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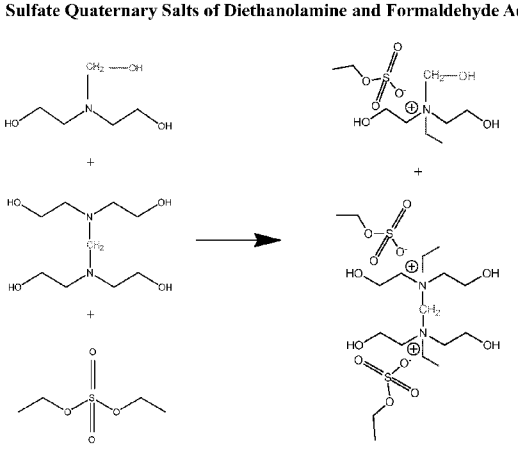

FIG. 13

(57) Abstract: New classes of temporary and/or permanent clay stabilization compositions including at least one quaternary salt of primary amines, secondary amines, tertiary amines, reaction products of these amines with at least one aldehyde, or mixtures and combinations thereof and to methods for making and using same, where the quaternary salts have reduced toxicity.

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PCT SPECIFICATION

TITLE: **ENVIRONMENTALLY FRIENDLY QUATERNARY SALTS OF AMINES AND THEIR USE AS TEMPORARY AND/OR PERMANENT CLAY STABILIZERS AND METHODS FOR MAKING AND USING SAME**

INVENTOR: **Duane S. TREYBIG, Alan RUSSELL and Aziz HIKEM**

ASSIGNEE: **CLEARWATER INTERNATIONAL LLC**

RELATED APPLICATIONS

[0001] This application claims the benefit of and priority to United States Provisional Patent Application Serial No. 61/790,299 filed 03/15/2013 (15 March 2013). This application is also related to United States Patent Serial Nos. 14/211,025 and 14/211,066, filed 03/14/2014 (14 March 2014).

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] Embodiments of the present invention relate to new classes of temporary and permanent clay stabilization compositions and to methods for making and using same.

[0002] More particularly, embodiment of the present invention relate to new classes of temporary and permanent clay stabilization compositions, where the compositions includes one or a plurality of quaternary salts of primary, secondary, tertiary amines, mono, di and tri alkanol amines, mono, di, tri alkyleneether amines, or mixtures and combinations thereof. The invention also related to methods for making and using same.

2. Description of the Related Art

[0003] Clay stabilizer is a chemical additive used in stimulation treatments to prevent the migration or swelling of clay particles in reaction to water-base fluid. There are two types of clay stabilizers, temporary and permanent. There is a need for more environmentally friendly clay stabilizers and a need for more permanent clay stabilizers, especially those that are environmentally friendly.

[0004] During drilling and/or completion, zones that comprise shales and/or reactive clays can become unstable, when they are in contact with water in a drilling fluid. These zones contain clays that have been dehydrated over geologic time by overburden pressure. When these zone are exposed to a water containing material such as a drilling fluid, the clays osmotically imbibe water from the drilling fluid and swell. The swelling of the shale induces stresses, loss of mechanical strength, and shale failure. See Thomas W. Beihoffer et al in the May 16, 1992 Oil & Gas Journal, page 47 et seq., entitled "Cationic Polymer Drilling Fluid Can Sometimes Replace Oil-based Mud" for a more in depth explanation of the problem of drilling through clay containing zones. Shale crumbling into the borehole ("sloughing") can ultimately place a burden on the drill bit which makes it impossible to

retrieve.

[0005] Salts such as potassium chloride have been widely used in drilling treatments to convert the formation material from the sodium form by ion exchange to, for example, the potassium form which is less vulnerable to swelling; also the use of high concentrations of potassium salts affects the osmotic balance and tends to inhibit the flow of water away from the high potassium salt concentration fluids into the shale. However, it is difficult to maintain the required high concentrations of potassium salts in the drilling fluids. In addition, the physical introduction of such salts causes difficulties with the use of the viscosifying materials typically used for drilling. Inorganic salts can also have a harmful effect on the environment if released.

[0006] There are three general types of amine and/or quaternary ammonium cation sources which have been suggested for clay treatment during drilling operations and hydrocarbon recovery. The three types include: (a) compounds having a single-site quaternary ammonium cation and amine, (b) compounds having a few (two to about six) amine or quaternary ammonium cation sites, sometimes referred herein as "oligo-cationics", and (c) quaternary ammonium or amine polymers, which may have from about six to thousands of cationic sites. Such prior art clay control compounds are disclosed in United States Pat. Nos. 2,761,835; 2,761,840; 2,761,836; 4,842,073; 5,211,239; 2,761,843; 3,349,032; 4,447,342; 4,374,739; 4,366,071 and 6,921,742, incorporated herein by reference.

[0007] Although there are numerous examples of clay control additives, there is still a need in the art for new clay control additives, especially environmentally friendly clay control additives.

SUMMARY OF THE INVENTION

[0008] Embodiments of the present invention provide clay stabilizing compositions of this invention include one or more quaternary salts of primary, secondary, tertiary amines, mono, di and tri alkanol amines, mono, di, tri alkyleneether amines, or mixtures and combinations thereof.

[0009] Embodiments of the present invention provide clay stabilizing compositions of this invention include at least one quaternary salt compounds of Formula (**I**) and/or a reaction product of compounds of Formula (I) with at least one aldehyde:

$$[R^1R^2R^3N(R^0)_j]^+A^- \quad \textbf{(I)}$$

where:

A and $\mathbf{R^0}$ are derived from the general formula $\mathbf{R^0A}$ selected from the formulas consisting of $\mathbf{R^IR^{II}SO_4}$, $\mathbf{R^ISO_3H}$, $\mathbf{R^{III}Cl}$, **ArCl**, $\mathbf{ArR^{IV}Cl}$, $\mathbf{R^VO(R^{VI}O)R^{VI}Cl}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}Cl}$, or mixtures and combinations thereof, where $\mathbf{R^I}$, $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, and $\mathbf{R^V}$ are the same or different carbyl groups, **Ar** is an aryl group, and $\mathbf{R^{IV}}$ and $\mathbf{R^{VI}}$ are the same or different linking carbyl groups, where $\mathbf{R^0}$ is selected from the group consisting of a hydrogen atom (**H**), $\mathbf{R^I}$ or $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, **Ar**,

ArR^{IV}, $R^{V}O(R^{VI}O)R^{VII}$, $ClR^{VI}O(R^{VI}O)R^{VI}$, $R^{VI}O(R^{VI}O)R^{VI}$, and mixtures thereof and A^- is selected from the group consisting of $R^{I}SO_4^-$ or $R^{II}SO_4^-$, $R^{I}SO_3^-$, Cl^-, $[R^{VI}O(R^{VI}O)R^{VI}Cl]^-$, $[R^{VI}O(R^{VI}O)R^{VI}]^{2-}$, and mixtures thereof,

R^1, R^2, and R^3 are the same or different and are either a hydrogen atom (**H**), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms, an R^aOH group, an $R^a(OR^{aa})_nOH$ group, an R^aOR group, an $R^a(OR^{aa})_nOR'$ group, or mixtures and combinations thereof, provided at least one of the R^1, R^2, and R^3 groups is not a hydrogen atom,

j is an integer having a value between 1 and the maximum number of **NH** moieties plus 1,

R^a and R^{aa} are the same or different linear or branched carbyl linking groups having between 1 and 20 carbon atoms, and

R and **R'** are linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms.

[0010] Embodiments of the present invention provide drilling fluids including an effective amount of at least one clay stabilizing composition of this invention. Embodiments of the present invention provide completion fluids including an effective amount of at least one clay stabilizing composition of this invention. Embodiments of the present invention provide fracturing fluids including an effective amount of at least one clay stabilizing composition of this invention.

[0011] Embodiments of the present invention provide methods for making compounds of this invention. Embodiments of the present invention provide methods for drilling using a drilling fluid including at least one clay stabilizing composition of this invention. Embodiments of the present invention provide methods for completing using a completion fluid including at least one clay stabilizing composition of this invention. Embodiments of the present invention provide methods for fracturing using a fracturing fluid including at least one clay stabilizing composition of this invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The invention can be better understood with reference to the following detailed description together with the appended illustrative drawings in which like elements are numbered the same:

[0013] **Figure 1A-C** depict structures of exemplary of compounds of **Formulas** (**I-III**).

[0014] **Figure 2** depicts water release data for 71.7 wt.% choline chloride available as Bio Add 1200 from Shrieve Chemical Company from Weatherford Wyoming Bentonite.

[0015] **Figure 3** depicts water release data for 40.3 wt.% choline chloride available as Bio Add 1200 from Shrieve Chemical Company from Weatherford Wyoming Bentonite.

[0016] **Figure 4** depicts water release data for XC-197 in the range of 1.5 wt.% to 3 wt.%. XC-197 is a clay control additive available from Pchem, A Weatherford Company. The plot shows the behavior of XC-197 for 1 wt.% Charles B. Chrystle Co. clay versus 1 wt.% Weatherford Wyoming Bentonite.

[0017] Figure 5 depicts water release data for XC-197 in the range between 2 gpt and 10 gpt. XC-197 is a clay control additive available from Pchem, A Weatherford Company. The plot shows the behavior of XC-197 for 1 wt.% Weatherford Wyoming Bentonite.

[0018] Figure 6 depicts components of Huntsman Amine C9 including their chemical names and structures used in the preparation of the quaternary salts of **Example 1** and **Example 2**.

[0019] Figure 7 depicts chemical structures of diethyl sulfate quaternary salts of Huntsman C9 amine as set forth in **Example 1**.

[0020] Figure 8 depicts water release data for the quaternary salts of **Example 1** from Weatherford Wyoming Bentonite.

[0021] Figure 9 depicts chemical structures of dimethyl sulfate quaternary salts of Huntsman C9 amine as set forth in **Example 2**.

[0022] Figure 10 depicts water release data for the quaternary salts of **Example 2** from Weatherford Wyoming Bentonite.

[0023] Figure 11 depicts water release data for the quaternary salts of **Examples 1 and Example 2** from Cream Bentonite from Charles B. Chrystle.

[0024] Figure 12 depicts chemical structures of possible reaction products of the reaction of diethanolamine and formaldehyde as described in **Example 3**.

[0025] Figure 13 depicts chemical structures of possible diethyl sulfate quaternary salts of the reaction products of **Example 3**.

[0026] Figure 14 depicts water release data for the quaternary salts of **Example 3** from Weatherford Wyoming Bentonite.

[0027] Figure 15 depicts chemical structure of a possible benzyl chloride quaternary salt of triethanol amine of **Example 4**.

[0028] Figure 16 depicts water release data for the quaternary salt of **Example 4** from Weatherford Wyoming Bentonite.

[0029] Figure 17 depicts chemical structure of a possible diethyl sulfate quaternary salt of the triethanol amine of **Example 5**.

[0030] Figure 18 depicts water release data for the quaternary salt of **Example 5** from Weatherford Wyoming Bentonite.

DETAILED DESCRIPTION OF THE INVENTION

[0031] The inventors have found that new quaternary clay stabilizing compositions including one or a plurality of a new class of quaternary salt clay stabilization additives that have reduced toxicity and equivalent water release properties as conventional clay stabilization compounds. The inventors have found that one such new class of quaternary salt clay stabilization additives includes one or more

quaternary salts of primary, secondary, tertiary amines, mono-, di-, and tri-alkanol amines, mono-, di-, tri-alkyleneether amines, or mixtures and combinations thereof. The inventors have also found that one such new class of quaternary salt clay stabilization additives includes one or more quaternary salts of a reaction product of primary amines, secondary amines, monoalkanol amines, dialkanol amines, monoalkyleneether amines, dialkyleneether amines, or mixtures and combinations thereof with an aldehyde or an aldehyde donor. The inventors have also found that the quaternary salts of compounds of **Formula (I)**, **Formula (II)**, and/or **Formula (III)** represent new quaternary salt clay stabilizing compounds. We have also found that some of these new quaternary salt clay stabilizing compounds have reduced adverse environmental effects compared to conventional quaternary salt clay stabilizing compounds. We have found that the new quaternary clay stabilizing compounds are effective both as temporary and permanent clay stabilizers, are effective clay stabilizers with reduced corrosion propensity for downhole and surface equipment such as piping, casing, pumps, etc. and many of the compounds have improved environmental properties including reduced toxicity to microorganisms and vertebrates. We have also found that the compounds may be tailored by selecting the amines and the quaternarizing agents needed to render them more environmentally friendly and less toxic.

[0032] Embodiments of the present invention also broadly relates to drilling fluids including an effective amount of at least one clay stabilizing composition of this invention.

[0033] Embodiments of the present invention also broadly relates to completion fluids including an effective amount of at least one clay stabilizing composition of this invention.

[0034] Embodiments of the present invention also broadly relates to fracturing fluids including an effective amount of at least one clay stabilizing composition of this invention.

[0035] Embodiments of the present invention also broadly relates to methods for making compounds of the **Formula (I)**, **Formula (II)**, and/or **Formula (III)**.

[0036] Embodiments of the present invention also broadly relates to methods for drilling using a drilling fluid including at least one clay stabilizing composition of this invention.

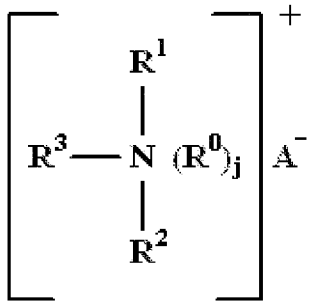
[0037] Embodiments of the present invention also broadly relates to methods for completing using a completion fluid including at least one clay stabilizing composition of this invention.

[0038] Embodiments of the present invention also broadly relates to methods for fracturing using a fracturing fluid including at least one clay stabilizing composition of this invention.

[0039] In certain embodiments of this invention, the compounds of this invention may also include morpholine amine corrosion inhibitors such as C6 amine available from Huntsman Corporation in the final stages of preparation so that the morpholine amines impart improved anti-corrosion characteristics to the formulation. The inventors have found that by adding C6 amine to the reaction

mixtures during preparation, the morpholine amines imparted needed anti-corrosion characteristics to the compositions. The inventors believe that the new compounds are well suited as clay stabilizers, corrosion inhibitors, scale inhibitors, de-emulsifiers, and/or collectors in ore floatation and other oil field and mining applications. These compositions are particularly useful as clay stabilizers that are environmentally friendly.

[0040] Embodiments of the present invention provide clay stabilizing compositions of this invention include one or more quaternary salts of compounds of **Formula (II)**:



where:

A and $\mathbf{R^0}$ are derived from the general formula $\mathbf{R^0A}$ selected from the formulas consisting of $\mathbf{R^IR^{II}SO_4}$, $\mathbf{R^ISO_3H}$, $\mathbf{R^{III}Cl}$, **ArCl**, $\mathbf{ArR^{IV}Cl}$, $\mathbf{R^VO(R^{VI}O)R^{VI}Cl}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}Cl}$, or mixtures and combinations thereof, where **H**, $\mathbf{R^I}$, $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, and $\mathbf{R^V}$ are the same or different carbyl groups, **Ar** is an aryl group, and $\mathbf{R^{IV}}$ and $\mathbf{R^{VI}}$ are the same or different linking carbyl groups, where $\mathbf{R^0}$ is selected from the group consisting of a hydrogen atom (**H**), $\mathbf{R^I}$ or $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, **Ar**, $\mathbf{ArR^{IV}}$, $\mathbf{R^VO(R^{VI}O)R^{VII}}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}}$, $\mathbf{R^{VI}O(R^{VI}O)R^{VI}}$, and mixtures thereof and $\mathbf{A^-}$ is selected from the group consisting of $\mathbf{R^ISO_4^-}$ or $\mathbf{R^{II}SO_4^-}$, $\mathbf{R^ISO_3^-}$, $\mathbf{Cl^-}$, $\mathbf{[R^{VI}O(R^{VI}O)R^{VI}Cl]^-}$, $\mathbf{[R^{VI}O(R^{VI}O)R^{VI}]^{2-}}$, and mixtures thereof,

$\mathbf{R^1}$, $\mathbf{R^2}$, and $\mathbf{R^3}$ are the same or different and are either a hydrogen atom (H), a linear, branched, or cyclic carbyl group having between 1 and 20 carbon atoms, an $\mathbf{R^aOH}$ group, an $\mathbf{R^a(OR^{aa})_nOH}$ group, an $\mathbf{R^aOR}$ group, an $\mathbf{R^a(OR^{aa})_nOR'}$ group, or mixtures and combinations thereof, provided at least one of the $\mathbf{R^1}$, $\mathbf{R^2}$, and $\mathbf{R^3}$ groups is not a hydrogen atom,

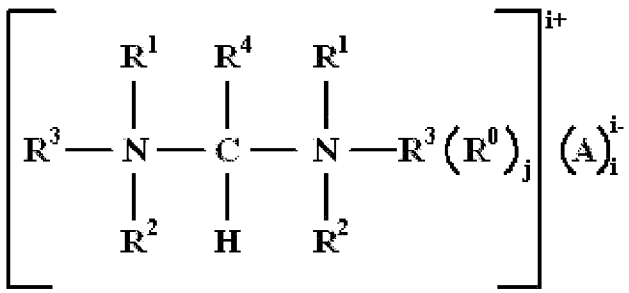
j is an integer having a value between 1 and the maximum number of **NH** moieties plus 1,

$\mathbf{R^a}$ and $\mathbf{R^{aa}}$ are the same or different linear or branched carbyl linking groups having between 1 and 20 carbon atoms, and

R and **R'** are linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms.

[0041] Embodiments of the present invention provide clay stabilizing compositions of this invention include one or more quaternary salts of a reaction product of primary amines, secondary amines, monoalkanol amines, dialkanol amines, monoalkyleneether amines, dialkyleneether amines, or mixtures and combinations thereof with an aldehyde or an aldehyde donor.

[0042] Embodiments of the present invention provide clay stabilizing compositions of this invention include a reaction product of compounds of Formula (**II**) with at least one aldehyde to form quaternary salt compounds of **Formula (III)**:



where:

A and $\mathbf{R^0}$ are as set forth above,

$\mathbf{R^1}$, $\mathbf{R^2}$, and $\mathbf{R^3}$ are the same or different and are independently either a hydrogen atom (H), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms, an $\mathbf{R^aOH}$ group, an $\mathbf{R^a(OR^{aa})_nOH}$ group, an $\mathbf{R^aOR}$ group, an $\mathbf{R^a(OR^{aa})_nOR'}$ group, or mixtures and combinations thereof, provided at least one of the $\mathbf{R^1}$, $\mathbf{R^2}$, and $\mathbf{R^3}$ groups is not a hydrogen atom,

j is an integer having a value between 1 and the maximum number of **NH** moieties plus 1,

$\mathbf{R^a}$ and $\mathbf{R^{aa}}$ are the same or different linear or branched carbyl linking groups having between 1 and 20 carbon atoms,

R and **R'** are the same or different linear, branched or cyclic carbyl groups having between 1 and 20 carbon atoms,

$\mathbf{R^4}$ is a hydrogen atom (H), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms and are derived from an aldehyde having the structure $\mathbf{R^4CHO}$, and

i is an integer having a value between 1 and 2.

[0043] **Figures 1A-C** show illustrative examples of compounds of **Formula (I)**, **Formula (II)**, and **Formula (III)** and reaction products of compounds of **Formula (I)** having **NH** moieties with aldehydes.

[0044] The quaternary salts of this invention are prepared by reacting monoamino compounds or reaction products of monoamino compounds having at least one **NH** moiety with one aldehyde or plurality of aldehydes with an effective amount of at least one alkylating agent $\mathbf{R^0A}$ sufficient to alkylate any **NH** moiety or all remaining **NH** moieties and converting at least 40% of the tertiary amines present in the compounds into quaternary salts. In certain embodiments, the effective amount sufficient to alkylate any **NH** moiety or all remaining **NH** moieties and converting at least 50% of the tertiary amines present in the compounds into quaternary salts. In other embodiments, the effective amount sufficient to alkylate any **NH** moiety or all remaining **NH** moieties and converting at least

60% of the tertiary amines present in the compounds into quaternary salts. In other embodiments, the effective amount sufficient to alkylate any **NH** moiety or all remaining **NH** moieties and converting at least 70% of the tertiary amines present in the compounds into quaternary salts. In other embodiments, the effective amount sufficient to alkylate any **NH** moiety or all remaining **NH** moieties and converting at least 80% of the tertiary amines present in the compounds into quaternary salts. In other embodiments, the effective amount sufficient to alkylate any **NH** moiety or all remaining **NH** moieties and converting at least 90% of the tertiary amines present in the compounds into quaternary salts. In other embodiments, the effective amount sufficient to alkylate any **NH** moiety or all remaining **NH** moieties and converting at least 95% of the tertiary amines present in the compounds into quaternary salts.

[0045] For example, diethanolamine, a secondary amine, may be reacted with sufficient $\mathbf{R^0A}$ to alkylate the diethanolamine to form $\mathbf{R^0}$-diethanolamine and then to convert 40 mole % of the resulting tertiary amines to $\mathbf{R^0}$,$\mathbf{R^0}$-diethanolammonium **A** salts.

[0046] In another example, diethanolamine, another secondary amine, may be reacted with an aldehyde to alkylate or dimerize the diethanolamine. The reaction product is then reacted with sufficient $\mathbf{R^0A}$ to convert at least 40% of the tertiary amines present in the compounds into corresponding quaternary salts.

[0047] In certain embodiments, the quaternary salts of the amines of this invention and the quaternary salts of reaction products of amines and aldehydes may also include polyamines or mixtures of polyamines to augment the properties of the clay stabilization compositions of this invention.

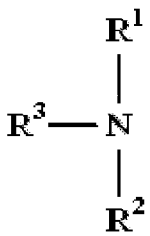
SUITABLE REAGENTS

Amines, Alkanol Amines, and Alkyleneether Amines

[0048] Suitable amines, alkanol amines, and alkyleneether amines for use in the invention include, without limitation, any linear, branched or cyclic carbyl amine having between about 1 carbon atoms to about 40 carbon atoms. In certain embodiments, the amines are primary amines, secondary amines, tertiary amines, or mixtures or combinations thereof. The carbyl group may be any carbon containing group having between 1 and 30 carbon atoms. In certain embodiments, the carbyl groups are linear, branched, and/or cyclic alkyl groups, alkenyl groups, alkynyl groups, or mixtures and combinations thereof. In other embodiments, the carbyl groups are aryl groups, alkaryl groups, arylalkyl groups, or mixtures and combinations thereof. In other embodiments, the carbyl groups are alkanol groups, ether groups, polyether alkanol groups, or mixtures and combinations thereof. Exemplary examples include, without limitation, monocarbylamines, dicarbylamines, tricarbylamines, or mixtures and combinations thereof. Exemplary examples include, without limitation, monoalkylamine, dialkylamine, trialkylamines, monoalkanolamines, dialkanolamines, trialkanolamines,

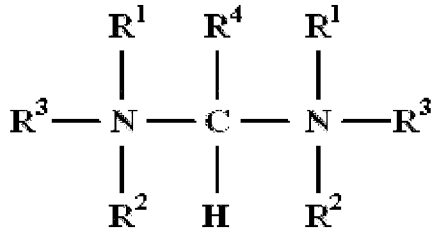
monoetheramines, dietheramines, trietheramines, cyclicamines, heterocyclic amines, alkylated analogs, alkoxylated analogs, alkylalkanolamines, dialkylalkanolamines, alkyldialkanolamines, alkyletheramines, dialkyletheramines, alkyldietheramines, alkanoletheramines, dialkanoletheramines, alkanoldietheramines, or mixtures and combinations thereof. Exemplary examples of suitable amines include, without limitation, ethoxylated amines, ethoxylated morpholine amines, alkanolamines, ethyleneamines, alkylated ethoxylated amines, alkylated ethoxylated morpholine amines, alkylated alkanolamines, alkylated ethyleneamines, alkylated amines, or mixtures and combinations thereof. The alkylating agents include, without limitation, formaldehyde, paraformaldehyde, glyoxal, other formaldehyde donors, or mixtures and combinations thereof.

[0049] In certain embodiments, the amines, alkanol amines, and alkyleneether amines suitable for this invention include alkanolamines of the general formula:



where $\mathbf{R^1}$, $\mathbf{R^2}$, and $\mathbf{R^3}$ are the same or different and are either a hydrogen atom (**H**), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms, an $\mathbf{R^aOH}$ group, an $\mathbf{R^a(OR^{aa})_nOH}$ group, an $\mathbf{R^aOR}$ group, an $\mathbf{R^a(OR^{aa})_nOR'}$ group, or mixtures and combinations thereof, provided at least one of the $\mathbf{R^1}$, $\mathbf{R^2}$, and $\mathbf{R^3}$ groups is not a hydrogen atom, $\mathbf{R^a}$ and $\mathbf{R^{aa}}$ are the same or different linear or branched carbyl linking groups having between 1 and 20 carbon atoms, and **R** and **R'** are the same or different linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms. Exemplary examples of linear, branched or cyclic carbyl linking groups include, without limitation, methylene groups, ethylene groups, propylene group, butylene groups, pentylene groups, hexylene group, higher alkylene groups, cyclopentylene group, cyclohexylene group, phenylene groups, benzylene groups, alkalated analog thereof, or mixtures and combinations thereof and the linear, branched, or cyclic carbyl groups are analogs having two attachment sites. Exemplary amines include, without limitation monoalkanol amines such as methanolamine, ethanolamine, or higher alkanol amines, dialkanolamines such as dimethanolamine, diethanolamine, N-(2-hydroxyethyl) ethylenediamine, 2-(2-(2-hydroxyethoxy)ethyl-methylamino)ethanol, bis(2-hydroxyethoxyethyl) methylamine, or mixtures and combinations thereof.

