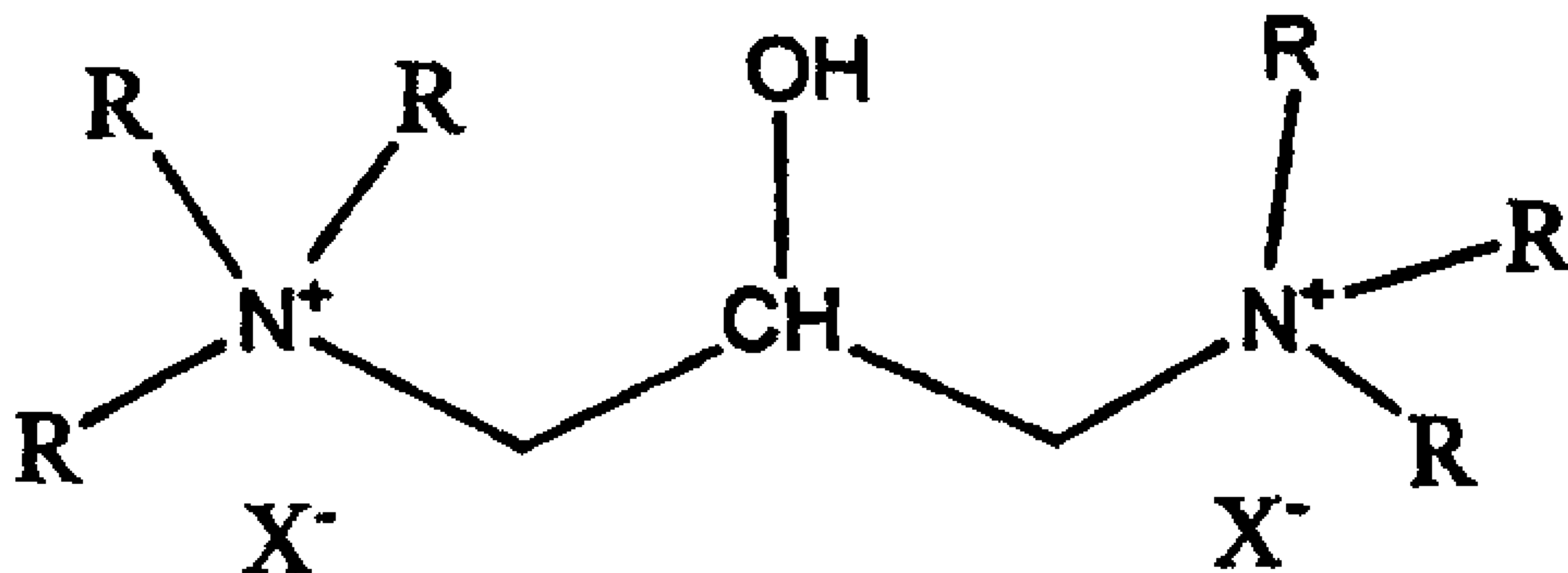




(86) Date de dépôt PCT/PCT Filing Date: 2008/03/06
(87) Date publication PCT/PCT Publication Date: 2008/09/18
(45) Date de délivrance/Issue Date: 2012/05/15
(85) Entrée phase nationale/National Entry: 2009/09/11
(86) N° demande PCT/PCT Application No.: US 2008/055994
(87) N° publication PCT/PCT Publication No.: 2008/112481
(30) Priorités/Priorities: 2007/03/13 (US60/894,646);
2007/05/30 (US60/940,833)

(51) Cl.Int./Int.Cl. *C09K 8/04* (2006.01),
C09K 8/68 (2006.01), *E21B 21/14* (2006.01)
(72) Inventeurs/Inventors:
PATEL, ARVIND D., US;
STAMATAKIS, EMANUEL, US
(73) Propriétaire/Owner:
M-I L.L.C., US
(74) Agent: FINLAYSON & SINGLEHURST

(54) Titre : AGENT D'INHIBITION D'HYDRATATION DE SCHISTE ARGILEUX ET PROCEDE D'UTILISATION
(54) Title: SHALE HYDRATION INHIBITION AGENT AND METHOD OF USE

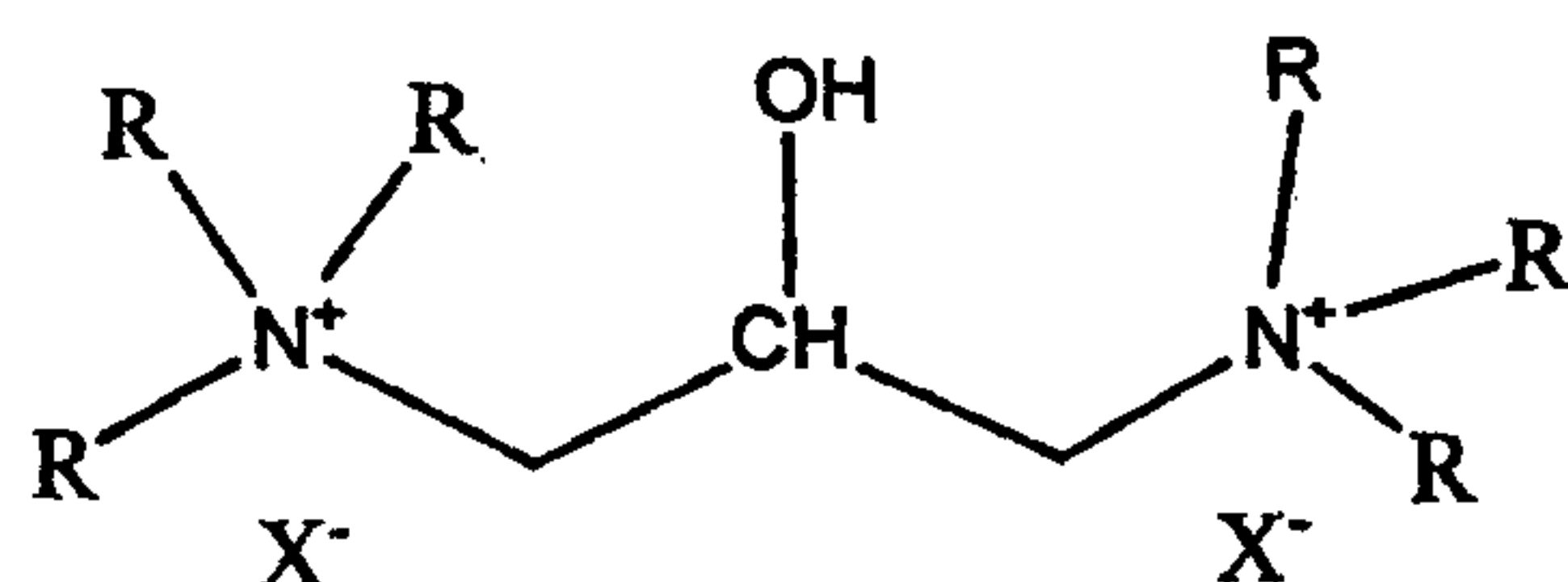


(57) Abrégé/Abstract:

A water-base fluid for use in drilling, cementing, workover, fracturing and abandonment of subterranean wells through a formation containing a shale which swells in the presence of water. In one illustrative embodiment, the drilling fluid includes, an aqueous based continuous phase, a weighting agent, and a shale hydration inhibition agent. The shale hydration inhibition agent should have the general formula: (see above formula) in which R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms, and X is an anion. The shale hydration inhibition agent is present in sufficient concentration to substantially reduce the swelling of shale drilling cuttings upon contact with the drilling fluid. The drilling fluid may be formulated to include a wide variety of components of aqueous based drilling fluids, such as weighting agents, fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials known to one of skill in the art. The fluids may also be used in the disposal by reinjection of drilling cutting into a selected subterranean disposal formation.

ABSTRACT

A water-base fluid for use in drilling, cementing, workover, fracturing and abandonment of subterranean wells through a formation containing a shale which swells in the presence of water. In one illustrative embodiment, the drilling fluid includes, an aqueous based continuous phase, a weighting agent, and a shale hydration inhibition agent. The shale hydration inhibition agent should have the general formula:



in which R is independently selected

from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms, and X is an anion. The shale hydration inhibition agent is present in sufficient concentration to substantially reduce the swelling of shale drilling cuttings upon contact with the drilling fluid. The drilling fluid may be formulated to include a wide variety of components of aqueous based drilling fluids, such as weighting agents, fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials known to one of skill in the art. The fluids may also be used in the disposal by reinjection of drilling cutting into a selected subterranean disposal formation.

SHALE HYDRATION INHIBITION AGENT AND METHOD OF USE

BACKGROUND

- [0002]** In rotary drilling of subterranean wells numerous functions and characteristics are expected of a drilling fluid. A drilling fluid should circulate throughout the well and carry cuttings from beneath the bit, transport the cuttings up the annulus, and allow their separation at the surface. At the same time, the drilling fluid is 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 borehole's uncased sections. The drilling fluid should also form a thin, low permeability filter cake that seals openings in formations penetrated by the bit and act to reduce the unwanted influx of formation fluids from permeable rocks.
- [0003]** Drilling fluids are typically classified according to their base material. In oil base fluids, solid particles are suspended in oil, and water or brine may be emulsified with the oil. The oil is typically the continuous phase. In water base fluids, solid particles are suspended in water or brine, and oil may be emulsified in the water. The water is typically the continuous phase. Pneumatic fluids are a third class of drilling fluids in which a high velocity stream of air or natural gas removes drill cuttings.
- [0004]** The formation solids that become dispersed in a drilling fluid are typically the cuttings produced by the drill bit's action and the solids produced by borehole instability. Where the formation solids are clay minerals that swell, the presence of either type of formation solids in the drilling fluid can greatly increase drilling time and costs. 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 borehole, and inhibits formation of the thin filter cake that

seals formations. Clay swelling can also create other drilling problems such as loss of circulation or stuck pipe that slow drilling and increase drilling costs.

[0005] Clay swelling is a phenomenon in which water molecules surround a clay crystal structure and position themselves to increase the structure's c-spacing thus resulting in an increase in volume. Two types of swelling may occur: surface hydration and osmotic swelling.

[0006] Surface hydration is one type of swelling in which water molecules are adsorbed on crystal surfaces. Hydrogen bonding holds a layer of water molecules to the oxygen atoms exposed on the crystal surfaces. Subsequent layers of water molecules align to form a quasi-crystalline structure between unit layers, which results in an increased c-spacing. Virtually all types of clays swell in this manner.

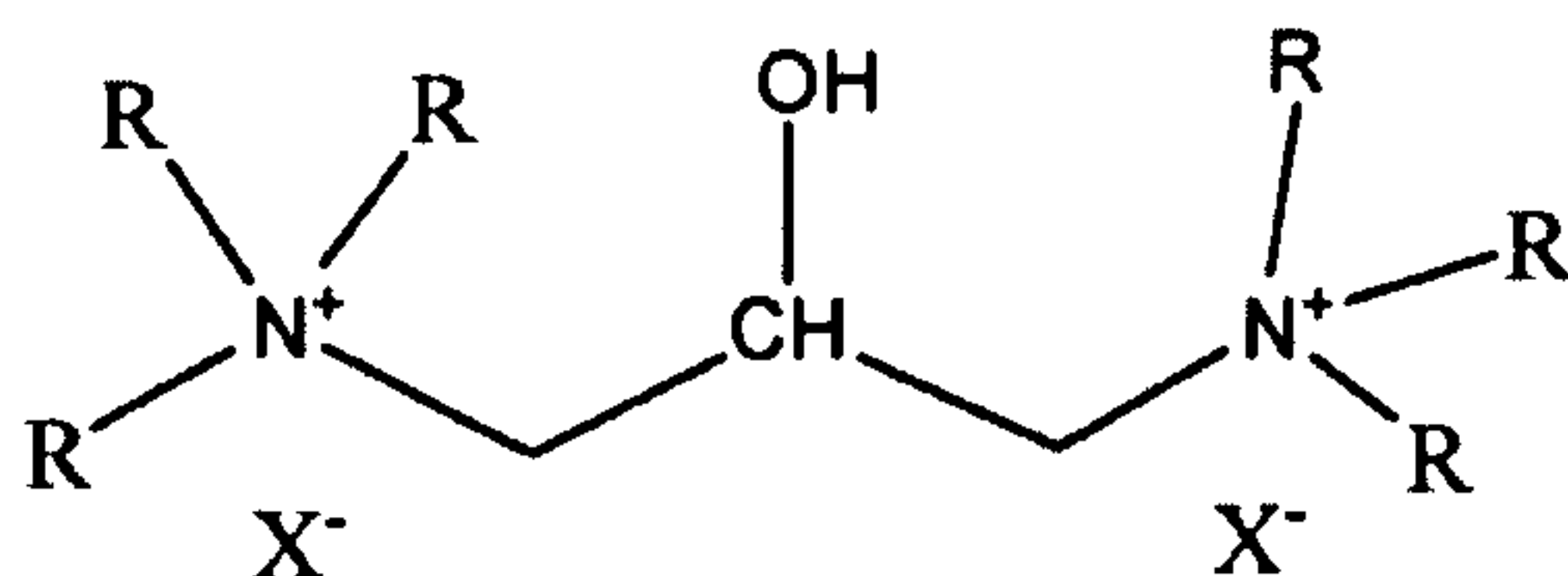
[0007] Osmotic swelling is a type of swelling where the concentration of cations between unit layers in a clay mineral is higher than the cation concentration in the surrounding water, water is osmotically drawn between the unit layers and the c-spacing is increased. Osmotic swelling results in larger overall volume increases than surface hydration. However, only certain clays, like sodium montmorillonite, swell in this manner.

[0008] Although a number of compounds are known for their effectiveness in inhibiting reactive shale formations, several factors affect the practicality of using swelling inhibitor additives in drilling fluids. First, the inhibitor must be compatible with the other drilling fluid components. The driller of subterranean wells must be able to control the rheological properties of drilling fluids by using additives such as bentonite, anionic polymers and weighting agents. Thus, drilling fluid additives should also provide desirable results but should not inhibit the desired performance of other additives. However, many swelling inhibitors will react with other drilling fluid components, resulting in severe flocculation or precipitation.

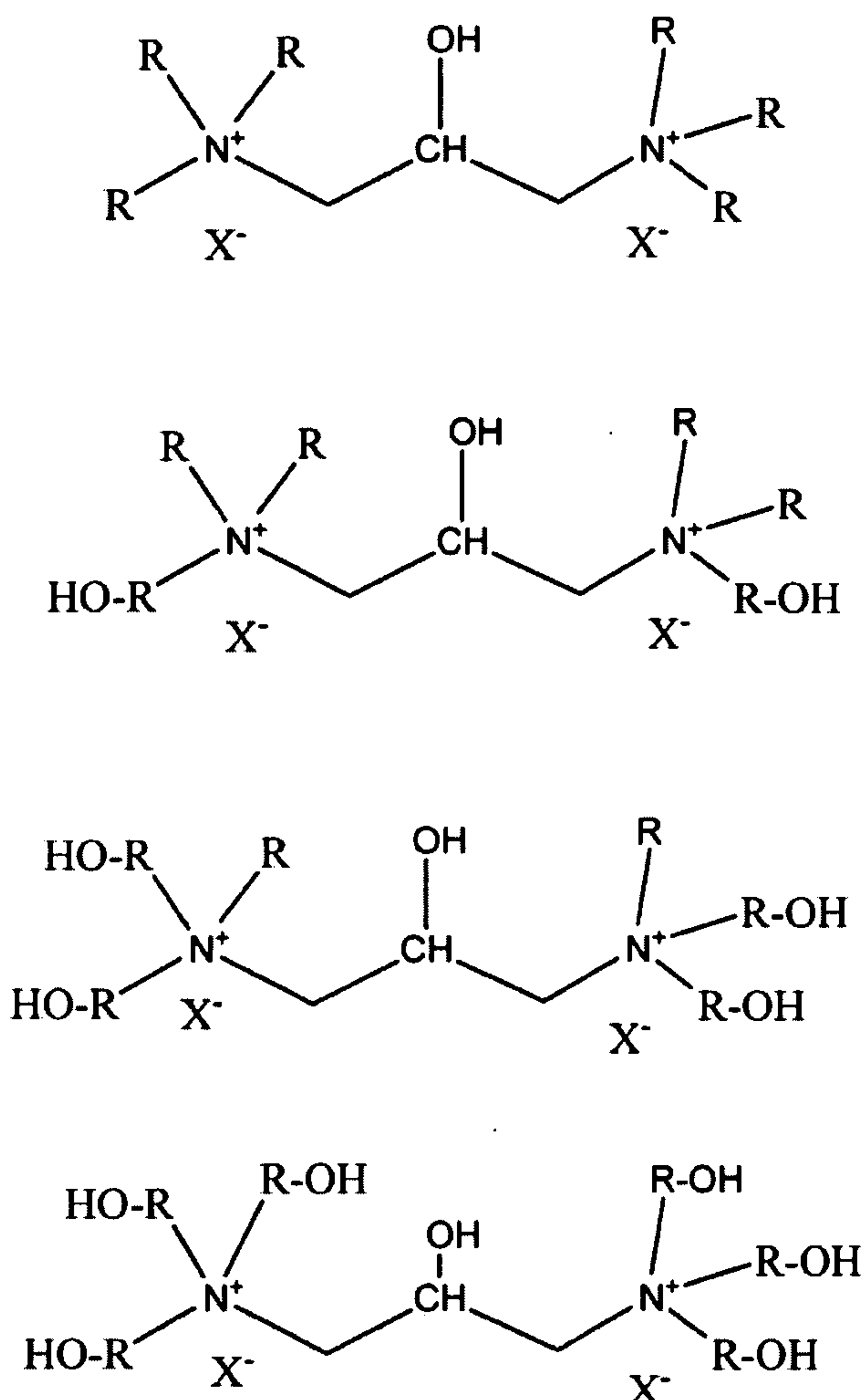
[0009] Second, current drilling fluid components must be environmentally acceptable. As drilling operations impact on plant and animal life, drilling fluid additives should have low toxicity levels and should be easy to handle and to use to minimize the dangers of environmental pollution and harm to personnel. Moreover, in the oil and gas industry today, it is desirable that additives work both onshore and offshore and in fresh and salt water environments.

SUMMARY

[0010] Upon consideration of the present disclosure, one of skill in the art should understand and appreciate that one illustrative embodiment of the claimed subject matter includes a water-base drilling fluid for use in drilling wells through a formation containing a shale which swells in the presence of water. In such an illustrative embodiment, the drilling fluid includes, an aqueous based continuous phase, a weighting agent, and a shale hydration inhibition agent. The shale hydration inhibition agent should have the general formula:



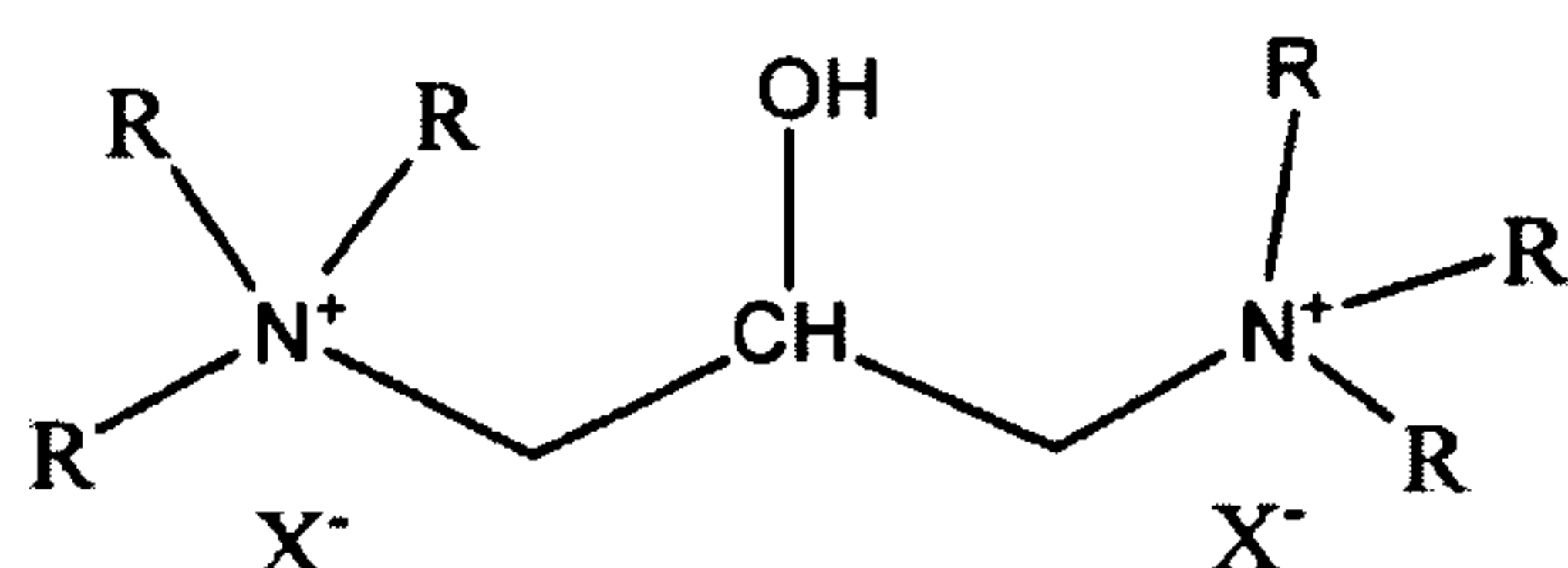
in which R is independently selected from alkyls and hydroxyl alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10 carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. The shale hydration inhibition agent is present in sufficient concentration to substantially reduce the swelling of shale drilling cuttings upon contact with the drilling fluid. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of the reaction of tertiary amine and epichlorohydrine. In a particularly preferred illustrative embodiment, the shale hydration inhibition agent is selected from:



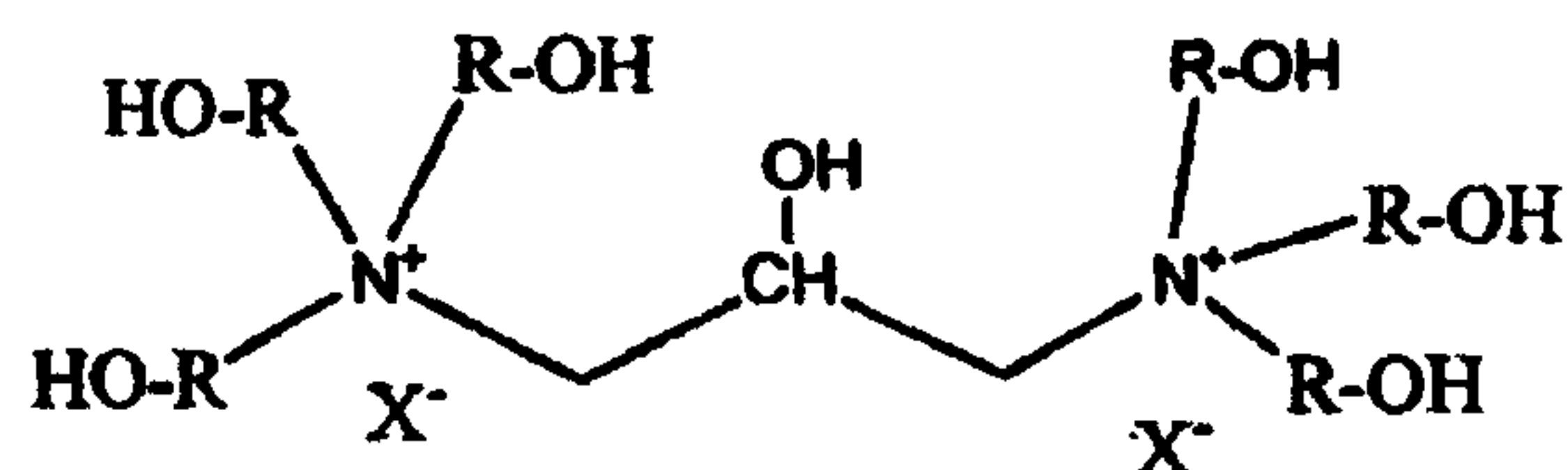
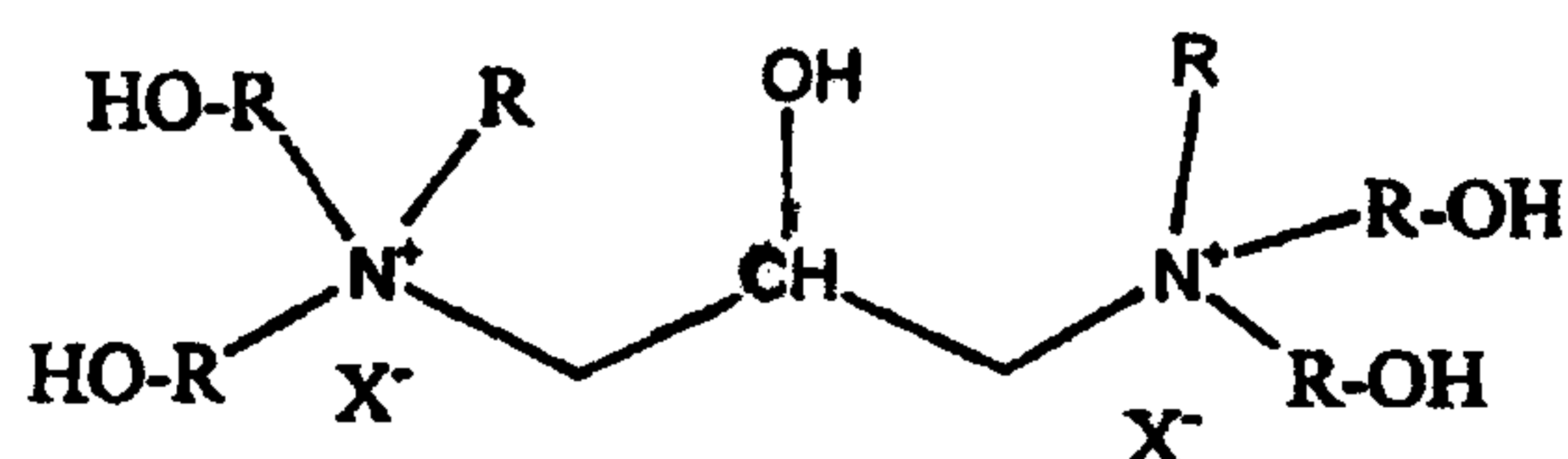
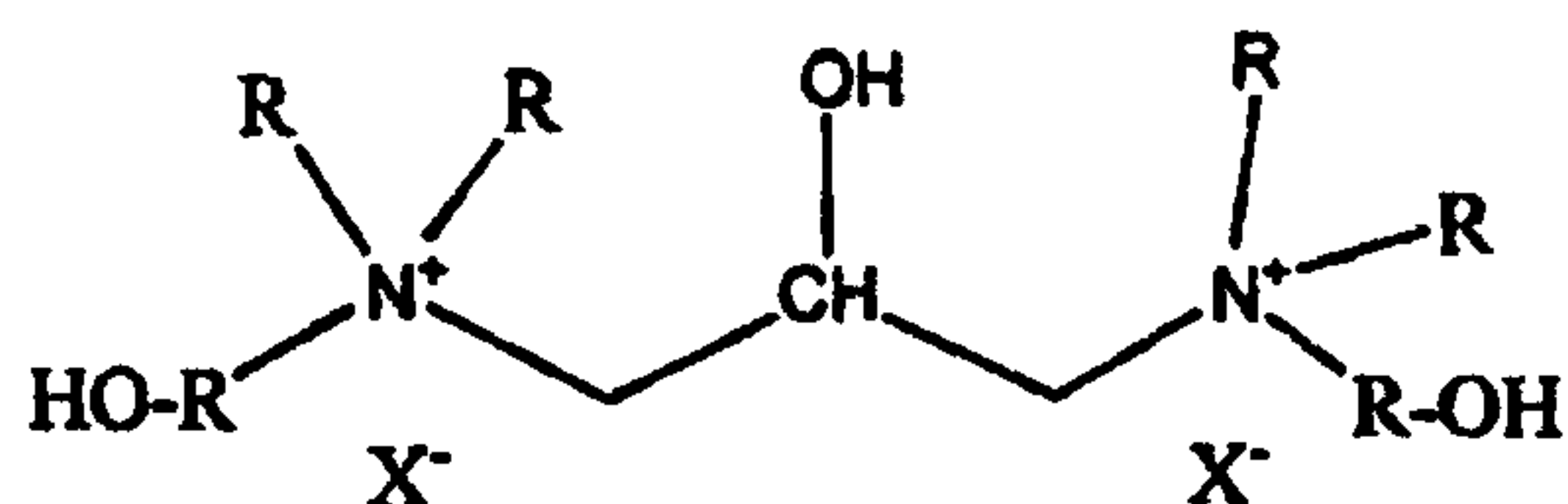
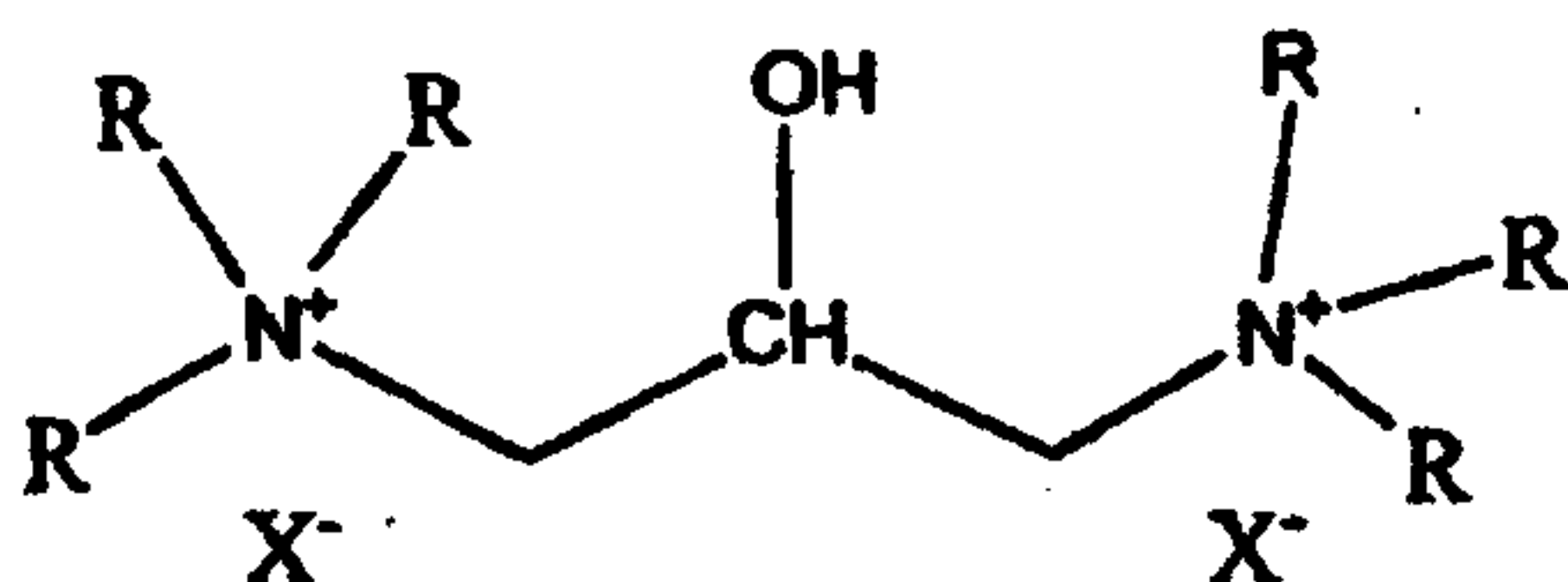
as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another embodiment, R comprises 1 to 10 carbon atoms; and in another embodiment R comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. The illustrative drilling fluid is formulated such that the aqueous based continuous phase is selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected from mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic

salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may also include a wide variety of conventional components of aqueous based drilling fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