[0050] In certain embodiments, the reaction product of amines, alkanol amines, and alkyleneether amines suitable for this invention include alkanolamines of the general formula:



where R^1, R^2, and R^3 are the same or different and are either a hydrogen atom (H), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms, an R^aOH group, an $R^a(OR^{aa})_nOH$ group, an R^aOR group, an $R^a(OR^{aa})_nOR'$ group, or mixtures and combinations thereof, provided at least one of the R^1, R^2 , and R^3 groups is not a hydrogen atom, R^4 is a hydrogen atom (H), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms and are derived from an aldehyde having the structure R^4CHO, R^a and R^{aa} are the same or different linear or branched carbyl linking groups having between 1 and 20 carbon atoms, and R and R' are the same or different linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms. Exemplary examples of linear, branched or cyclic carbyl linking groups include, without limitation, methylene groups, ethylene groups, propylene group, butylene groups, pentylene groups, hexylene group, higher alkylene groups, cyclopentylene group, cyclohexylene group, phenylene groups, benzylene groups, alkylated analog thereof, or mixtures and combinations thereof and the linear, branched, or cyclic carbyl groups are analogs having two attachment sites. Exemplary amines include, without limitation, monoetheralkylamines such as methoxymethylamine, ethoxyethylamine, or higher alkoxyalkylamines, dietheralkylamines such as dimethoxyethylamine, diethoxydiethylamine, N-(2-methoxyethyl)ethylenediamine, 2-(2-(2-ethoxy)ethyl-methylamino)ethane, bis(2-ethoxyethyl)methylamine, or mixtures and combinations thereof.

[0051] Other suitable amines include, without limitation, ethyleneamines such as ethylenediamine, monoethanolamine, diethylentriamine, 2-aminoethylethanolamine, triethylenetetramine, 5-ethyl-1,4,7-triazabicyclo[4.3.0]non-4,6-diene, 5-ethyl-1,4,7-triazabicyclo[4.3.0]non-6-ene, N-(2-aminoethyl)piperazine, 4-(2-aminoethyl)diethylenetriamine, N-(2-piperazinylethyl)ethylenediamine, tetraethylenepentamine, 4-(2-aminoethyl)triethylenetetramine, pentaethylenehexamine (PEHA), hexaethyleneheptamine (HEHA), heptaethyleneoctamine (HEOA), higher molecular weight ethyleneamine and piperazine oligomers, their piperazine constituents thereof, Molex ethyleneamines such as Molex A-1328, Molex A-1320, Molex A-1303, Molex 1783L, and the corresponding alkylated ethyleneamines and hydoxylated ethyleneamines, 1,4-dimethylpiperazine, tetramethylethylenediamine, other alkylated ethyleneamines, or mixtures and combinations thereof. Other amines include, without limitation, aminocyclohexane, 1,2-diaminocyclohexane, 4-(2-aminoethyl)morpholine, propyleneamines, propylenediamines, similar amines, or mixtures and combinations thereof. In certain embodiments, the compositions of this invention include secondary

alkanolamines, ethyleneamines, alkylated ethylenamines, alkylated amines, hydroxylated amine, which may be partially or totally alkylated with methyl chloride, benzyl chloride, dimethyl sulfate, diethyl sulfate, 1-chlorohexadecane, formaldehyde, paraformaldehyde, glyoxal and other alkylating agents. In other embodiments, the compositions of this invention include tertiary alkanolamines, secondary alkanolamines, partially alkylated or totally alkylated ethyleneamines, amines or mixtures and combinations thereof. Other amines include amine head's which are a combination of hexamethylenediamine, tetramethylenediamine, 3-aminopropan-1-ol, 2-methyl-1,5-pentanediamine, 2-aminocyclopentanemethylamine, and 1,2-cyclohexanediamine.

[0052] Suitable quaternizing agents for forming the **A** counterions include, without limitation, compounds of the general formula $\mathbf{R^0A}$ including, without limitation, dialkylsulfates, where the alkyl groups are the same or different and have between 1 and 6 carbon atoms, chloroalkylbenzenes such as benzylchloride, 1,4-chloromethylbenzene, *etc.*, where the alkyl group has between 1 and 6 carbon atoms, alkylchlorides, where the alkyl group has between 1 and 24 carbon atoms, chloroethers, where the alkyl group has between 4 and 24 carbon atoms, and alkylsulfonates, where the alkyl group is a straight chain alkyl group, or branched alkyl group, or cyclic alkyl group has between 1 to 24 carbon atoms. In all of these compounds one or more of carbon atoms may be replaced by oxygen atoms. Exemplary examples of dialkylsulfate compounds include, without limitation, dimethylsulfate, methylethylsulfate, diethylsulfate, dipropylsulfate, methylpropylsulfate, ethylpropylsulfate, higher dialkyl sulfates and mixed dialkyl sulfates, or mixtures and combinations thereof. Exemplary examples of chloroalkylbenzenes include, without limitation, benzyl chloride, chloroxylene, chloroethylbenzene, chloropropylbenzene, chlorobutylbenzene, higher chloroalkylbenzenes, or mixtures and combinations thereof. Exemplary examples of alkylchlorides include, without limitation, methyl chloride, ethyl chloride, propyl chloride, butyl chloride, pentyl chloride, hexyl chloride, heptyl chloride, octyl chloride,1-chlorohexadecane, higher alkyl chloride, or mixtures and combinations. Exemplary examples of chloroethers include, without limitation, chloroethylethanolether, dichloroethylether, higher chlorinated ethers, or mixtures and combinations. Exemplary examples of alkylsulfonates are methylsulfonate, ethane sulfonic acid, 1-butane sulfonic acid, petroleum sulfonic acids, benzenesulfonic acid, toluene sulfonic acid, dedecylbenzene sulfonic acid, and mixtures or combination thereof.

[0053] Huntsman C-6 amine may be added to these quaternaries to raise the pH. Huntsman C-6 amine is a mixture of 2-(2-(4-morpholinyl)ethoxy)ethanol, 4-(2-(2-aminoethoxy)ethyl)morpholine, 4-(4-morpholinyl)ethoxyethyl)morpholine.

[0054] Suitable cyclic amines include, without limitation, imidazolidines, oxazolidines, piperazines, morpholines, similar higher heterocyclic amines, and mixtures or combinations thereof.

[0055] Suitable polyamines for use in the invention include, without limitation, any linear, branched, or cyclic carbyl polyamines having between about 1 carbon atoms to about 40 carbon atoms. The carbyl group may be alkanol groups, ether groups, amino groups, polyether alkanol groups, polyamine groups, or mixtures and combinations thereof. Exemplary examples include, without limitation, alkylpolyamine, alkanolpolyamines, alkylalkanolpolyamines, etherpolyamines, cyclicpolyamines, heterocyclic polyamines, alkylated analogs, alkoxylated analogs, and mixtures and combinations thereof. Exemplary examples of suitable polyamines include, without limitation, α,ω-linear or branched diamines, α,ω-alkyleneoxide diamines, a,w-alkyleneamino diamines, or mixtures and combinations thereof. Exemplary examples of suitable polyamines include, without limitation, ethoxylated polyamines, ethoxylated morpholine polyamines, alkanol polyamines, ethylene polyamines, alkylated ethoxylated polyamines, alkylated ethoxylated morpholine polyamines, alkylated polyamines, alkylated ethylene polyamines, alkylated polyamines, or mixtures and combinations thereof. The alkylating agents include, without limitation, formaldehyde, paraformaldehyde, glyoxal, other formaldehyde donors, or mixtures and combinations thereof.

EXPERIMENTS OF THE INVENTION

[0056] Referring now to **Figures 2-5**, clay testing of prior art clay control additives are shown. Looking at **Figure 2**, a plot of water release data from Weatherford Wyoming Bentonite using a 71.7 wt.% choline chloride solution is shown. Looking at **Figure 3**, a plot of water release data from Weatherford Wyoming Bentonite using a 40.3 wt.% choline chloride solution is shown. Looking at **Figure 4**, a plot of water release data from 1% Charles B. Chystle Co. Cream Bentonite compared to Weatherford Wyoming Bentonite for XC-197 at different GPT values is shown. Looking at **Figure 5**, a plot of water release data from Weatherford Wyoming Bentonite using XC-197 is shown.

EXAMPLE 1

[0057] 324.09 grams of C9 amine from Huntsman and 80.81 grams of water were added to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column, and Friedrichs column on top. C9 amine is a blend of 2-(2-(2-hydroxyethoxy)ethyl-methylamino)ethanol and bis(2-hydroxyethoxyethyl)methylamine shown pictorially in **Figure 6**. The reaction mixture was agitated and heated to 190°F. 250.26 grams diethyl sulfate were added dropwise from an addition funnel over a 84 minute period, while maintaining the temperature below 215°F. The reaction mixture was held at a temperature of 200°F for 81 minutes. The reaction mixture had a Total Amine Value (TAV) of 46.89 and a pH of 8.11. The reaction mixture was cooled to a temperature below 150°F and 48 grams of a 31% HCl solution was added to adjust the pH to a pH of 3.09. Finally, 135 grams of water were added to the reaction mixture to yield a product having 70.0% solids and a final pH of 3.15. **Figure 7** depicts the chemical structures of the diethyl sulfate quaternary salts of C9

amines, while **Figure 8** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 1**.

EXAMPLE 2

[0058] 324.03 grams of C9 amine from Huntsman and 103.70 grams water were added to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column and Friedrichs column on top. C9 amine is a blend of 2-(2-(2-hydroxyethoxy)ethyl-methylamino)ethanol and bis(2-hydroxyethoxyethyl)methylamine shown pictorially in **Figure 6**. The reaction mixtures was agitated and heated to 180°F. 204.32 grams of dimethyl sulfate was added dropwise from an addition funnel over a 56 minute period, while the temperature of the reaction mixtures was maintained 244°F. The reaction mixtures was held at a temperature between 187°F and 207°F for 3 hours and 53 minutes. The reaction mixture had a TAV of 31.97 and pH of 7.75. The reaction mixture was cooled to a temperature below 166°F and 64.01 grams of 31% HCl was added the reaction mixture to adjust the pH of the reaction mixture to a pH of 2.33. 2.91 grams of Huntsman C-9 amine were then added to adjust the pH of the reaction mixture to a pH of 2.14. 97.90 grams of water was then added to the reaction product to yield a product having 69.4 % solids and a final pH of 2.4. **Figure 9** depicts the chemical structures of the dimethyl sulfate quaternary salts of C9 amines, while **Figure 10** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 2**. **Figure 11** shows a plot of water release data for the clay control additives of **Example 1** and **Example 2** using Cream Bentonite from Charles B. Chrystle.

EXAMPLE 3

[0059] 169.66 grams diethanolamine and 221.65 grams of water were added to a liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column, and Friedrichs column on top. The reaction mixture was heated to 113°F with agitation. 64.86 grams of 37% formaldehyde in water was added dropwise to the reaction mixture over a 23 minute period. **Figure 12** shows possible amines formed in this reaction mixture. 250.43 grams diethyl sulfate was added between 100° and 204°F in a 176 minute period. Reactor contents are a yellowish colored liquid with a pH of 2.8. 30.65 grams C6 Amine from Huntsman is added with an addition funnel to the reactor contents between 207° and 230°F to give a black colored liquid with a final pH of 5.67 and TAV of 7.62. **Figure 13** shows chemical structures of possible diethyl sulfate quaternary salts of the reaction mixture of this example, while **Figure 14** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 3**.

EXAMPLE 4

[0060] Add triethanolamine (351.0 grams) and water (82.8 grams) to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column and Friedrichs column on top.

The reaction mixture was heated to at temperature of 153°F with agitation. 283.68 grams of benzyl chloride were added dropwise from an addition funnel over a 182 minute period of time, while the reaction mixture was maintained at a temperature between 167°F and 227°F. 112.15 grams of water was added to the reaction mixture to yield a product having 77.58 % solids and being the form of a slight yellow transparent liquid. **Figure 15** shows a possible chemical structure of the benzyl chloride quaternary salts of triethanolamine, while **Figure 16** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 4**.

EXAMPLE 5

[0061] 319.96 grams of triethanolamine and 82.83 grams of water were added to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column, and Friedrichs column on top. The reaction mixture was heated to a temperature of 127°F with agitation. 314.93 grams of diethyl sulfate (DES) were added dropwise from addition funnel over a 63 minute period, while the reaction mixture was maintained at a temperature below 250°F. 82.95 grams of water were added to give a product having 78.13 % solids and in the form of a golden yellow transparent liquid having a TAV of 9.76 and pH of 5.95. **Figure 17** depicts the chemical structures of the diethyl sulfate quaternary salts of triethanolamine, while **Figure 18** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 5**.

EXAMPLE 6

Clay Stabilization Test

Clay Solution Preparation

[0062] To make 100 mL of a clay solution, measure 1g of Cream Bentonite Clay or Weatherford Bentonite Clay material. Add 99g of distilled water and shake bottle until all the clay is dissolved.

Blank Preparation

[0063] Measure 100 ml of clay solution in a graduated cylinder. Shake 10 times. Record separation time and clay precipitation.

Test Sample Preparation

[0064] Measure 100 mL of clay solution in a graduated cylinder and add 0.5 mL of the desired clay stabilizer. Shake 10 times. Record separation time and clay coagulation. Record clay deposition, swelling and water release. The results are tabulated in **Table I**.

TABLE I

Clay Stability

Clay Stabilizer	Dosage (wt.%/100 mL)	Final Water (mL)
Blank	0	15% (Top)
Choline Chloride	0.5	27 mL/60 minutes (Top)

Example 1	0.5	30 mL/60 minutes (Top)
Example 2	0.5	31 mL/60 minutes (Top)
Example 5	0.5	20 mL/60 minutes (Middle)

The data in **Table 1** indicates that **Example 1** and **Example 2** break the water out faster than choline chloride and break out more water than choline chloride.

EXAMPLE 7

[0065] Acute toxicity survival tests of **Example 3**, **Example 4**, and **Example 5** and tetramethylammonium chloride (TMAC) were performed using Fathead Minnow (pimephales promelas). Because the expected toxicity of these chemical was unknown, the testing was performed in a phased approach consisting of an initial "range-finding" test, where test concentrations were progressively increased by orders of magnitude to determine a threshold toxicity range. Once the range where no minnows survived was identified, the "range-finding" test was followed by a "definitive" test, where test concentrations were progressively increased by a factor of two to determine specific toxicity ranges. As a consequence, the "definitive" test gave a more precise LC50 value. LC50 was determined using a log-normal transformation coupled with linear regression between the bracketing no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC). Both the range finding and definitive tests were run on **Example 4** and **Example 5**. Only the ranging finding test was run for TMAC and **Example 3**. The LC-50's are summarized in **Table II**.

TABLE II

Acute Toxicity Minnow Survival Test Results

Clay Stabilizer	LC50
tetramethylammonium chloride (TMAC)	737 mg/L
Example 3	379 mg/L
Example 4	3160 mg/L
Example 5	6030 mg/L

In terms of toxicity to Flathead Minnows, **Example 4** and **Example 5** are much less toxic than TMAC. **Example 3** and TMAC exhibit similar Flathead Minnows toxicity values.

EXAMPLE 8

[0066] 362 grams of ethyleneamine E-100 from Huntsman was charged to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column, and Friedrichs column on top. Ethyleneamine E-100 is a complex mixture of various linear, cyclic, and branched products with a number-average molecular weight between 250 and 300 g/mole.

$H_2NCH_2CH_2(NHCH_2CH_2)_xNH_2$ where (x = 3, 4, 5, and higher) including tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), hexaethyleneheptamine (HEHA), and higher molecular weight product polyamines. The reaction mixtures were agitated and heated to a temperature of 180°F. 482 grams of diethyl sulfate (DES) was added dropwise from an addition funnel over a 120 minute period of time, while the reaction mixture was maintained at a temperature below 250°F. The reaction mixture was then maintained at a temperature between 187°F and 250°F for 3 hours. The reaction mixture was cooled down to a temperature to 200°F, then 138 grams of water were added. The reaction mixture was cooled to keep the reaction mixture temperature below 166°F. 18 grams of 31 % HCl was added to the reaction mixture to give a product having 90.31 % solids, a TAV of 151mg KOH/g and a final pH of 7.8.

EXAMPLE 9

[0067] 290 grams of Amine Heads II from Ascend were charged to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column, and Friedrichs column on top. Amine Heads II is a mixture of hexamethylenediamine (HMDA), tetramethylendiamine (TMDA), 1,2 diaminocyclohexane, hexamethyleneimine (HMI). The reaction mixtures was agitated and heated to a temperature of 180°F. 710 grams diethyl sulfate (DES) was added dropwise from an addition funnel over a 120 minute period of time, while the reaction mixture was maintained at a temperature below 250°F. The reaction temperature was then maintained at a temperature between 187°F and 250°F for 3 hours to yield a product having 93.24% solids, a TAV of 0 mg KOH/g and a final pH of 2.4. The composition of Amine Heads II is given in **Table III**.

TABLE III

Amine Heads II Composition

Components	CAS No	Concentration range	Units
1,2-cyclohexanediamine	694-83-7	>25.0 - <55.0	%
hexamethylenediamine	124-09-4	>10.0 - <30.0	%
water	7732-18-5	>10.0 - <20.0	%
tetramethylenediamine	110-60-1	>7.0 - <20.0	%
3-aminopropan-1-ol	156-87-6	>5.0 - <15.0	%
2-aminocyclopentanemethylamine	21544-02-5	>1.0 - <5.0	%
1,5-pentanediamine, 2-methyl	15520-10-2	>1.0 - <5.0	%

EXAMPLE 10

[0068] 120.02 grams; 1.15 moles of aminoethylethanolamine (AEEA) and 266.09 grams of water were added into a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column, and Friedrichs column on top. The reaction mixtures was agitated and heated to

a temperature of 89°F. 181.04 grams; 2.23 moles of 37% formaldehyde in water were added dropwise from an addition funnel at a rate where temperature remained below 114°F. The reaction mixtures was then heated to a temperature of 180°F. A possible reaction scheme for reactions that occurred in this example is shown in **Figure 19**; while this reaction scheme is possible, the inventors are not meaning to be bound thereby. 144.7 grams; 1.14 moles of benzyl chloride were then added dropwise from an addition funnel over a 14 minute period, while the reaction mixture was maintained at a temperature between 180°F and 212°F. The reaction mixture was in the form of an orange opaque liquid. The reaction mixture was maintained at a temperature between 180° and 204°F for 2 hours and 58 minutes. The reaction mixture was in the form of a dark purple transparent liquid having 46.10 % solids. 91.59 grams of water were then added to the reaction mixture to yield a product having 40 wt.% solids.

EXAMPLE 11

[0069] 120.05 grams; 1.15 moles aminoethylethanolamine (AEEA) and 308.54 grams water were added into a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column and Friedrichs column on top. TAV was 303. The reaction mixture was agitated and heated to 96°F. 187.05 grams; 2.3 moles of 37 % formaldehyde in water were added dropwise from an addition funnel at a rate where temperature remained below 131°F. TAV was 194. A possible reaction scheme is shown in **Figure 19**. The reaction mixture was maintained at a temperature between 128° to 131°F for an additional 25 minutes and heated to 180°F. 82 grams; 0.57 moles dichloroethylether were added dropwise from addition funnel in 10 minutes. Reactor contents were an orange transparent liquid. The reaction mixture was maintained at a temperature between 184°F and 229°F for 17 hours and 49 minutes. TAV was 61.5. The reaction product was a 69.9 wt. % dark burgundy transparent liquid. 237 grams of water were added to give a solution with 40 wt. % solids. **Figure 20** depicts the chemical structures of the dichloroethylether quaternary salts of di-(3-hydroxyethylimidazolidenyl)methane. **Figure 21** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 11**. **Figure 22** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 11**. Bentonite.

EXAMPLE 12

[0070] 120.02 grams; 1.15 moles of aminoethylethanolamine (AEEA) and 264.86 grams water were added into a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column and Friedrichs column on top. The reaction mixture was agitated and heated to 97°F. 187.23 grams; 2.30 moles of 37 % formaldehyde in water were added dropwise from an addition funnel at a rate in 14 minutes where the temperature remained below 140°F. The reaction scheme is shown

in **Figure 19**. The reaction mixtures was maintained at a temperature between 134° to 199°F for 14 minutes. The reaction mixture was heated to 180°F. 140.20 grams; 1.10 moles of benzyl chloride were added dropwise from addition funnel in 20 minutes. The reactor contents are a red brown transparent liquid. The reaction mixtures was maintained at a temperature between 199° and 217°F for 5 hours. TAV was 17. 67.23 grams of water were added to give a solution with 40 wt. % solids. **Figure 20** depicts the chemical structures of the benzyl chloride quaternary salts of triethanolamine. **Figure 23** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 12**.

EXAMPLE 13A

[0071] 120.13 grams; 1.15 moles aminoethylethanolamine (AEEA) and 238.95 grams water were added into a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column and Friedrichs column on top. TAV was 363. The reaction mixtures was agitated and heated to 95°F. 187.60 grams; 2.30 moles of 37 % formaldehyde in water were added dropwise from an addition funnel at a rate in 45 minutes, where the temperature remained below 140°F. The reactor contents are a lime green transparent liquid and had a TAV of 144. The reaction scheme is shown in **Figure 19**. The reaction mixtures was maintained at a temperature between 127° to 155°F for 30 minutes. The reaction mixture was heated to 174°F. 175.97 grams; 0.985 moles diethyl sulfate were added dropwise from addition funnel in 45 minutes. The reactor contents were a burgundy transparent liquid. The reaction mixtures was maintained at a temperature between 100°F and 218°F for 4 hours and 45 minutes. TAV was 24. 166 grams of water were added to give a burgundy colored solution with 39.72 wt. % solids and had a TAV of 18.34. **Figure 20** depicts the chemical structures of the diethyl sulfate quaternary salts of triethanolamine. **Figure 24** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 13A**.

EXAMPLE 13B

[0072] 200 grams Molex Amine 1328 (a mixture of aminoethylethanolamine, N-(2-aminoethyl)piperazine, 5-ethyl-1,4,7-triazabicyclo[4.3.0]non-4,6-diene, 5-ethyl-1,4,7-triazabicyclo[4.3.0]non-6-ene, triethylene tetraamine, and other polyamines) and 400 grams water were added into a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column and Friedrichs column on top. The reaction mixture was heated and maintained at a temperature of 180°F. 398 grams diethyl sulfate were added dropwise from addition funnel. The reaction mixture was maintained at a temperature of 180°F for 2 hours. The reaction product was an amber liquid with a pH of 6.7 and 59.3 wt. % solids.

EXAMPLE 14

[0073] 277 grams; 0.99 moles tetrahydroxyethyl diethylenetriamine (THEDEA) and 413 grams

water were added into a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column and Friedrichs column on top. The reaction mixture was agitated and heated to 175°F. 310 grams; 2.01 moles of diethyl sulfate were added dropwise from addition funnel in 90 minutes. The reactor contents were a orange to red transparent liquid. The reaction mixture was maintained at a temperature between 175°F and 200°F for 4 hours. The final product has 56% solids and had a TAV of 9. **Figure 25** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 14**.

EXAMPLE 15

[0074] 336 g (1.45 mole) of tetrahydroxyethyl diethylenetriamine and 423 g out of 447 g total water were added to a 2 liter pressure reactor kettle. 47 g of 37% inhibited formaldehyde were added dropwise from an addition funnel. The rate of addition was adjusted to maintain reaction temperature of below 140°F. After formaldehyde addition was complete, the reaction mixture was maintained at a temperature of 130°F for 1 hour, then the temperature was increased to 150°F. The reaction scheme is shown in **Figure 26**. Charge 112g out of 126 g (2.50 moles) total of methyl chloride in even increments over a 2 hour period, maintaining the temperature of between 175°F and 225°F. The methyl chloride quaternary salts are shown structurally in **Figure 27**. After methyl chloride addition was complete, the reaction mixture was maintained at a temperature of 200°F for one hour. Use reserved 14 g of methyl chloride to adjust the pH of the reaction mixture to a pH below 5.5 and adjust the total amine value to below 20. Use reserved 24 g of water to adjust the reaction mixture to have a 50 wt. % solids solution. The appearance of the final product was clear to pale yellow transparent liquid. **Figure 28** shows a plot of water release data from Weatherford Wyoming Bentonite using the clay control additive of **Example 15**.

EXAMPLE 16

[0075] 75.3grams methanol and 407.2 grams ETHYLENEAMINE E-100 from Huntsman were added to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column and Friedrichs column on top. ETHYLENEAMINE E-100 is a mixture of tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), hexaethyleneheptamine (HEHA), and higher molecular weight products. E-100 is a complex mixture of various linear, cyclic, and branched products with a number-average molecular weight of 250-300 g/mole. $H_2NCH_2CH_2$ $(NHCH_2CH2)_xNH_2$ where (x=3, 4, 5 and higher). The reaction mixture was agitated and 185 grams of formalin solution (37% Active) were added dropwise from an addition funnel, while the reaction mixture was maintained at a temperature between 130°F -140°F. When all the formalin was added, 250 grams diethyl sulfate (DES) was added dropwise from an addition funnel over a 100 minute period of time, while the reaction mixture was maintained at a temperature below 200°F. The reaction mixture was maintained

at a temperature between 187°F and 200°F for 2 hours. The reaction mixture was then cooled down to a temperature of 150°F. 82.5 grams of methanol was then added to yield a product having 78.52 % solids, a TAV of 295mg KOH/g and a final pH of 9.2.

EXAMPLE 17

[0076] 275.2 grams Amine Heads II from Ascend were charged to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column and Friedrichs column on top. Amine Heads II is a mixture of hexamethylenediamine (HMDA), tetramethylendiamine (TMDA), 1,2-diaminocyclohexane, hexamethyleneimine (HMI). The reaction mixture was agitated and 724.8 grams diethyl sulfate were added dropwise from an addition funnel, while maintaining the temperature between 187°F and 200°F for 3 hours to give a product with 94.12 % solids, TVA of 0 mg KOH/g and a final pH: 1.45

EXAMPLE 18

[0077] 267.3 grams of 3-methoxypropylamine were added to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column, and Friedrichs column on top. The reaction mixture was agitated and 202.9 grams of formalin solution (37% Active) was added dropwise from an addition funnel, while the reaction mixture was maintained at a temperature between 130°F and 140°F. When all the formalin was added, then 385.4 grams of diethyl sulfate (DES) were added dropwise from an addition funnel, while the reaction mixture was maintained at a temperature below 200°F. The reaction mixture was then maintained at a temperature between 187°F and 200°F for 2 hours. The reaction mixture was cooled down to a temperature of 150°F. 144.4 grams of water were added to give a product with 48.89 % solids, a TAV of 362.70 mg KOH/g and a final pH of 11.32.

EXAMPLE 19

Step 1

[0078] 100 grams methanol and 542.9 grams of ETHYLENEAMINE E-100 from Huntsman was added to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column, and Friedrichs column on top. ETHYLENEAMINE E-100 is a mixture of tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), hexaethyleneheptamine (HEHA), and higher molecular weight products. ETHYLENEAMINE E-100 is a complex mixture of various linear, cyclic, and branched products with a number-average molecular weight of 250-300 g/mole. $H_2NCH_2CH_2(NHCH_2CH2)_xNH_2$ where (x=3, 4, 5 and higher). The reaction mixture was agitated and 246.7grams of formalin solution (37% Active) were added dropwise from an addition funnel, while the reaction mixture was maintained at a temperature between 130°F and 140°F. The reaction mixture was mixed for 1 hour and then 110.4grams of methanol were added to yield a product having 59.62 % solids, a TAV of 487mg KOH/g and a final pH of 11.9.

Step 2

[0079] 750 grams of the product of **step 1** was added to a 1 liter resin kettle equipped with a thermocouple, thermocouple well, Vigreux distillation column, and Friedrichs column on top. 250 grams of methylsulfonic acid were added dropwise from an addition funnel. The reaction mixtures was maintained at a temperature between 187°F and 200°F for 1 hour. The reaction mixture was cooled down to a temperature below 100°F to yield a product having 73.37 % solids, a TAV of 230mg KOH/g and a final pH: 8.6

EXAMPLE 20

[0080] This Example compares the Linear Swell after 23 hours for Bentonite (blank), **Example 9**, and Comparative Example (Choline Chloride; CC-120). The lower the curve the better the Linear Swell.

[0081] The Linear Swell Meter was OFITE 115V Dynamic Linear Swell Meter Model # 150-80. 14g of Bentonite was added to a pelletizer/compactor and 10,000 psi pressure was applied for 30 minutes. The pellet was removed from the compactor. Ensure all components of the Linear Swell Meter are clean: transfer stand, cap for wafer tube, bottom plate, magnetic stir bar, Teflon washer, and cup. With both the screens in the linear swell meter cell, the swell meter was zeroed out by clicking on the specific cell(s) to be zeroed out and clicked "apply". One of the screens from the cell was removed and the pellet was added on top of the other screen. The other screen was put on top of the pellet. The transfer stand was gently placed on top of the pellet. The cell was placed on the magnetic stir plate underneath the linear variable differential transformer (LVDT) to make sure that the spindle was directly centered on top of the transfer stand. The fluid to be tested was poured through the hole on the cap for the wafer tube, the box was checked to start the cell and "apply" was clicked. Doing this will start the test for the specific cell. The test results are tabulated in **Table IV**.

TABLE IV

The Linear Swell after 23 hours Data

Sample	Description	Concentration	% Swell
Blank	Bentonite		98.5
Comparative Example	Choline Chloride (CC-120)	6000 ppm	88.9
Example 9	Amine Heads II/Et_2SO_4	6000 ppm	75.9

[0082] Diethyl sulfate quaternary salts of Amine Head II (**Example 8**) swelled the clay less than choline chloride.

EXAMPLE 21

Water Release Clay Stabilization Test

Clay Solution Preparation

[0083] To make 1 wt. % clay solution, 23g of Wyoming Bentonite Clay and 2277 g of distilled water were added to a bottle and shaken until all the clay was dissolved.

Blank Preparation

[0084] Measure 100 mL of clay solution into a graduated cylinder. The clay solution was shaken 10 times. The clay solution separation time and clay precipitation was recorded.

Test Sample Preparation

[0085] Measure 100 mL of clay solution into 6 graduated cylinders. To each graduated cylinders was added 0.1 mL, 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL, and 1.0 mL of Examples 1-5, 8-19. The addition of the clay stabilizers at 0.1 mL, 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL, and 1.0 mL in 100 mL of a clay solution corresponds to 1, 2, 4, 6, 8 and 10 Gallons per Thousand (or gpt). Invert the cylinders 20 times. Start timer and record separation time and clay coagulation. Record clay deposition, swelling and water release. The water release volumes at 60 minutes are tabulated in **Table V**.

TABLE V

Water Release Clay Stabilization Test Results

Example	WR* 0.5 gpt	WR* 1.0 gpt	WR* 2.0 gpt	WR* 4.0 gpt	WR* 6.0 gpt	WR* 8.0 gpt	WR* 10.0 gpt
TW**	n.a.	n.a.	0	0	0	1	2
1	n.a.	n.a.	23	30	29	28	29
2	n.a.	n.a.	0	29	33	35	36
3	n.a.	n.a.	4	26	32	34	36
4	n.a.	n.a.	27	33	34	33	32
5	n.a.	n.a.	2	9	22	26	31
8	33	33	28	29	28	26	25
9	3	45	3	46	45	45	44
10	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11	n.a.	n.a.	1	11	28	26	26
12	n.a.	n.a.	0	10	14	14	14
13	n.a.	n.a.	0	0	30	33	33
14	n.a.	n.a.	27	32	31	30	30
15	3	27	32	31	28	20	18
16	n.a.	n.a.	22	20	18	18	14
17	n.a.	n.a.	38	43	43	42	42
18	n.a	n.a.	12	33	34	33	33
19	n.a.	n.a.	33	30	27	26	23

* water release at 60 minutes

** tap water

EXAMPLE 22

Capillary Suction Timer Clay Stabilization Test

Rock Sample Preparation

[0086] A rock sample was placed in a Gyral Grinder and grinding of the rock sample was begun. The rock sample was ground for 1 hour using a timer. The ground rock sample was placed into a 200-mesh sieve. The aggregate that passed through the sieve was placed in a pan for testing and placed to the side.

Mixture Preparation

[0087] Using a 100mL volumetric flask, a solution was prepared that will be used to mix with the rock sample. At least one solution should be prepared as the sample with straight tap water will be used as a reference blank. 100g of solution was added to a 250mL beaker equipped with a magnetic stir bar. A specified amount of each shale inhibitor was added to the beaker. The beaker was placed on stir plate and stirring was begun at a speed at which a vortex reaches the bottom of the beaker. 2g of the untreated Bentonite sample was added and a timer was set for 5 minutes. After 5 minutes, the stir plate was turned off, the solution was poured into a 100mL graduated cylinder, and a timer was set for 15 minutes. After 15 minutes, the mixture was poured back into the beaker, the beaker was placed on the magnetic stir plate and stirring was restarted on the plate. Wait until the vortex returned and the clay had become dispersed.

Test Procedure

[0088] A Venture Innovations capillary suction timer (CST) from Venture Chemicals, Inc. in Lafayette , LA was used in the tests. Before each test, the test head, filter paper, and stainless steel funnel were cleaned and dried. Make sure the cable from the test head was plugged into the control box and the reading on the control box display was reset to zero. A piece of 7×9cm CST filter paper from Venture Innovations Inc. (part no. IFP-9053) was placed on the test head with the stainless steel probes facing down. The stainless steel funnel was fitted into the test head.

[0089] Using a 5-mL syringe, 5-mL of sample was withdrawn from the vortex. Consecutive samples were removed from the same position in the vortex, where the previous sample was taken. A 5 mL sample was charged into the stainless steel funnel. The 5 mL sample charge was repeated twice more. Instrument started automatically when a beep sounds from the control box. When this beep sounded, the timer started. After the second beep, the timer stopped and the time in seconds was displayed. The data was recorded in seconds and tabulation in **Table VI**.

TABLE VI
Capillary Suction Timer Clay Stabilization Test Results

Example	CST Concentration (ppm)	CST Time (seconds)
Tap Water		906.35

1	4000	43
2	Not tested	Not tested
3	Not tested	Not tested
4	4000	18
5	4000	90
5	5000	68
5	6000	92
8	4000	17
8	6000	17
9	6000	15
10	6000	323
11	6000	55
12	Not tested	Not tested
13	6000	38
14	2000	394
15	6000	19
16	6000	19
17	6000	15
18	6000	19
19	6000	18

[0090] The data clearly shows that the amine quaternary salts represent a reduced toxicity option to prior art more toxic clay control additives and stabilize the clay in a shorter period of time compared to prior art clay stabilizers.

[0091] All references cited herein are incorporated by reference. Although the invention has been disclosed with reference to its preferred embodiments, from reading this description those of skill in the art may appreciate changes and modification that may be made which do not depart from the scope and spirit of the invention as described above and claimed hereafter.

CLAIMS

We claim:

1. A clay stabilize composition comprising:

compounds of **Formula (I)**:

$$[R^1R^2R^3N(R^0)_j]^+A^- \quad \textbf{(I)},$$

reaction products of at least one compounds of **Formula (I)** with at least one aldehyde of the general formula R^4CHO, and

mixtures or combinations thereof,

where:

A and R^0 are derived from the general formula R^0A selected from the formulas consisting of $R^IR^{II}SO_4$, R^ISO_3H, $R^{III}Cl$, $ArCl$, $ArR^{IV}Cl$, $R^VO(R^{VI}O)R^{VI}Cl$, $ClR^{VI}O(R^{VI}O)R^{VI}Cl$, or mixtures and combinations thereof, where R^I, R^{II}, R^{III}, and R^V are the same or different carbyl groups, **Ar** is an aryl group, and R^{IV} and R^{VI} are the same or different linking carbyl groups, where R^0 is selected from the group consisting of hydrogen atom (**H**), R^I or R^{II}, R^{III}, **Ar**, ArR^{IV}, $R^VO(R^{VI}O)R^{VII}$, $ClR^{VI}O(R^{VI}O)R^{VI}$, $R^{VI}O(R^{VI}O)R^{VI}$, and mixtures thereof and A^- is selected from the group consisting of $R^ISO_4^-$ or $R^{II}SO_4^-$, $R^ISO_3^-$, Cl^-, $[R^{VI}O(R^{VI}O)R^{VI}Cl]^-$, $[R^{VI}O(R^{VI}O)R^{VI}]^{2-}$, and mixtures thereof,

R^1, R^2, and R^3 are the same or different and are either a hydrogen atom (H), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms, an R^aOH group, an $R^a(OR^{aa})_nOH$ group, an R^aOR group, an $R^a(OR^{aa})_nOR'$ group, or mixtures and combinations thereof, provided at least one of the R^1, R^2, and R^3 groups is not a hydrogen atom,

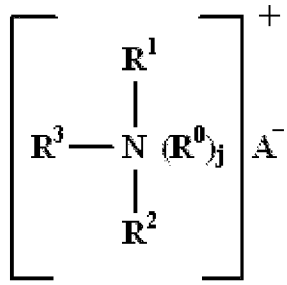
j is an integer having a value between 1 and the maximum number of **NH** moieties plus 1,

R^4 is a hydrogen atom (H), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms,

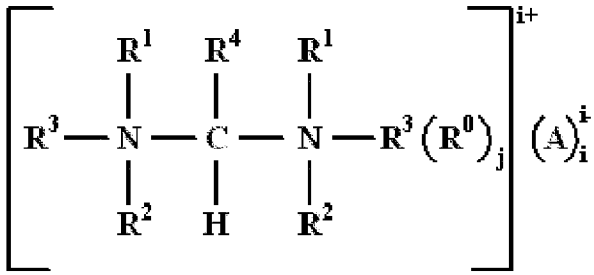
R^a and R^{aa} are the same or different linear or branched carbyl linking groups having between 1 and 20 carbon atoms, and

R and **R'** are linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms.

2. The composition of claim 1, wherein the quaternary salts are selected from compounds of **Formula (II)**

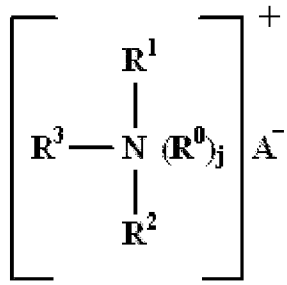


compounds of **Formula (III)**:

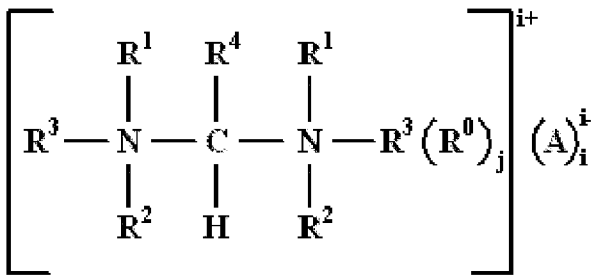


mixtures or combinations thereof.

3. The composition of claim 1, wherein the quaternary salts are selected from compounds of **Formula (II)**:



4. The composition of claim 1, wherein the quaternary salts are selected from compounds of **Formula (III)**:



5. The clay stabilize composition of claim 1, comprise quaternary salts of:

(a) (i) primary amines, secondary amines, and tertiary amines, (ii) monoalkanol amines, dialkanol amines, and trialkanol amines, (iii) monoalkyleneether amines,

dialkyleneether amines, trialkyleneether amines, (iv) alkyl-alkanol amines, alkyl-dialkanol amines, and dialkyl-alkanol amines, (v) alkyl-alkyleneether amines, dialkyl-alkyleneether amines, and alkyl-dialkyleneether amines, (vi) alkyl-alkanol-alkyleneether amines, and (vii) alkanol-alkyleneether amines, dialkanol-alkyleneether amines, and alkanol-dialkyleneether amines;

(b) reaction products of (i) primary amines, secondary amines, and tertiary amines, (ii) monoalkanol amines, dialkanol amines, and trialkanol amines, (iii) monoalkyleneether amines, dialkyleneether amines, trialkyleneether amines, (iv) alkyl-alkanol amines, alkyl-dialkanol amines, and dialkyl-alkanol amines, (v) alkyl-alkyleneether amines, dialkyl-alkyleneether amines, and alkyl-dialkyleneether amines, (vi) alkyl-alkanol-alkyleneether amines, (vii) alkanol-alkyleneether amines, dialkanol-alkyleneether amines, and alkanol-dialkyleneether amines or (viii) mixtures and combinations thereof with an aldehyde, an aldehyde donor, or mixtures and combinations thereof; or

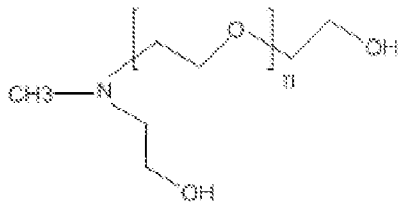
(c) mixtures and combinations thereof,

where the quaternizing agent comprise a compound of the general formula $\mathbf{R^0A}$ selected from the formulas consisting of $\mathbf{R^IR^{II}SO_4}$, $\mathbf{R^ISO_3H}$, $\mathbf{R^{III}Cl}$, $\mathbf{ArCl}$, $\mathbf{ArR^{IV}Cl}$, $\mathbf{R^VO(R^{VI}O)R^{VI}Cl}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}Cl}$, or mixtures and combinations thereof, where $\mathbf{R^I}$, $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, and $\mathbf{R^V}$ are the same or different carbyl groups, **Ar** is an aryl group, and $\mathbf{R^{IV}}$ and $\mathbf{R^{VI}}$ are the same or different linking carbyl groups, where $\mathbf{R^0}$ is selected from the group consisting of hydrogen atom (**H**), $\mathbf{R^I}$ or $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, **Ar**, $\mathbf{ArR^{IV}}$, $\mathbf{R^VO(R^{VI}O)R^{VII}}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}}$, $\mathbf{R^{VI}O(R^{VI}O)R^{VI}}$, and mixtures thereof and $\mathbf{A^-}$ is selected from the group consisting of $\mathbf{R^ISO_4^-}$ or $\mathbf{R^{II}SO_4^-}$, $\mathbf{R^ISO_3^-}$, $\mathbf{Cl^-}$, $\mathbf{[R^{VI}O(R^{VI}O)R^{VI}Cl]^-}$, $\mathbf{[R^{VI}O(R^{VI}O)R^{VI}]^{2-}}$, and mixtures thereof.

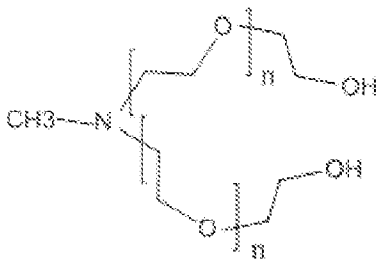
6. The composition of claim 5, wherein the clay stabilize composition comprises at least one quaternary salt of (i) primary amines, secondary amines, and tertiary amines, (ii) monoalkanol amines, dialkanol amines, and trialkanol amines, (iii) monoalkyleneether amines, dialkyleneether amines, trialkyleneether amines, (iv) alkyl-alkanol amines, alkyl-dialkanol amines, and dialkyl-alkanol amines, (v) alkyl-alkyleneether amines, dialkyl-alkyleneether amines, and alkyl-dialkyleneether amines, (vi) alkyl-alkanol-alkyleneether amines, and (vii) alkanol-alkyleneether amines, dialkanol-alkyleneether amines, and alkanol-dialkyleneether amines and (viii) mixtures or combinations thereof.

7. The composition of claim 6, wherein:

the tertiary amines are a compound of the general formula:



or



or

mixtures and combinations thereof, where **n** is an integer having a value between 0 and 10, and

R^0A is selected from the group consisting of dimethyl sulfate, diethyl sulfate, benzyl chloride, methyl chloride, dichloroethylether, methane sulfonic acid, and mixtures or combinations thereof.

8. The composition of claim 7, wherein **R^0A** is selected from the group consisting of diethylsulfate, dimethylsulfate, and mixtures or combinations thereof in the presence or absence of HCl.

9. The composition of claim 6, wherein the trialkanolamine is triethanolamine and **R^0A** is selected from the group consisting of diethyl sulfate, dimethyl sulfate, dichloroethylether, and mixtures or combinations thereof.

10. The composition of claim 9, wherein **R^0A** is diethyl sulfate.

11. The composition of claim 1, wherein the quaternary salts further comprise a mixture of 1,2-cyclohexanediamine, hexamethylenediamine, tetramethylenediamine, 3-aminopropan-1-ol, 2-aminocyclopentanemethylamine and 2-methyl-1,5,pentanediamine and **R^0A** is selected from the group consisting of dimethylsulfate, diethylsulfate, benzylchloride, methylchloride, dichloroethylether, and mixtures or combinations thereof.

12. The composition of claim 11, wherein **R^0A** is with diethyl sulfate.

13. The composition of claim 1, further comprising a corrosion system including a mixture of 2-

(2-(4-morpholinyl)ethoxy)ethanol, 4-(2-2-aminoethoxy)ethyl) morpholine, and 4-(4-morpholinyl) ethoxyethyl) morpholine.

14. The composition of claim 1, wherein the clay stabilize composition comprises at least one quaternary salt of a reaction product.

15. The composition of claim 14 wherein the reaction products comprise reactions of:

amines of the general formula:

$$R^{11}R^{12}NH$$

and formaldehyde or a formaldehyde donor,

where R^{11} and R^{12} is a hydrogen atom, a linear, branched, or cyclic carbyl group having between 1 and 20 carbon atoms, provided that both R^{11} and R^{12} are not a hydrogen atom and R^0A is selected from the group consisting of methyl chloride, benzyl chloride, dimethylsulfate, diethylsulfate, dichloroethylether, and mixtures or combinations thereof.

16. The composition of 15, further comprising a corrosion system including a mixture of 2-(2-(4-morpholinyl)ethoxy)ethanol, 4-(2-2-aminoethoxy)ethyl) morpholine, and 4-(4-morpholinyl) ethoxyethyl) morpholine

17. The composition of claim 15, wherein R^{11} is hydrogen and R^{12} is a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms.

18. The composition of claim 15, wherein the amines are given by the general formula:

$$H_3CO(CH_2)_nNH_2$$

where **n** is an integer having a value between 1 to 10.

19. The composition of claim 15, where the amine comprises $H_3CO(CH2)_3NH_2$.

20. The composition of claim 15, wherein the dialkanolamine comprises $HN(CH_2CH_2OH)_2$.

21. The composition claims of 15-20, further comprising a corrosion system including a mixture of 2-(2-(4-morpholinyl)ethoxy)ethanol, 4-(2-2-aminoethoxy)ethyl) morpholine, and 4-(4-morpholinyl) ethoxyethyl) morpholine

22. A method for stabilizing clay during drilling comprising:

drilling into a clay containing formation with a drilling fluid including an effective amount of a clay stabilize composition comprising compounds of **Formula (I)**:

$$[R^1R^2R^3N(R^0)_j]^+A^- \quad \textbf{(I)}$$

and reaction products of at least one compounds of **Formula (I)** with at least one aldehyde of the general formula R^4CHO,

where:

A and R^0 are derived from the general formula R^0A selected from the formulas consisting of $R^IR^{II}SO_4$, R^ISO_3H, $R^{III}Cl$, **ArCl**, $ArR^{IV}Cl$, $R^VO(R^{VI}O)R^{VI}Cl$, $ClR^{VI}O(R^{VI}O)R^{VI}Cl$, or mixtures and combinations thereof, where R^I, R^{II}, R^{III}, and R^V are the same or different carbyl groups, **Ar** is an aryl group, and R^{IV} and R^{VI} are the same or different linking carbyl groups, where R^0 is selected from the group consisting of hydrogen atom (**H**), R^I or R^{II}, R^{III}, **Ar**, ArR^{IV}, $R^VO(R^{VI}O)R^{VII}$, $ClR^{VI}O(R^{VI}O)R^{VI}$, $R^{VI}O(R^{VI}O)R^{VI}$, and mixtures thereof and A^- is selected from the group consisting of $R^ISO_4^-$ or $R^{II}SO_4^-$, $R^ISO_3^-$, Cl^-, $[R^{VI}O(R^{VI}O)R^{VI}Cl]^-$, $[R^{VI}O(R^{VI}O)R^{VI}]^{2-}$, and mixtures thereof,

R^1, R^2, and R^3 are the same or different and are either a hydrogen atom (H), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms, an R^aOH group, an $R^a(OR^{aa})_nOH$ group, an R^aOR group, an $R^a(OR^{aa})_nOR'$ group, or mixtures and combinations thereof, provided at least one of the R^1, R^2, and R^3 groups is not a hydrogen atom,

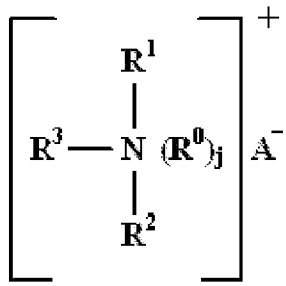
j is an integer having a value between 1 and the maximum number of **NH** moieties plus 1,

R^4 is a hydrogen atom (H), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms,

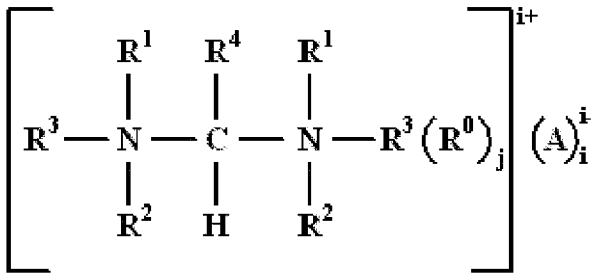
R^a and R^{aa} are the same or different linear or branched carbyl linking groups having between 1 and 20 carbon atoms, and

R and **R'** are linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms.

23. The method of claim 22, wherein the quaternary salts are selected from compounds of **Formula (II)**

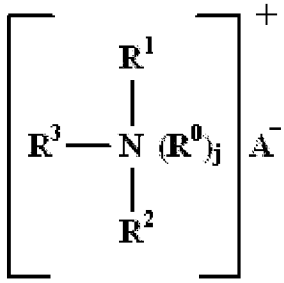


compounds of **Formula (III)**:

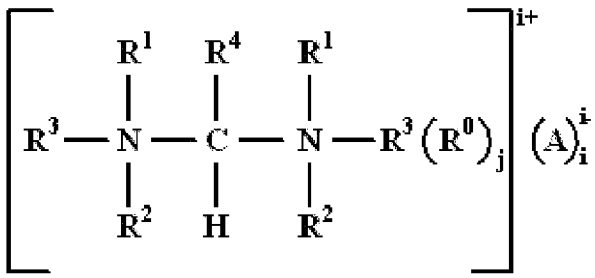


and mixtures or combinations thereof.