[0011] The scope of the claimed subject matter also encompasses a fracturing fluid for use in a subterranean well in which the subterranean well penetrates through one or more subterranean formation composed of a shale that swells in the presence of water. One illustrative fluid is formulated to include an aqueous based continuous phase, a viscosifying agent and a shale hydration inhibition agent which is present in sufficient concentration to substantially reduce the swelling of shale. In one illustrative embodiment, the shale hydration inhibition agent has the formula:



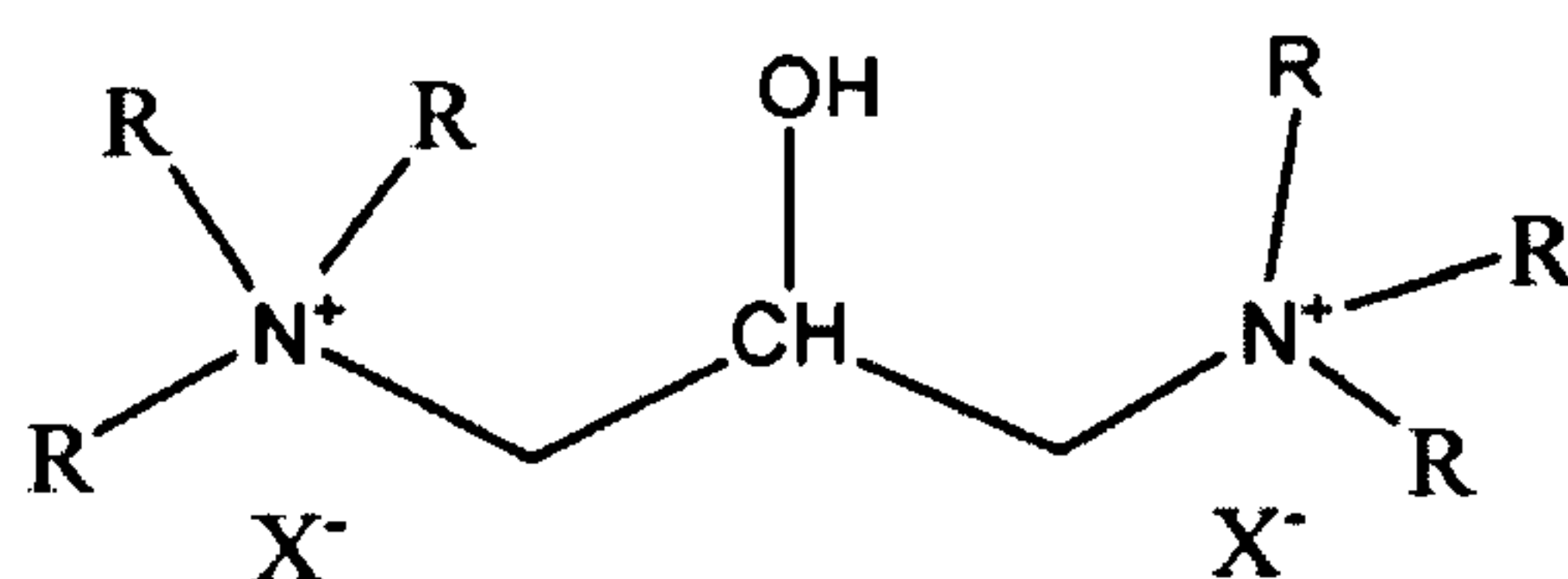
in which R is independently selected from alkyls and hydroxyl alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10 carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. Alternatively, the shale hydration inhibition agent of the illustrative fluid may be selected from:



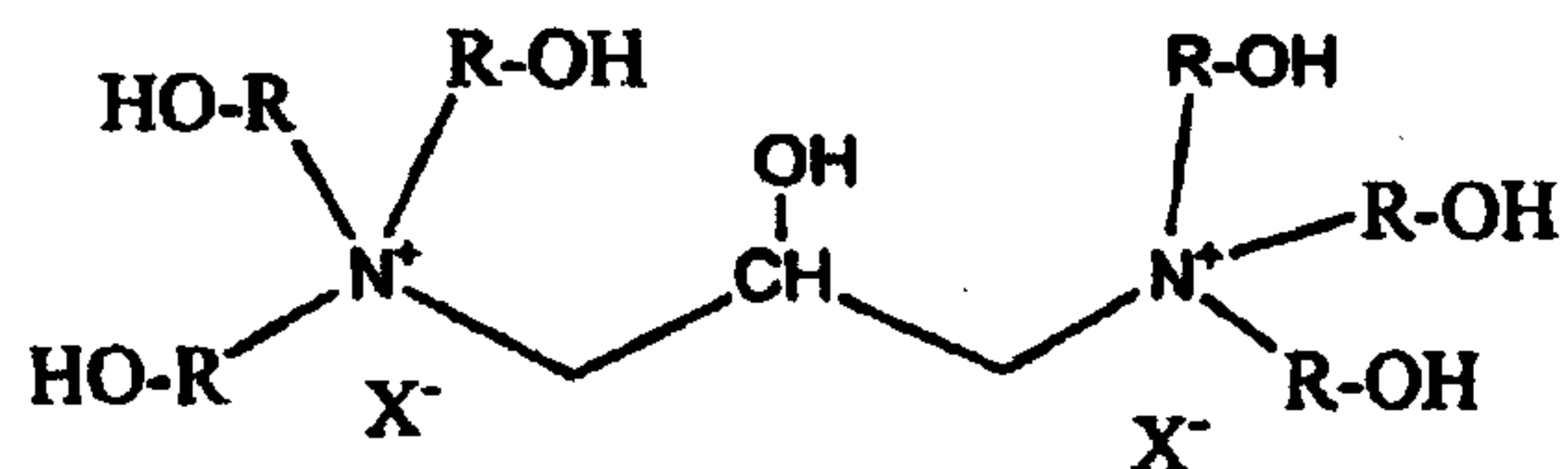
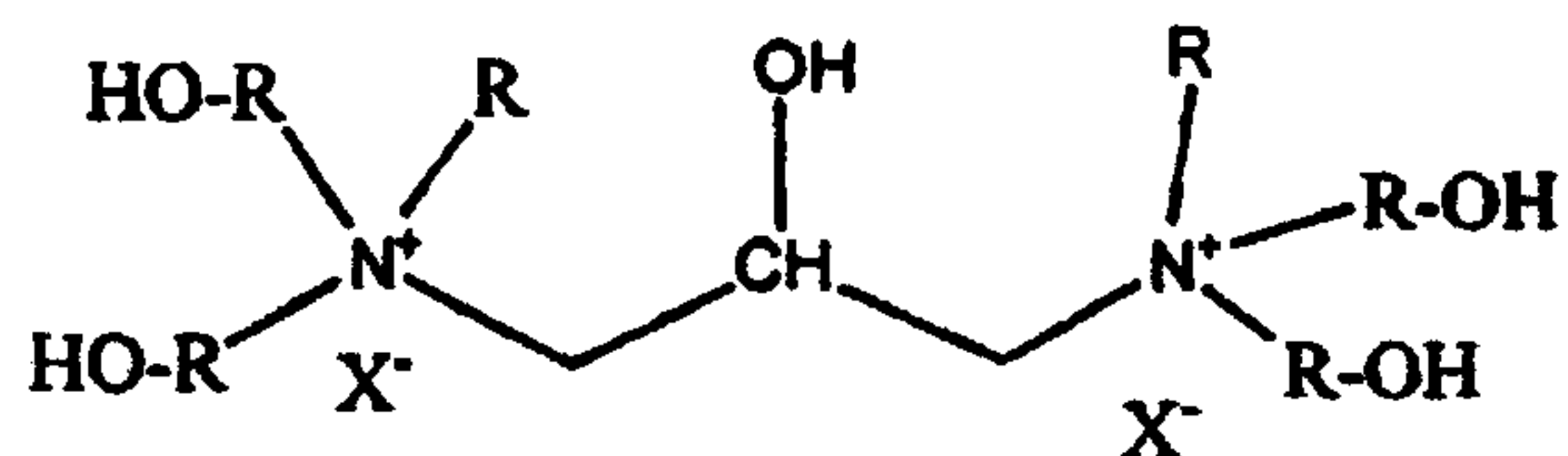
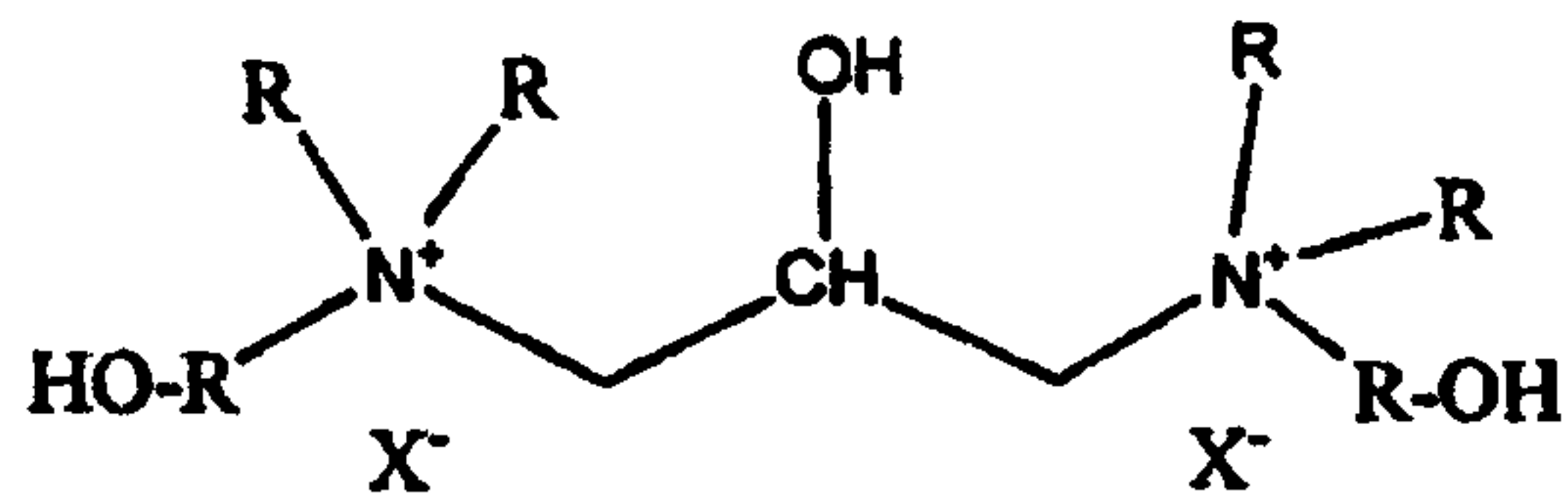
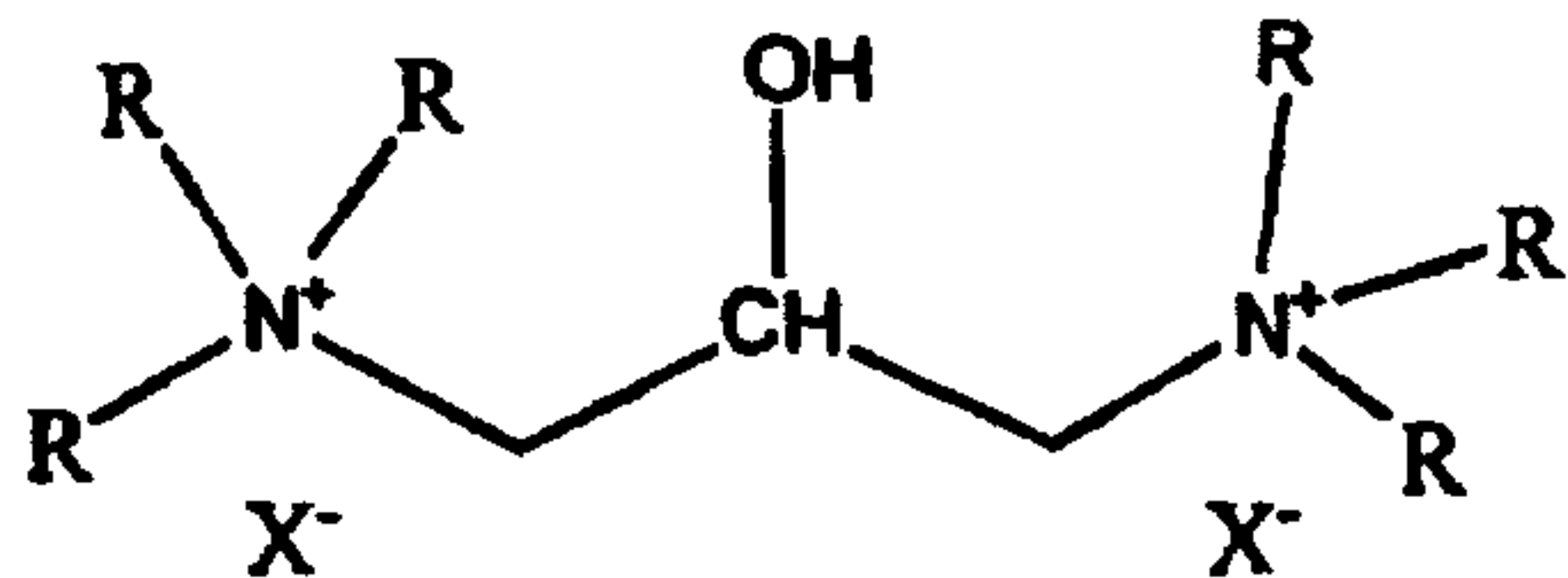
as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another embodiment, R comprises 1 to 10 carbon atoms; and in another embodiment R comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of the reaction of tertiary amine and epichlorohydrine. Preferred tertiary amines are trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethylamine, and tripropanolamine. The illustrative fluid is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and

combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may also include a wide variety of conventional components of fracturing fluids, such as propants such as sand, gravel, glass beads, ceramic materials and the like, acid release agents, fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

[0012] It should also be appreciated that the claimed subject matter inherently includes components such as: an aqueous based continuous phase; a swellable shale material; and a shale hydration inhibition agent present in sufficient concentration to substantially reduce the swelling of the swellable shale material. Such a composition may be formed during the course of drilling a subterranean well, but also may be deliberately made if drill cuttings reinjection is to be carried out. In one illustrative embodiment, the shale hydration inhibition agent has the formula:



in which R is independently selected from alkyls and hydroxyl alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10 carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. Alternatively, the shale hydration inhibition agent of the illustrative fluid may be selected from:



as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another embodiment, R comprises 1 to 10 carbon atoms; and in another embodiment R comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of the reaction of tertiary amine and epichlorohydrine. Preferred tertiary amines are trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethanolamine, and tripropanolamine. The illustrative composition is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and

combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative composition. The illustrative composition may also include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

[0013] One of skill in the art should appreciate that the fluids of the claimed subject matter are useful during the course of the drilling, cementing, fracturing, maintenance and production, workover, abandonment of a well as other operations associated with subterranean wells. The claimed subject matter also includes a method of reducing the toxicity of a wellbore fluid for use in subterranean operations, the method including circulating in the well a water-based wellbore fluid formulated to produce $EC_{50}(15)$ values greater than 50%. It should also be appreciated by one of skill in the art that the claimed subject matter inherently includes a method of reducing the swelling of shale clay in a well, the method including circulating in the well a water-base drilling fluid formulated as is substantially disclosed herein. These and other features of the claimed subject matter are more fully set forth in the following description of illustrative embodiments of the claimed subject matter.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

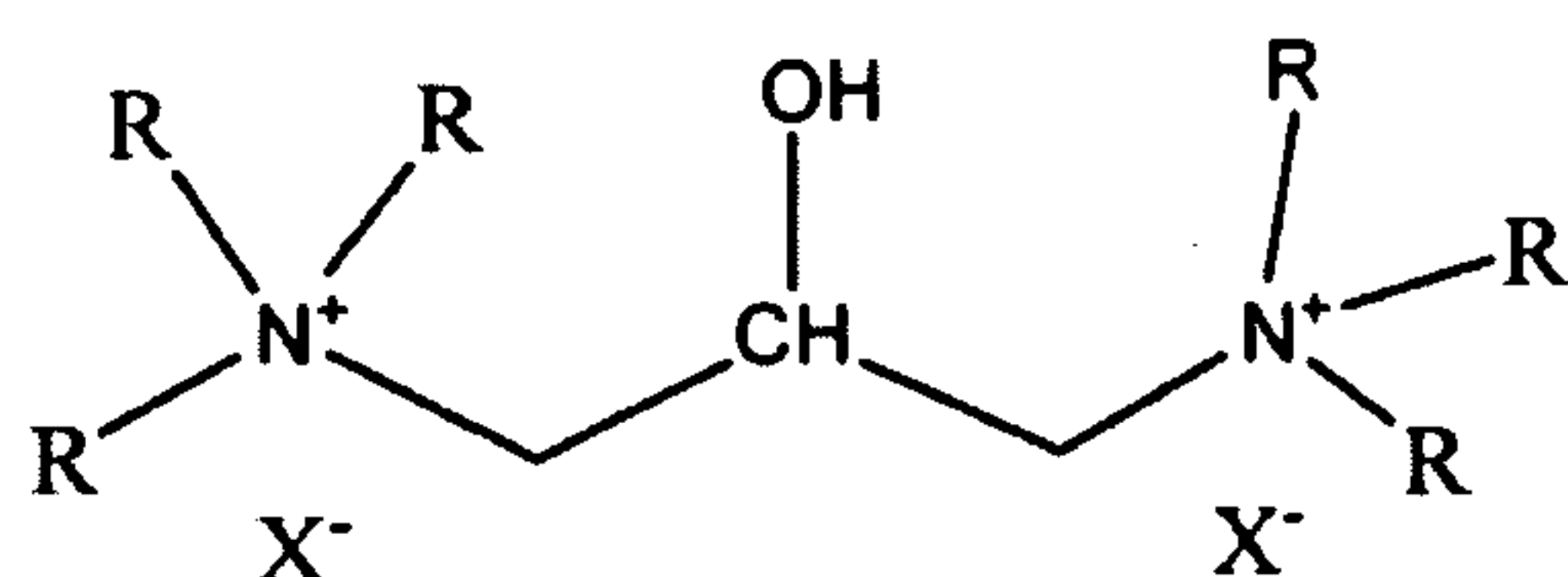
[0014] The claimed subject matter is directed to a water-base drilling fluid for use in drilling wells through a formation containing a shale which swells in the presence of water. Generally the drilling fluid of the claimed subject matter may be formulated to include an aqueous continuous phase and a shale hydration inhibition agent. As disclosed below, the drilling fluids of the claimed subject matter may optionally include additional components, such as weighting agents, viscosity agents, fluid loss control agents, bridging agents, lubricants, anti-bit balling agents, corrosion inhibition agents, alkali reserve materials and buffering agents, surfactants and suspending

agents, rate of penetration enhancing agents and the like that one of skill in the art should understand may be added to an aqueous based drilling fluid.

[0015] The aqueous based continuous phase may generally be any water based fluid phase that is compatible with the formulation of a drilling fluid and is compatible with the shale hydration inhibition agents disclosed herein. In one preferred embodiment, the aqueous based continuous phase is selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds and mixtures thereof. The amount of the aqueous based continuous phase should be sufficient to form a water based drilling fluid. This amount may range from nearly 100% of the drilling fluid to less than 30 % of the drilling fluid by volume. Preferably, the aqueous based continuous phase is from about 95 to about 30 % by volume and preferably from about 90 to about 40 % by volume of the drilling fluid.