24. The method of claim 22, wherein the quaternary salts are selected from compounds of **Formula (II)**:



25. The method of claim 22, wherein the quaternary salts are selected from compounds of **Formula (III)**:



26. The method of claim 1, comprise quaternary salts of:

(a) (i) primary amines, secondary amines, and tertiary amines, (ii) monoalkanol amines, dialkanol amines, and trialkanol amines, (iii) monoalkyleneether amines, dialkyleneether amines, trialkyleneether amines, (iv) alkyl-alkanol amines, alkyl-dialkanol amines, and dialkyl-alkanol amines, (v) alkyl-alkyleneether amines, dialkyl-alkyleneether amines, and alkyl-dialkyleneether amines, (vi) alkyl-alkanol-alkyleneether amines, and (vii) alkanol-alkyleneether amines, dialkanol-alkyleneether amines, and alkanol-dialkyleneether amines;

(b) reaction products of (i) primary amines, secondary amines, and tertiary amines, (ii)

monoalkanol amines, dialkanol amines, and trialkanol amines, (iii) monoalkyleneether amines, dialkyleneether amines, trialkyleneether amines, (iv) alkyl-alkanol amines, alkyl-dialkanol amines, and dialkyl-alkanol amines, (v) alkyl-alkyleneether amines, dialkyl-alkyleneether amines, and alkyl-dialkyleneether amines, (vi) alkyl-alkanol-alkyleneether amines, (vii) alkanol-alkyleneether amines, dialkanol-alkyleneether amines, and alkanol-dialkyleneether amines or (viii) mixtures and combinations thereof with an aldehyde, an aldehyde donor, or mixtures and combinations thereof; or

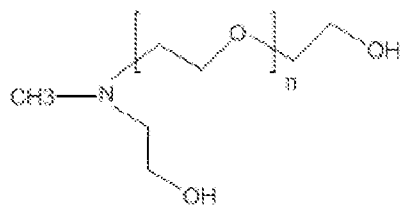
(c) mixtures and combinations thereof,

where the quaternizing agent comprise a compound of the general formula $\mathbf{R^0A}$ selected from the formulas consisting of $\mathbf{R^IR^{II}SO_4}$, $\mathbf{R^ISO_3H}$, $\mathbf{R^{III}Cl}$, **ArCl**, $\mathbf{ArR^{IV}Cl}$, $\mathbf{R^VO(R^{VI}O)R^{VI}Cl}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}Cl}$, or mixtures and combinations thereof, where a hydrogen atom (**H**), $\mathbf{R^I}$, $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, and $\mathbf{R^V}$ are the same or different carbyl groups, **Ar** is an aryl group, and $\mathbf{R^{IV}}$ and $\mathbf{R^{VI}}$ are the same or different linking carbyl groups, where $\mathbf{R^0}$ is selected from the group consisting of hydrogen atom (**H**), $\mathbf{R^I}$ or $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, **Ar**, $\mathbf{ArR^{IV}}$, $\mathbf{R^VO(R^{VI}O)R^{VII}}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}}$, $\mathbf{R^{VI}O(R^{VI}O)R^{VI}}$, and mixtures thereof and $\mathbf{A^-}$ is selected from the group consisting of $\mathbf{R^ISO_4^-}$ or $\mathbf{R^{II}SO_4^-}$, $\mathbf{R^ISO_3^-}$, $\mathbf{Cl^-}$, $\mathbf{[R^{VI}O(R^{VI}O)R^{VI}Cl]^-}$, $\mathbf{[R^{VI}O(R^{VI}O)R^{VI}]^{2-}}$, and mixtures thereof.

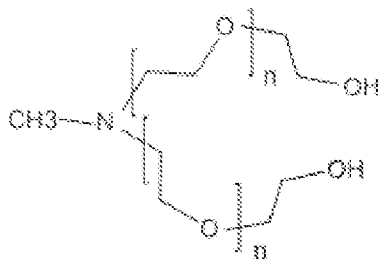
27. The method of claim 26, wherein the clay stabilize composition comprises at least one quaternary salt of (i) primary amines, secondary amines, and tertiary amines, (ii) monoalkanol amines, dialkanol amines, and trialkanol amines, (iii) monoalkyleneether amines, dialkyleneether amines, trialkyleneether amines, (iv) alkyl-alkanol amines, alkyl-dialkanol amines, and dialkyl-alkanol amines, (v) alkyl-alkyleneether amines, dialkyl-alkyleneether amines, and alkyl-dialkyleneether amines, (vi) alkyl-alkanol-alkyleneether amines, and (vii) alkanol-alkyleneether amines, dialkanol-alkyleneether amines, and alkanol-dialkyleneether amines and (viii) mixtures or combinations thereof.

28. The method of claim 27, wherein:

the tertiary amines are a compound of the general formula:



or



or

mixtures and combinations thereof, where **n** is an integer having a value between 0 and 10, and

R^0A is selected from the group consisting of dimethyl sulfate, diethyl sulfate, benzyl chloride, methyl chloride, dichloroethylether, and mixtures or combinations thereof.

29. The method of claim 28, wherein **R^0A** is selected from the group consisting of diethylsulfate, dimethylsulfate, and mixtures or combinations thereof in the presence or absence of HCl.

30. The method of claim 27, wherein the trialkanolamine is triethanolamine and **R^0A** is selected from the group consisting of diethyl sulfate, dimethyl sulfate, dichloroethylether, and mixtures or combinations thereof.

31. The method of claim 30, wherein **R^0A** is diethyl sulfate.

32. The method of claim 22, wherein the quaternary salts further comprise a mixture of 1,2-cyclohexanediamine, hexamethylenediamine, tetramethylenediamine, 3-aminopropan-1-ol, 2-aminocyclopentanemethylamine and 2-methyl-1,5,pentanediamine and **R^0A** is selected from the group consisting of dimethylsulfate, diethylsulfate, benzylchloride, methylchloride, dichloroethylether, and mixtures or combinations thereof.

33. The method of claim 32, wherein **R^0A** is with diethyl sulfate.

34. The method of claim 22, wherein the clay stabilizing compositions further includes a corrosion system includes a mixture of 2-(2-(4-morpholinyl)ethoxy)ethanol, 4-(2-2-aminoethoxy)ethyl) morpholine, and 4-(4-morpholinyl) ethoxyethyl) morpholine.

35. The method of claim 22, wherein the clay stabilize composition comprises at least one quaternary salt of a reaction product.

36. The method of claim 35, wherein the reaction products comprise reactions of:

amines of the general formula:

$$R^{11}R^{12}NH$$

and formaldehyde or a formaldehyde donor,

where R^{11} and R^{12} is a hydrogen atom, a linear, branched, or cyclic carbyl group having between 1 and 20 carbon atoms, provided that both R^{11} and R^{12} are not a hydrogen atom and R^0A is selected from the group consisting of methyl chloride, benzyl chloride, dimethylsulfate, diethylsulfate, dichloroethylether, and mixtures or combinations thereof.

37. The method of 36, wherein the clay stabilizing compositions further includes a corrosion system includes a mixture of 2-(2-(4-morpholinyl)ethoxy)ethanol, 4-(2-2-aminoethoxy)ethyl) morpholine, and 4-(4-morpholinyl) ethoxyethyl) morpholine

38. The method of claim 36, wherein R^{11} is hydrogen and R^{12} is a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms.

39. The method of claim 36, wherein the amines are given by the general formula:

$$H_3CO(CH_2)_nNH_2$$

where **n** is an integer having a value between 1 to 10.

40. The method of claim 36, where the amine comprises $H_3CO(CH2)_3NH_2$.

41. The method of claim 36, wherein the dialkanolamine comprises $HN(CH_2CH_2OH)_2$.

42. The method claims of 36-41, wherein the clay stabilizing compositions further includes a corrosion system includes a mixture of 2-(2-(4-morpholinyl)ethoxy)ethanol, 4-(2-2-aminoethoxy)ethyl) morpholine, and 4-(4-morpholinyl) ethoxyethyl) morpholine.

43. A method for stabilizing clay during production comprising:

pumping into a clay containing formation with a completion fluid including an effective amount of a clay stabilize composition comprising compounds of **Formula (I)**:

$$[R^1R^2R^3N(R^0)_j]^+A^- \quad \textbf{(I)}$$

and reaction products of at least one compounds of Formula (I) with at least one aldehyde of the

general formula $\mathbf{R^4CHO}$,

where:

A and $\mathbf{R^0}$ are derived from the general formula $\mathbf{R^0A}$ selected from the formulas consisting of $\mathbf{R^IR^{II}SO_4}$, $\mathbf{R^ISO_3H}$, $\mathbf{R^{III}Cl}$, **ArCl**, $\mathbf{ArR^{IV}Cl}$, $\mathbf{R^VO(R^{VI}O)R^{VI}Cl}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}Cl}$, or mixtures and combinations thereof, where $\mathbf{R^I}$, $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, and $\mathbf{R^V}$ are the same or different carbyl groups, **Ar** is an aryl group, and $\mathbf{R^{IV}}$ and $\mathbf{R^{VI}}$ are the same or different linking carbyl groups, where $\mathbf{R^0}$ is selected from the group consisting of hydrogen atom (**H**), $\mathbf{R^I}$ or $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, **Ar**, $\mathbf{ArR^{IV}}$, $\mathbf{R^VO(R^{VI}O)R^{VII}}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}}$, $\mathbf{R^{VI}O(R^{VI}O)R^{VI}}$, and mixtures thereof and $\mathbf{A^-}$ is selected from the group consisting of $\mathbf{R^ISO_4^-}$ or $\mathbf{R^{II}SO_4^-}$, $\mathbf{R^ISO_3^-}$, $\mathbf{Cl^-}$, $\mathbf{[R^{VI}O(R^{VI}O)R^{VI}Cl]^-}$, $\mathbf{[R^{VI}O(R^{VI}O)R^{VI}]^{2-}}$, and mixtures thereof,

$\mathbf{R^1}$, $\mathbf{R^2}$, and $\mathbf{R^3}$ are the same or different and are either a hydrogen atom (H), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms, an $\mathbf{R^aOH}$ group, an $\mathbf{R^a(OR^{aa})_nOH}$ group, an $\mathbf{R^aOR}$ group, an $\mathbf{R^a(OR^{aa})_nOR'}$ group, or mixtures and combinations thereof, provided at least one of the $\mathbf{R^1}$, $\mathbf{R^2}$, and $\mathbf{R^3}$ groups is not a hydrogen atom,

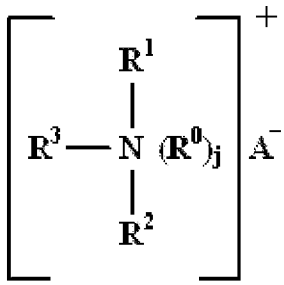
j is an integer having a value between 1 and the maximum number of **NH** moieties plus 1,

$\mathbf{R^4}$ is a hydrogen atom (H), a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms,

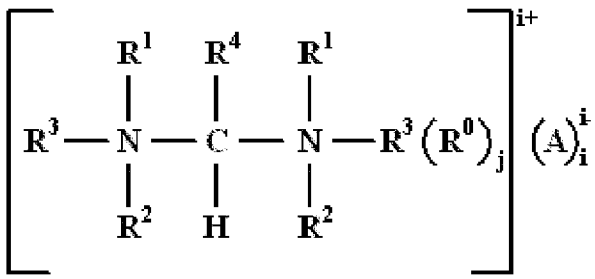
$\mathbf{R^a}$ and $\mathbf{R^{aa}}$ are the same or different linear or branched carbyl linking groups having between 1 and 20 carbon atoms, and

R and **R'** are linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms.

44. The method of claim 43, wherein the quaternary salts are selected from compounds of **Formula (II)**

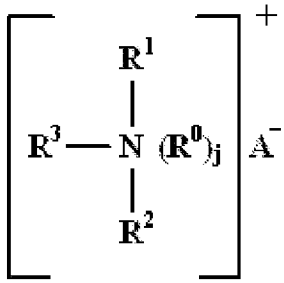


compounds of **Formula (III)**:

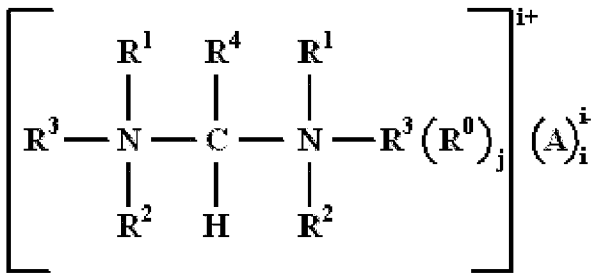


and mixtures or combinations thereof.

45. The method of claim 43, wherein the quaternary salts are selected from compounds of **Formula (II)**:



46. The method of claim 43, wherein the quaternary salts are selected from compounds of **Formula (III)**:



47. The method of claim 43, comprise quaternary salts of:

(a) (i) primary amines, secondary amines, and tertiary amines, (ii) monoalkanol amines, dialkanol amines, and trialkanol amines, (iii) monoalkyleneether amines, dialkyleneether amines, trialkyleneether amines, (iv) alkyl-alkanol amines, alkyl-dialkanol amines, and dialkyl-alkanol amines, (v) alkyl-alkyleneether amines, dialkyl-alkyleneether amines, and alkyl-dialkyleneether amines, (vi) alkyl-alkanol-alkyleneether amines, and (vii) alkanol-alkyleneether amines, dialkanol-alkyleneether amines, and alkanol-dialkyleneether amines;

(b) reaction products of (i) primary amines, secondary amines, and tertiary amines, (ii) monoalkanol amines, dialkanol amines, and trialkanol amines, (iii) monoalkyleneether

amines, dialkyleneether amines, trialkyleneether amines, (iv) alkyl-alkanol amines, alkyl-dialkanol amines, and dialkyl-alkanol amines, (v) alkyl-alkyleneether amines, dialkyl-alkyleneether amines, and alkyl-dialkyleneether amines, (vi) alkyl-alkanol-alkyleneether amines, (vii) alkanol-alkyleneether amines, dialkanol-alkyleneether amines, and alkanol-dialkyleneether amines or (viii) mixtures and combinations thereof with an aldehyde, an aldehyde donor, or mixtures and combinations thereof; or

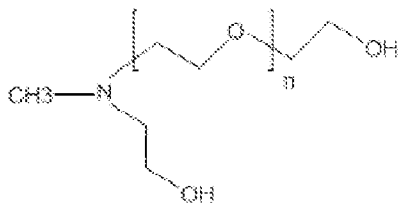
(c) mixtures and combinations thereof,

where the quaternizing agent comprise a compound of the general formula $\mathbf{R^0A}$ selected from the formulas consisting of $\mathbf{R^IR^{II}SO_4}$, $\mathbf{R^ISO_3H}$, $\mathbf{R^{III}Cl}$, $\mathbf{ArCl}$, $\mathbf{ArR^{IV}Cl}$, $\mathbf{R^VO(R^{VI}O)R^{VI}Cl}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}Cl}$, or mixtures and combinations thereof, where $\mathbf{R^I}$, $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, and $\mathbf{R^V}$ are the same or different carbyl groups, **Ar** is an aryl group, and $\mathbf{R^{IV}}$ and $\mathbf{R^{VI}}$ are the same or different linking carbyl groups, where $\mathbf{R^0}$ is selected from the group consisting of hydrogen atom (**H**), $\mathbf{R^I}$ or $\mathbf{R^{II}}$, $\mathbf{R^{III}}$, **Ar**, $\mathbf{ArR^{IV}}$, $\mathbf{R^VO(R^{VI}O)R^{VII}}$, $\mathbf{ClR^{VI}O(R^{VI}O)R^{VI}}$, $\mathbf{R^{VI}O(R^{VI}O)R^{VI}}$, and mixtures thereof and $\mathbf{A^-}$ is selected from the group consisting of $\mathbf{R^ISO_4^-}$ or $\mathbf{R^{II}SO_4^-}$, $\mathbf{R^ISO_3^-}$, $\mathbf{Cl^-}$, $\mathbf{[R^{VI}O(R^{VI}O)R^{VI}Cl]^-}$, $\mathbf{[R^{VI}O(R^{VI}O)R^{VI}]^{2-}}$, and mixtures thereof.

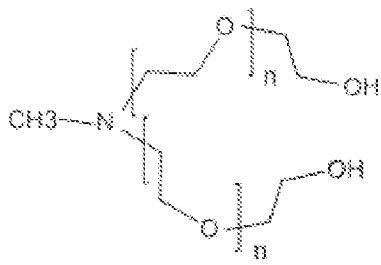
48. The method of claim 47, wherein the clay stabilize composition comprises at least one quaternary salt of (i) primary amines, secondary amines, and tertiary amines, (ii) monoalkanol amines, dialkanol amines, and trialkanol amines, (iii) monoalkyleneether amines, dialkyleneether amines, trialkyleneether amines, (iv) alkyl-alkanol amines, alkyl-dialkanol amines, and dialkyl-alkanol amines, (v) alkyl-alkyleneether amines, dialkyl-alkyleneether amines, and alkyl-dialkyleneether amines, (vi) alkyl-alkanol-alkyleneether amines, and (vii) alkanol-alkyleneether amines, dialkanol-alkyleneether amines, and alkanol-dialkyleneether amines and (viii) mixtures or combinations thereof.

49. The method of claim 48, wherein:

the tertiary amines are a compound of the general formula:



or



or

mixtures and combinations thereof, where **n** is an integer having a value between 0 and 10, and

$\mathbf{R^0A}$ is selected from the group consisting of dimethyl sulfate, diethyl sulfate, benzyl chloride, methyl chloride, dichloroethylether, and mixtures or combinations thereof.

50. The method of claim 49, wherein $\mathbf{R^0A}$ is selected from the group consisting of diethylsulfate, dimethylsulfate, and mixtures or combinations thereof in the presence or absence of HCl.

51. The method of claim 48, wherein the trialkanolamine is triethanolamine and $\mathbf{R^0A}$ is selected from the group consisting of diethyl sulfate, dimethyl sulfate, dichloroethylether, and mixtures or combinations thereof.

52. The method of claim 51, wherein $\mathbf{R^0A}$ is diethyl sulfate.

53. The method of claim 43, wherein the quaternary salts further comprise a mixture of 1,2-cyclohexanediamine, hexamethylenediamine, tetramethylenediamine, 3-aminopropan-1-ol, 2-aminocyclopentanemethylamine and 2-methyl-1,5,pentanediamine and $\mathbf{R^0A}$ is selected from the group consisting of dimethylsulfate, diethylsulfate, benzylchloride, methylchloride, dichloroethylether, and mixtures or combinations thereof.

54. The method of claim 53, wherein $\mathbf{R^0A}$ is with diethyl sulfate.

55. The method of claim 43, wherein the clay stabilizing compositions further includes a corrosion system includes a mixture of 2-(2-(4-morpholinyl)ethoxy)ethanol, 4-(2-2-aminoethoxy)ethyl) morpholine, and 4-(4-morpholinyl) ethoxyethyl) morpholine.

56. The method of claim 43, wherein the clay stabilize composition comprises at least one quaternary salt of a reaction product.

57. The method of claim 56, wherein the reaction products comprise reactions of:

amines of the general formula:

$$R^{11}R^{12}NH$$

and formaldehyde or a formaldehyde donor,

where R^{11} and R^{12} is a hydrogen atom, a linear, branched, or cyclic carbyl group having between 1 and 20 carbon atoms, provided that both R^{11} and R^{12} are not a hydrogen atom and R^0A is selected from the group consisting of methyl chloride, benzyl chloride, dimethylsulfate, diethylsulfate, dichloroethylether, and mixtures or combinations thereof.

58. The method of 57, wherein the clay stabilizing compositions further includes a corrosion system includes a mixture of 2-(2-(4-morpholinyl)ethoxy)ethanol, 4-(2-2-aminoethoxy)ethyl) morpholine, and 4-(4-morpholinyl) ethoxyethyl) morpholine

59. The method of claim 57, wherein R^{11} is hydrogen and R^{12} is a linear, branched or cyclic carbyl group having between 1 and 20 carbon atoms.

60. The method of claim 57, wherein the amines are given by the general formula:

$$H_3CO(CH_2)_nNH_2$$

where **n** is an integer having a value between 1 to 10.

61. The method of claim 57, where the amine comprises $H_3CO(CH2)_3NH_2$.

62. The method of claim 57, wherein the dialkanolamine comprises $HN(CH_2CH_2OH)_2$.

63. The composition claims of 47-62, wherein the clay stabilizing compositions further includes a corrosion system includes a mixture of 2-(2-(4-morpholinyl)ethoxy)ethanol, 4-(2-2-aminoethoxy)ethyl) morpholine, and 4-(4-morpholinyl) ethoxyethyl) morpholine.

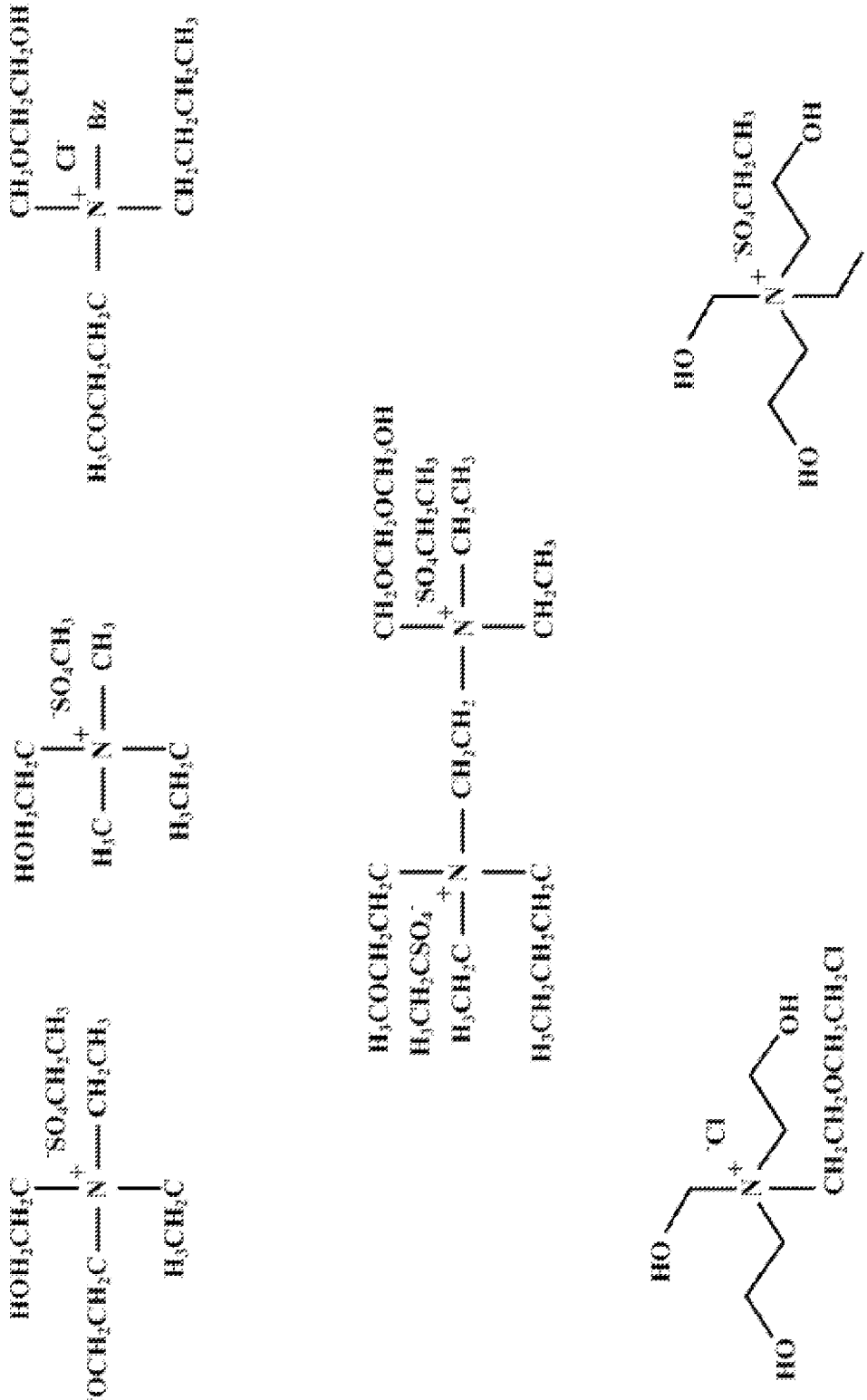


FIG. 1A

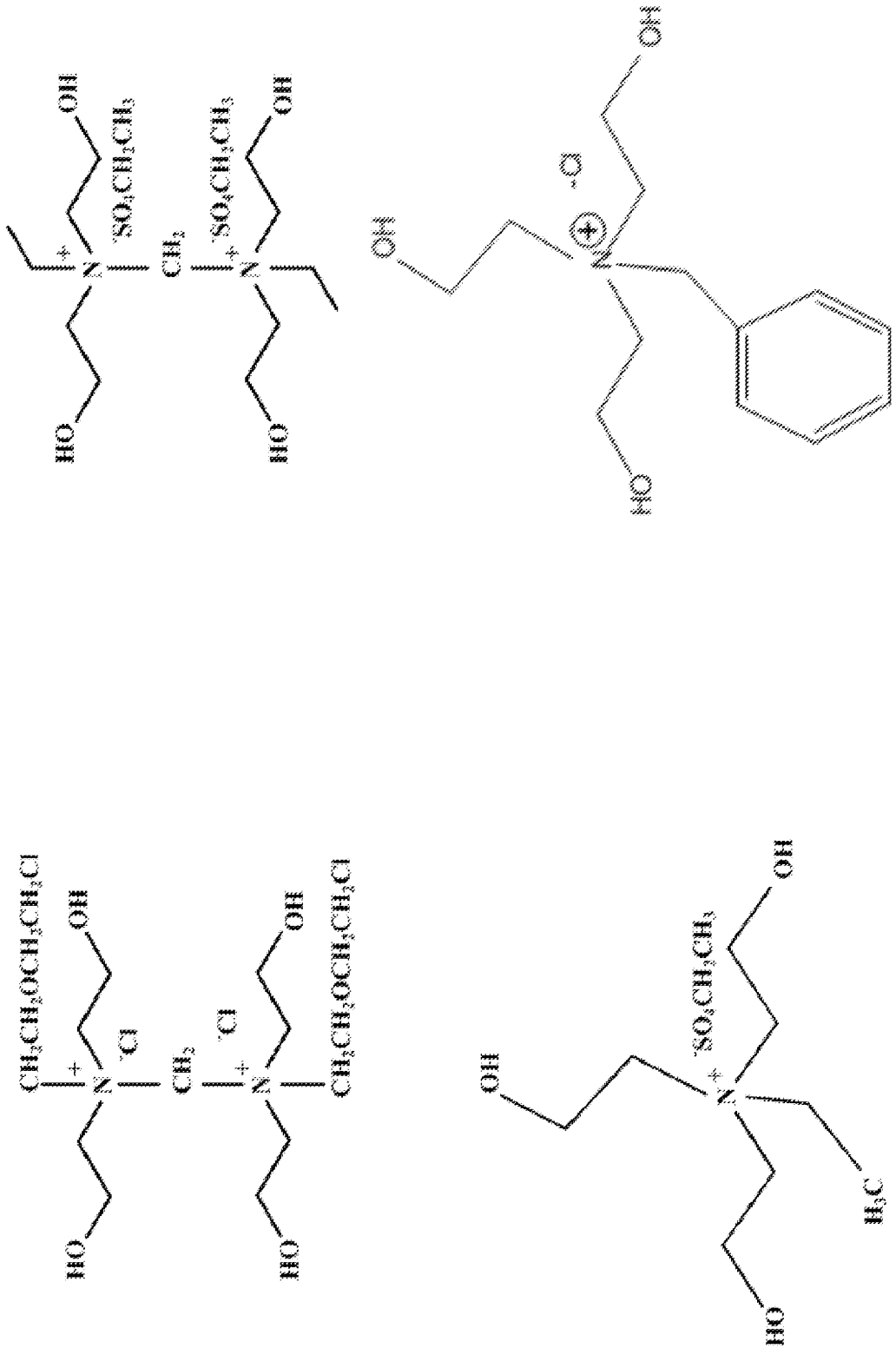


FIG. 1B

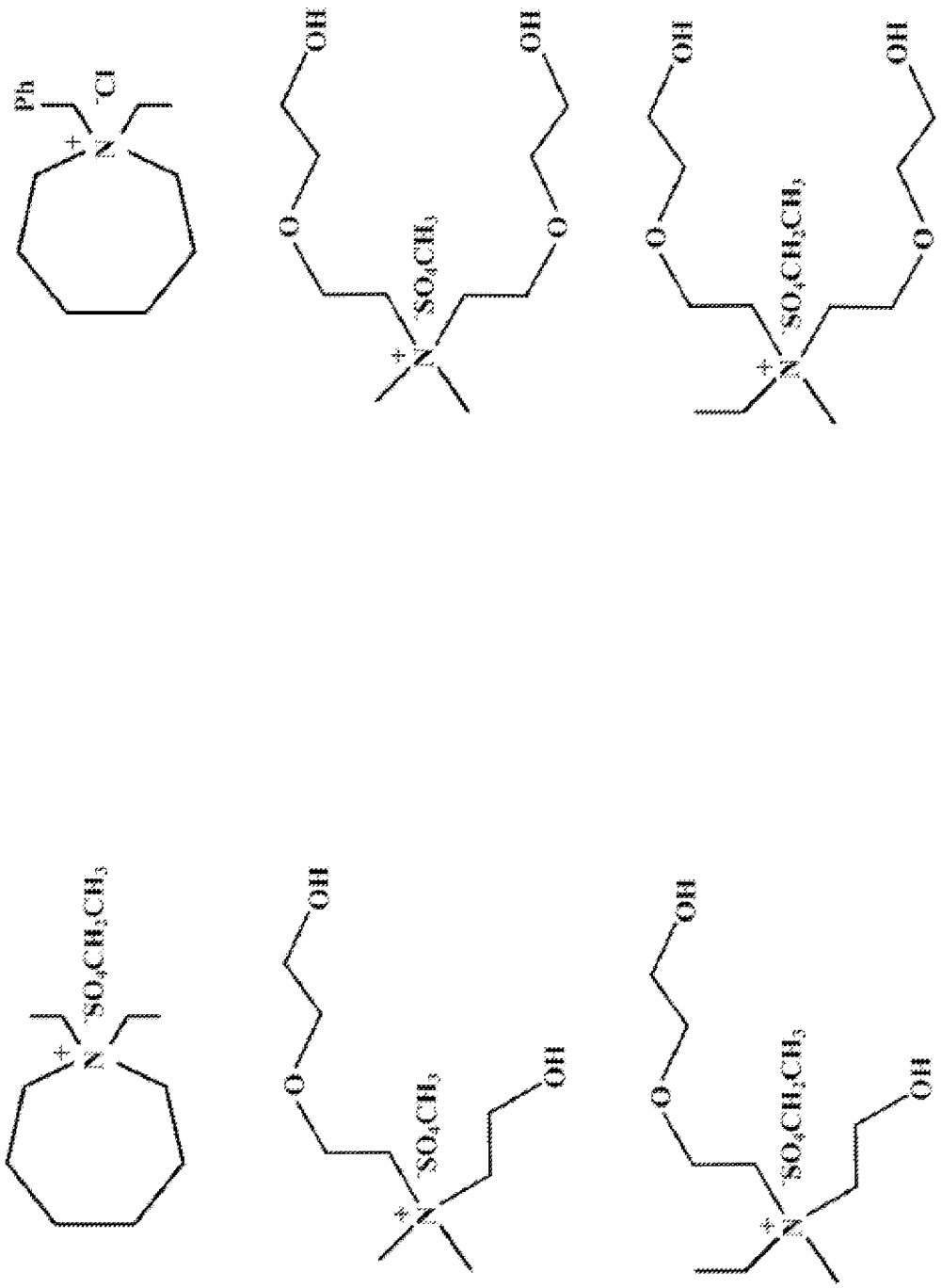


FIG. 1C

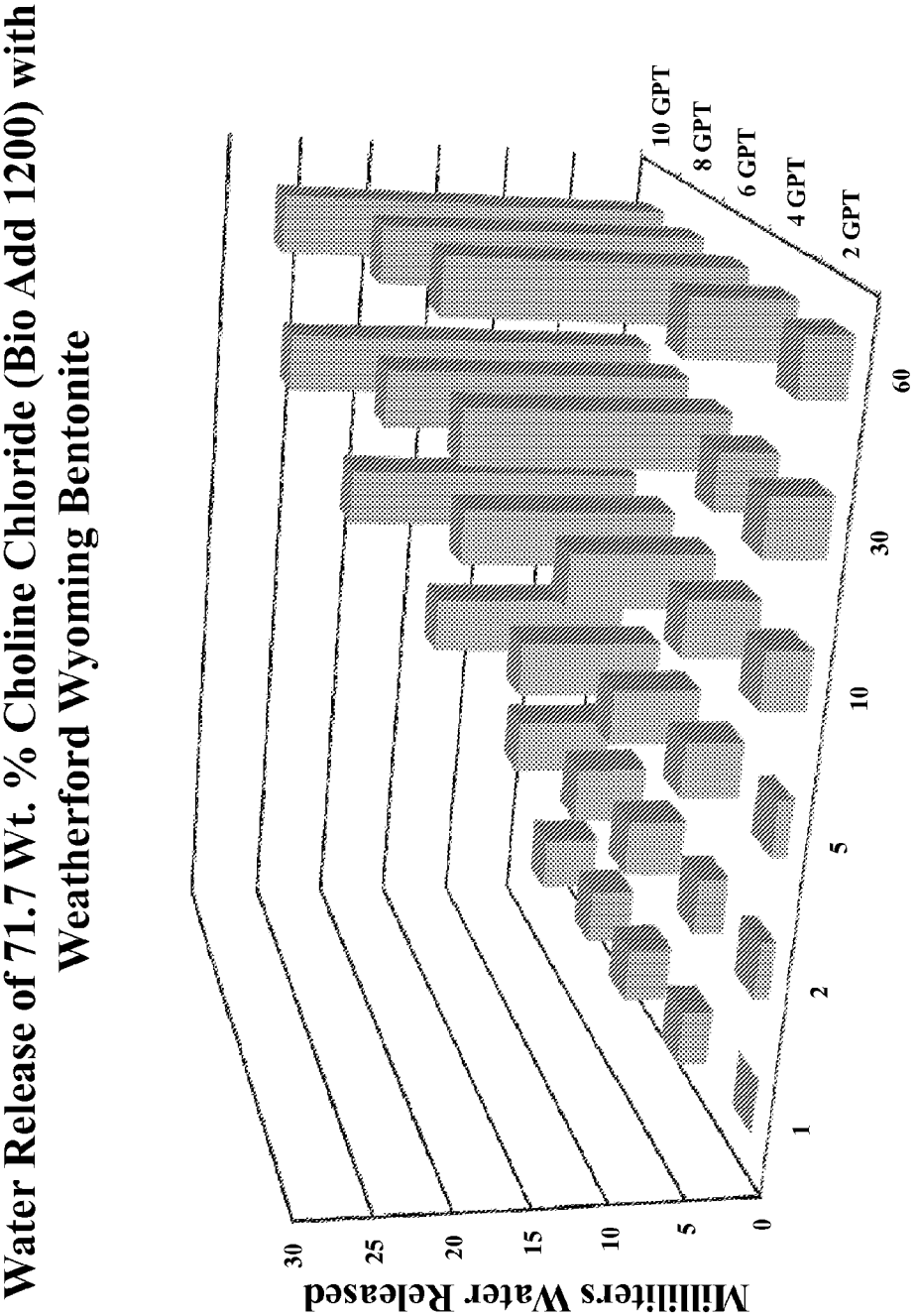

Water Release of 71.7 Wt. % Choline Chloride (Bio Add 1200) with Weatherford Wyoming Bentonite
Milliliters Water Released
0
5
10
15
20
25
30
Time (Minutes)
1
2
5
10
30
60
2 GPT
4 GPT
6 GPT
8 GPT
10 GPT

FIG. 2

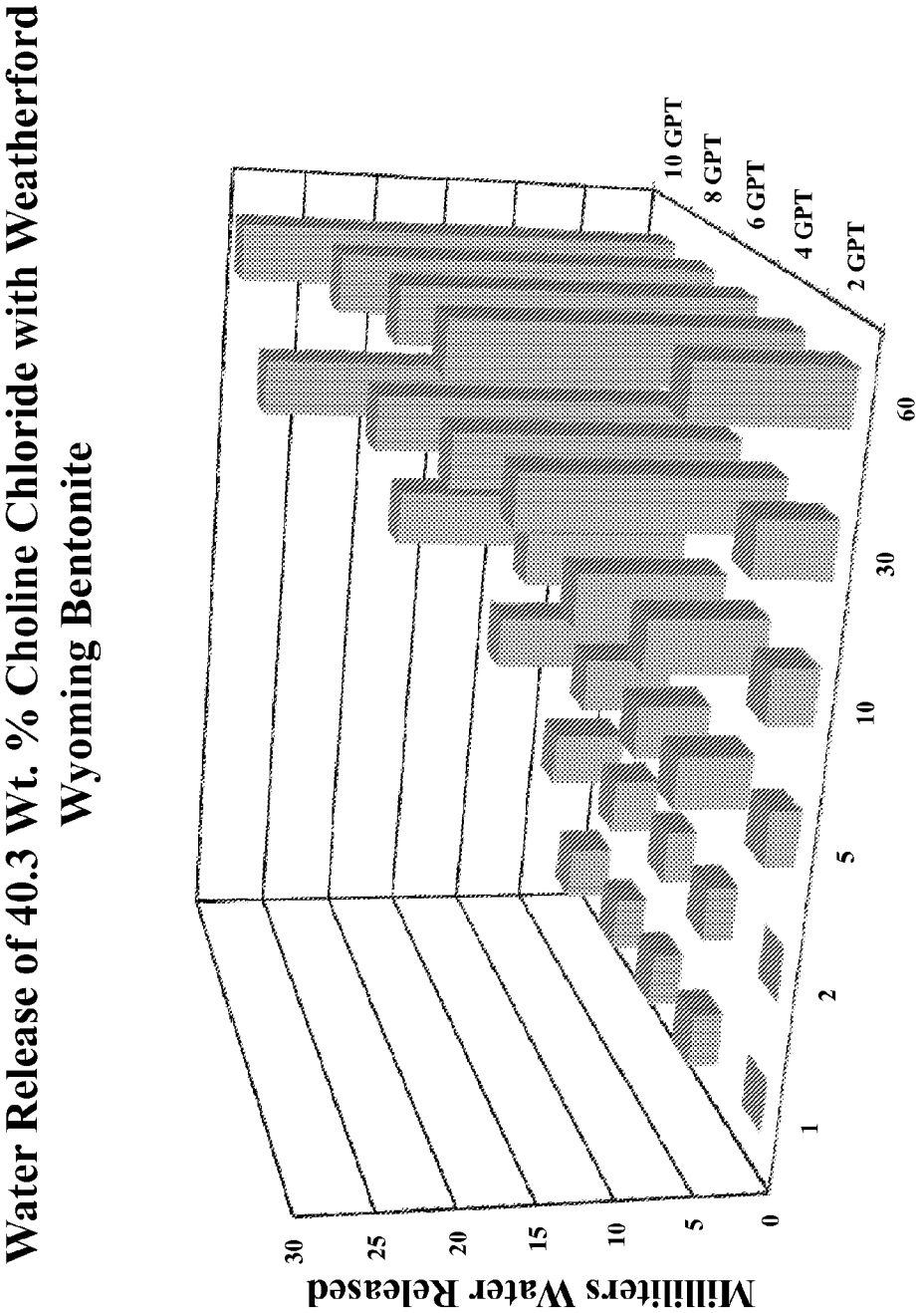

Water Release of 40.3 Wt. % Choline Chloride with Weatherford
Wyoming Bentonite
Milliliters Water Released
0
5
10
15
20
25
30
Time (Minutes)
1
2
5
10
30
60
2 GPT
4 GPT
6 GPT
8 GPT
10 GPT

FIG. 3

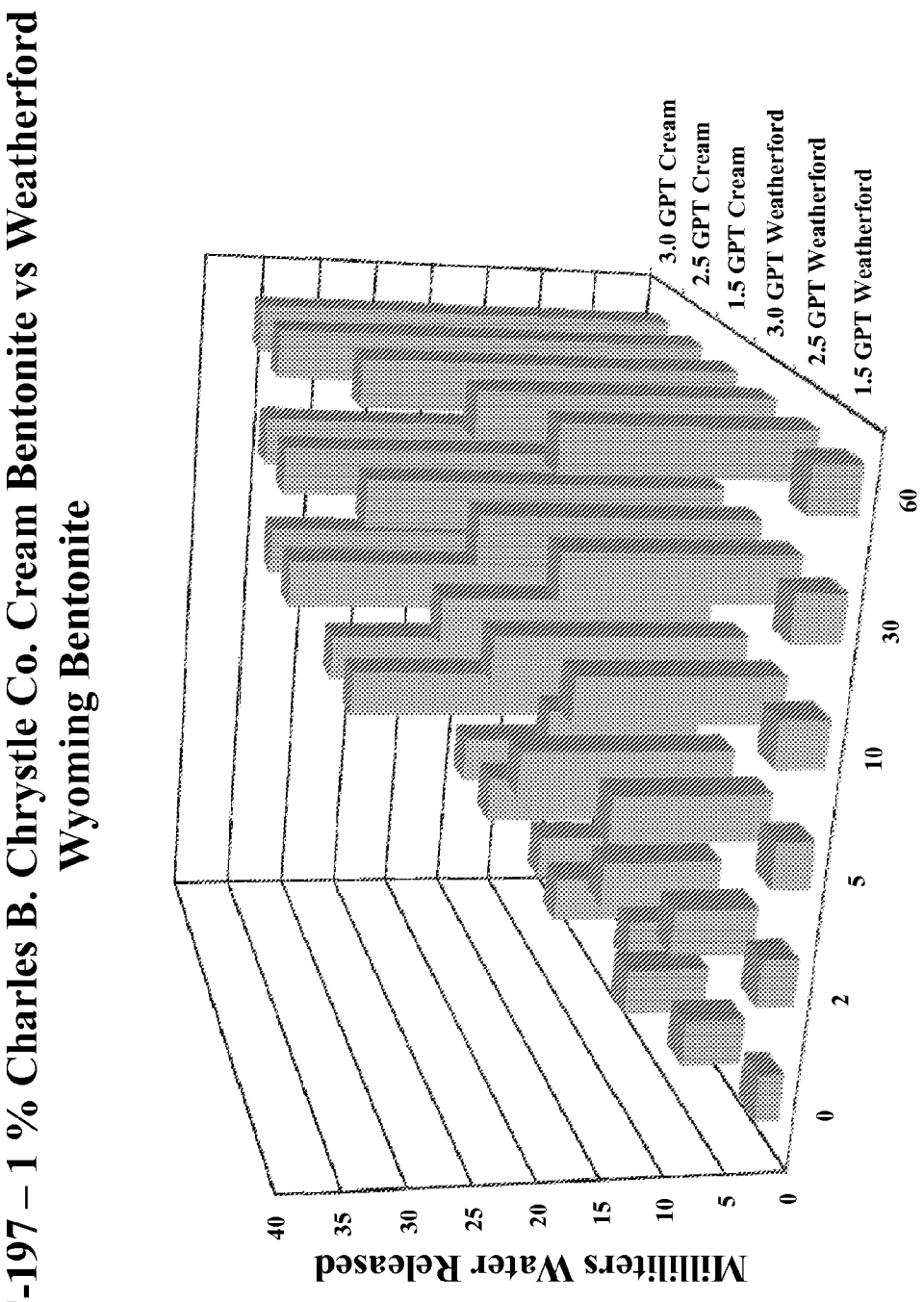

XC-197 – 1 % Charles B. Chrystle Co. Cream Bentonite vs Weatherford
Wyoming Bentonite
Milliliters Water Released
0
5
10
15
20
25
30
35
40
Time (Minutes)
0
2
5
10
30
60
3.0 GPT Cream
2.5 GPT Cream
1.5 GPT Cream
3.0 GPT Weatherford
2.5 GPT Weatherford
1.5 GPT Weatherford

FIG. 4

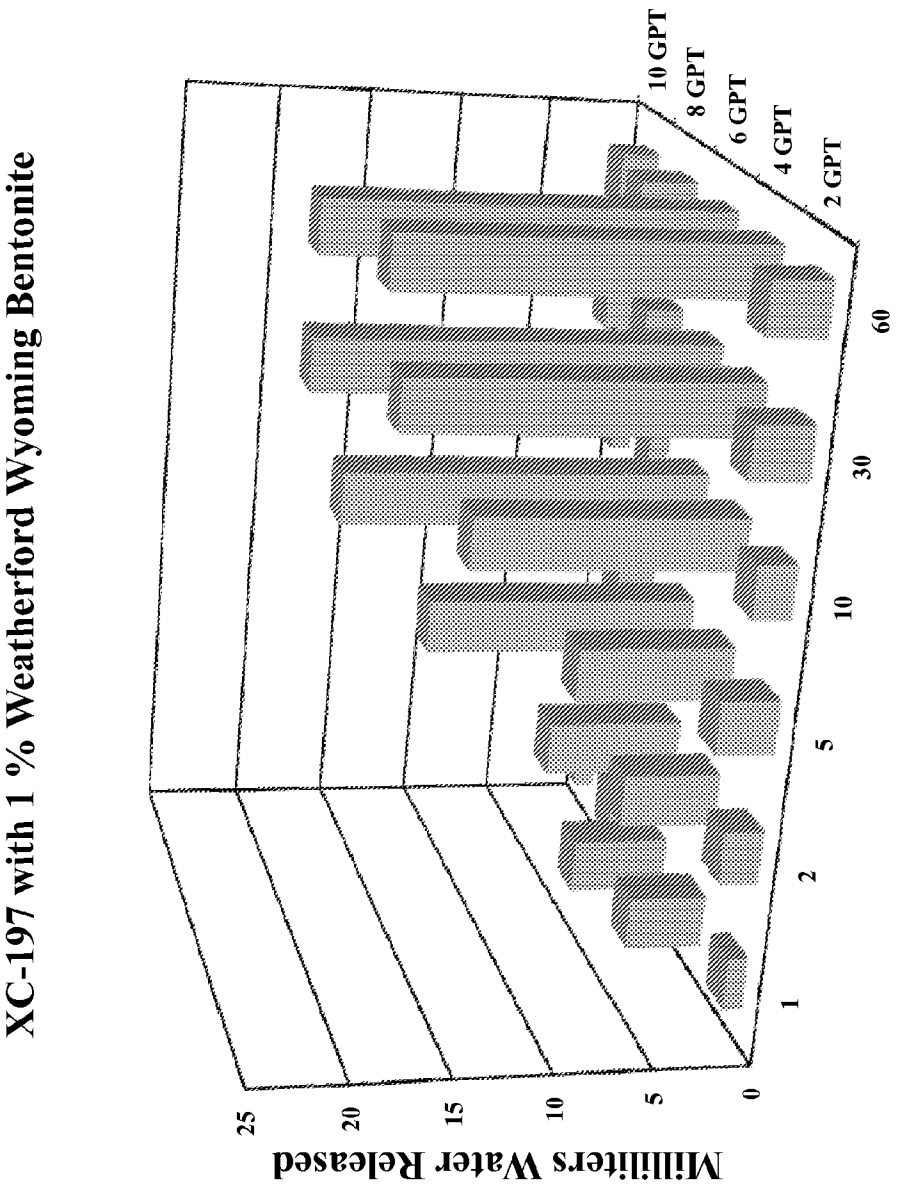
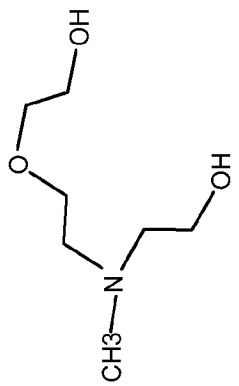
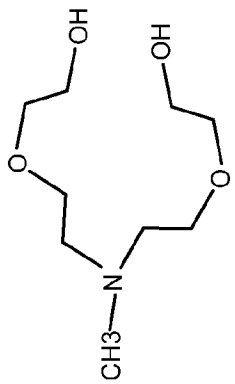

XC-197 with 1 % Weatherford Wyoming Bentonite
Milliliters Water Released
0
5
10
15
20
25
Time (Minutes)
1
2
5
10
30
60
2 GPT
4 GPT
6 GPT
8 GPT
10 GPT

FIG. 5

Huntsman C-9 (N-Methyldiethanolamine Bottoms)



2-[2-(2-Hydroxyethoxy)ethyl-methylamino]ethanol



N-Methyl-bis(N-hydroxyethoxyethyl)amine

FIG. 6

Diethyl Sulfate Quaternary Salt of Amine C-9 (Example 1)

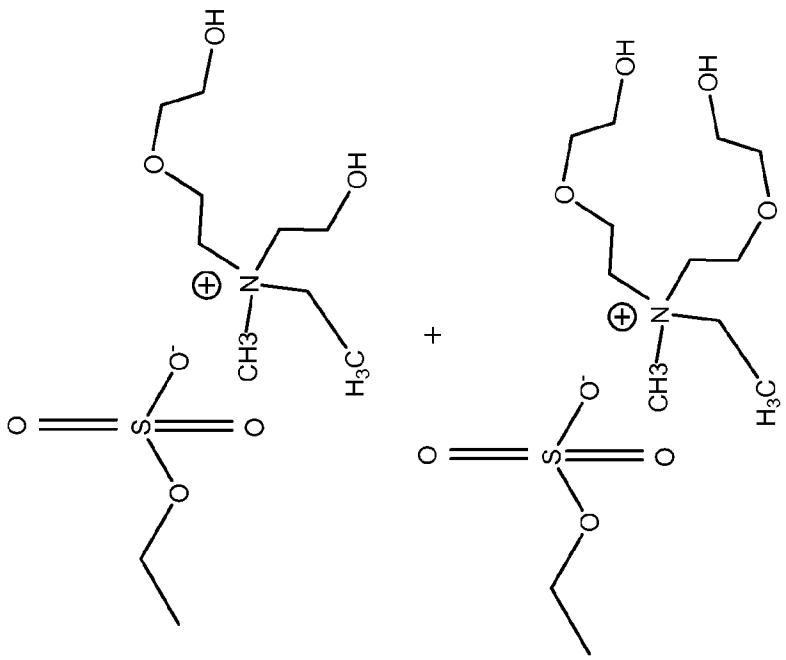


FIG. 7

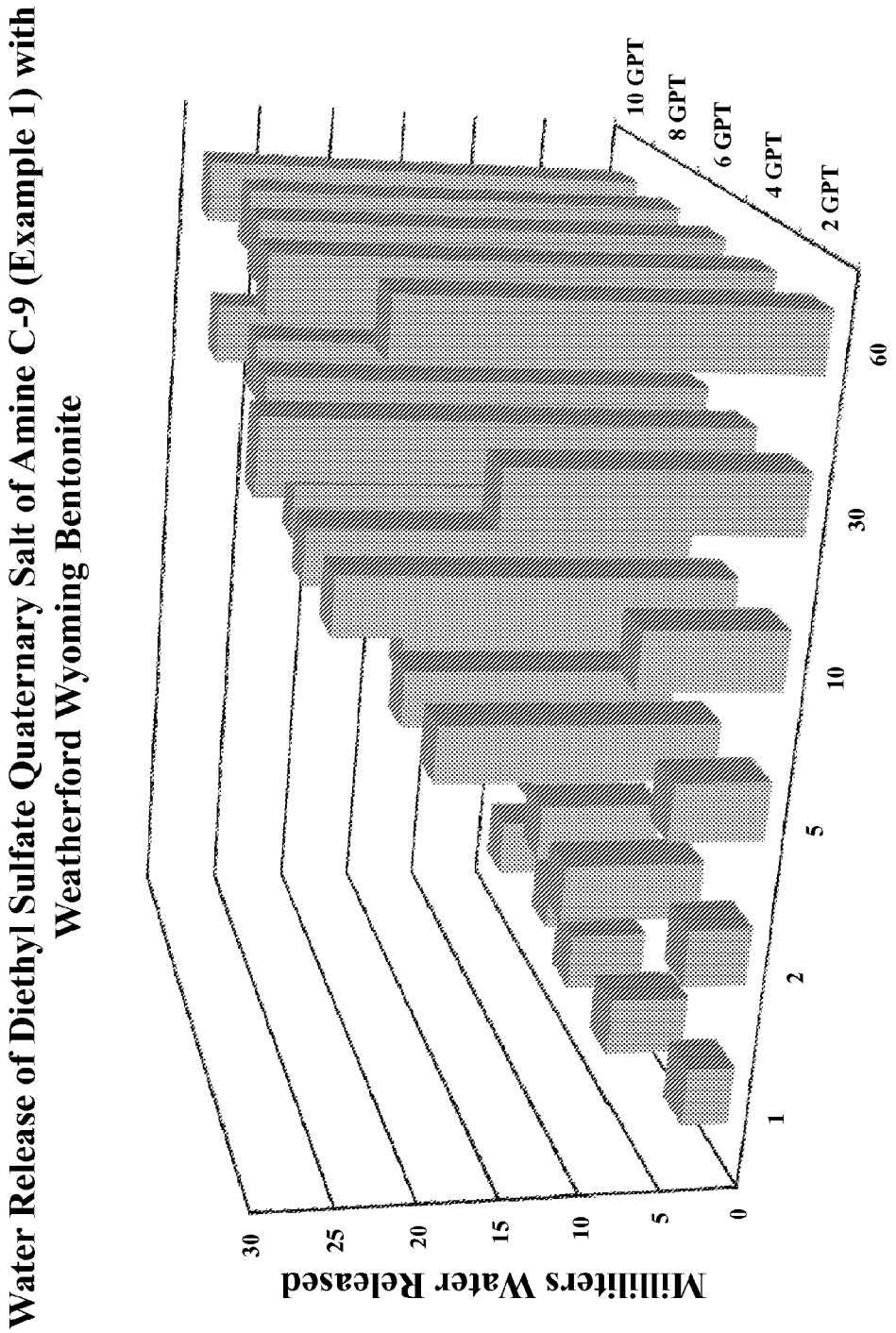

Water Release of Diethyl Sulfate Quaternary Salt of Amine C-9 (Example 1) with Weatherford Wyoming Bentonite
Milliliters Water Released
0
5
10
15
20
25
30
Time (Minutes)
1
2
5
10
30
60
2 GPT
4 GPT
6 GPT
8 GPT
10 GPT