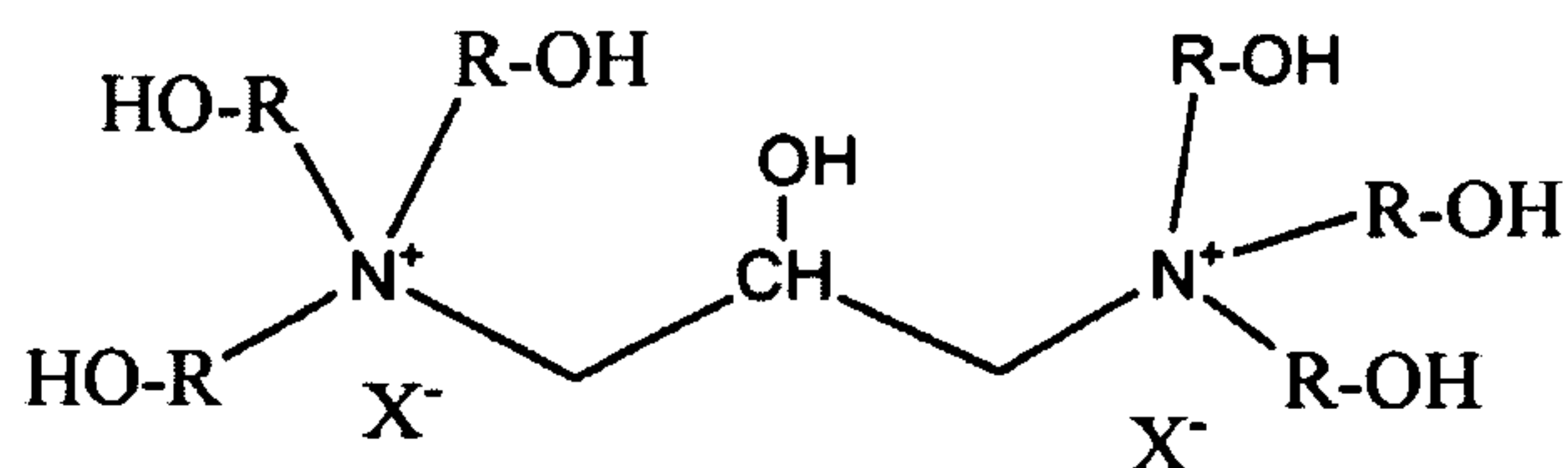
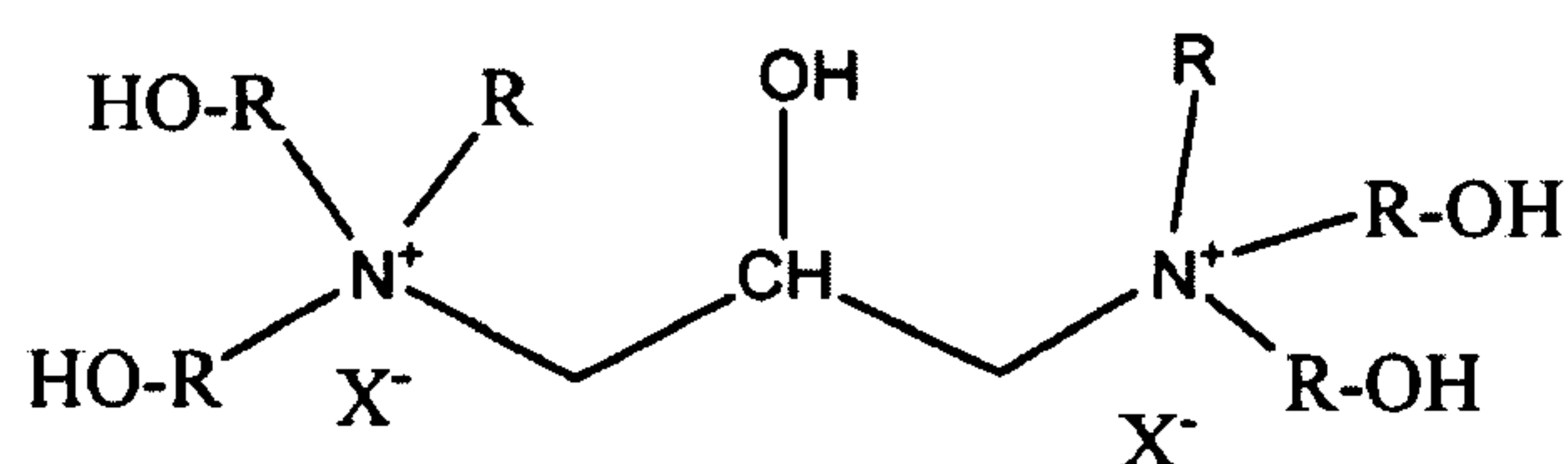
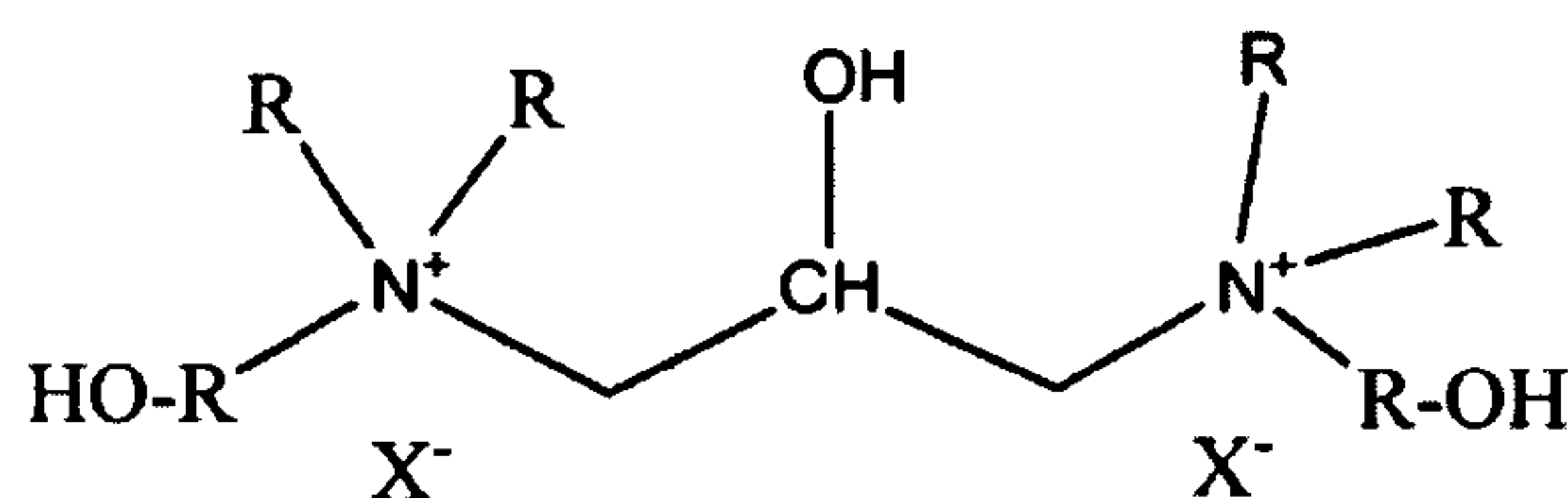
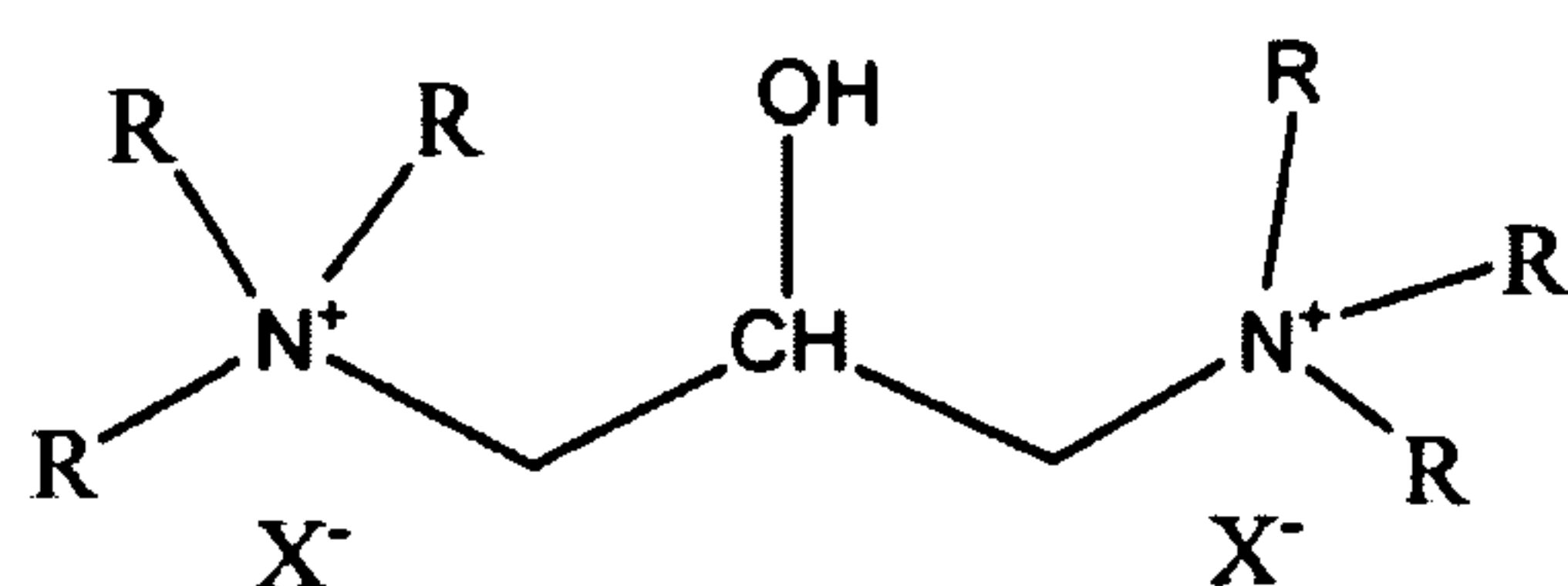
[0016] A shale hydration inhibition agent is included in the formulation of the drilling fluids of the claimed subject matter so that the hydration of shale and shale like formations is inhibited. Thus, the shale hydration inhibition agent should be present in sufficient concentration to reduce either or both the surface hydration based swelling and/or the osmotic based swelling of the shale clay. The exact amount of the shale 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 shale clay formation encountered. Generally however, the shale hydration inhibition agent of the claimed subject matter may be used in drilling fluids 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.

[0017] The shale hydration inhibition agent of the claimed subject matter should have the general formula:



in which R is independently selected from alkyls and hydroxyl alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl

alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10 carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. The shale hydration inhibition agent is present in sufficient concentration to substantially reduce the swelling of shale drilling cuttings upon contact with the drilling fluid. In a particularly preferred illustrative embodiment, the shale hydration inhibition agent of the illustrative composition may be selected from:



as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another embodiment, R comprises 1 to 10 carbon atoms; and in another embodiment R comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. .

- [0018]** When considering the illustrative shale hydration inhibition agents disclosed above, one skilled in organic synthesis should recognize that a wide variety of synthetic reaction pathways can be used to reach the above target molecules. It has been found that one desirable and economic way to achieve the target compounds is the reaction of a tertiary amine and epichlorohydrine. Preferred tertiary amines are trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethylamine, and tripropanolamine. The techniques, required apparatus, and reaction conditions for carrying out such reactions should be easily obtained from the appropriate literature by one of skill in the art of organic synthesis. In some instances the above compounds may be commercially available from specialty chemical suppliers although their use and application may be in a field other than drilling fluid formulation.
- [0019]** The drilling fluids of the claimed subject matter can include a weight material in order to increase the density of the fluid. The primary purpose for such weighting materials is to increase the density of the drilling fluid so as to prevent kick-backs and blow-outs. One of skill in the art should know and understand that the prevention of kick-backs and blow-outs is important to the safe day to day operations of a drilling rig. Thus the weight material is added to the drilling fluid in a functionally effective amount largely dependent on the nature of the formation being drilled. Weight materials suitable for use in the formulation of the drilling fluids of the claimed subject matter may be generally selected from any type of weighting materials be it in solid, particulate form, suspended in solution, dissolved in the aqueous phase as part of the preparation process or 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 may be utilized in the formulation of drilling fluids.
- [0020]** The drilling fluids of the claimed subject matter can include a viscosifying agent in order to alter or maintain the rheological properties of the fluid. The primary purpose for such viscosifying agents is to control the viscosity and potential changes in viscosity of the drilling fluid. Viscosity control is particularly important because often a subterranean formation may have a temperature significantly higher than the surface temperature. Thus a drilling fluid may undergo temperature extremes of

nearly freezing temperatures to nearly the boiling temperature of water or higher during the course of its transit from the surface to the drill bit and back. One of skill in the art should know and understand that such changes in temperature can result in significant changes in the rheological properties of fluids. Thus in order to control and/or moderate the rheology changes, viscosity agents and rheology control agents may be included in the formulation of the drilling fluid. Viscosifying agents suitable for use in the formulation of the drilling fluids of the claimed subject matter may be generally selected from any type of viscosifying agents suitable for use in aqueous based drilling fluids. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like.

[0021] In addition to the components noted above, the claimed drilling fluids may also be formulated to include materials generically referred to as alkali reserve and alkali buffering agent, gelling materials, thinners, and fluid loss control agents, as well as other compounds and materials which are optionally added to water base drilling fluid formulations. Of these additional materials, each can be added to the formulation in a concentration as rheologically and functionally required by drilling conditions.

[0022] One of skill in the art should appreciate that lime is the principle alkali reserve agent utilized in formulating water based drilling fluids. Alkali buffering agents, such as cyclic organic amines, sterically hindered amines, amides of fatty acids and the like may also be included to serve as a buffer against the loss of the alkali reserve agent. The drilling fluid may also contain anticorrosion agents as well to prevent corrosion of the metal components of the drilling operational equipment. Gelling materials are also often used in aqueous based drilling fluids and these include bentonite, sepiolite, clay, attapulgite clay, anionic high-molecular weight polymers and biopolymers. Thinners such as lignosulfonates are also often added to water-base drilling fluids. Typically lignosulfonates, modified lignosulfonates, polyphosphates and tannins are added. In other embodiments, low molecular weight polyacrylates can also be added as thinners. Thinners are added to a drilling fluid to reduce flow resistance and control gelation tendencies. Other functions performed by thinners include reducing

filtration and filter cake thickness, counteracting the effects of salts, minimizing the effects of water on the formations drilled, emulsifying oil in water, and stabilizing mud properties at elevated temperatures.

[0023] A variety of fluid loss control agents may be added to the drilling fluids of the claimed subject matter that are generally selected from a group consisting of synthetic organic polymers, biopolymers, and mixtures thereof. The fluid loss control agents such as modified lignite, polymers, modified starches and modified celluloses may also be added to the water base drilling fluid system of this invention. In one embodiment it is preferred that the additives of the invention should be selected to have low toxicity and to be compatible with common anionic drilling fluid additives such as polyanionic carboxymethylcellulose (PAC or CMC), polyacrylates, partially-hydrolyzed polyacrylamides (PHPA), lignosulfonates, xanthan gum, mixtures of these and the like.

[0024] The drilling fluid of the claimed subject matter may further contain an encapsulating agent generally selected from the group consisting of synthetic organic, inorganic and bio-polymers and mixtures thereof. The role of the encapsulating agent is to absorb at multiple points along the chain onto the clay particles, thus binding the particles together and encapsulating the cuttings. These 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, amphoteric, or non-ionic in nature.

[0025] Other additives that could be present in the drilling fluids of the claimed subject matter include products such as lubricants, penetration rate enhancers, defoamers, fluid loss circulation products and so forth. Such compounds should be known to one of ordinary skill in the art of formulating aqueous based drilling fluids.

[0026] The following examples are included to demonstrate preferred embodiments of the claimed subject matter. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the claimed subject matter, and thus can be considered to constitute preferred modes for its practice. However, 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 claimed subject matter.

[0027] Unless otherwise stated, all starting materials are commercially available and standard laboratory techniques and equipment are utilized. The tests were conducted in accordance with the procedures in API Bulletin RP 13B-2, 1990. The following abbreviations are sometimes used in describing the results discussed in the examples:

"PV" is plastic viscosity (CPS) which is one variable used in the calculation of viscosity characteristics of a drilling fluid.

"YP" is yield point (lbs/100 ft²) which is another variable used in the calculation of viscosity characteristics of drilling fluids.

"GELS" (lbs/100 ft²) is a measure of the suspending characteristics and the thixotropic properties of a drilling fluid.

"F/L" is API fluid loss and is a measure of fluid loss in milliliters of drilling fluid at 100 psi.

Example 1

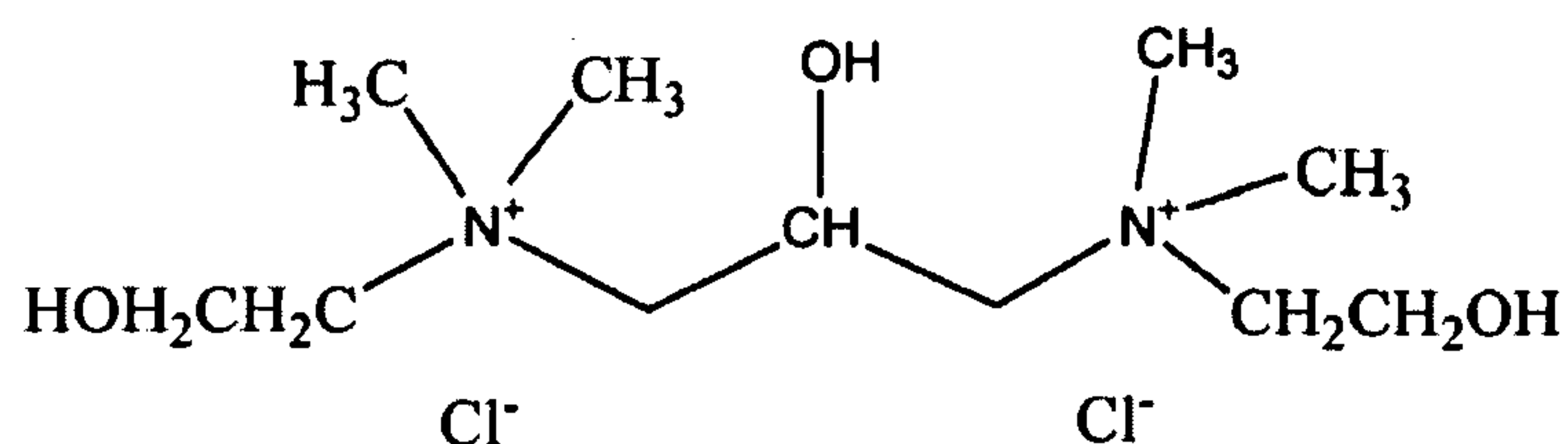
The drilling muds in Table 1 are formulated to illustrate the claimed subject matter:

Table 1

	A (ppb)	B (ppb)	C (ppb)
Fresh Water	285.0	285.0	275.0
DuoVis	1.0	1.0	1.0
Hydroxy ethyl carboxy methyl Starch (HECMS)	3.0	3.0	3.0
UltraCap®	2.0	2.0	2.0
Cola®Moist 200	10.5	-	-
Dimethylethanolamine- chlorhydrine BisQuat		10.5	-
Trimethanolamine Dichlorohydrin	-	-	10.5
Barite	175.0	175.0	175.0

[0028] In the above mud formulations, commercially available compounds have been used in the formulation of the drilling fluid, but one of skill in the art should appreciate that other similar compounds may be used instead. Ultracap is a cationic polyacrylamide available from M-I LLC.

[0029] Cola Moist 200 is a hydroxypropyl Bis-Hydroxyethyltrimonium Chloride having the formula



and which is commercially available from Colonial Chemicals, Inc..

The initial properties of the above muds are measured and detailed in Table 2:

Table 2

Properties (at 120°F)	A	B	C
Viscosity (cps) at			
600 rpm	84	78	85
300 rpm	58	54	60
200 rpm	44	43	48
100 rpm	28	30	33
6 rpm	7	9	8
3 rpm	6	7	7
Gels 10 sec.	8	8	8
10 min.	9	11	11
PV	26	24	25
YP	32	30	35

[0030] The muds were then heat-aged at 150°F for 16 hours. Table 3 details the heat-aged properties of the muds.

Table 3

Properties (after aging at 150°F for 16 hours)	A	B	C
Viscosity (cps) at 600 rpm	74	73	65
300 rpm	49	49	45
200 rpm	35	36	35
100 rpm	22	24	22
6 rpm	6	7	6
3 rpm	4	5	5
Gels 10 sec.	6	8	7
10 min.	7	8	7
PV	25	24	20
YP	24	25	25
API Fluid Loss (mL)	3.2	3.4	3.8
pH	8.2	8.6	8.2

[0031] Dispersion tests are run with Arne and Oxford Clay cuttings by hot rolling 10 g of cuttings in a one-barrel equivalent of mud for 16 hours at 150° F. After hot rolling the remaining cuttings are screened using a 20 mesh screen and washed with 10% potassium chloride water, dried and weighed to obtain the percentage recovered. The results of this evaluation are given in Table 4 and shows the improved shale inhibition performance of shale inhibition agents of this invention.

Table 4

(% cuttings recovered)	A	B	C
Arne Clay	89	94	98
Oxford Clay	94	95	94

[0032] To further demonstrate the performance of the drilling fluids formulated in accordance with the teachings of this invention, a test using a bulk hardness tester is

conducted. A BP Bulk Hardness Tester is a device designed to give an assessment of the hardness of shale cuttings exposed to drilling fluids, which in turn can be related to the inhibiting properties of the drilling fluid being evaluated. In this test, shale cuttings are hot rolled in the test drilling fluid at 150°F for 16 hours. Shale cuttings are screened and then placed into a BP Bulk Hardness Tester. The equipment is closed and using a torque wrench the force used to extrude the cuttings through a plate with holes in it is recorded. Depending on the hydration state and hardness of the cuttings and the drilling fluid used, a plateau region in torque is reached as extrusion of the cuttings begins to take place. Alternatively, the torque may continue to rise which tends to occur with harder cutting samples. Therefore, the higher the torque number obtained, the more inhibitive the drilling fluid system is considered. Illustrative data obtained using the three different mud formulations with three different cuttings are given below.

Table 5

Arne Clay	Bulk Hardness: (values in inch/lbs) Mud Formulation		
Turn No.	A	B	C
4	-	-	5
5	-	5	10
6	-	20	20
7	-	40	25
8	5	55	30
9	25	65	40
10	40	80	45
11	45	85	45
12	50	100	50
13	60	135	55
14	60	140	60
15	65	175	70
16	80	225	110
17	100	-	225
18	150	-	-
19	225	-	-

Table 6

Oxford Clay	Bulk Hardness: (values in inch/lbs) Mud Formulation		
Turn No.	A	B	C
4	5	-	-
5	10	5	5
6	10	5	5
7	15	5	5
8	25	10	10
9	55	15	35
10	110	35	140
11	150	75	150
12	170	140	140
13	185	175	150
14	215	210	170
15	225	225	180
16			210
17			225

[0033] To further demonstrate the toxicity performance of the drilling fluids formulated in accordance with the teachings of this invention, the Microtox[®] acute toxicity test is conducted on the samples. The Microtox[®] acute toxicity test operates on the basis of monitoring the level of light emission from luminescent bacteria. Luminescent bacteria produce light as a by-product of their cellular respiration. Exposure to toxic conditions result in a decrease in the rate of respiration, thereby reducing the rate of luminescence. Consequently, toxicity is measured as a percentage of luminescence lost. The test endpoint is measured as the effective concentration (EC) of a test sample that reduces light emission by a specific amount under defined conditions of time and temperature. Generally, the effective concentration is expressed as EC₅₀(15), which is the effective concentration of a sample which reduces light emission by 50% at 15 minutes at 15°C. One of skill in the art will appreciate that the length of time of exposure, and the minimum EC₅₀ values, will vary

depending on local legislation. In some embodiments, the additives of the present invention are added to a water-based wellbore fluid in concentrations resulting in EC₅₀(15) values greater than 50%; in other embodiments, EC₅₀(15) values greater than 70%; and in yet other embodiments, EC₅₀(15) values greater than 90%.

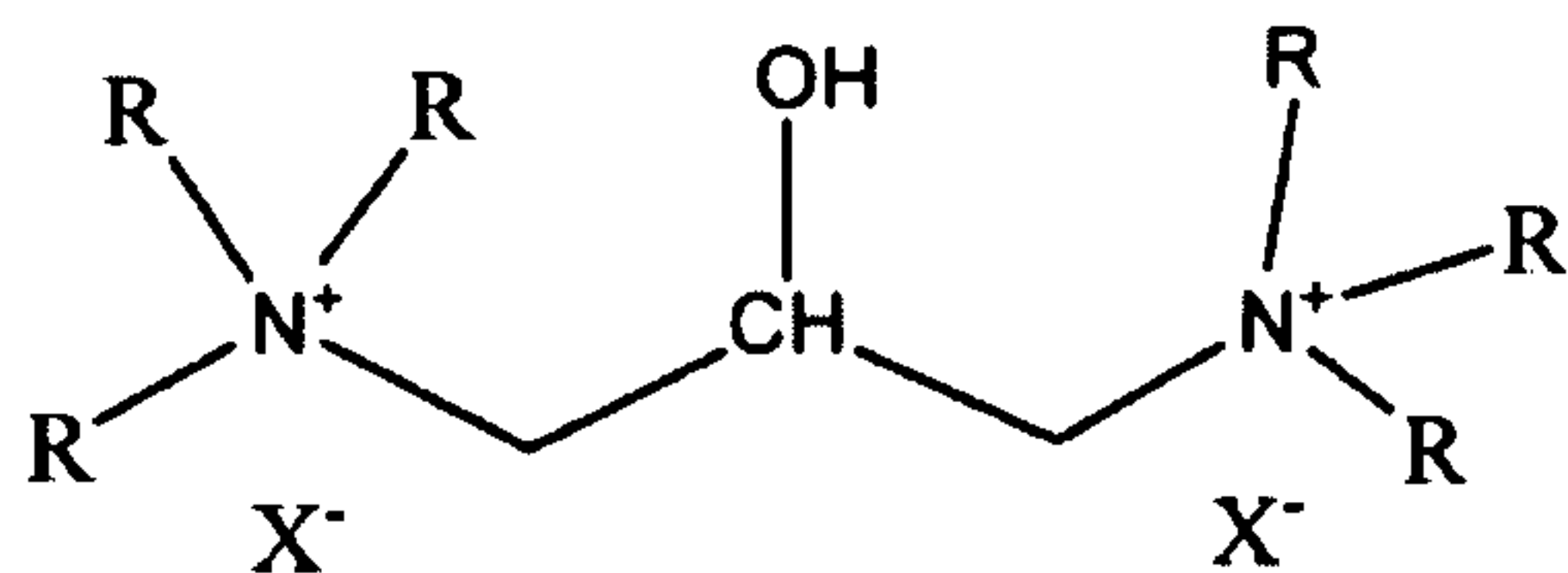
[0034] The samples were prepared and tested as specified in the Standard Procedure for Microtox Analysis published by the Western Canada Microtox Users Committee. The EC₅₀(15) was determined at 15°C. Table 8 details the EC₅₀(15) results for samples B and C.