FIG. 8

Dimethyl Sulfate Quaternary Salt of Amine C-9 (Example 2)

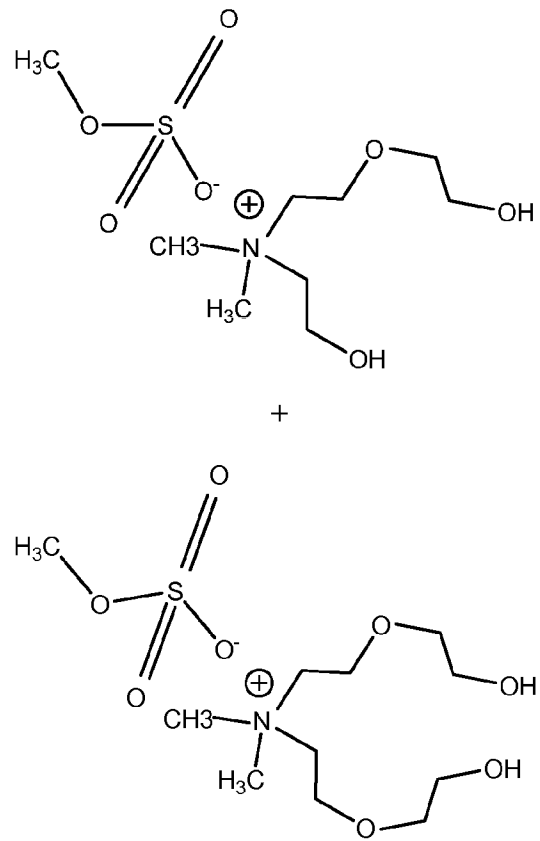


FIG. 9

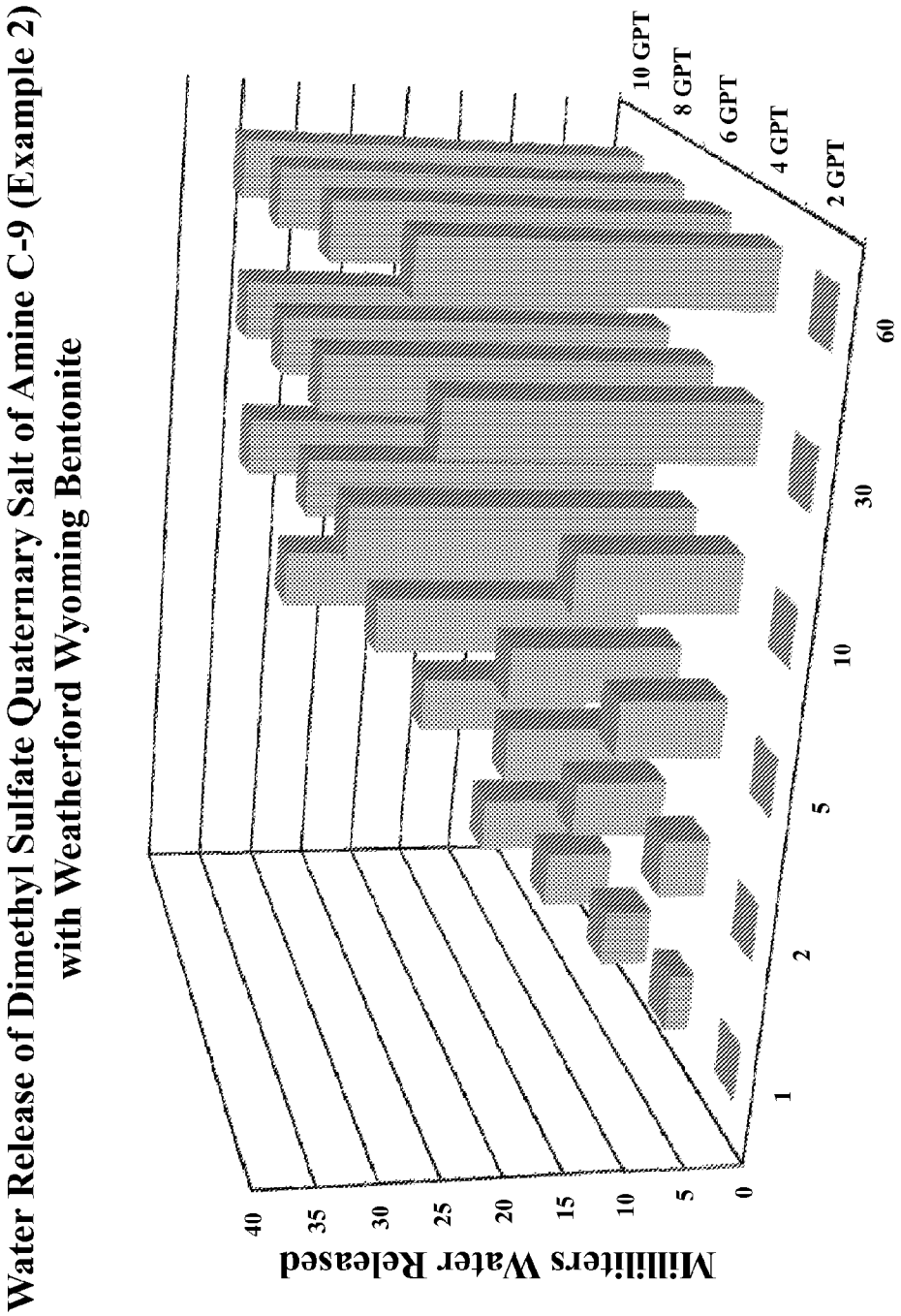

Water Release of Dimethyl Sulfate Quaternary Salt of Amine C-9 (Example 2) with Weatherford Wyoming Bentonite
Milliliters Water Released
0
5
10
15
20
25
30
35
40
Time (Minutes)
1
2
5
10
30
60
2 GPT
4 GPT
6 GPT
8 GPT
10 GPT

FIG. 10

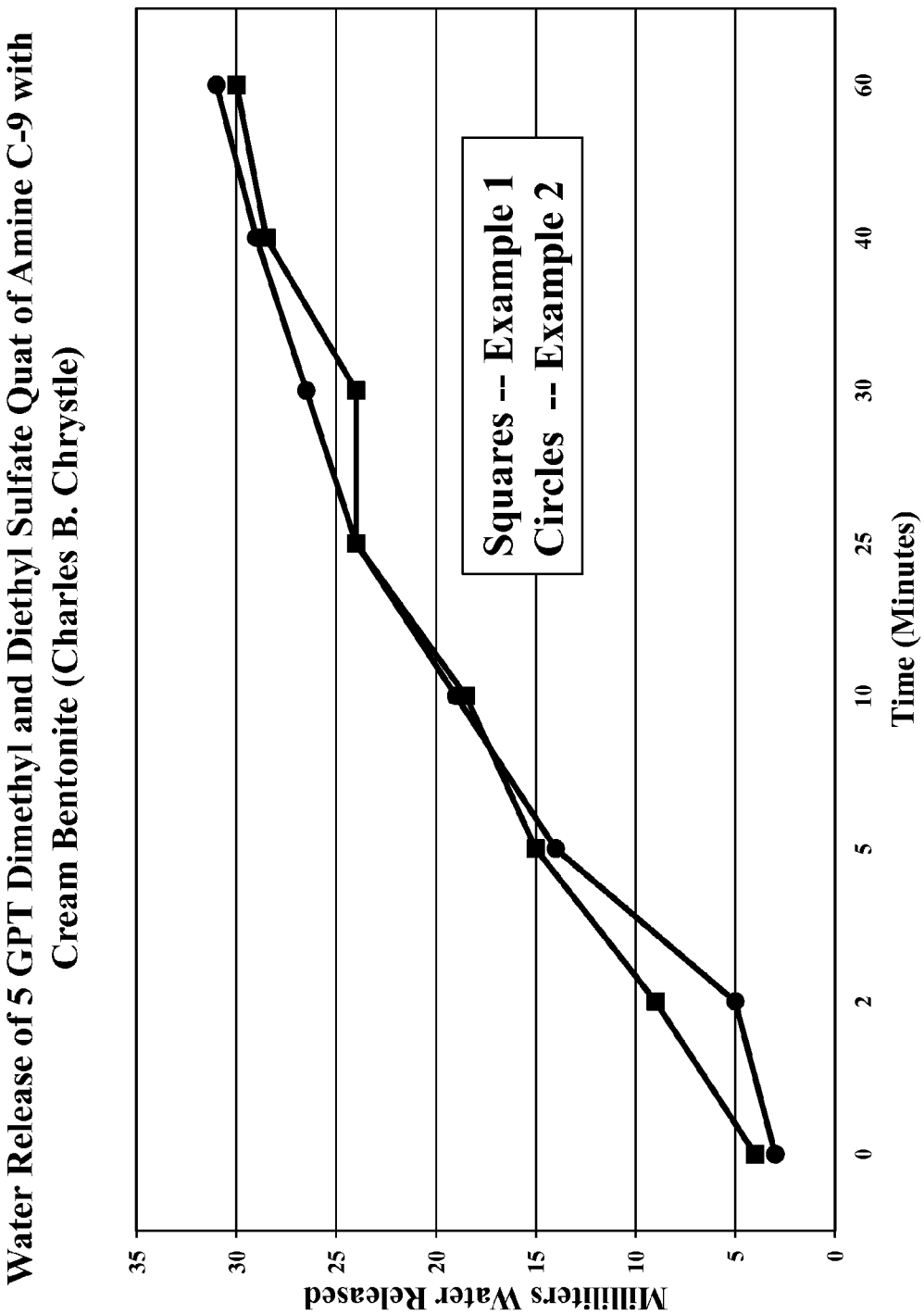

Water Release of 5 GPT Dimethyl and Diethyl Sulfate Quat of Amine C-9 with Cream Bentonite (Charles B. Chrystle)
Squares -- Example 1
Circles -- Example 2
Milliliters Water Released
Time (Minutes)
0
5
10
15
20
25
30
35
0
2
5
10
25
30
40
60

FIG. 11

Diethanolamine and Formaldehyde Reaction

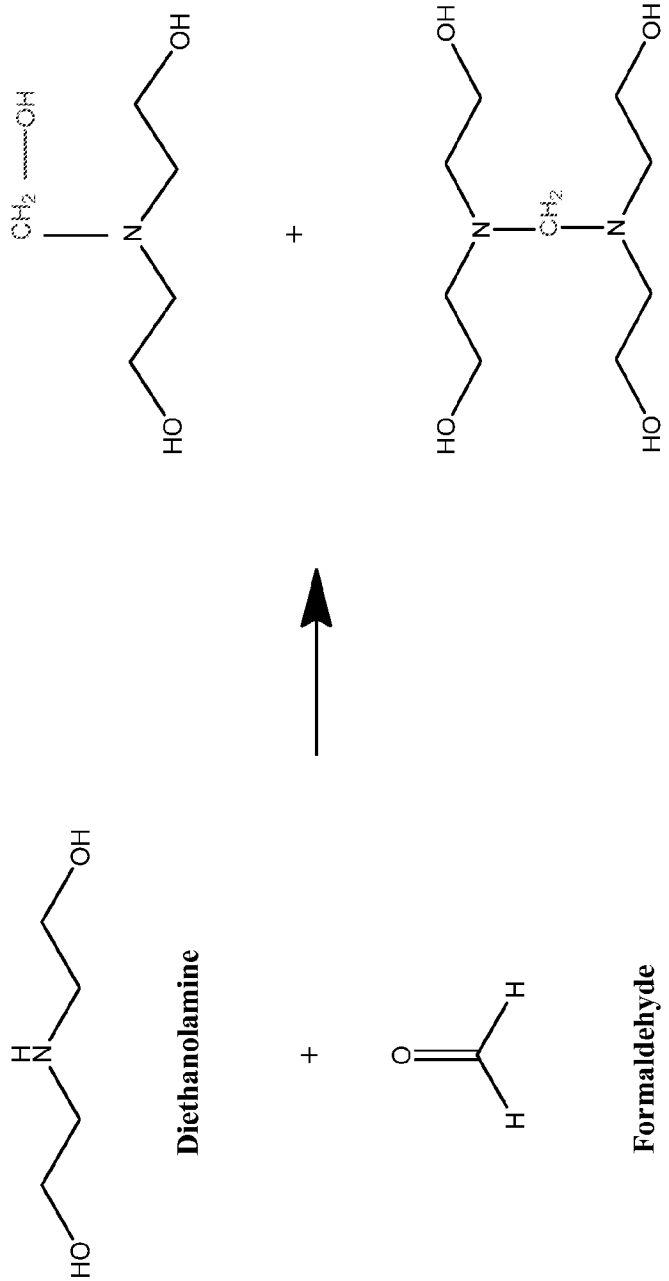


FIG. 12

Diethyl Sulfate Quaternary Salts of Diethanolamine and Formaldehyde Adducts

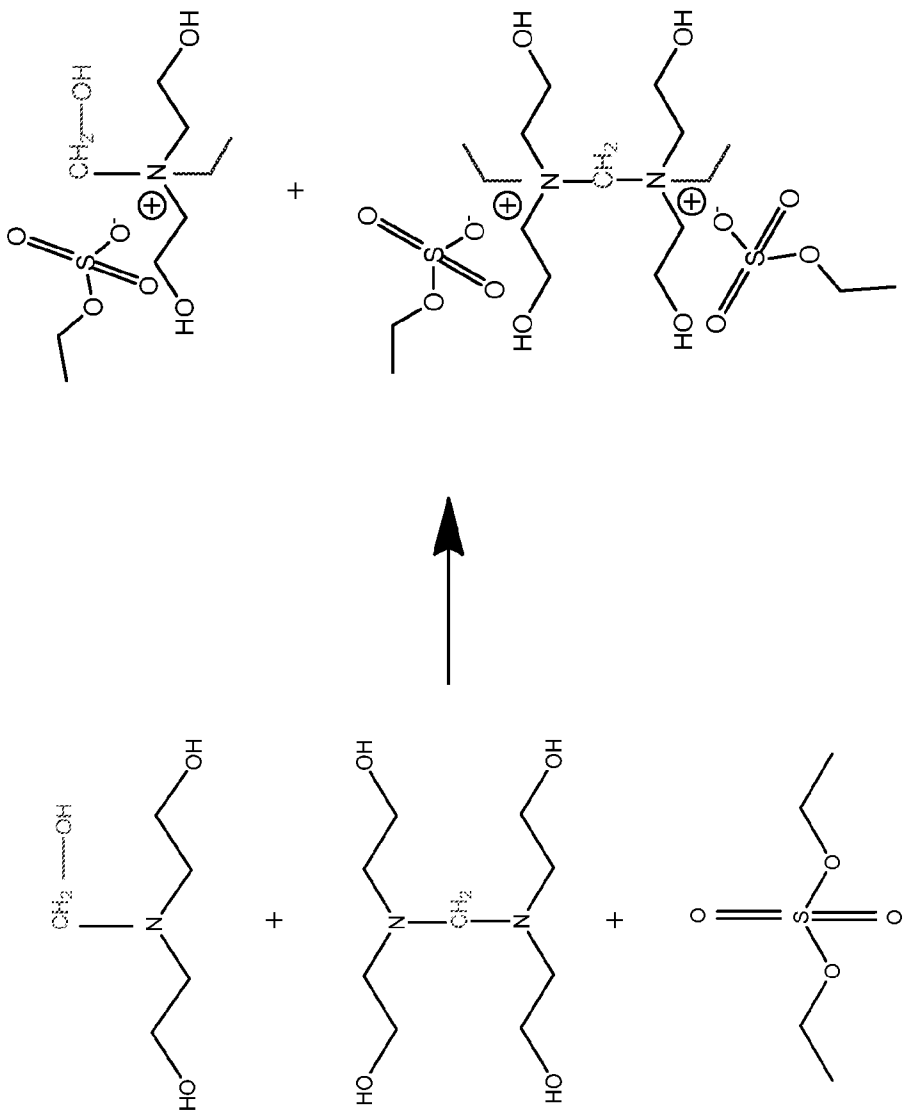


FIG. 13

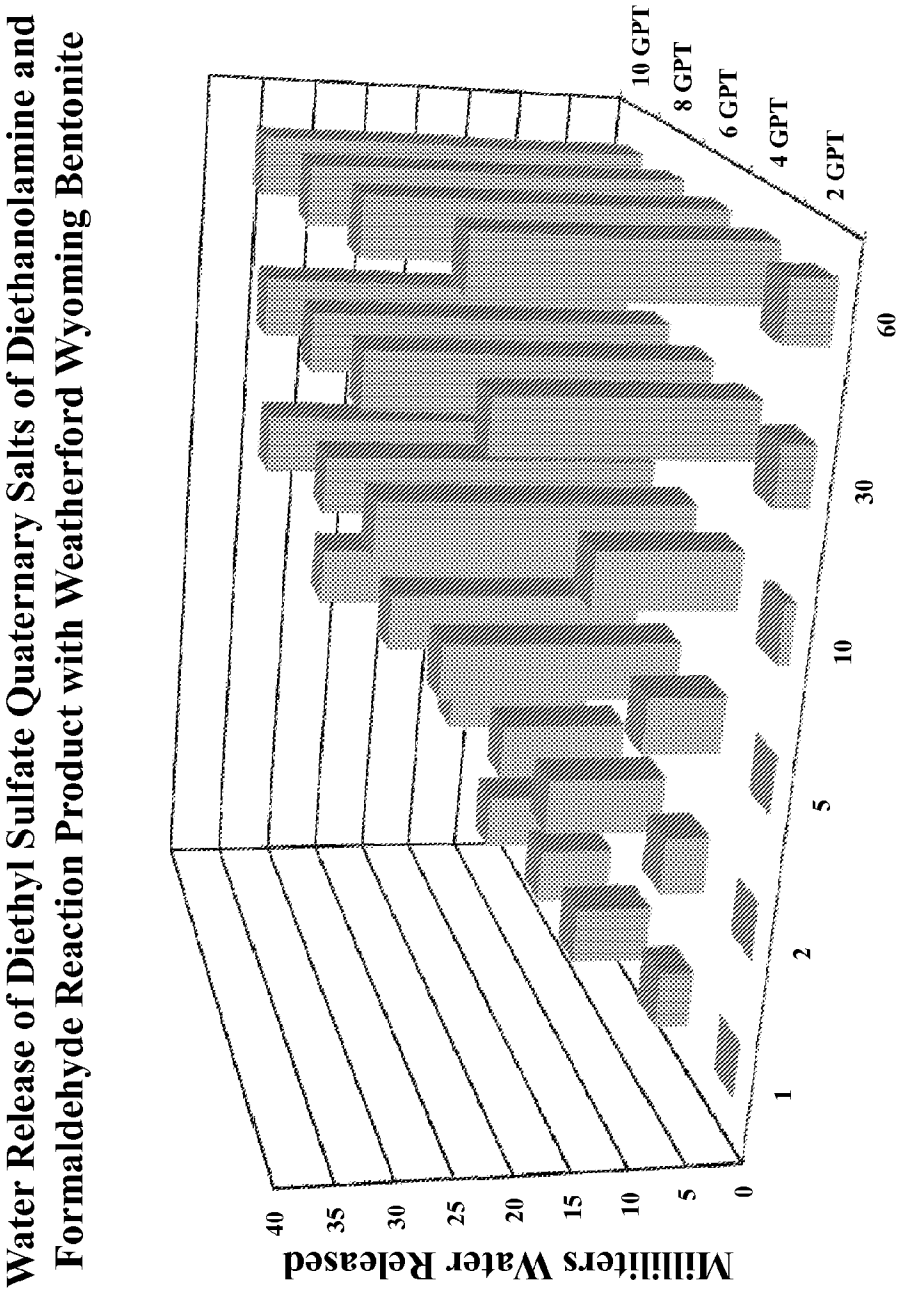

Water Release of Diethyl Sulfate Quaternary Salts of Diethanolamine and Formaldehyde Reaction Product with Weatherford Wyoming Bentonite
Milliliters Water Released
0
5
10
15
20
25
30
35
40
Time (Minutes)
1
2
5
10
30
60
10 GPT
8 GPT
6 GPT
4 GPT
2 GPT

FIG. 14

Benzyl Chloride Quat of Triethanolamine

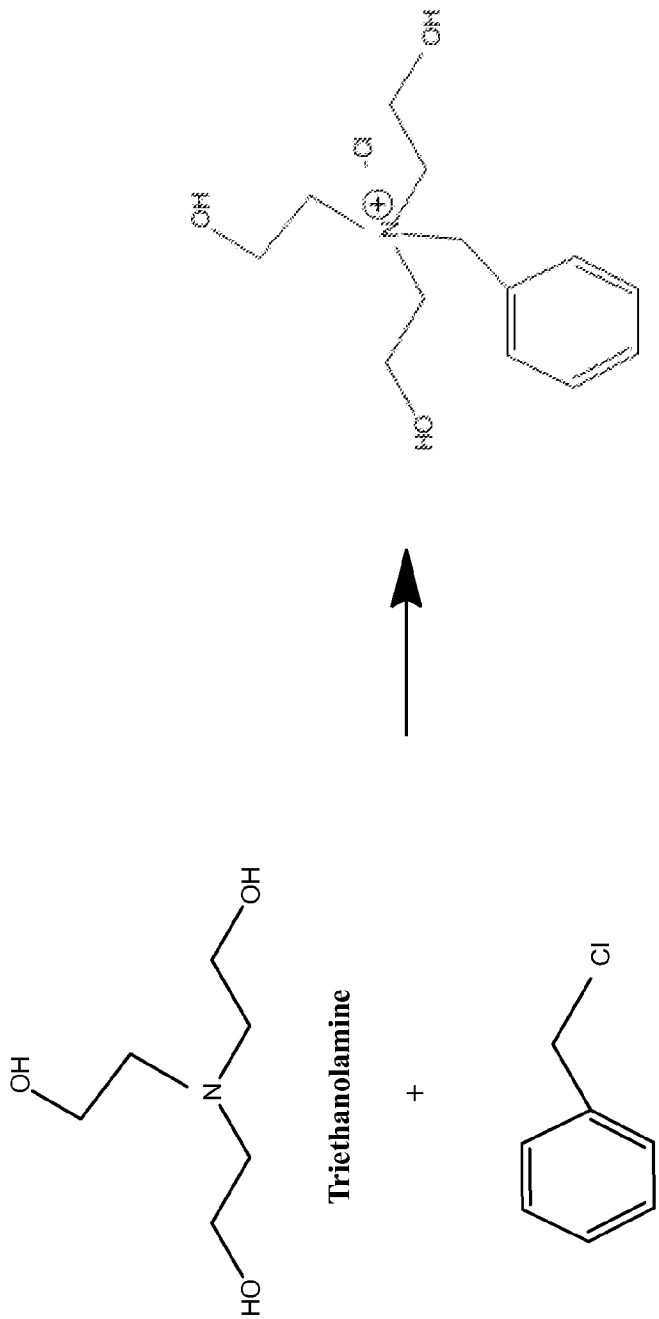


FIG. 15

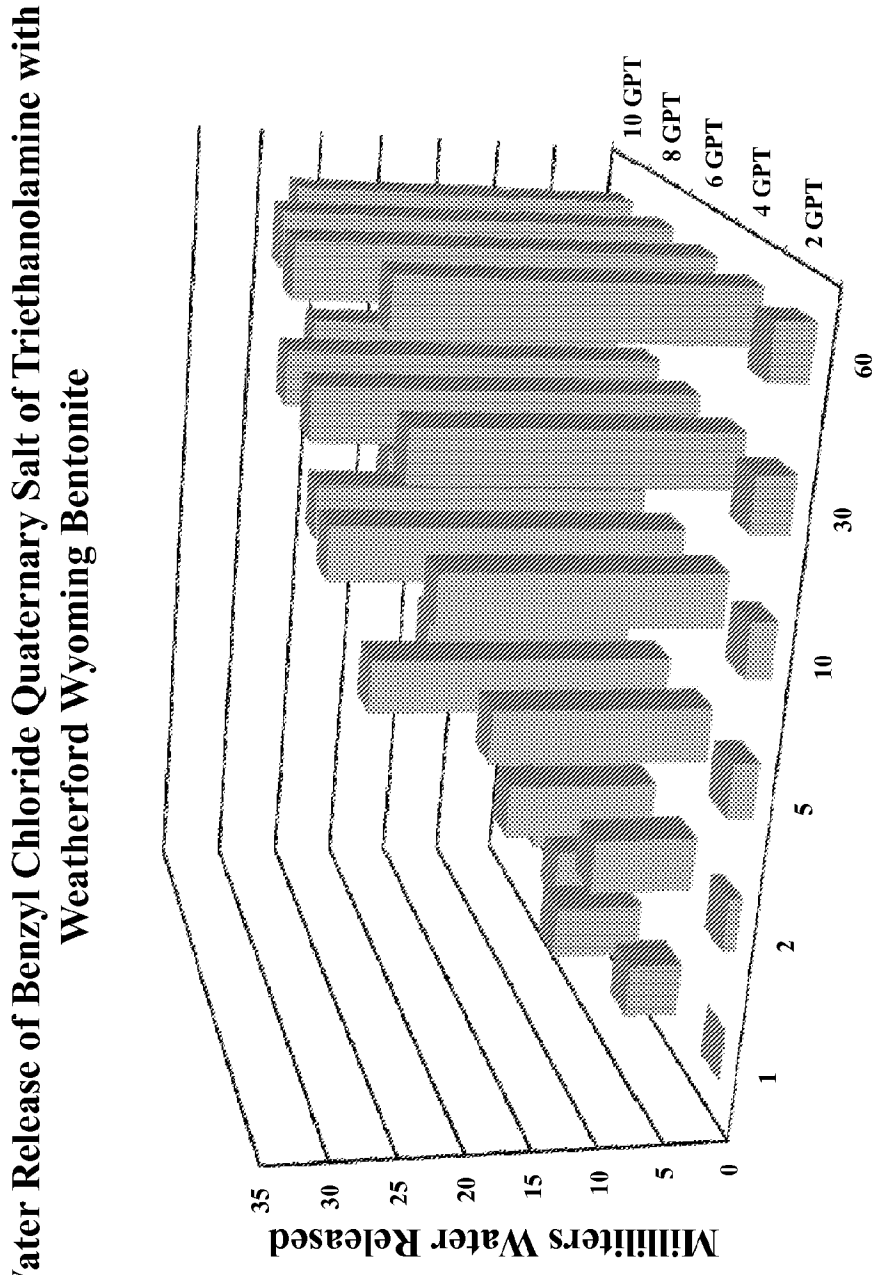

Water Release of Benzyl Chloride Quaternary Salt of Triethanolamine with Weatherford Wyoming Bentonite
Milliliters Water Released
0
5
10
15
20
25
30
35
Time (Minutes)
1
2
5
10
30
60
2 GPT
4 GPT
6 GPT
8 GPT
10 GPT

FIG. 16

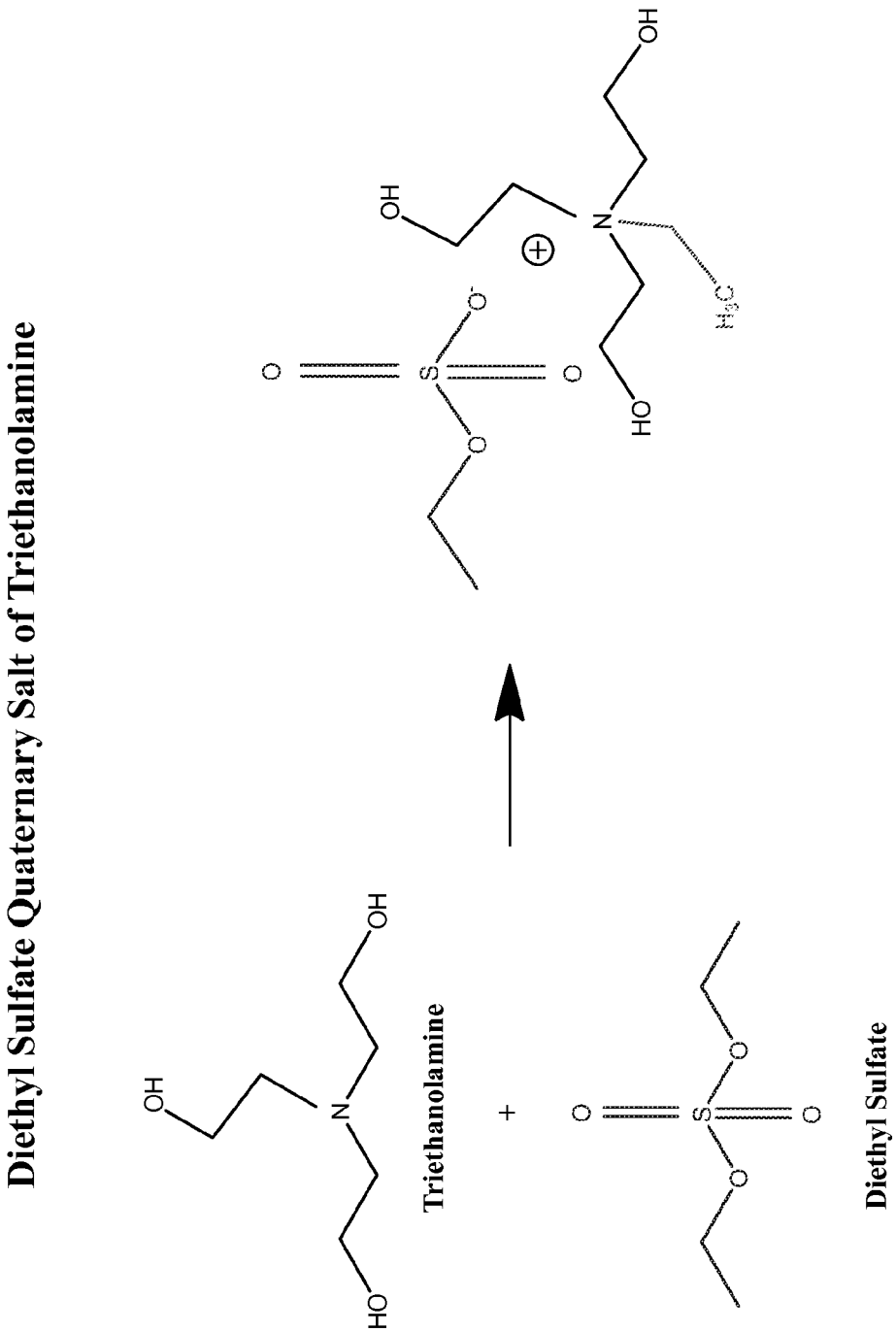

Diethyl Sulfate Quaternary Salt of Triethanolamine
Triethanolamine
Diethyl Sulfate

FIG. 17

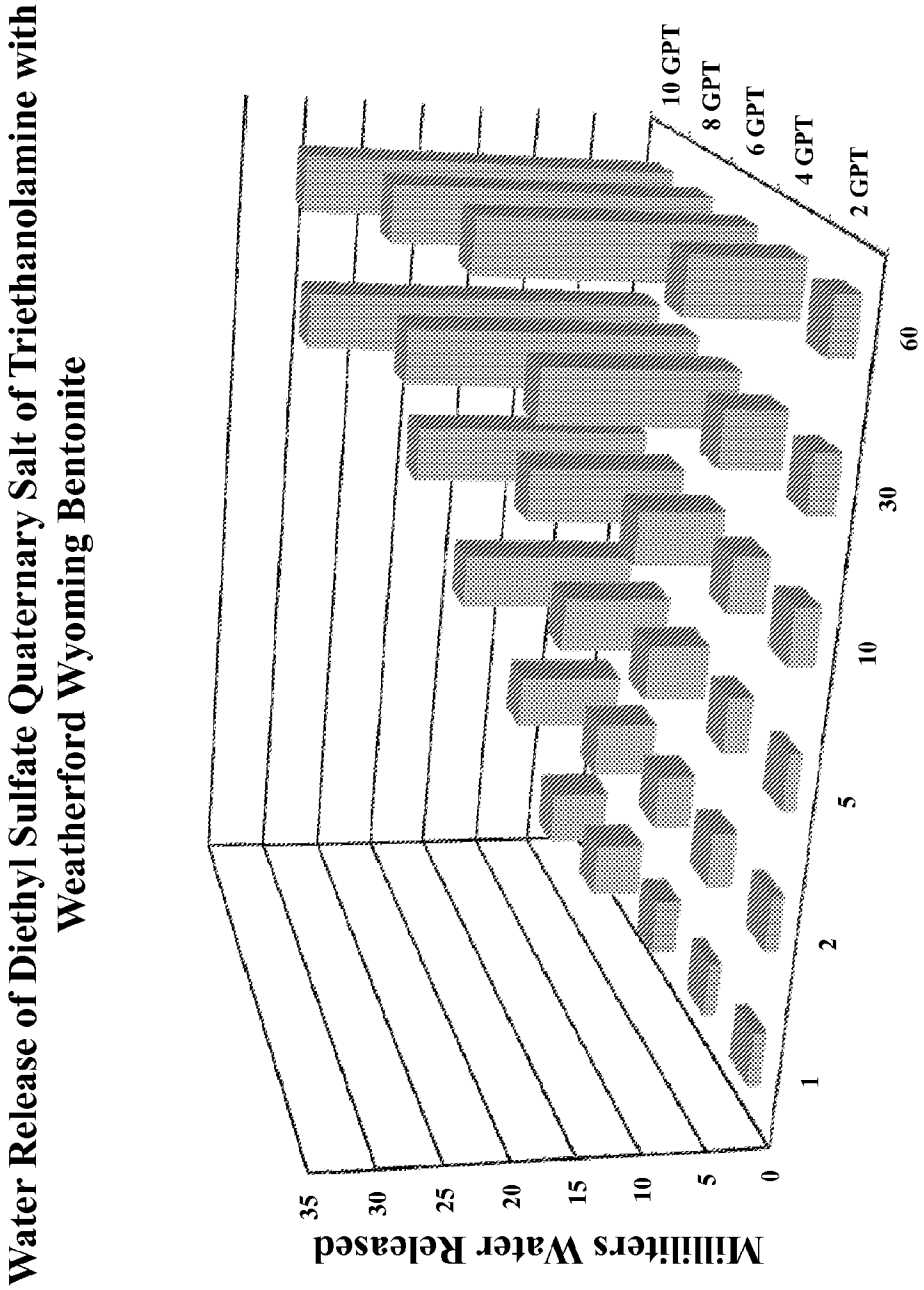

Water Release of Diethyl Sulfate Quaternary Salt of Triethanolamine with Weatherford Wyoming Bentonite
Milliliters Water Released
0
5
10
15
20
25
30
35
Time (Minutes)
1
2
5
10
30
60
2 GPT
4 GPT
6 GPT
8 GPT
10 GPT

FIG. 18

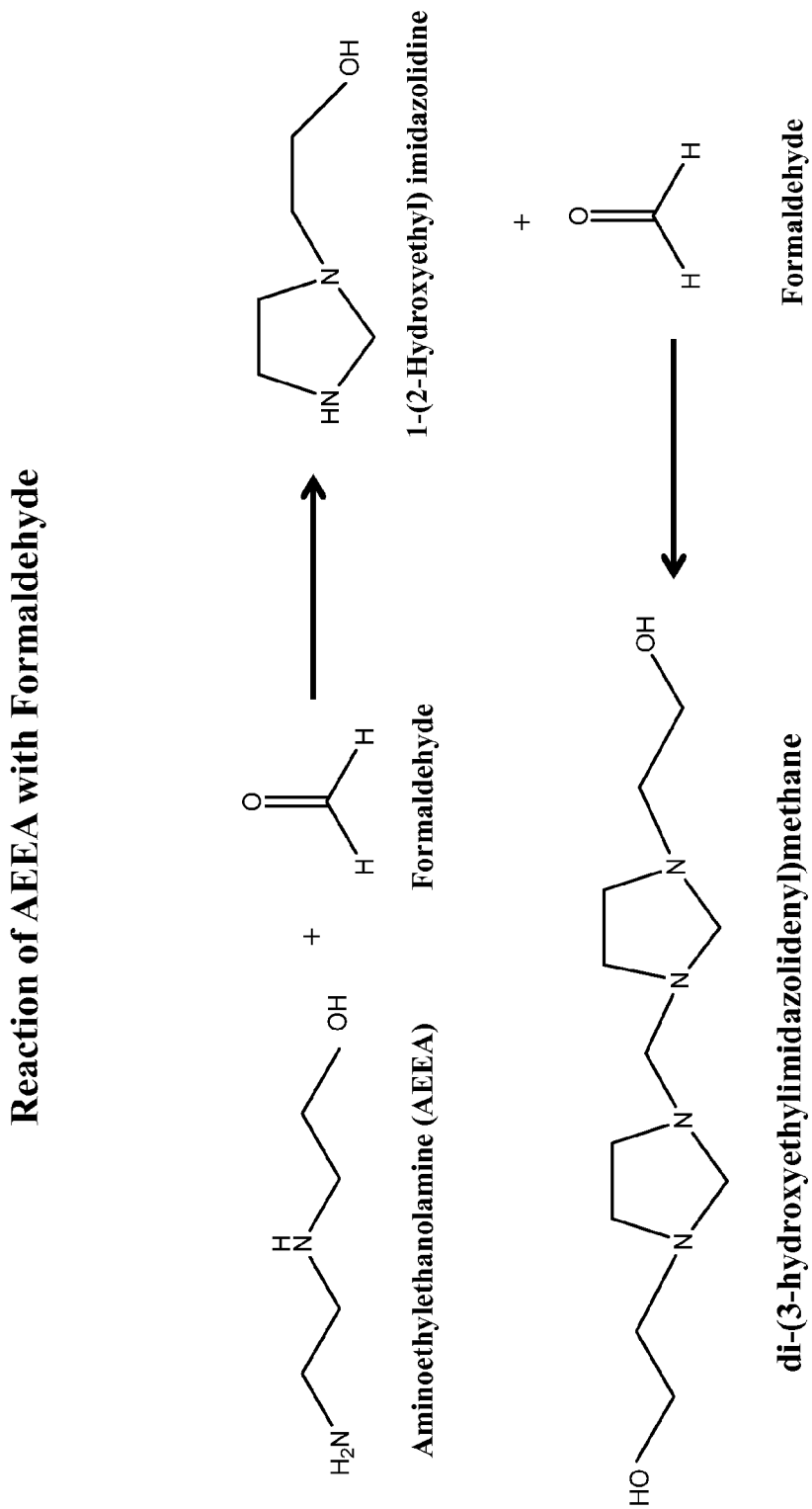

Reaction of AEEA with Formaldehyde
Aminoethylethanolamine (AEEA)
Formaldehyde
1-(2-Hydroxyethyl) imidazolidine
Formaldehyde
di-(3-hydroxyethylimidazolidenyl)methane

FIG. 19

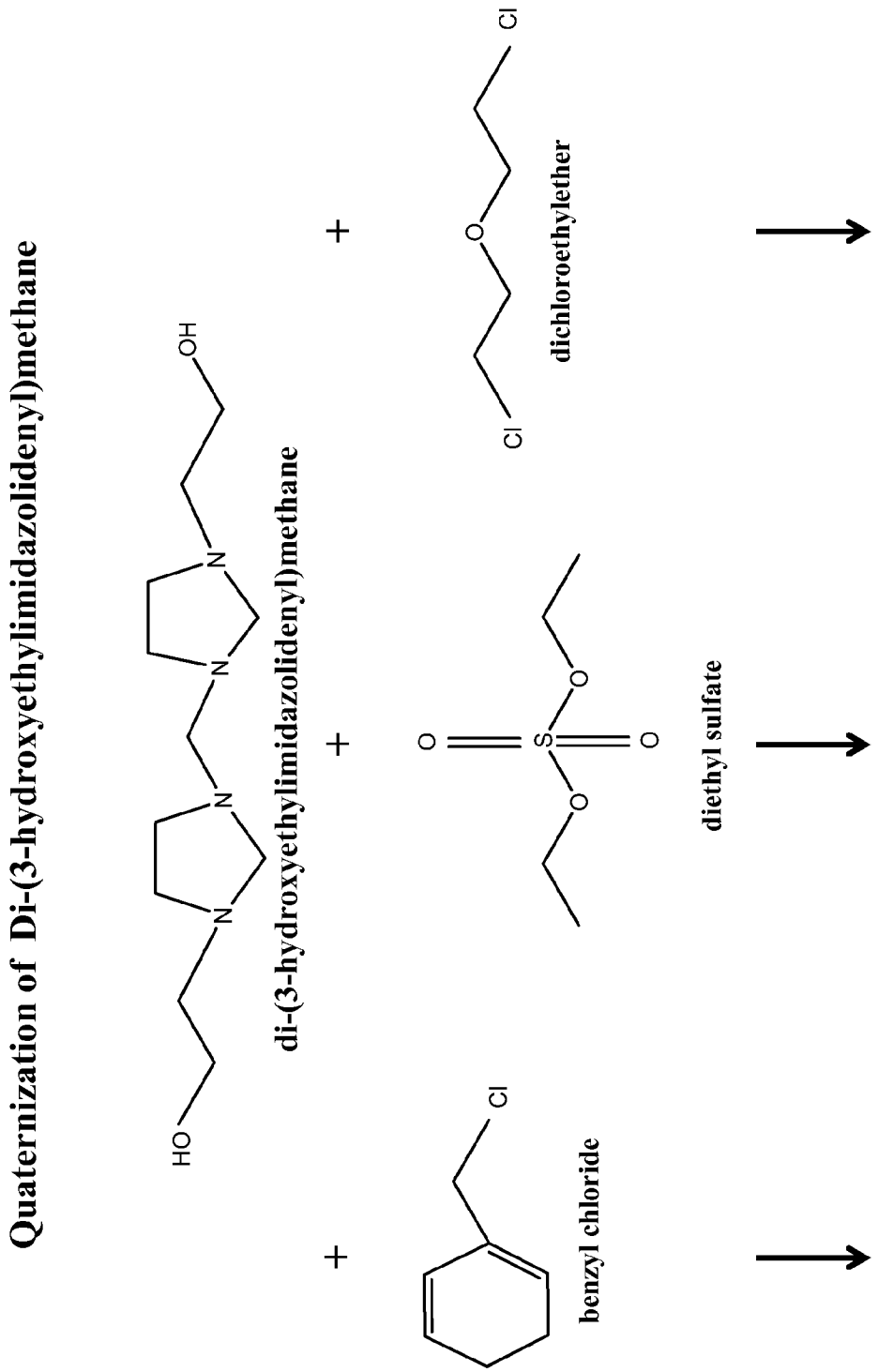

Quaternization of Di-(3-hydroxyethylimidazolidenyl)methane
di-(3-hydroxyethylimidazolidenyl)methane
dichloroethylether
benzyl chloride
diethyl sulfate

FIG. 20

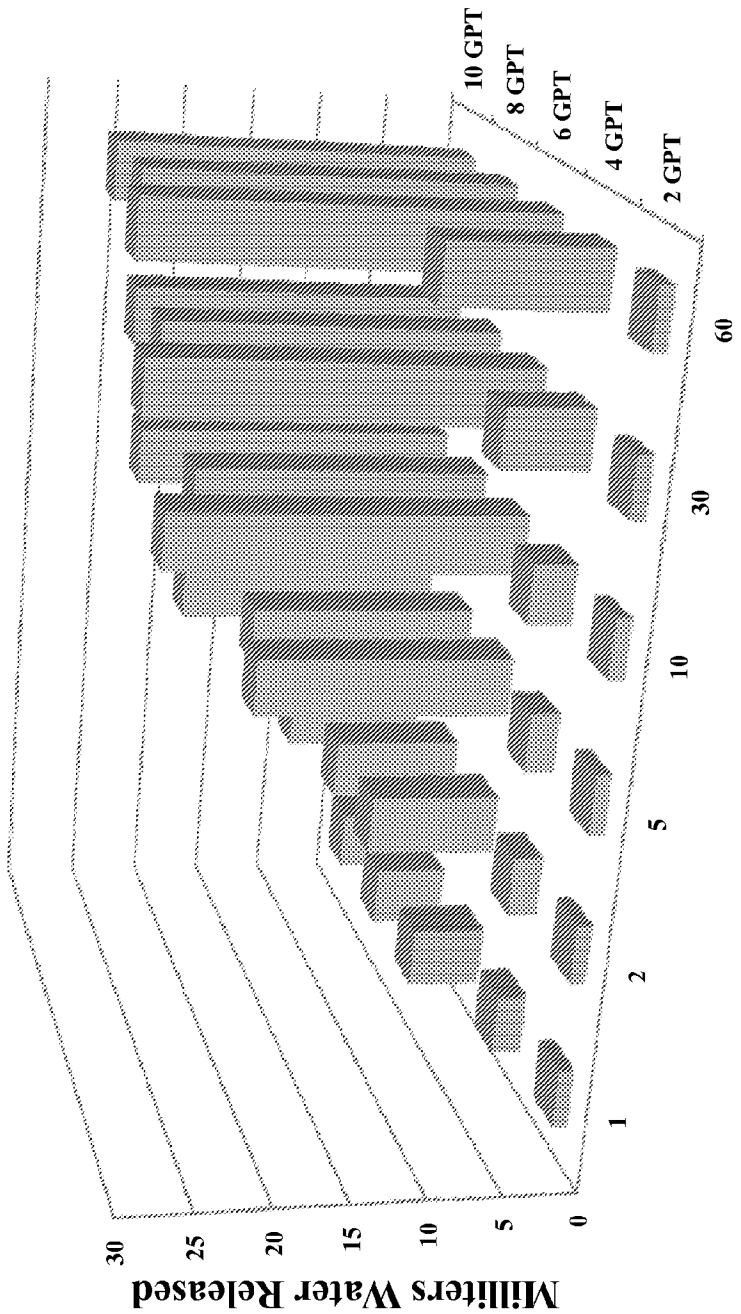

Water Release of Dichloroethylether Quat of Di-(3-hydroxyethylimidazolidenyl)methane with Weatherford Wyoming Bentonite
Milliters Water Released
30
25
20
15
10
5
0
1
2
5
10
30
60
Time (Minutes)
10 GPT
8 GPT
6 GPT
4 GPT
2 GPT

FIG. 21

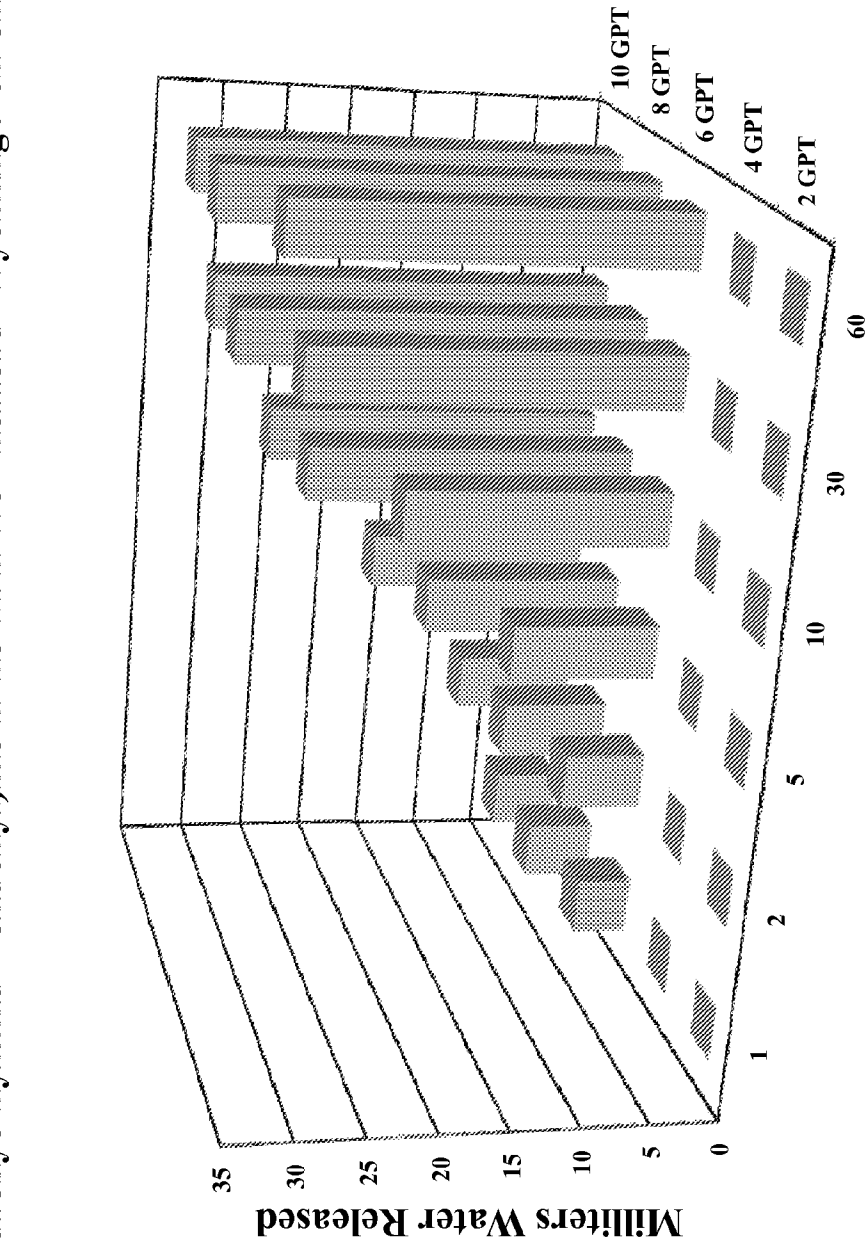

Water Release of Diethyl Sulfate Quaternary Salt of Di-(3-hydroxyethylimidazolidenyl)methane with Weatherford Wyoming Bentonite
Milliters Water Released
0
5
10
15
20
25
30
35
Time (Minutes)
1
2
5
10
30
60
2 GPT
4 GPT
6 GPT
8 GPT
10 GPT