Table 8

	A	B	C
EC ₅₀ (15)	> 90%	> 90%	88.66%

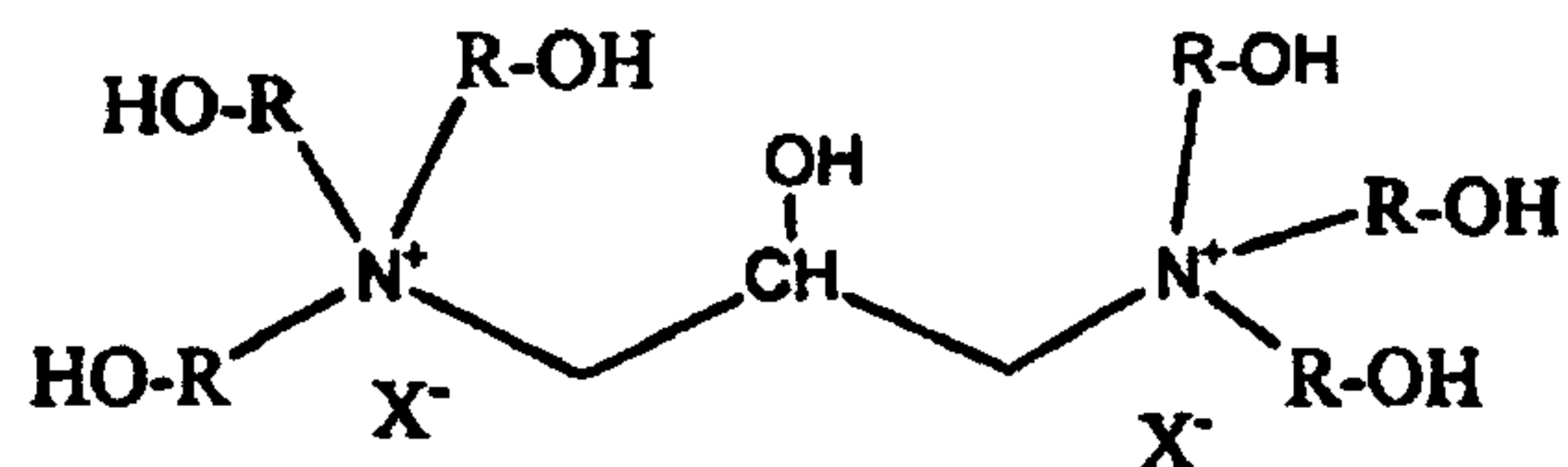
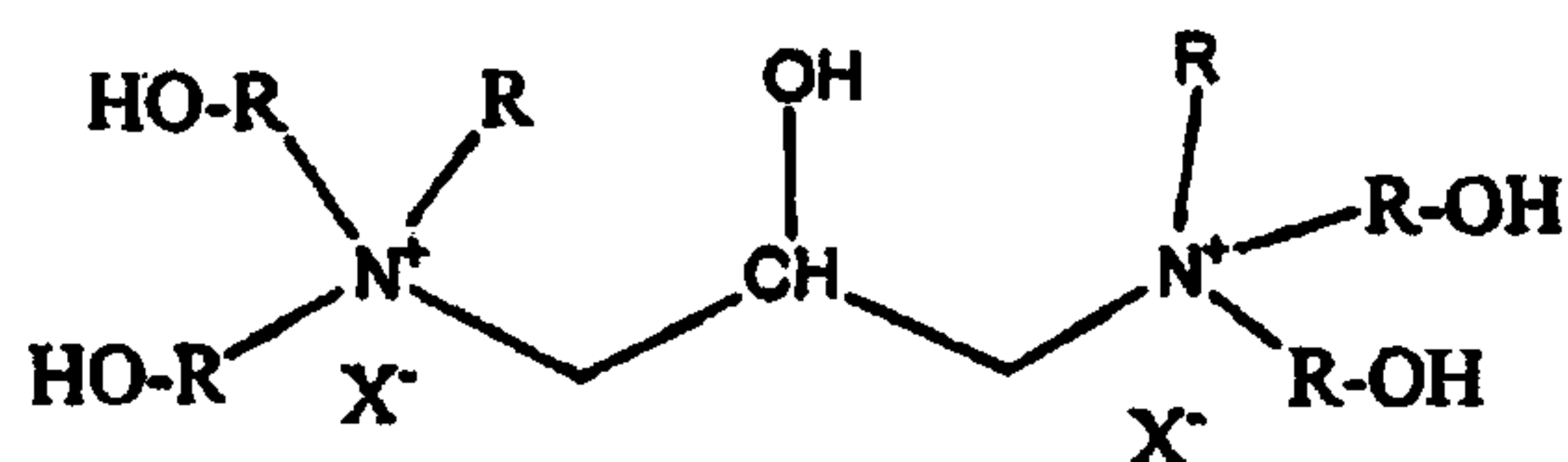
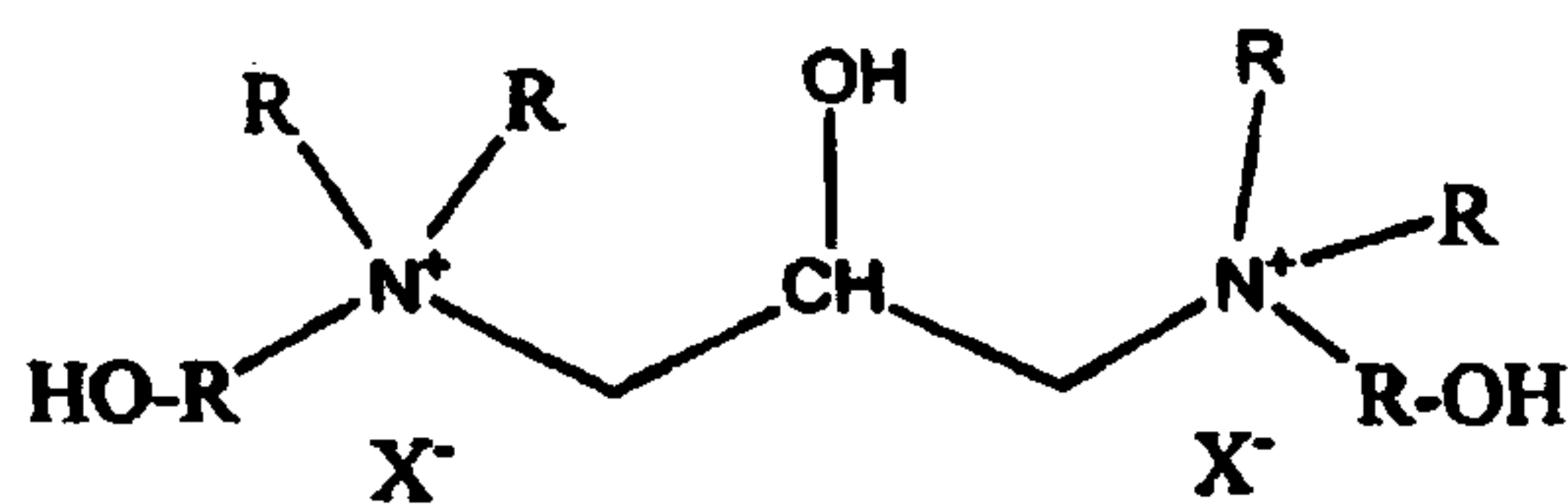
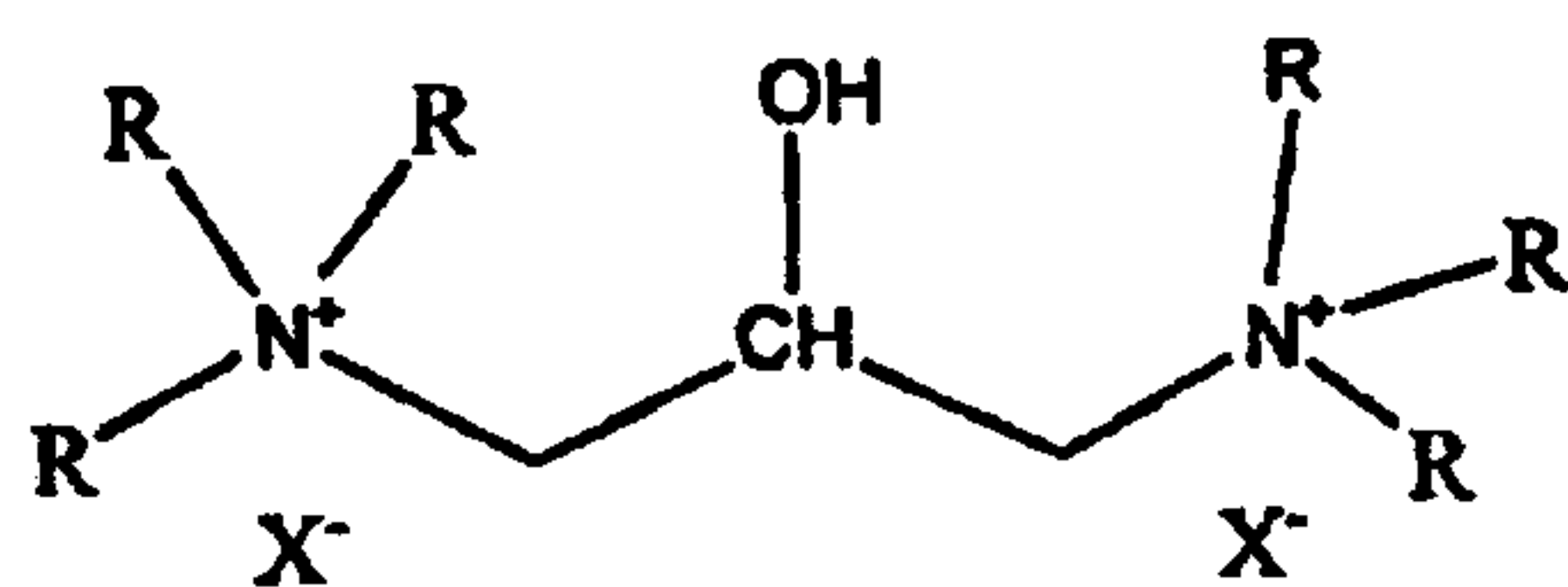
[0035] Upon review of the above data, one skilled in the art should observe that drilling fluids formulated according to the teachings of this invention prevent the hydration of various types of shale clays and thus are likely to provide good performance in drilling subterranean wells encountering such shale clays.

[0036] In view of the above disclosure, one of skill in the art should understand and appreciate that one illustrative embodiment of the claimed subject matter includes a water-base drilling fluid for use in drilling wells through a formation containing a shale which swells in the presence of water. In such an illustrative embodiment, the drilling fluid includes, an aqueous based continuous phase, a weighting agent, and a shale hydration inhibition agent. The shale hydration inhibition agent should have the general formula:



in which R is independently selected from alkyls and hydroxyl alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10

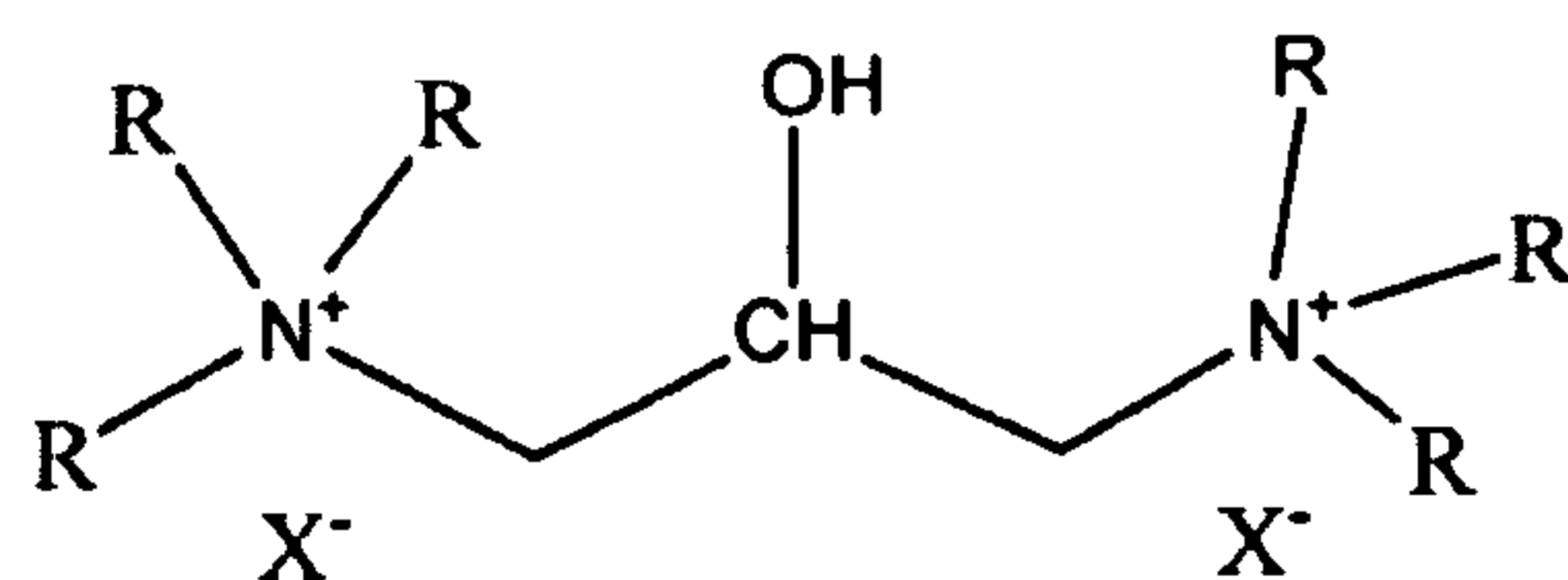
carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. The shale hydration inhibition agent is present in sufficient concentration to substantially reduce the swelling of shale drilling cuttings upon contact with the drilling fluid. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of the reaction of a tertiary amine and epichlorohydrine. Preferred tertiary amines are trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethylamine, and tripropanolamine. In a particularly preferred illustrative embodiment, the shale hydration inhibition agent is selected from:



as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another embodiment, R comprises 1 to 10 carbon atoms; and in another embodiment R

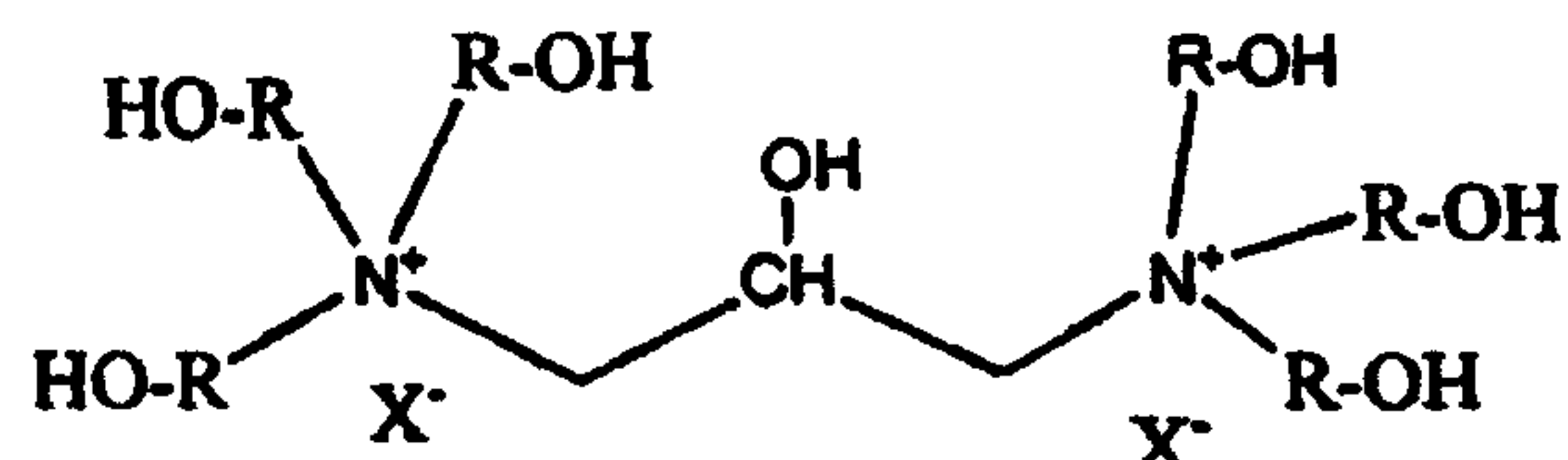
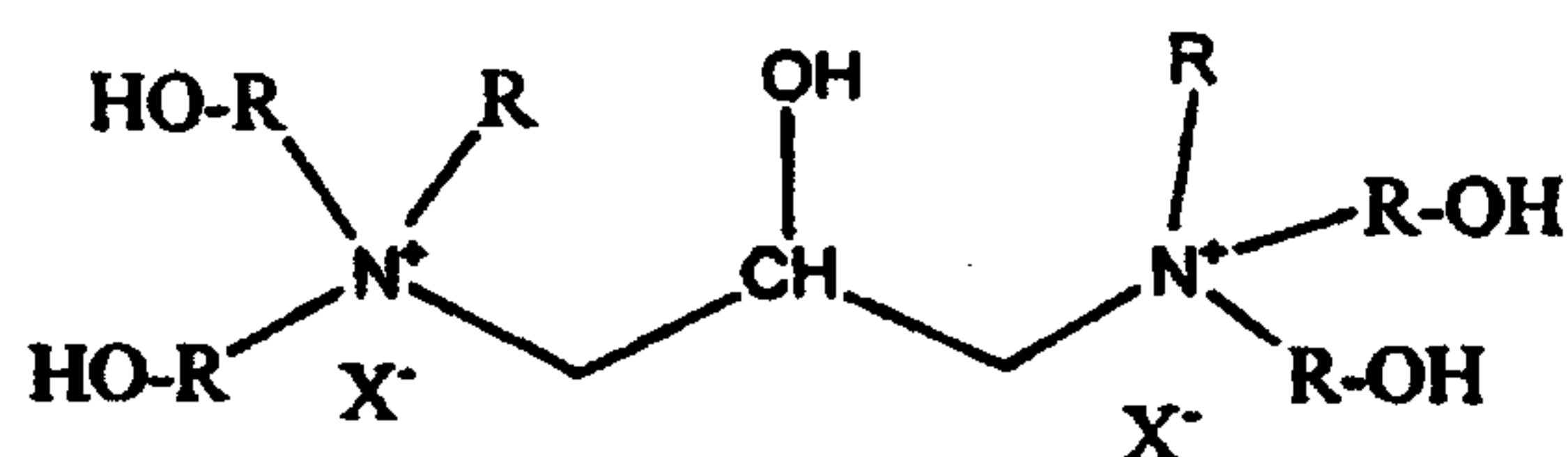
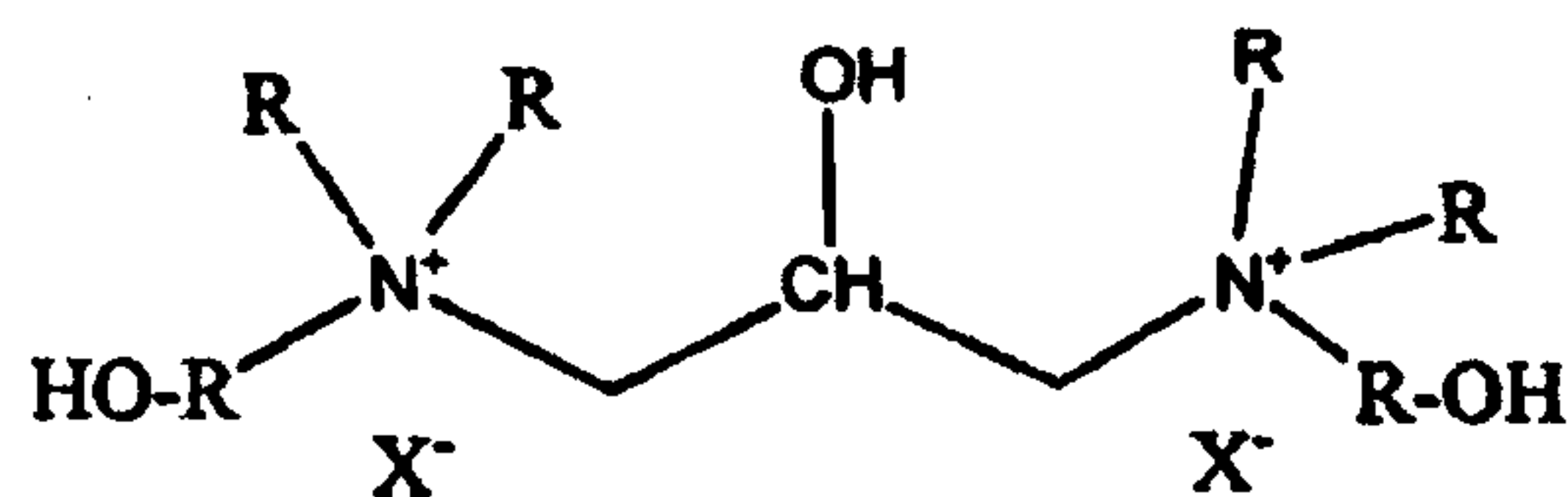
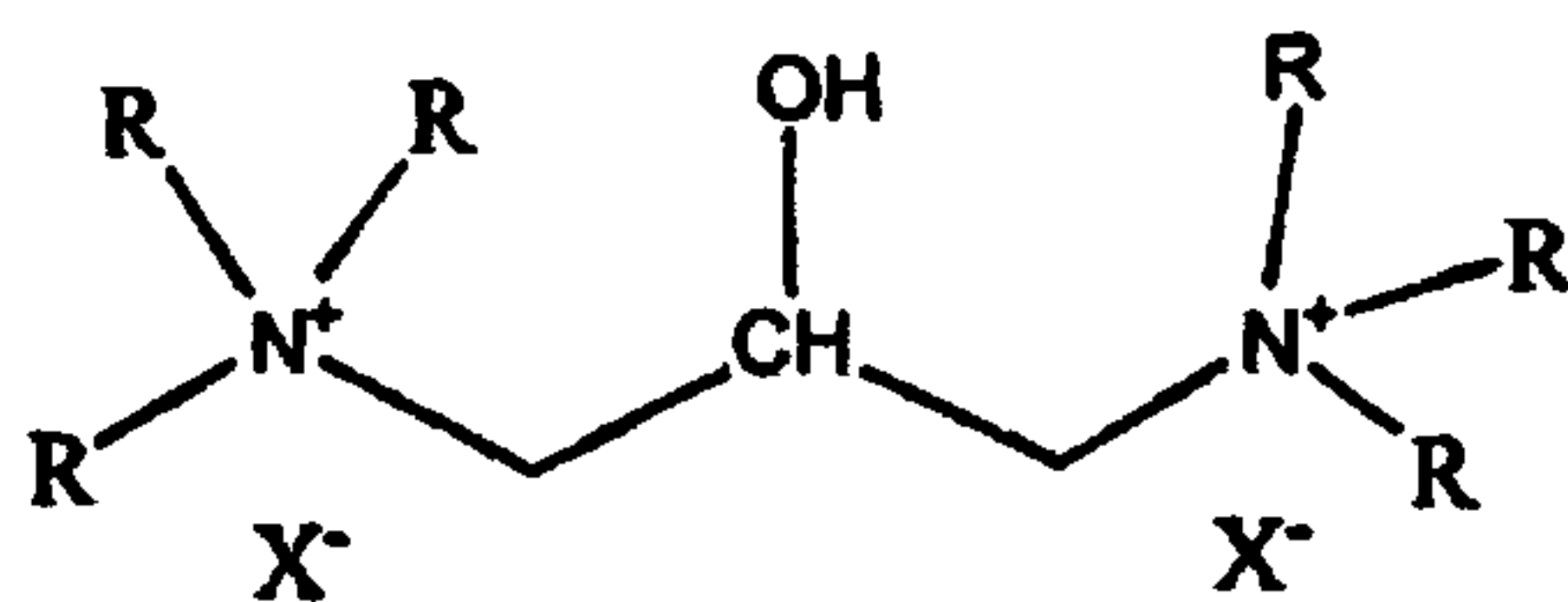
comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. The illustrative drilling fluid is formulated such that the aqueous based continuous phase is selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may also include a wide variety of conventional components of aqueous based drilling fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

[0037] The scope of the claimed subject matter also encompasses a fracturing fluid for use in a subterranean well in which the subterranean well penetrates through one or more subterranean formations composed of a shale that swells in the presence of water. One illustrative fluid is formulated to include an aqueous based continuous phase, a viscosifying agent and a shale hydration inhibition agent which is present in sufficient concentration to substantially reduce the swelling of shale. In one illustrative embodiment, the shale hydration inhibition agent has the formula:



in which R is independently selected from alkyls and hydroxyl alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10

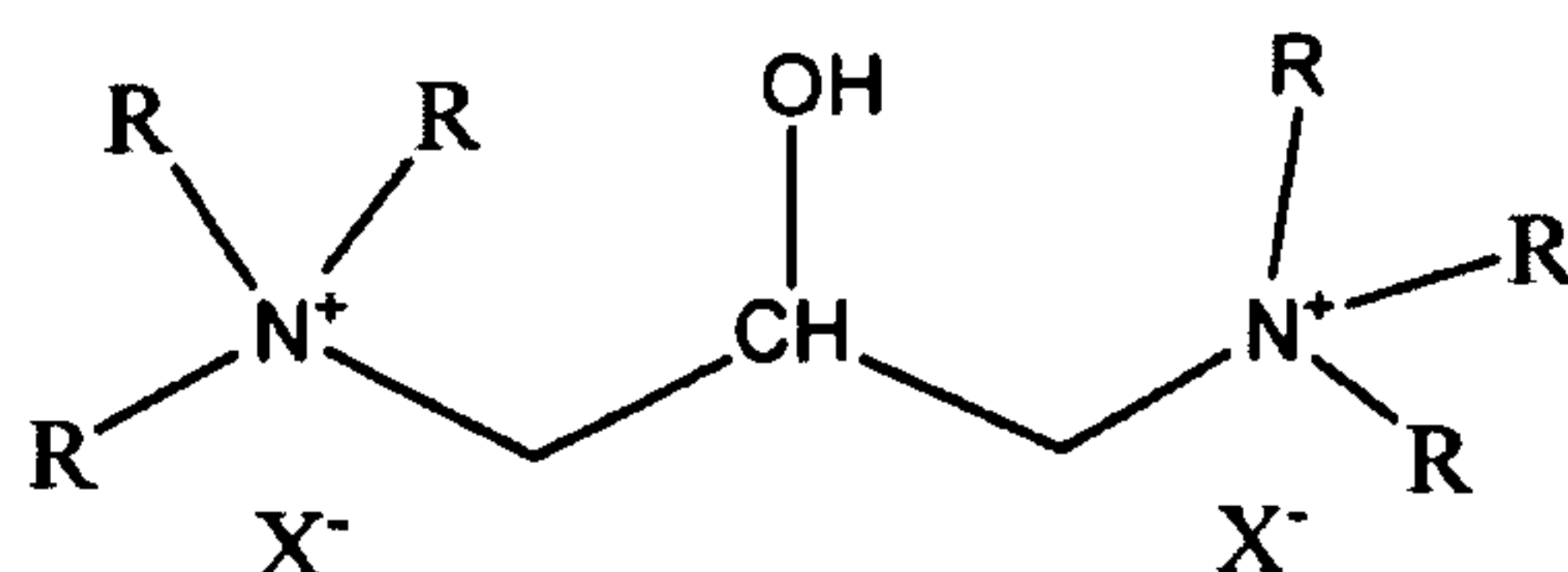
carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. Alternatively, the shale hydration inhibition agent of the illustrative fluid may be selected from:



as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another embodiment, R comprises 1 to 10 carbon atoms; and in another embodiment R comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of the reaction of a tertiary amine and epichlorohydrine. Preferred tertiary amines are trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethanolamine, and tripropanolamine. The illustrative fluid is formulated such that the aqueous based

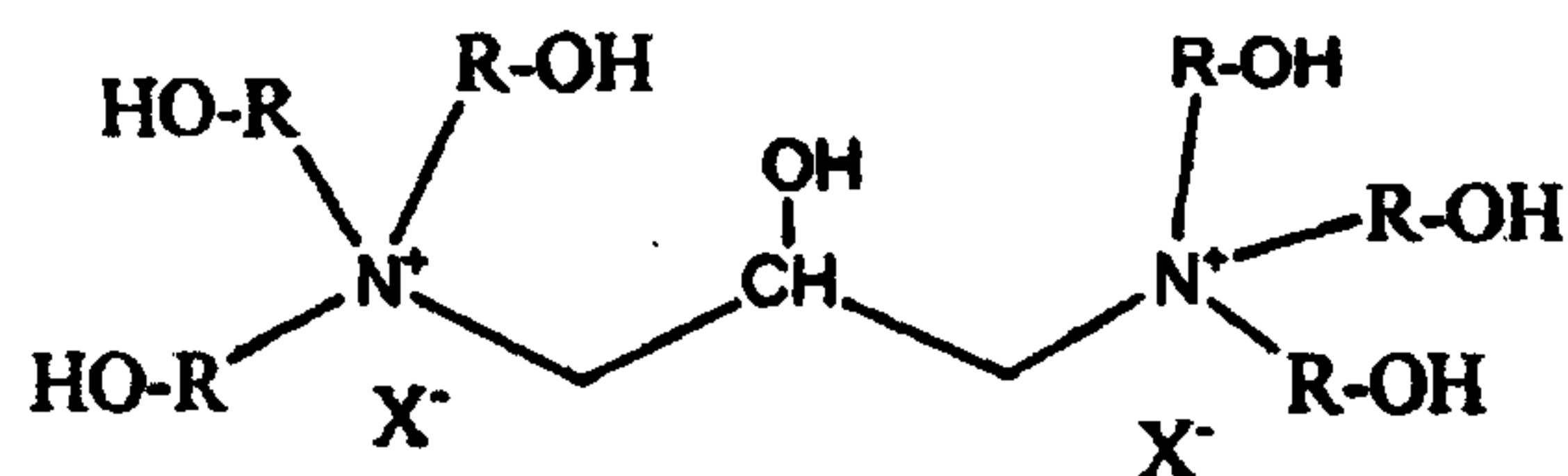
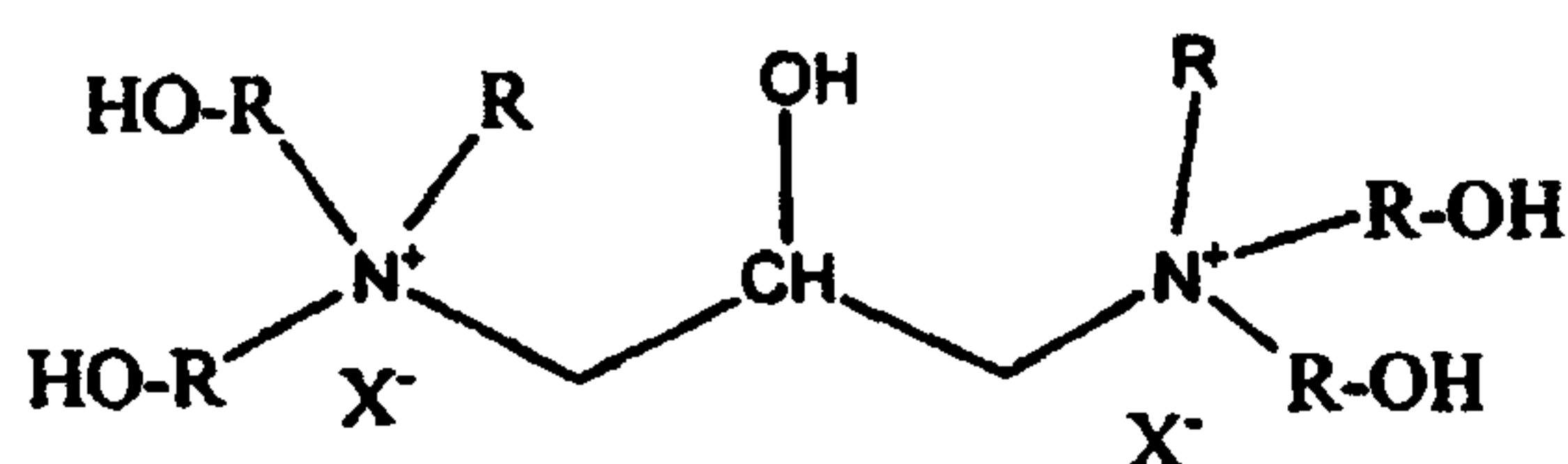
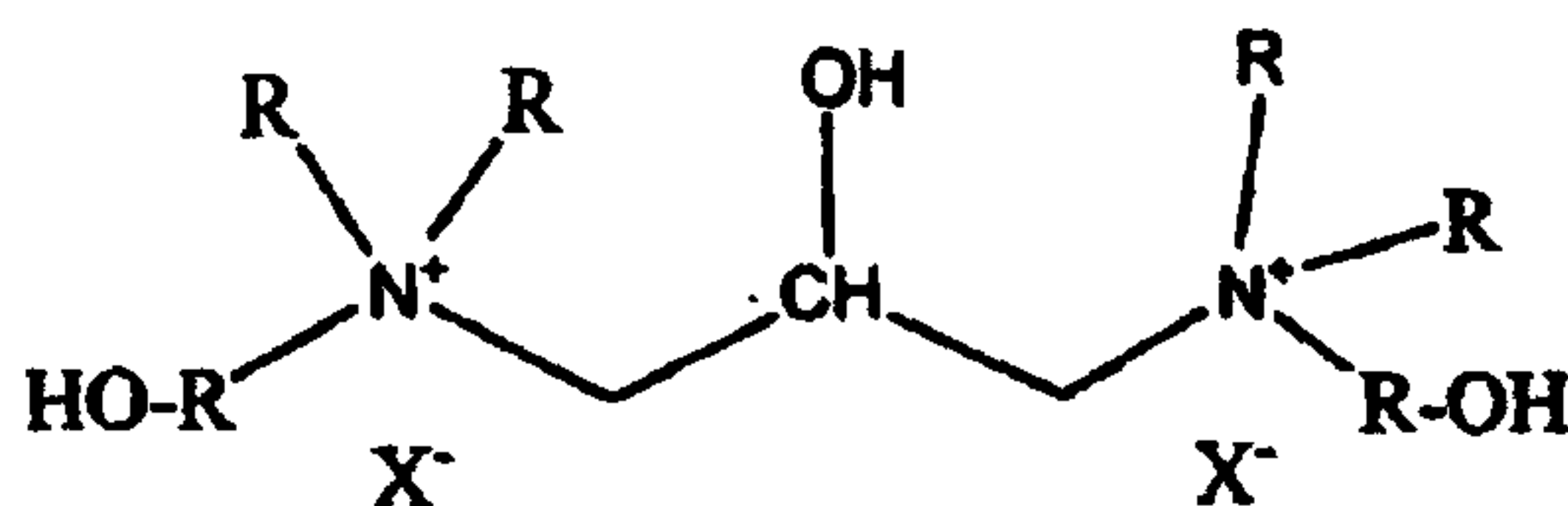
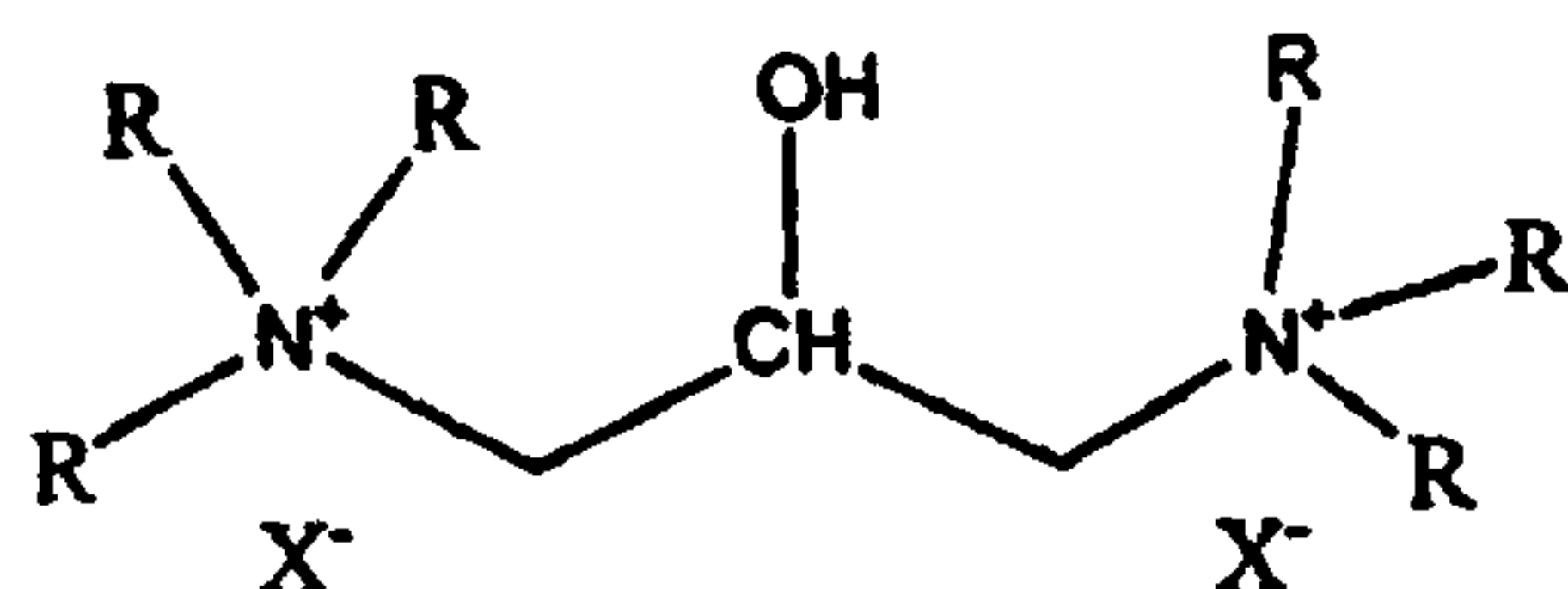
continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may also include a wide variety of conventional components of fracturing fluids, such as proppants such as sand, gravel, glass beads, ceramic materials and the like, acid release agents, fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

[0038] It should also be appreciated that the claimed subject matter inherently includes a composition that includes: an aqueous based continuous phase; a swellable shale material; and a shale hydration inhibition agent present in sufficient concentration to substantially reduce the swelling of the swellable shale material. Such a composition may be formed during the course of drilling a subterranean well, but also may be deliberately made if drill cuttings reinjection is to be carried out. In one illustrative embodiment, the shale hydration inhibition agent has the formula:



in which R is independently selected from alkyls and hydroxyl alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10 carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide

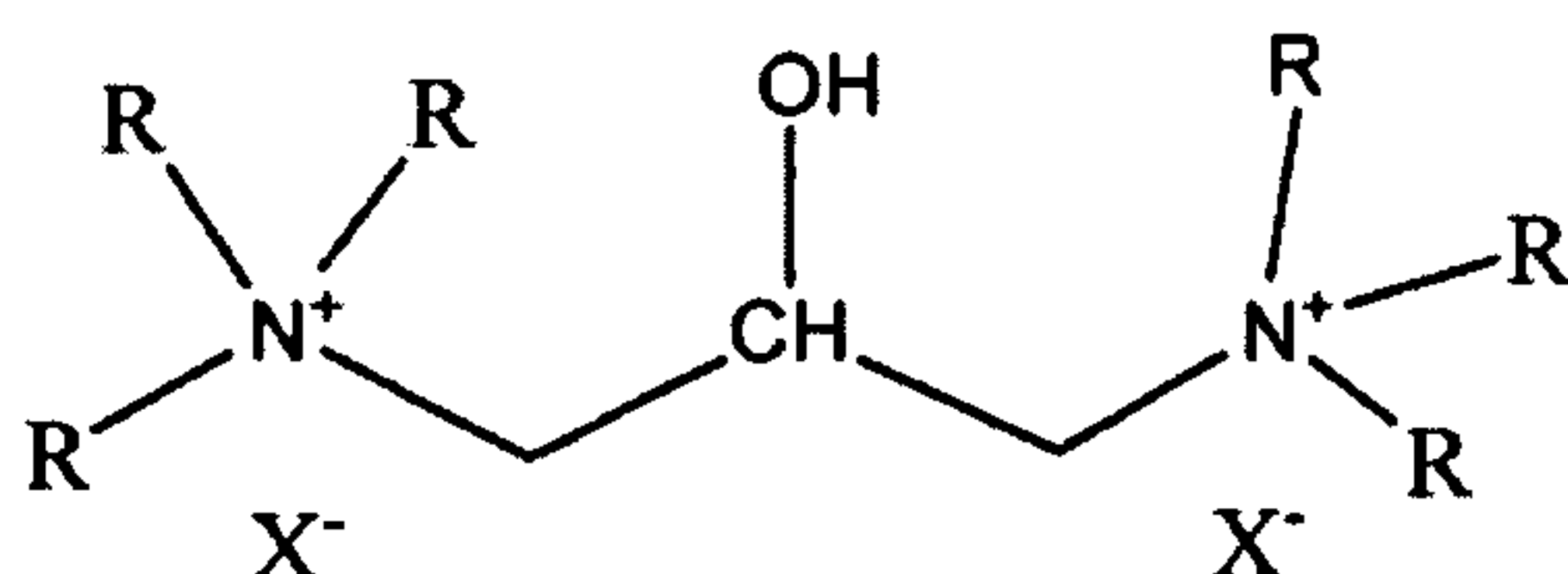
anions. Alternatively, the shale hydration inhibition agent of the illustrative composition may be selected from:



as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another embodiment, R comprises 1 to 10 carbon atoms, and in another embodiment R comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of the reaction of a tertiary amine and epichlorohydrine. Preferred tertiary amines are trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethylamine, and tripropanolamine. The illustrative composition is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations

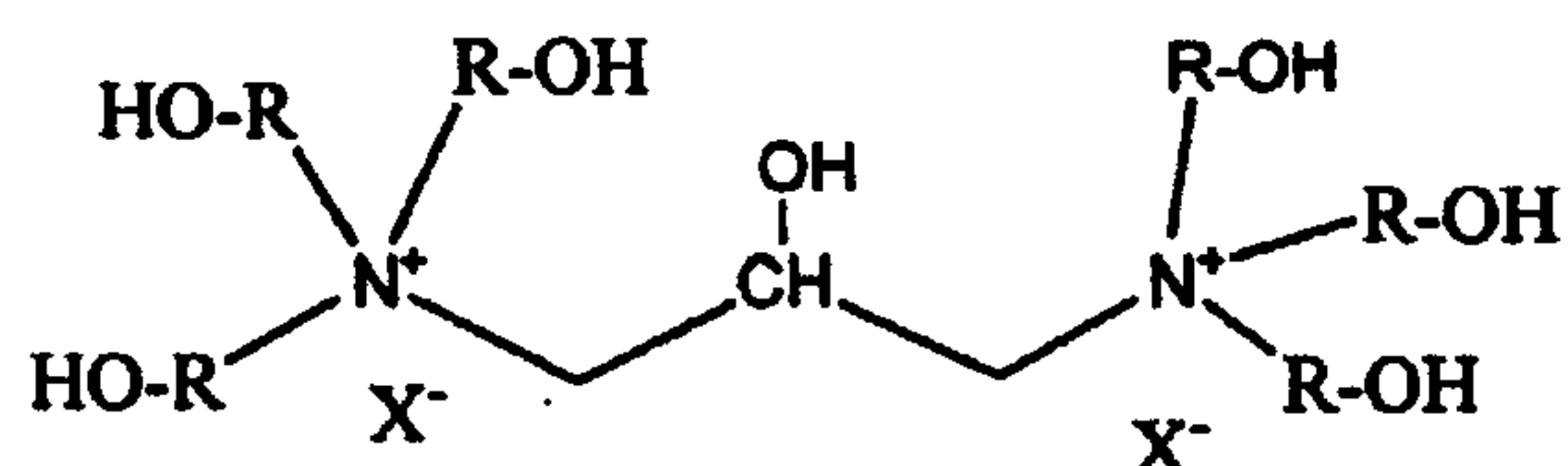
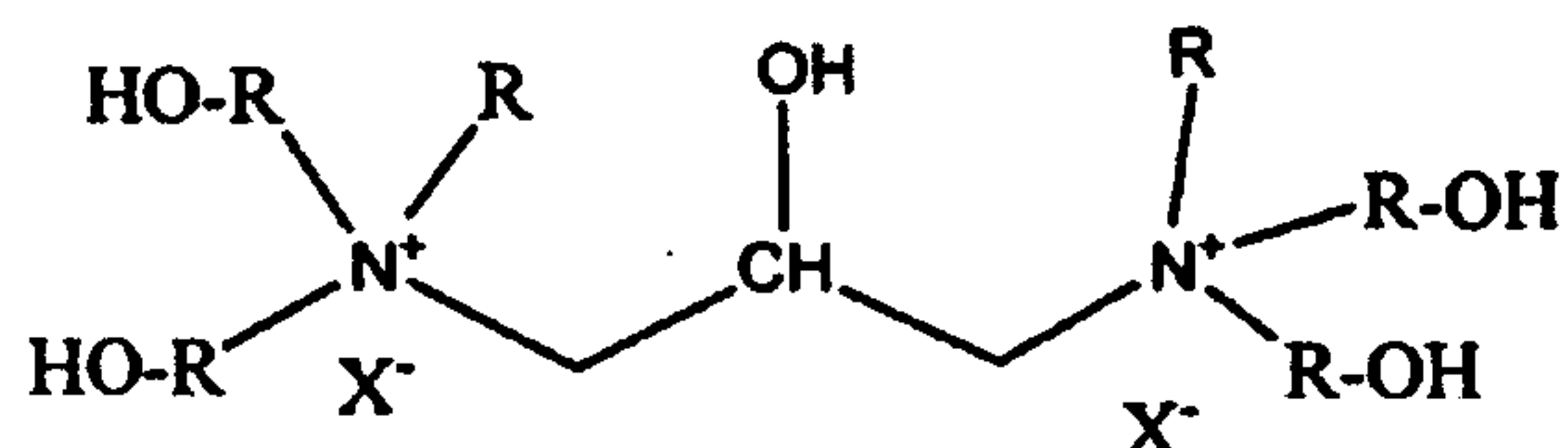
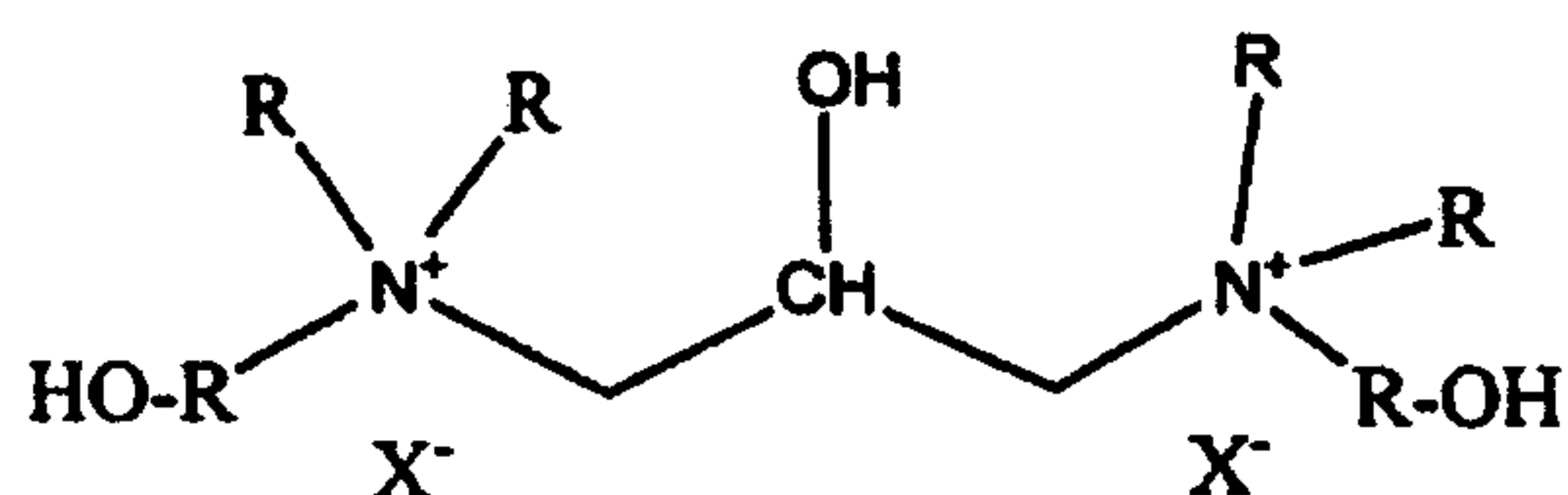
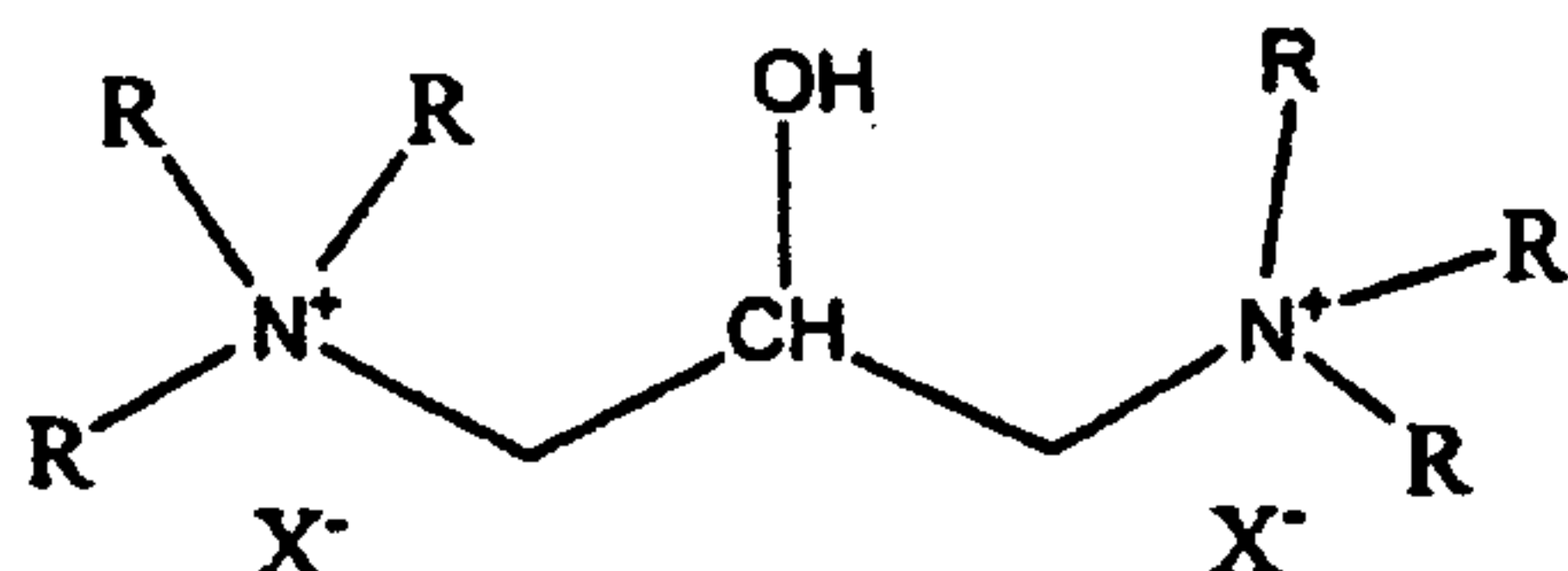
of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative composition. The illustrative composition may also include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

[0039] One of skill in the art should appreciate that the fluids of the claimed subject matter are useful during course of the drilling, cementing, fracturing, maintenance and production, workover, abandonment of a well or other operations associated with subterranean wells. In one illustrative embodiment, the fluids are utilized in a method involving the drilling a subterranean well through one or more subterranean formations containing a shale which swells in the presence of water. The illustrative method is carried out using conventional drilling means and techniques, however, the drilling fluid utilized is formulated to include: an aqueous based continuous phase; a weighting agent; and a shale hydration inhibition agent present in sufficient concentration to reduce the swelling of shale. In one illustrative embodiment, the shale hydration inhibition agent has the formula:



in which R is independently selected from alkyls and hydroxy alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10 carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some

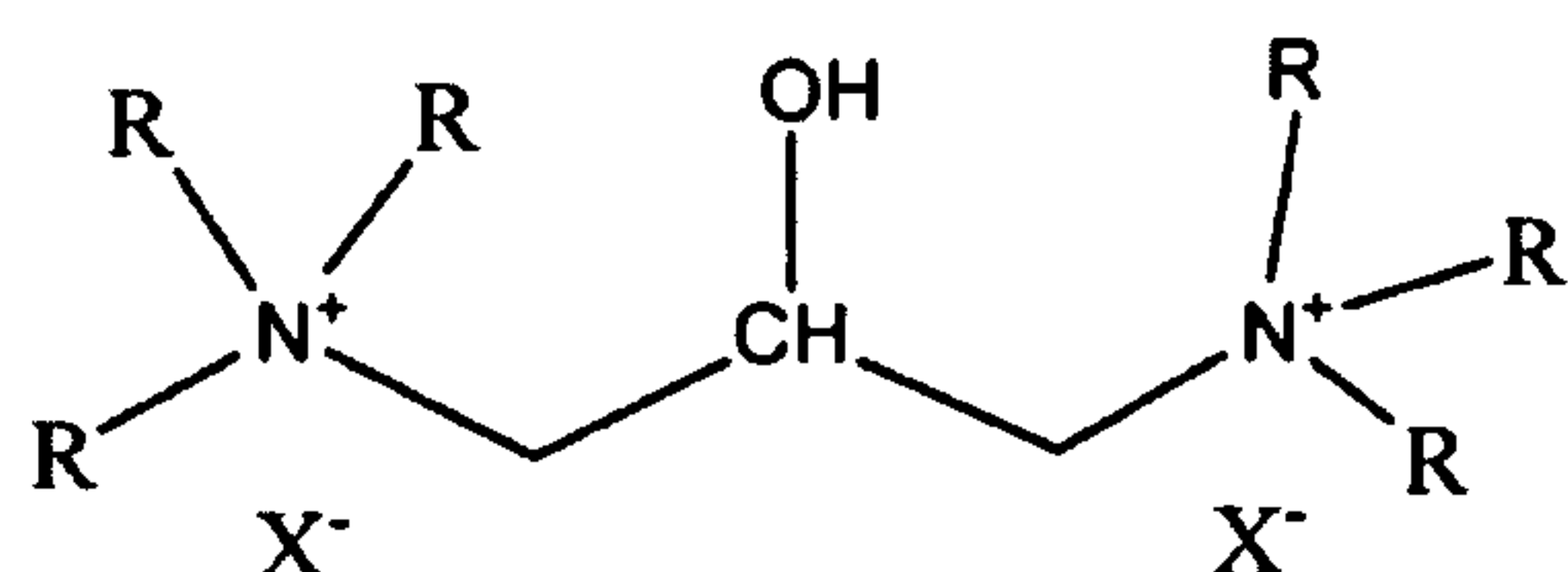
embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. Alternatively, the shale hydration inhibition agent of the illustrative composition may be selected from:



as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another embodiment, R comprises 1 to 10 carbon atoms; and in another embodiment R comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of the reaction of a tertiary amine and epichlorohydrine. Preferred tertiary amines are trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethanolamine, and tripropanolamine. The illustrative drilling fluid is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures

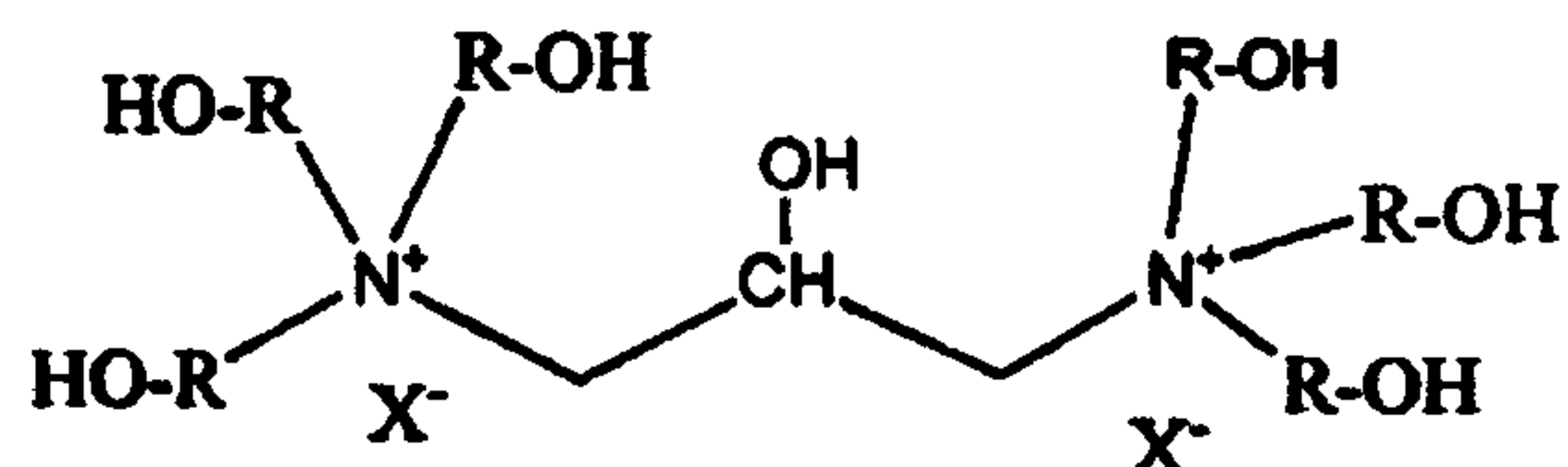
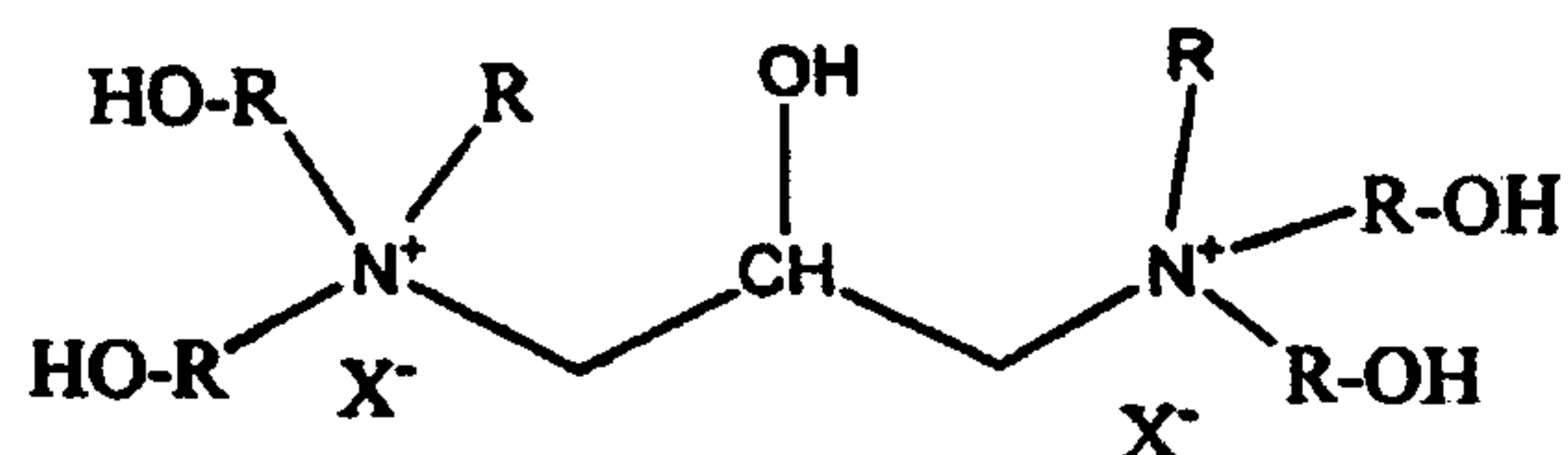
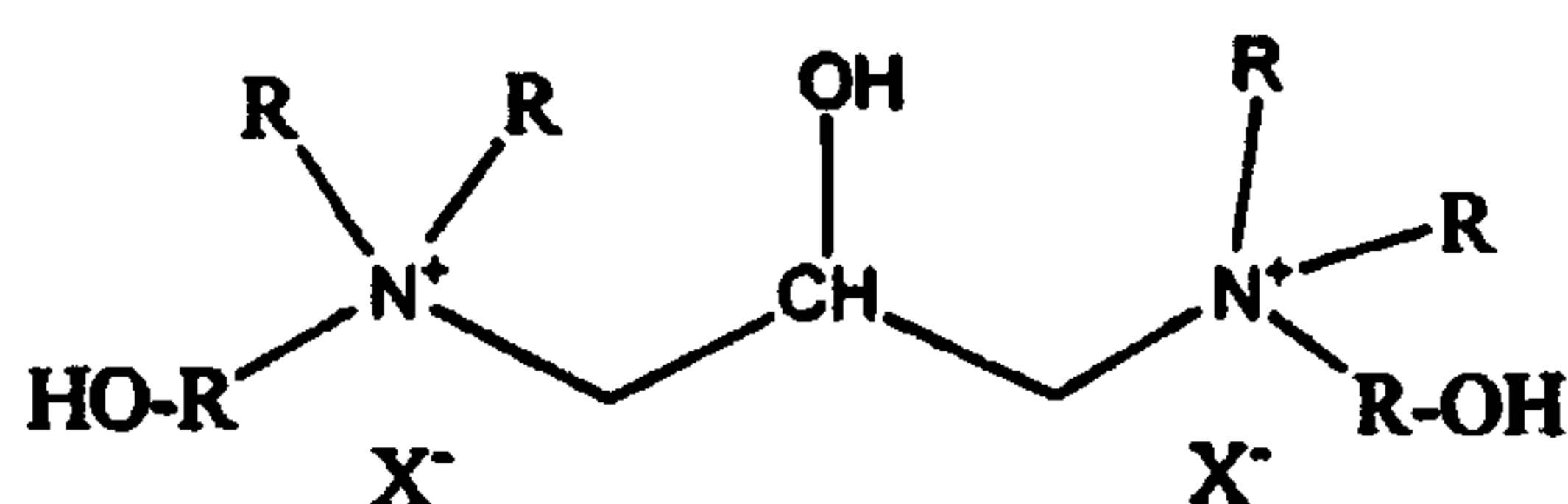
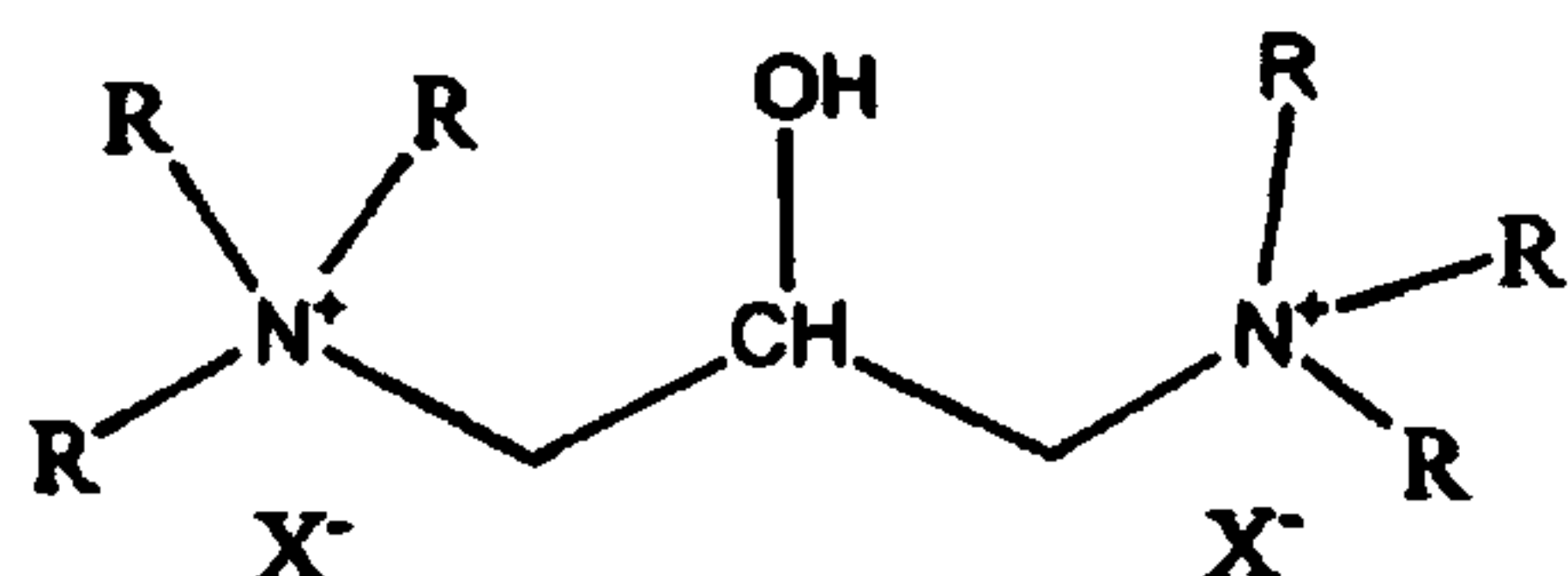
of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative drilling fluid. The illustrative drilling fluid may also include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