FIG. 22

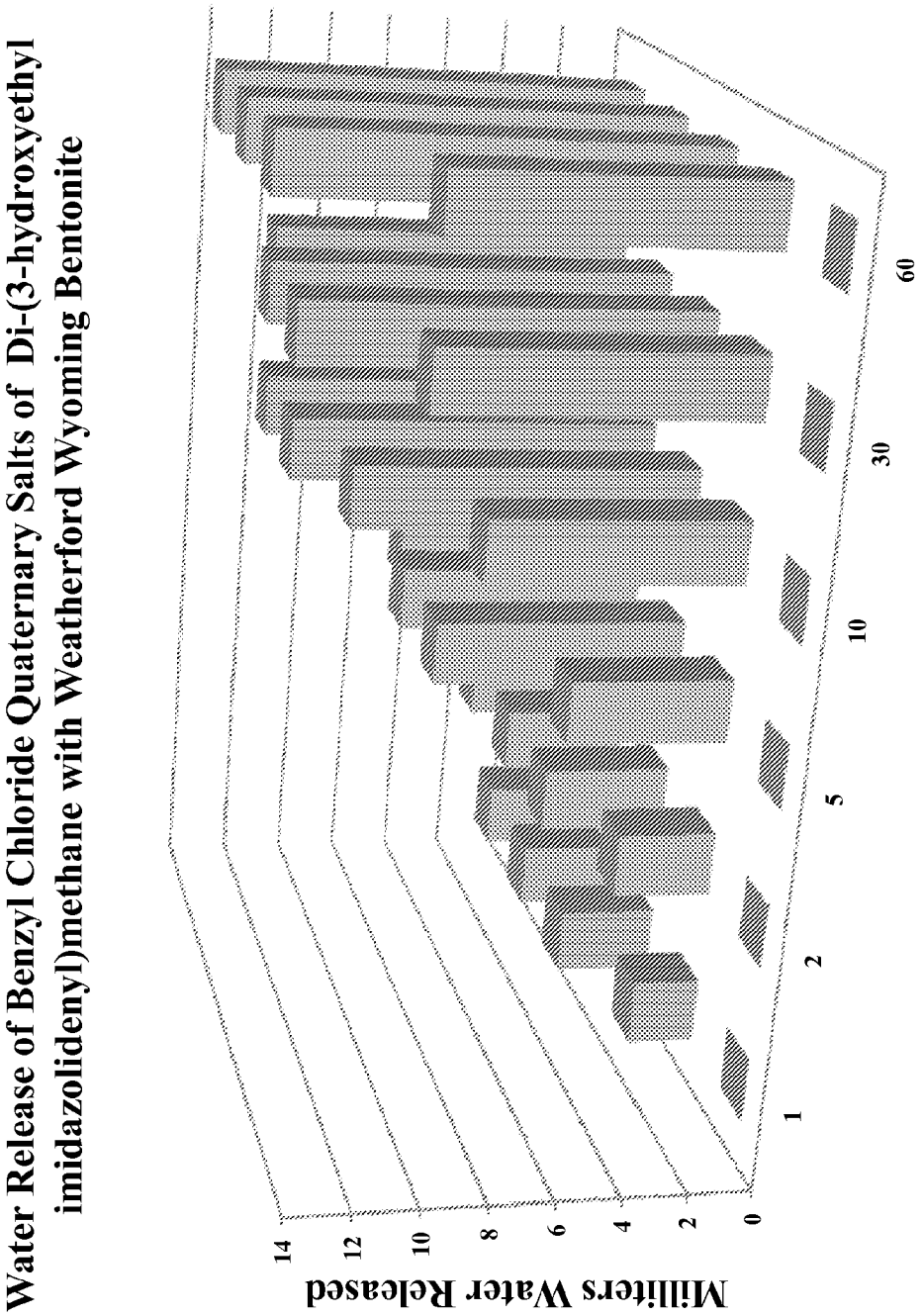

Water Release of Benzyl Chloride Quaternary Salts of Di-(3-hydroxyethyl imidazolidenyl)methane with Weatherford Wyoming Bentonite
Milliliters Water Released
0
2
4
6
8
10
12
14
1
2
5
10
30
60
Time (Minutes)

FIG. 23

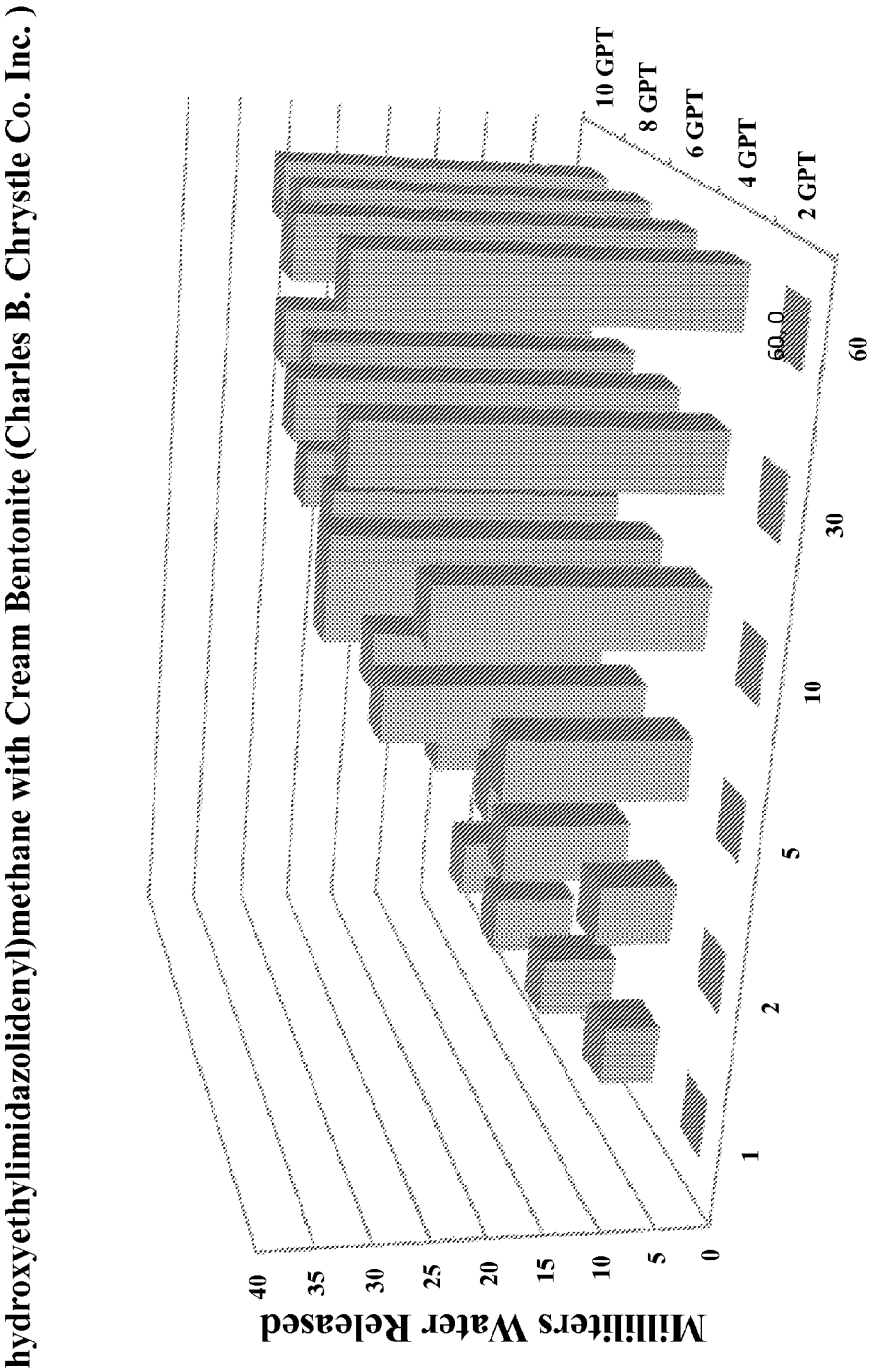

Water Release of Dichloroethylether Quaternary Salts of Di-(3-hydroxyethylimidazolidenyl)methane with Cream Bentonite (Charles B. Chrystle Co. Inc.)
Milliliters Water Released
0
5
10
15
20
25
30
35
40
Time (Minutes)
1
2
5
10
30
60
10 GPT
8 GPT
6 GPT
4 GPT
2 GPT

FIG. 24

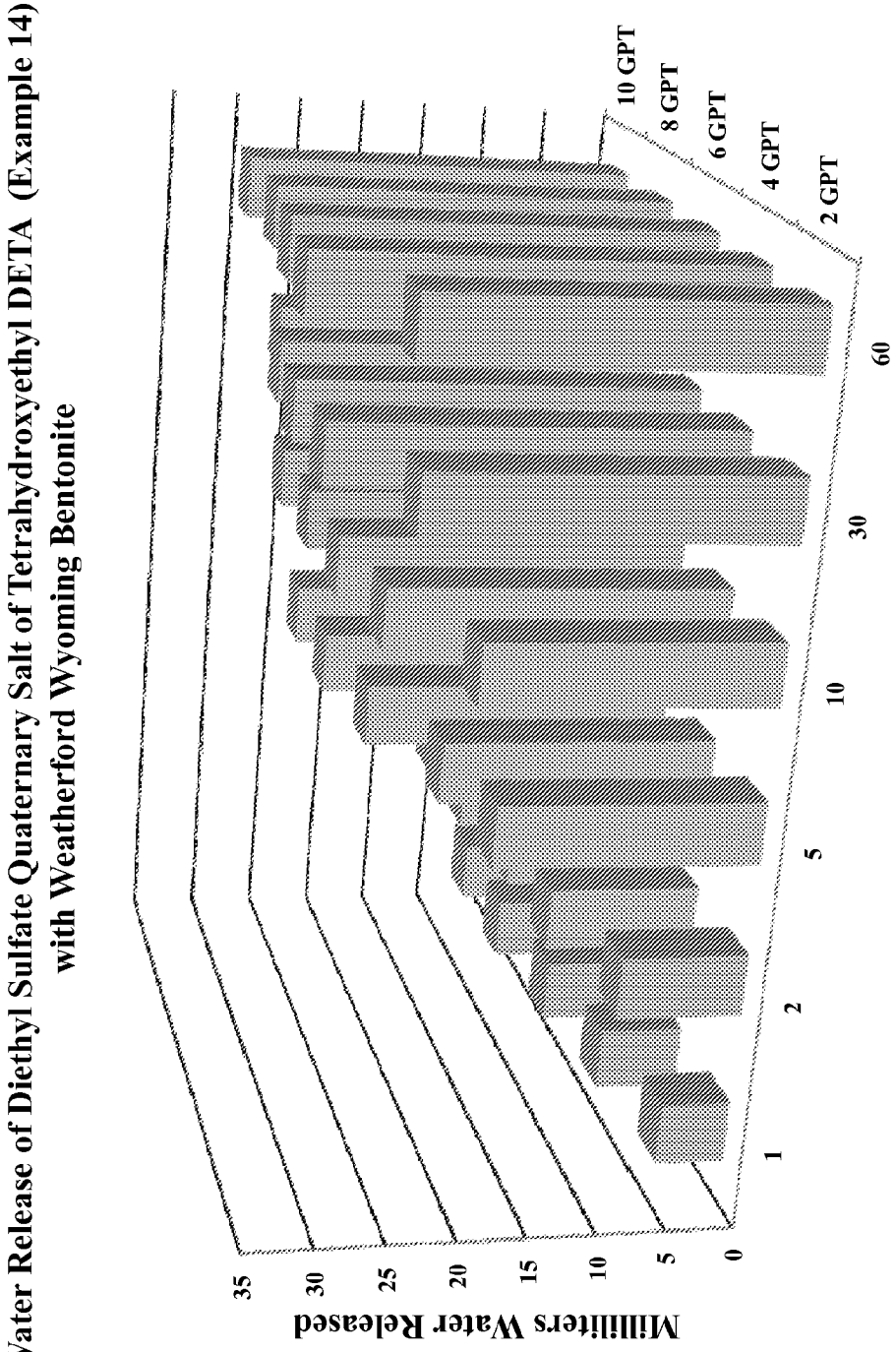

Water Release of Diethyl Sulfate Quaternary Salt of Tetrahydroxyethyl DETA (Example 14)
with Weatherford Wyoming Bentonite
Milliliters Water Released
0
5
10
15
20
25
30
35
1
2
5
10
30
60
Time (Minutes)
2 GPT
4 GPT
6 GPT
8 GPT
10 GPT

FIG. 25

Reaction of Tetrahydroxyethyldiethylenetriamine and Formaldehyde

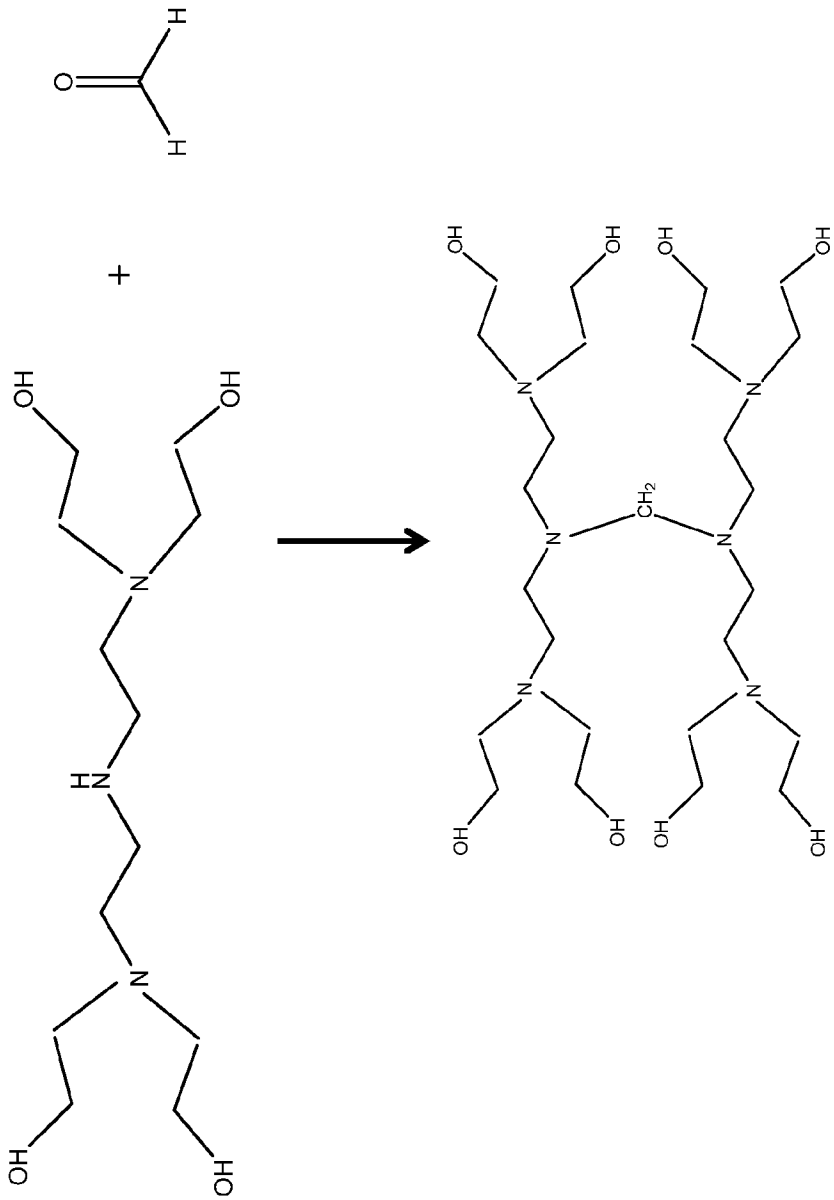


FIG. 26

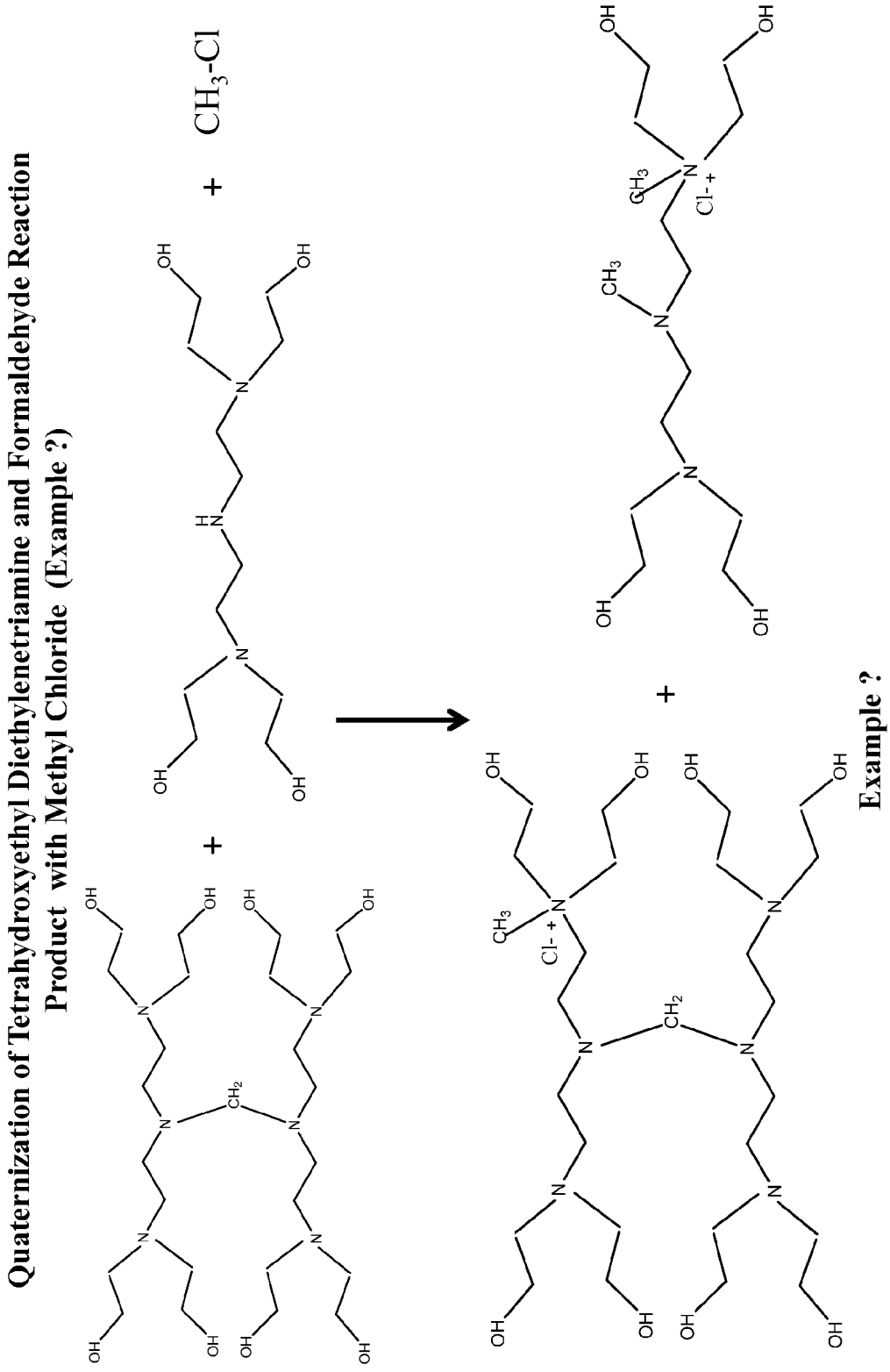

Quaternization of Tetrahydroxyethyl Diethylenetriamine and Formaldehyde Reaction
Product with Methyl Chloride (Example ?)
CH3-Cl
Example ?

FIG. 27

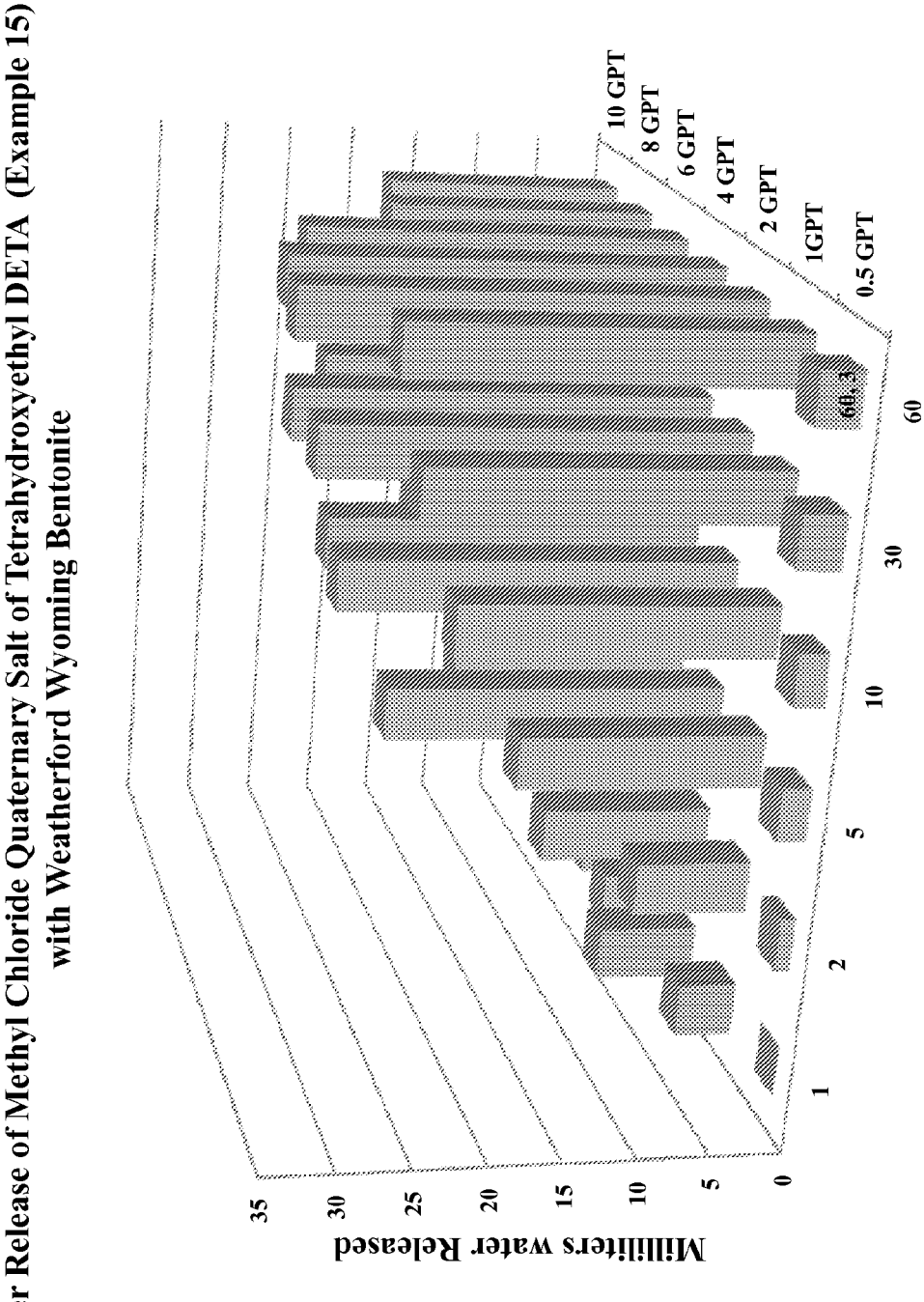

Water Release of Methyl Chloride Quaternary Salt of Tetrahydroxyethyl DETA (Example 15)
with Weatherford Wyoming Bentonite
Milliliters water Released
0
5
10
15
20
25
30
35
1
2
5
10
30
60
Time (Minutes)
10 GPT
8 GPT
6 GPT
4 GPT
2 GPT
1GPT
0.5 GPT
60.3

FIG. 28

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/028706

A. CLASSIFICATION OF SUBJECT MATTER

C09K 8/035(2006.01)i, C09K 8/18(2006.01)i, E21B 43/22(2006.01)i

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 8/035; C09K 8/68; C09K 8/04; C09K 8/22; C09K 7/02; E21B 43/26; C09K 8/18; E21B 43/22

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: clay stabilize composition, quaternary salt, amine, diethyl sulfate, aldehyde, drilling fluid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008-0227671 A1 (PATEL, ARVIND D.) 18 September 2008 See abstract; paragraphs [0015]-[0019] and [0042]; and claims 1-14.	1-20,22-41,43-62
A	US 5342530 A (AFTEN, CARL W. et al.) 30 August 1994 See columns 5-7; and claims 1-29.	1-20,22-41,43-62
A	US 7566686 B2 (KIPPIE, DAVID P. et al.) 28 July 2009 See abstract; columns 4 and 8; and claims 1	1-20,22-41,43-62
A	ANDERSON, R. L. et al. 'Clay swelling-a challenge in the oilfield.' Earth-Science Reviews. 2010, Vol. 98, No. 3, pages 201-216. See abstract; and pages 210-213.	1-20,22-41,43-62
A	US 5380706 A (HIMES, RONALD E. et al.) 10 January 1995 See abstract; and claims 1-14.	1-20,22-41,43-62

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"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
28 July 2014 (28.07.2014)	**28 July 2014 (28.07.2014)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
HONG, Sung Ran
Telephone No. +82-42-481-5405

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/028706

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 21, 42, 63
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2014/028706

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008-0227671 A1	18/09/2008	CA 2624737 A1	13/09/2008
		US 2011-190171 A1	04/08/2011
		US 7939473 B2	10/05/2011
		US 8298996 B2	30/10/2012
		WO 2008-112453 A1	18/09/2008
US 5342530 A	30/08/1994	US 5099923 A	31/03/1992
		US 5152906 A	06/10/1992
US 7566686 B2	28/07/2009	AU 2005-239638 A1	15/06/2006
		AU 2005-239638 B2	11/11/2010
		CA 2528014 A1	29/05/2006
		CA 2528014 C	20/07/2010
		GB 0524144 D0	04/01/2006
		GB 2420577 A	31/05/2006
		GB 2420577 B	23/09/2009
		NO 20055613 A	30/05/2006
		NO 20055613 D0	28/11/2005
		US 2006-0116296 A1	01/06/2006
		US 2008-0039345 A1	14/02/2008
		US 7268100 B2	11/09/2007
US 5380706 A	10/01/1995	EP 0545677 A1	09/06/1993