[0040] The claimed subject matter also includes a method of reducing the toxicity of a wellbore fluid for use in subterranean operations. One of skill in the art may appreciate that in some operations it may be desirable to provide non-toxic wellbore fluids. With this in mind, one of skill in the art may appreciate that in some embodiments, the method includes circulating a low-toxicity wellbore fluid in a wellbore, wherein the wellbore fluid is formulated to include: an aqueous based continuous phase and a shale hydration inhibition agent present in sufficient concentration to reduce the toxicity of the wellbore fluid. The shale hydration inhibition agent utilized in the formulation of the fluid is that which is substantive described above. That is to say the shale hydration inhibition agent utilized in one embodiment of the illustrative method has the formula:



in which R is independently selected from alkyls and hydroxy alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10 carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some

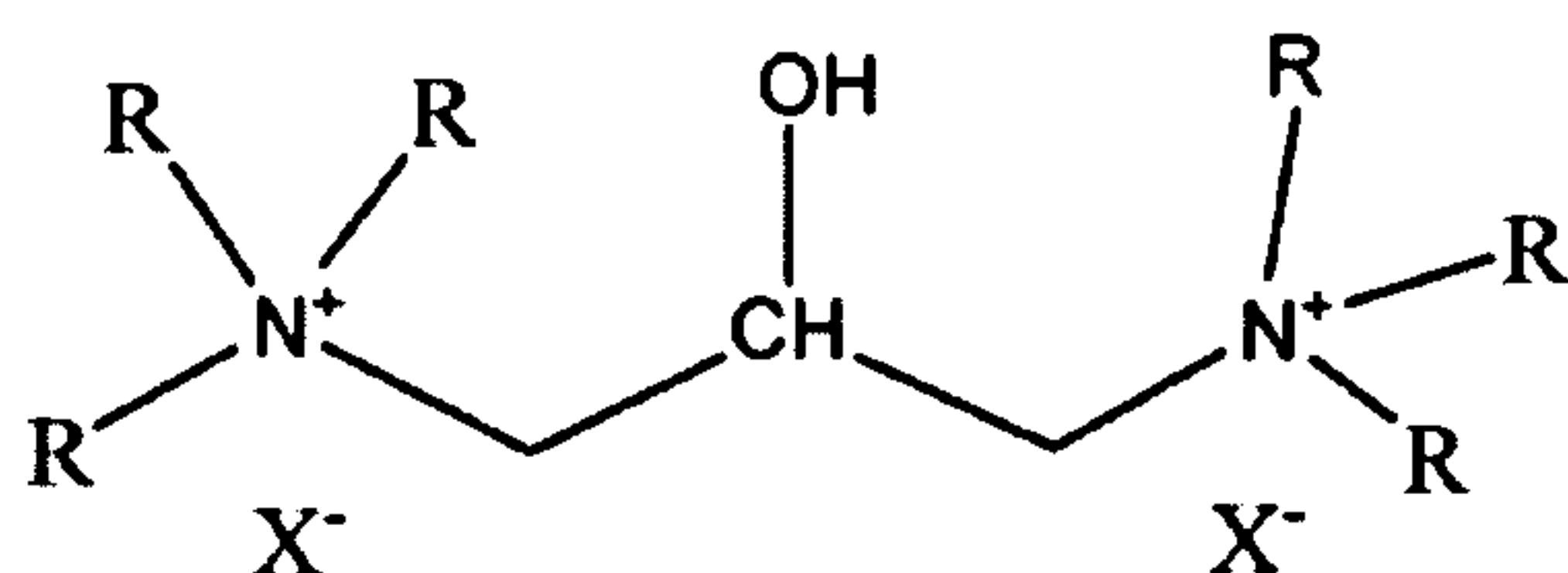
embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. Alternatively, the shale hydration inhibition agent of the illustrative composition may be selected from:



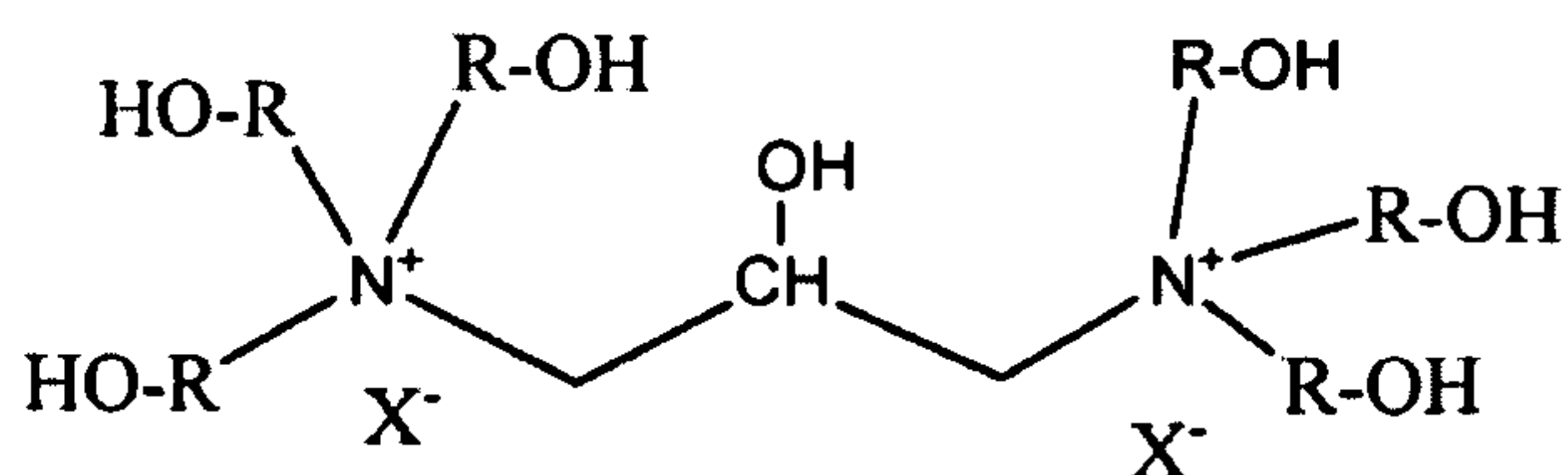
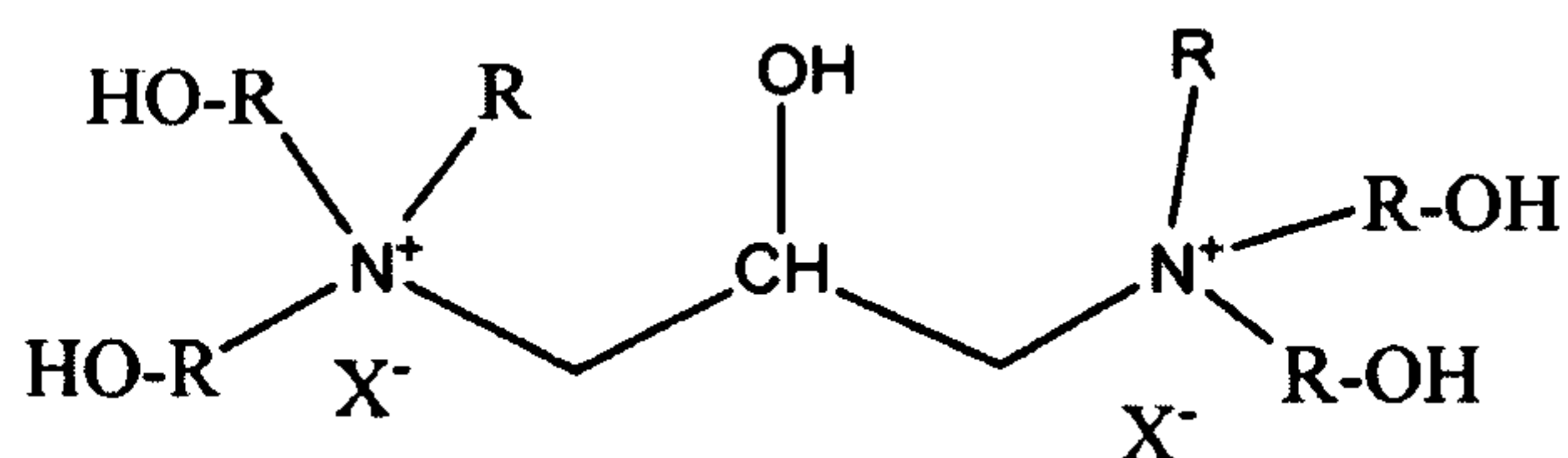
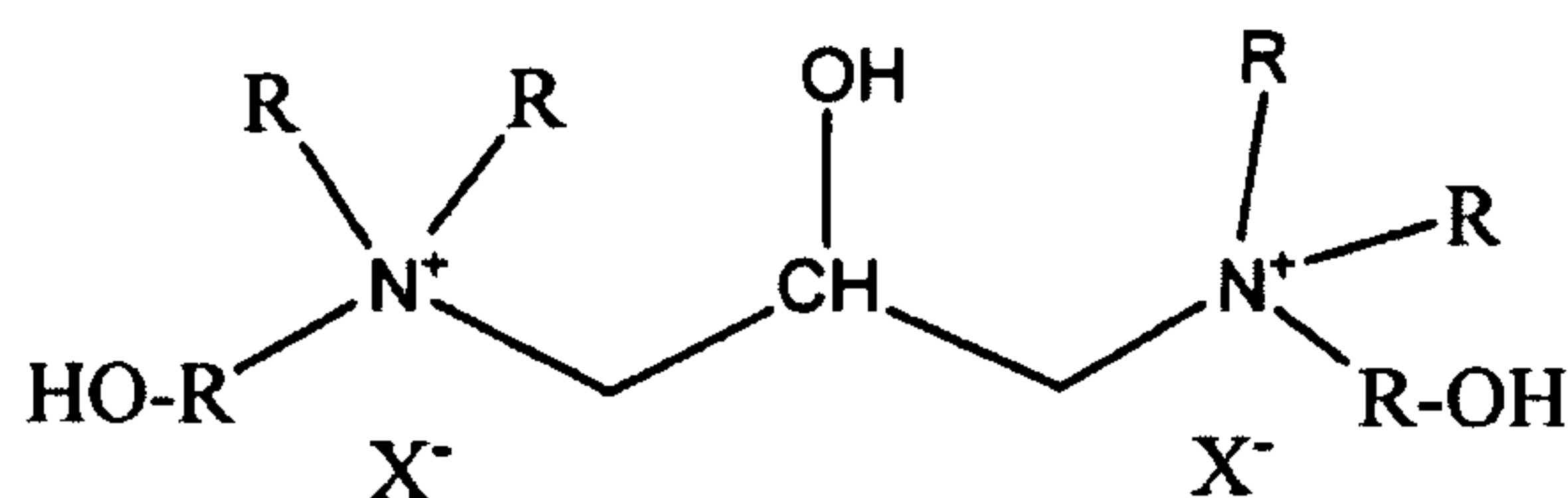
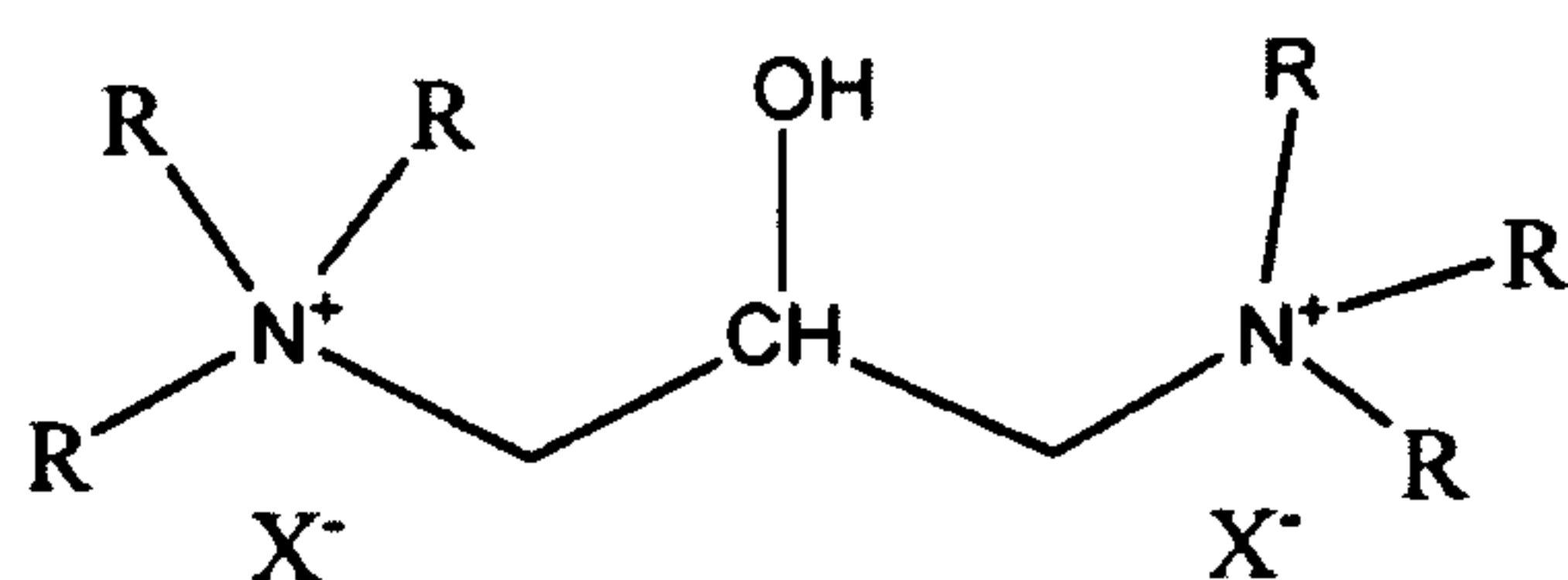
as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another embodiment, R comprises 1 to 10 carbon atoms; and in another embodiment R comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of the reaction of a tertiary amine and epichlorohydrine. Preferred tertiary amines are trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethanolamine, and tripropanolamine. The illustrative fluid is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of

water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may optionally include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about. In some embodiments, the wellbore fluids comprises EC₅₀(15) values greater than 50%. In other embodiments, the EC₅₀(15) values are greater than 70%, and in yet other embodiments, the EC₅₀(15) values are greater than 90%.

[0041] The claimed subject matter also includes a method of disposing of drill cuttings into a subterranean formation. As should be well known to one of skill in the art, this involves grinding the drill cuttings, which have been previously separated from the recirculating drilling fluid, in the presence of a fluid to form a slurry. The slurry is then injected by way of a well into a suitable subterranean formation for disposal. With this in mind a person of skill should appreciate that one illustrative embodiment of the claimed subject matter includes: grinding drill cuttings in a water-base fluid to form a slurry, in which the water based fluid is formulated to include: an aqueous based continuous phase and a shale hydration inhibition agent present in sufficient concentration to substantially reduce the swelling of the shale and then injecting the slurry into the subterranean formation designated for disposal of the cuttings. The shale hydration inhibition agent utilized in the formulation of the fluid is that which is substantive described above. That is to say the shale hydration inhibition agent utilized in one embodiment of the illustrative method has the formula:



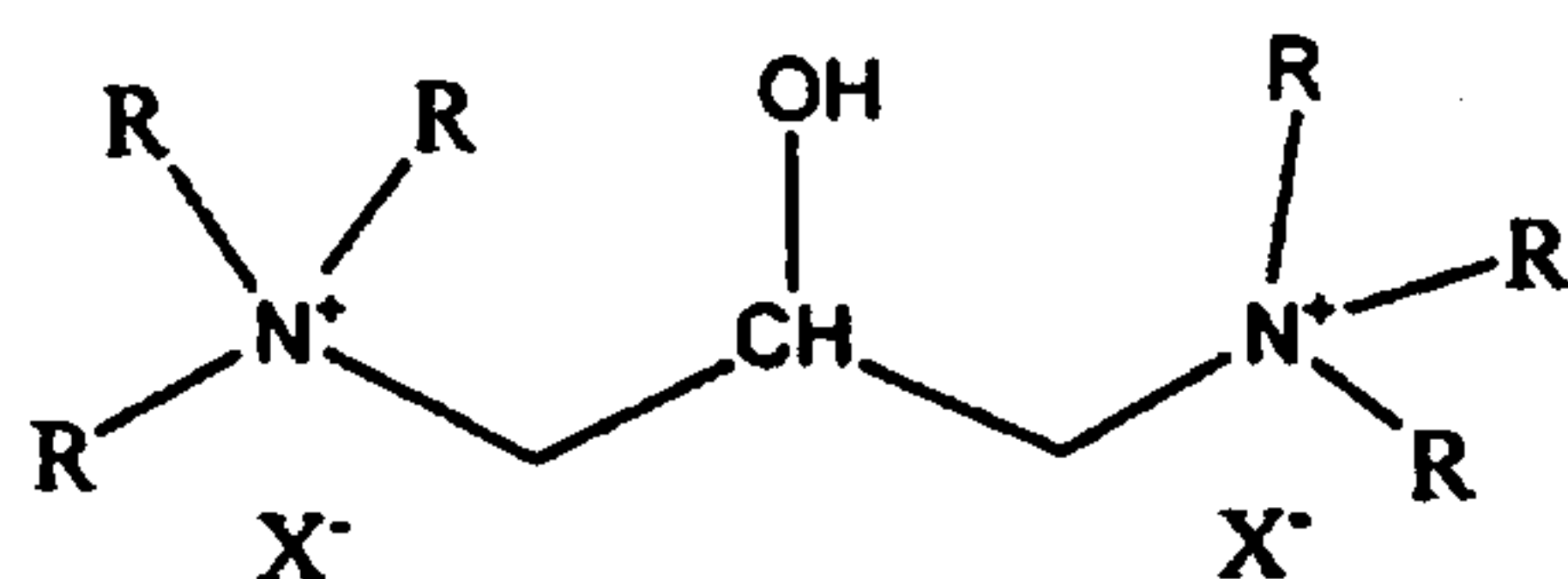
in which R is independently selected from alkyls and hydroxy alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10 carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. Alternatively, the shale hydration inhibition agent of the illustrative composition may be selected from:



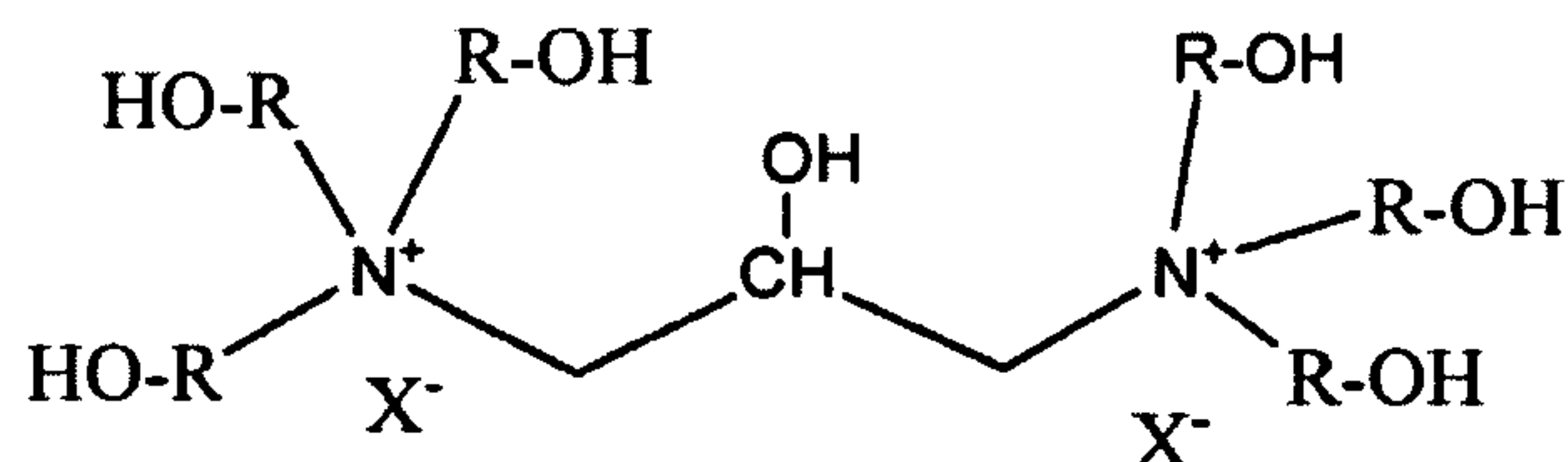
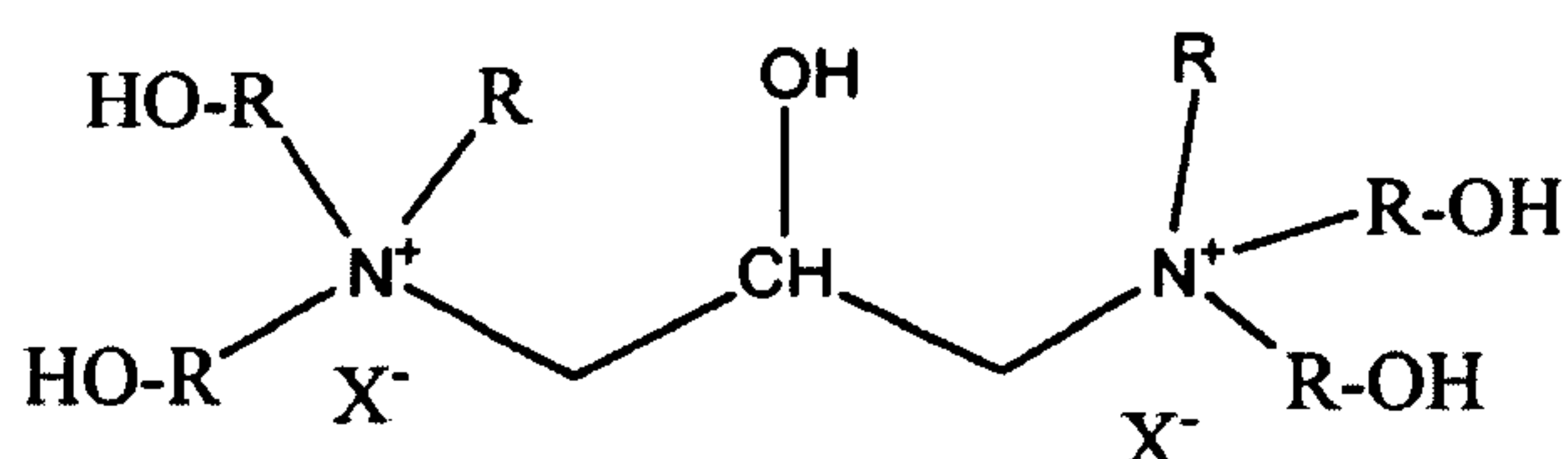
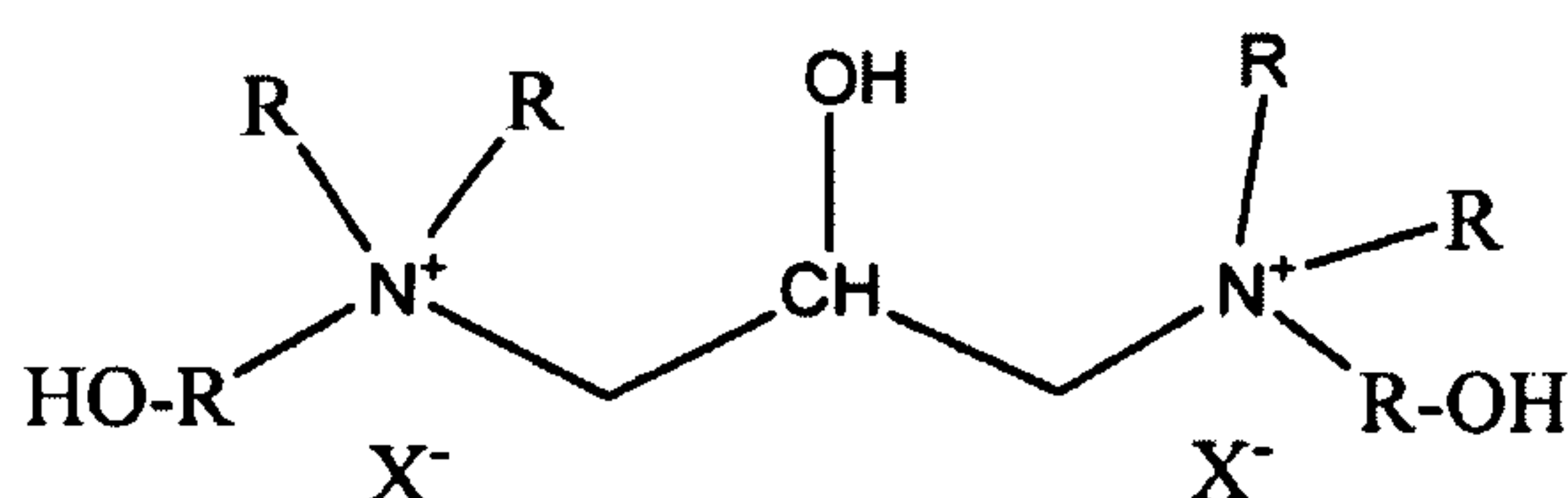
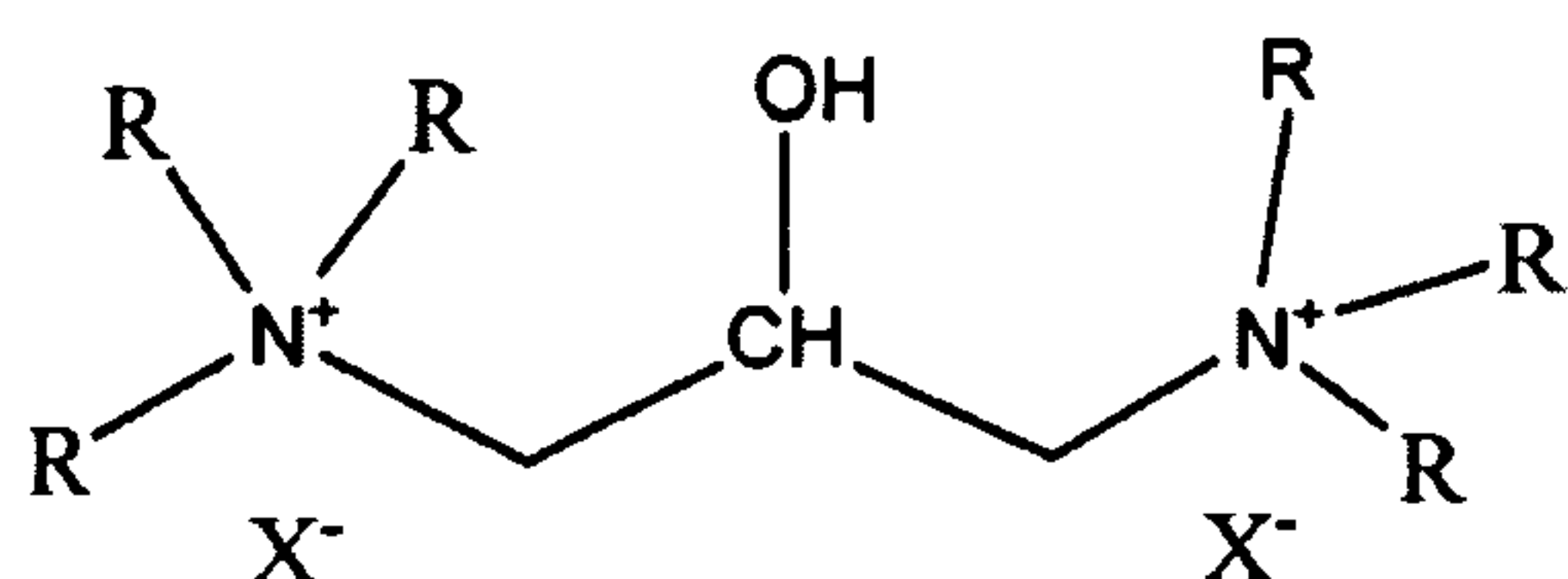
as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another

embodiment, R comprises 1 to 10 carbon atoms;, and in another embodiment R comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of the reaction of a tertiary amine and epichlorohydrine. Preferred tertiary amines are trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethylamine, and tripropanolamine. The illustrative fluid is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may optionally include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

[0042] It should also be appreciated by one of skill in the art that the claimed subject matter inherently includes a method of reducing the swelling of shale clay in a well comprising circulating in the well a water-base drilling fluid formulated as is substantially disclosed herein. One such illustrative fluid includes: an aqueous based continuous phase and a shale hydration inhibition agent present in sufficient concentration to reduce the swelling of the shale. That is to say the shale hydration inhibition agent utilized in one embodiment of the illustrative method has the formula:



in which R is independently selected from alkyls and hydroxy alkyls, and X is an anion. In one embodiment, R is independently selected from alkyls and hydroxyl alkyls comprising 1 to 15 carbon atoms; in another embodiment, comprising 1 to 10 carbon atoms; and in another embodiment, comprising 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. Alternatively, the shale hydration inhibition agent of the illustrative composition may be selected from:



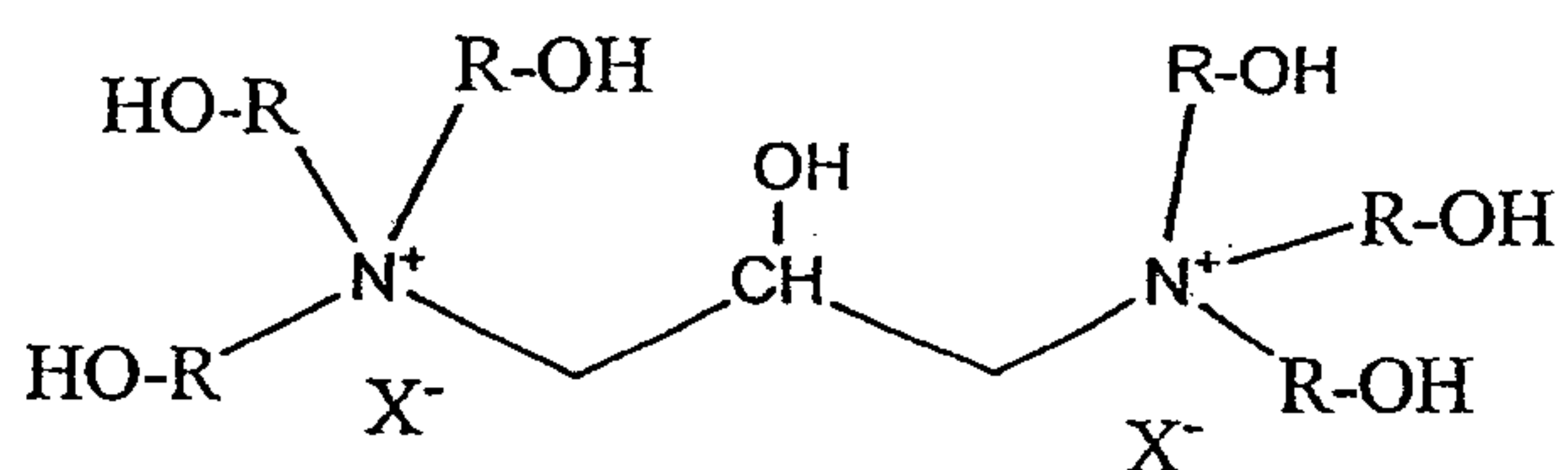
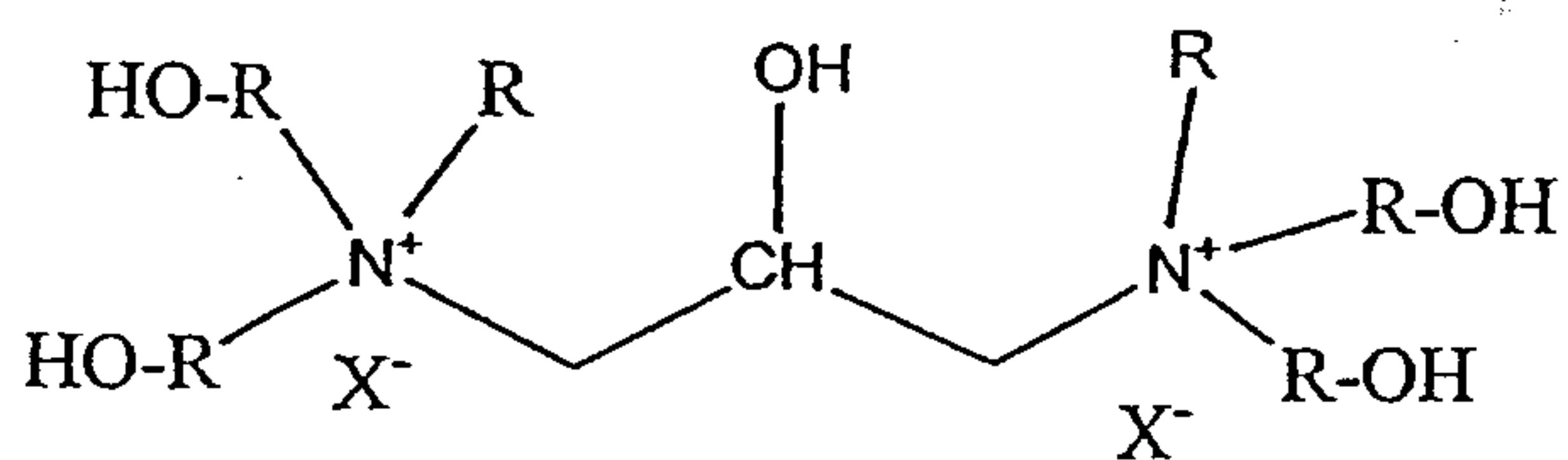
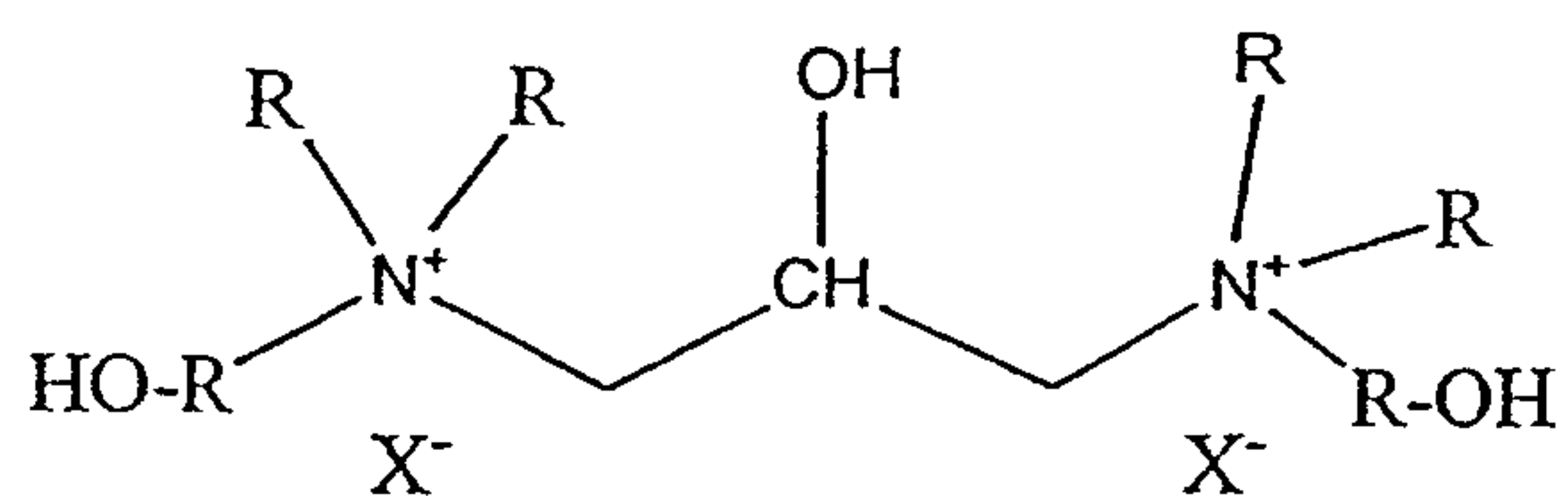
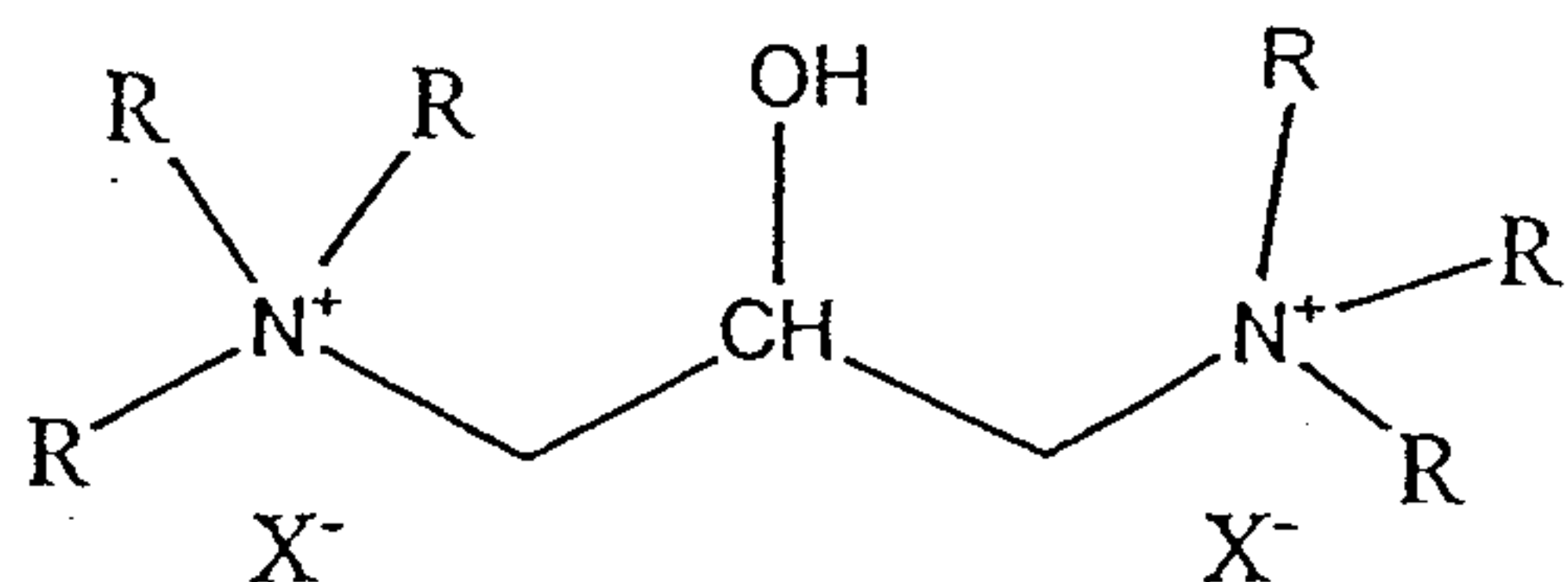
as well as mixtures of these, wherein X is an anion, and R is an alkyl side chain. In one embodiment, R is an alkyl chain comprising 1 to 15 carbon atoms; in another embodiment, R comprises 1 to 10 carbon atoms; and in another embodiment R comprises 1 to 7 carbon atoms. In some embodiments, X is selected from halide, sulfate, phosphate, carbonate, and hydroxide anions. As noted above, the illustrative shale hydration inhibition agent is preferably the reaction product of the reaction of a

tertiary amine and epichlorohydrine. Preferred tertiary amines are trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethylaniline, and tripropanolamine. Alternatively the shale hydration inhibition agent may be the reaction product of the reaction of diethanolamine and acrylonitrile. The illustrative fluid is formulated such that the aqueous based continuous phase may be selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds as well as mixtures and combinations of these and similar aqueous based fluids that should be known to one of skill in the art. In one illustrative embodiment, an optional viscosifying agent is included in the drilling fluid and the viscosifying agent is preferably selected mixtures and combinations of compounds that should be known to one of skill in the art such as xanthan gums, starches, modified starches and synthetic viscosifiers such as polyacrylamides, and the like. A weighting material such as barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, as well as mixtures and combinations of these and similar compounds that should be known to one of skill in the art may also be included into the formulation of the illustrative fluid. The illustrative fluid may optionally include a wide variety of conventional components of drilling and well bore fluids, such as fluid loss control agents, suspending agents, viscosifying agents, rheology control agents, as well as other compounds and materials that one of skill in the art would be knowledgeable about.

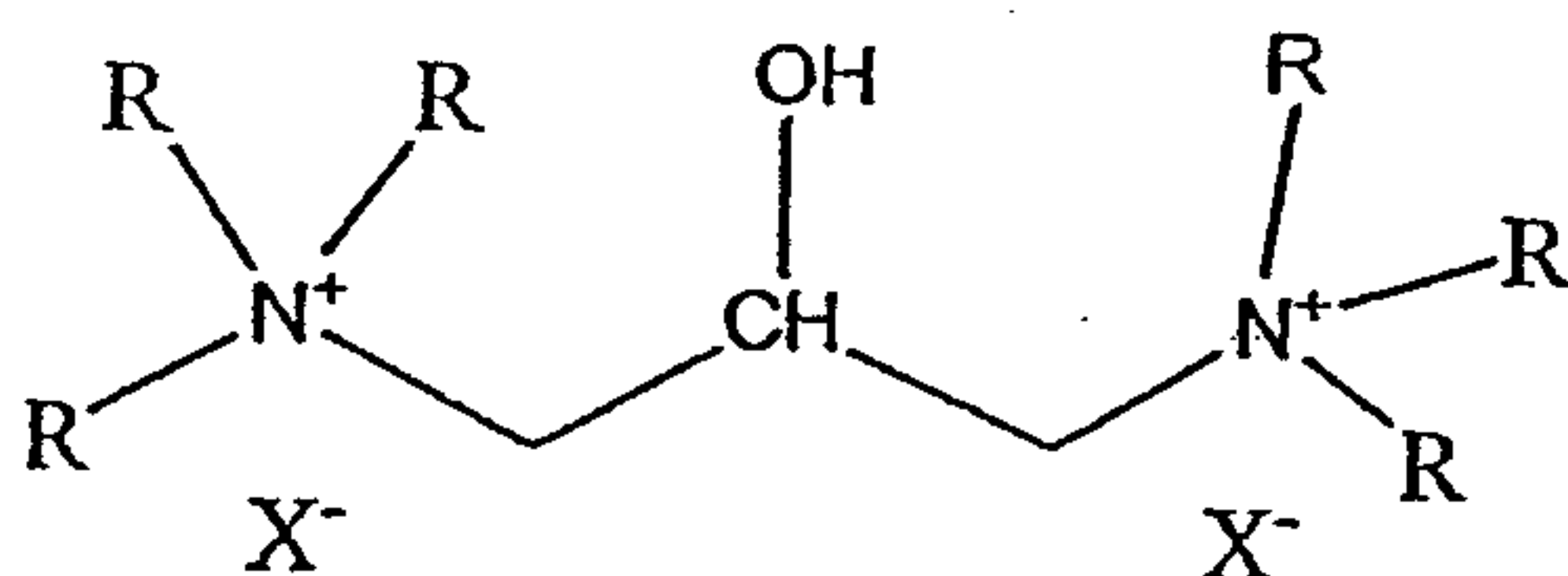
[0043] While the compositions and methods of this claimed subject matter have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the process described herein without departing from the concept and scope of the claimed subject matter. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the scope and concept of the claimed subject matter as it is set out in the following claims.

WHAT IS CLAIMED IS:

1. A drilling fluid for use in drilling a subterranean well through one or more subterranean formations containing a shale which swells in the presence of water, the fluid comprising:
- an aqueous based continuous phase;
 - a viscosifying agent and
 - a shale hydration inhibition agent, wherein the shale hydration inhibition agent is selected from:

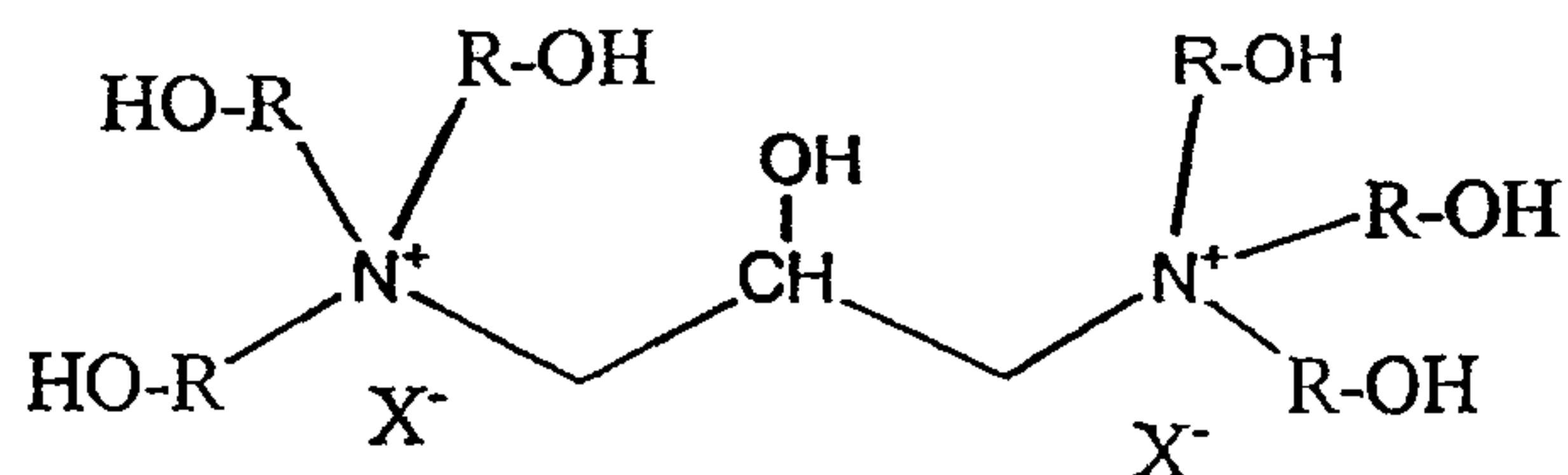
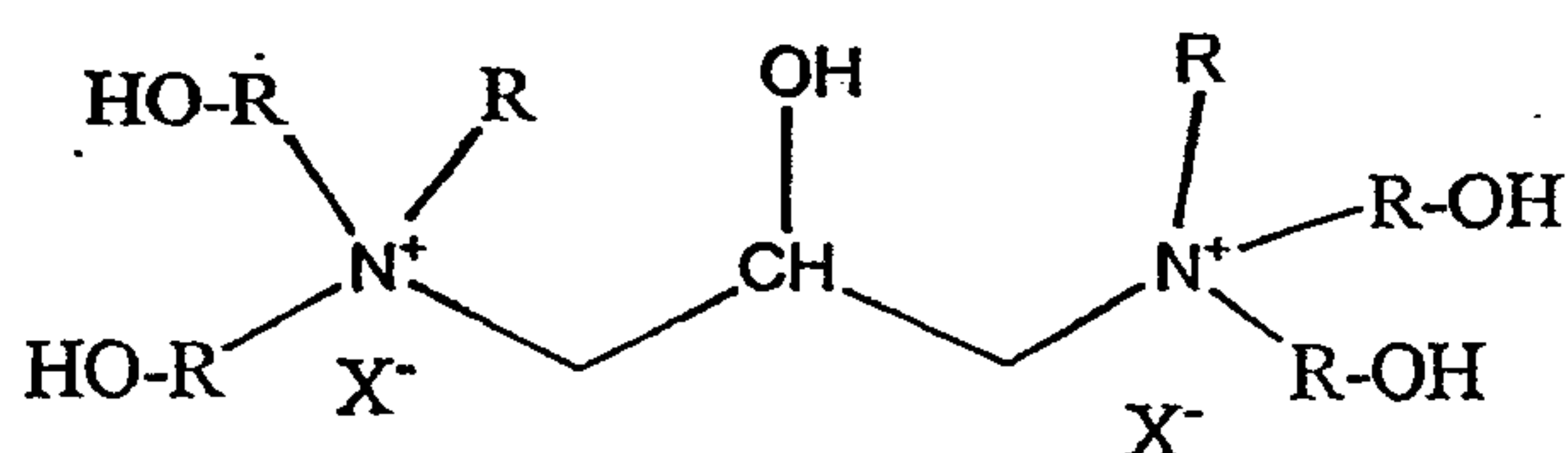
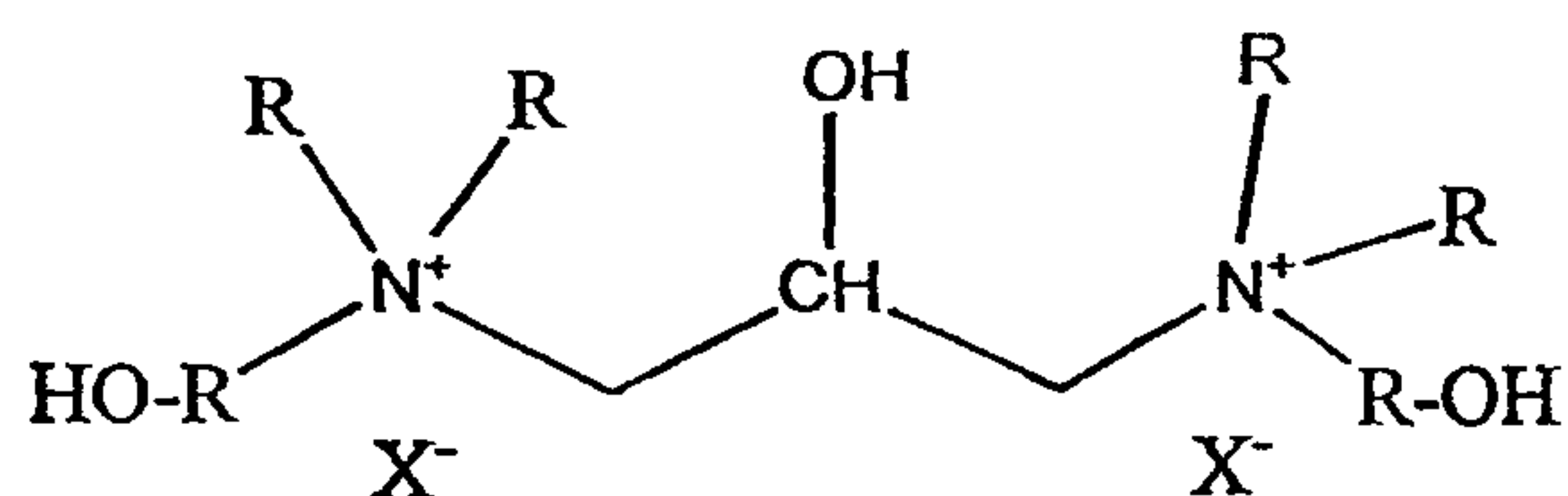
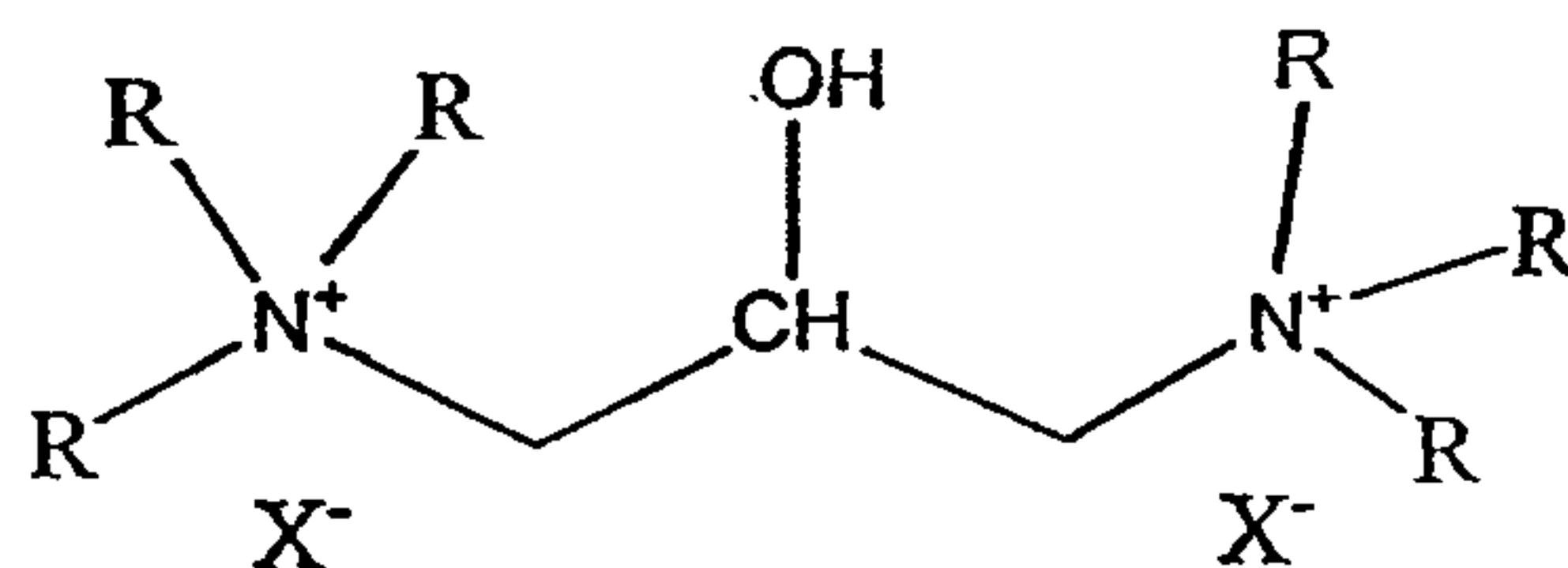


as well as mixtures of these, wherein R is an alkyl chain comprising 1 to 15 carbon atoms, and X is an anion;

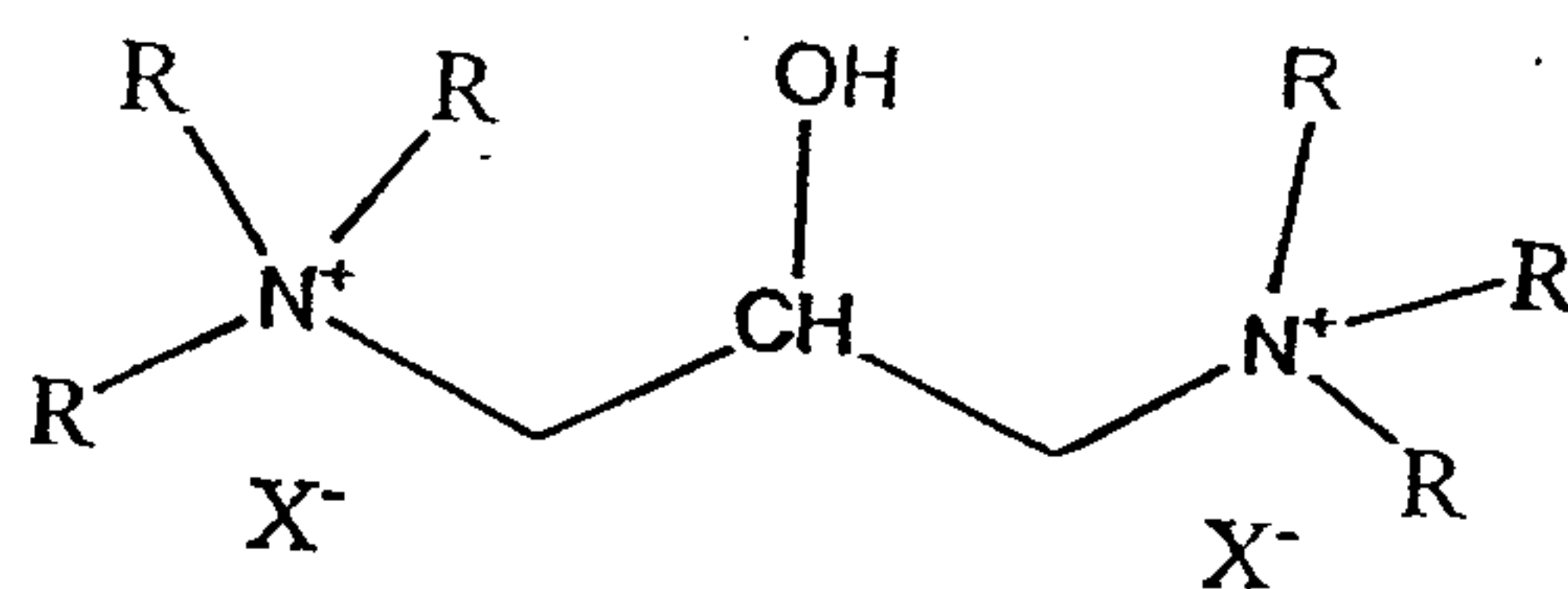


and wherein the shale hydration inhibition agent is present in sufficient concentration to reduce the swelling of shale.

2. The composition of claim 1 further comprising a weighing material selected from the group consisting of barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, and mixtures thereof.
3. A fracturing fluid for use in a subterranean well through one or more subterranean formations containing a shale which swells in the presence of water, the fluid comprising:
 - an aqueous based continuous phase;
 - a viscosifying agent and
 - a shale hydration inhibition agent, wherein the shale hydration inhibition agent is selected from:



as well as mixtures of these, wherein R is an alkyl chain comprising 1 to 15 carbon atoms, and X is an anion;



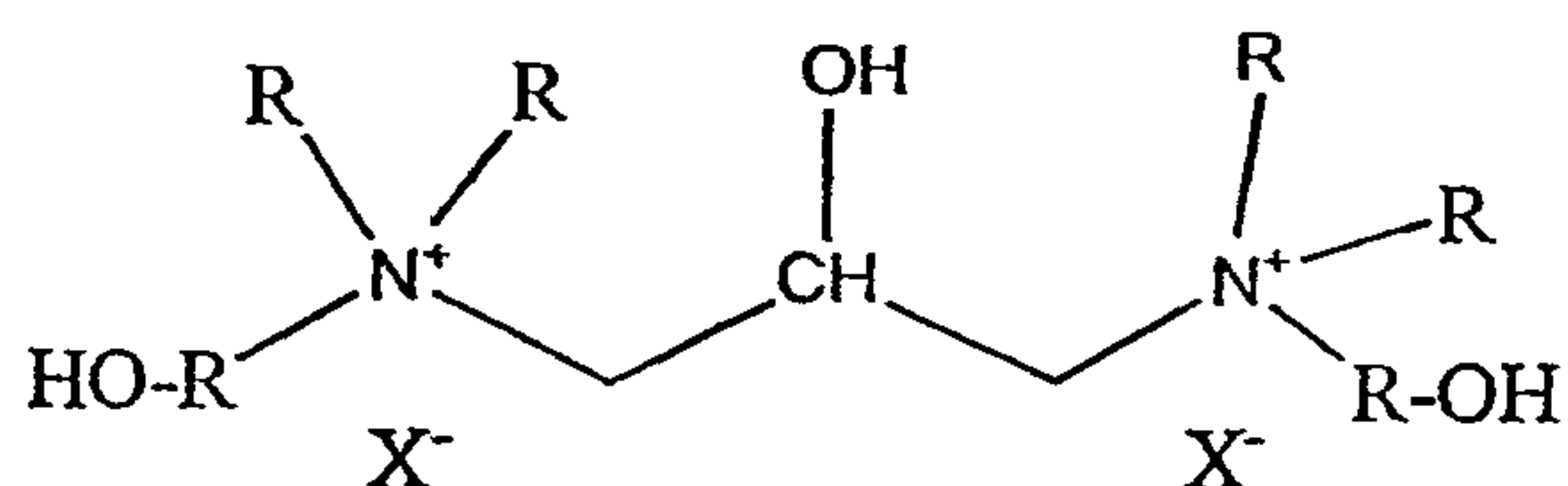
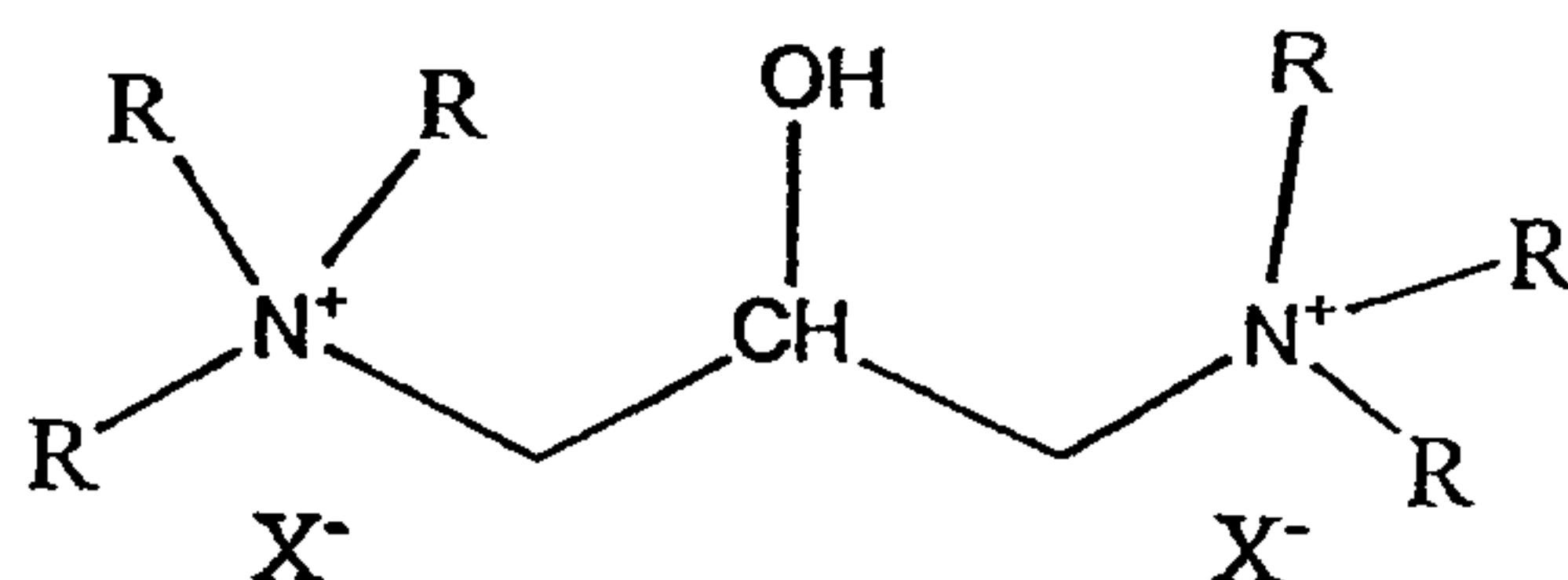
and wherein the shale hydration inhibition agent is present in sufficient concentration to reduce the swelling of shale.

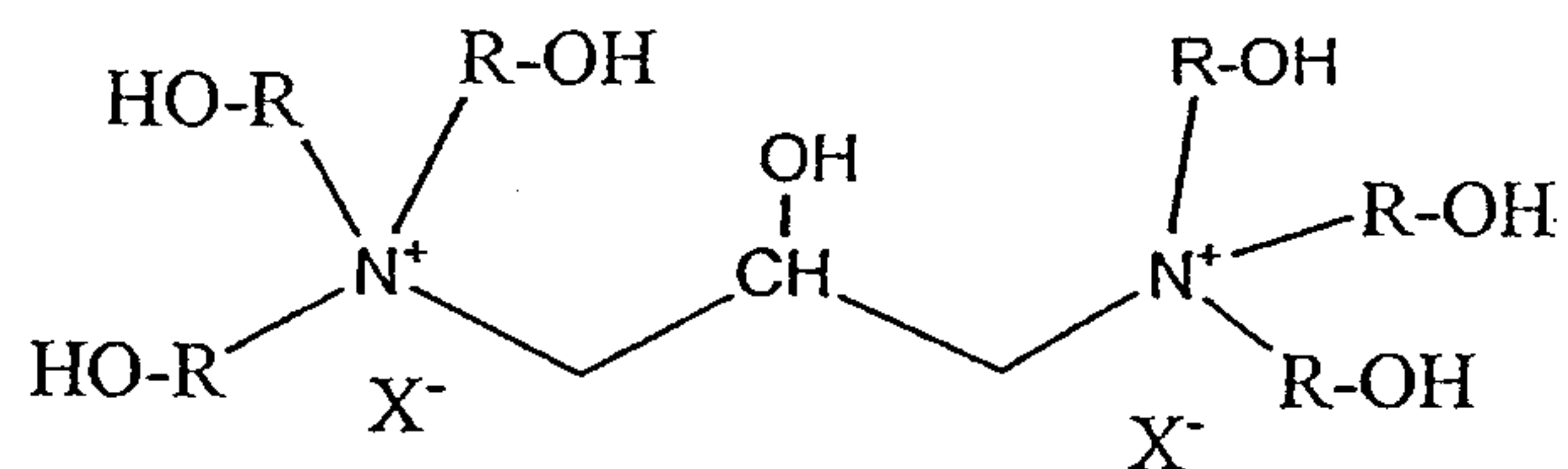
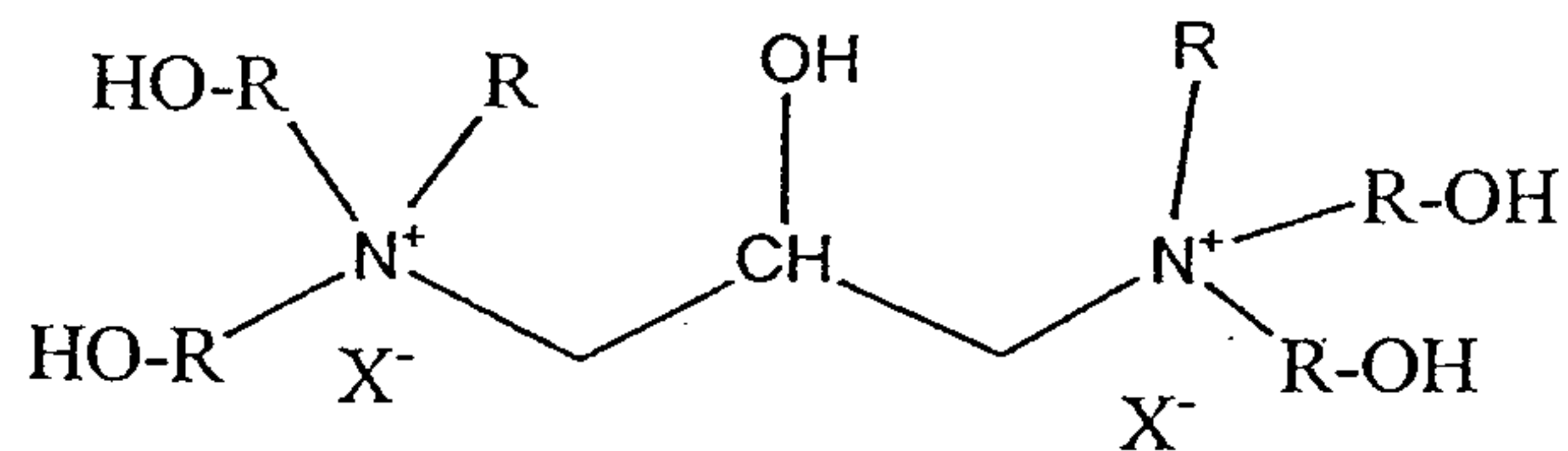
4. The composition of claim 3 further comprising a weighting material selected from the group consisting of barite, calcite, hematite, iron oxide, calcium carbonate, organic and inorganic salts, and mixtures thereof.

5. A method of decreasing the toxicity of a water-based wellbore fluid comprising circulating in the well a water-base drilling fluid comprising:

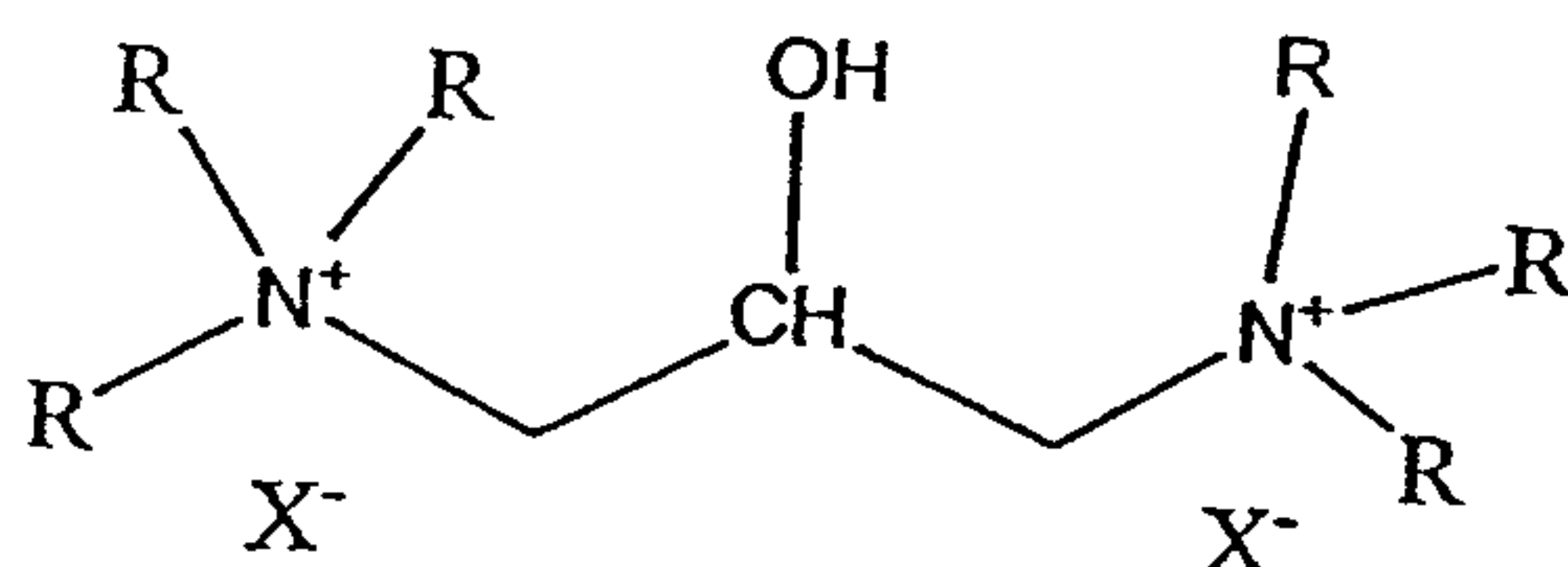
an aqueous based continuous phase and

a shale hydration inhibition agent, wherein the shale hydration inhibition agent is selected from:





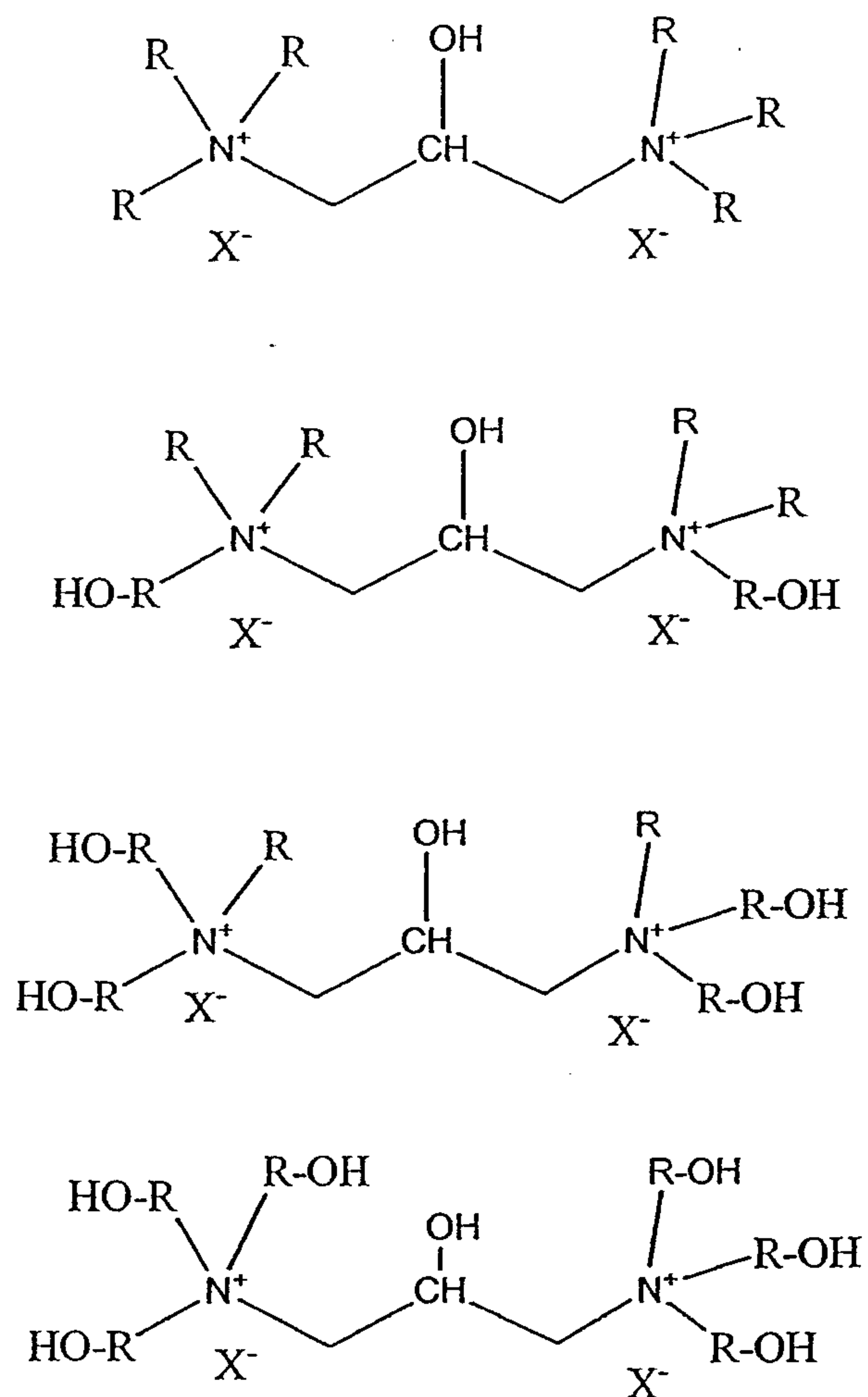
as well as mixtures of these, wherein R is an alkyl chain comprising 1 to 15 carbon atoms, and X is an anion;



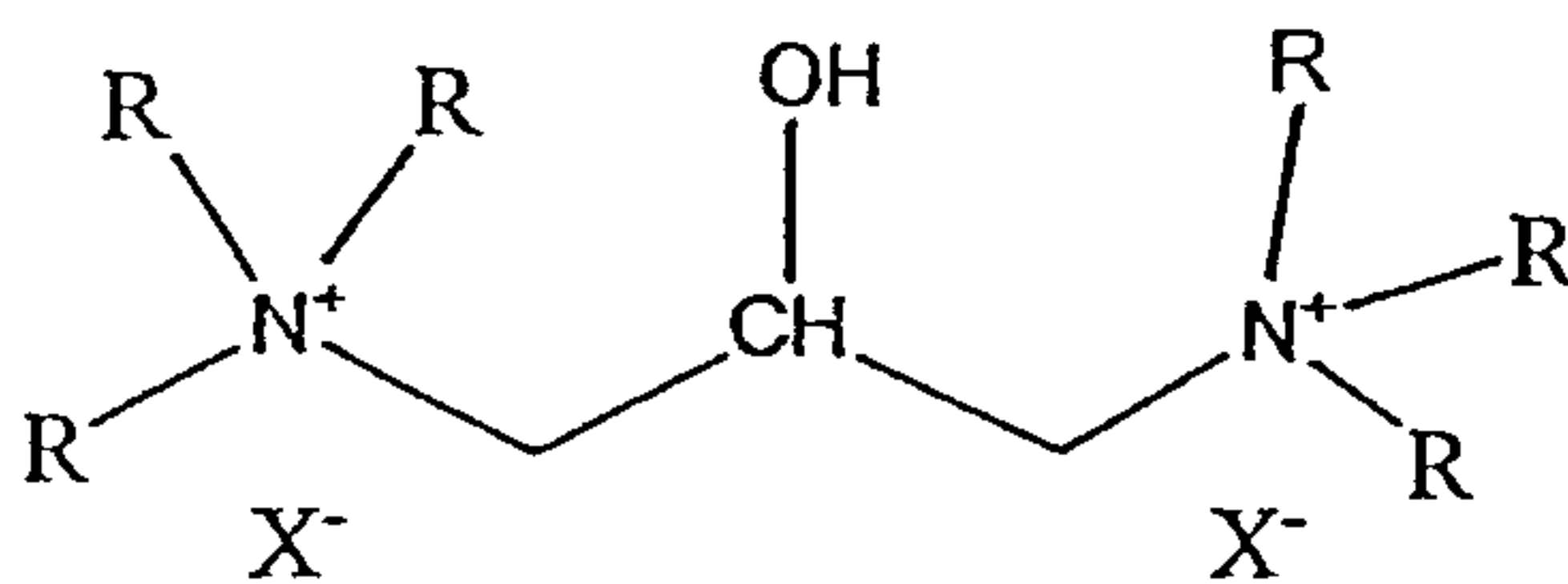
and wherein the shale hydration inhibition agent is present in sufficient concentration to reduce the toxicity of the wellbore fluid.

6. The method of claim 5 wherein the shale hydration inhibition agent is the reaction product of the reaction of a tertiary amine and epichlorohydrine.
7. The method of claim 5 wherein the wellbore fluid comprises EC₅₀(15) values greater than 50%.
8. The method of claim 5 wherein the wellbore fluid comprises EC₅₀(15) values greater than 90%.
9. A method of reducing the swelling of shale clay in a well comprising circulating in the well a water-base drilling fluid comprising:
 - an aqueous based continuous phase and

a shale hydration inhibition agent wherein the shale hydration inhibition agent is selected from:



as well as mixtures of these wherein R is an alkyl chain comprising 1 to 15 carbon atoms, and X is an anion;



and wherein the shale hydration inhibition agent is present in sufficient concentration to reduce the swelling of shale.

10. The method of claim 9 wherein the shale hydration inhibition agent is the reaction product of the reaction of a tertiary amine and epichlorohydrin.
11. The method of claim 10 wherein the tertiary amine is selected from the group consisting of: trimethanolamine, dimethylethanolamine, triethanolamine, diethanolmethanolamine, and tripropanolamine.
12. The method of claim 9 wherein the aqueous based continuous phase is selected from: fresh water, sea water, brine, mixtures of water and water soluble organic compounds and mixtures thereof.

