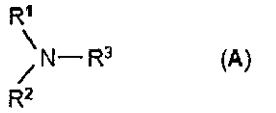
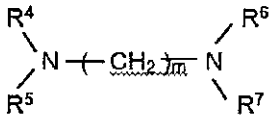
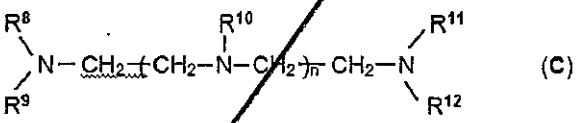
It is claimed:

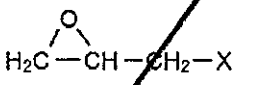
1. A method for mitigating the effects of clay in aggregates, comprising:

introducing to clay contained in a plurality of aggregates, in an amount of 0.1% to 100% by weight based on dry weight of the clay contained in said aggregates, a water-soluble functionalized polyamine comprising a water-soluble polyamine formed by reacting at least one of the amine compounds represented by the structural formulae (A) through (C) below with an epoxy compound represented by the structural formula (D) below:


(A)


(B)

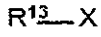

(C)


(D)

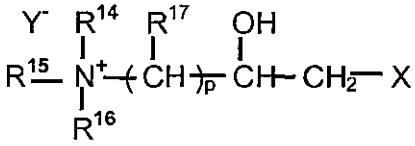
wherein R^1 to R^{12} each independently represent hydrogen or a C_1 to C_3 alkyl group; "m" and "n" each independently represent an integer of 1 to 6; "X" represents chlorine, bromine, iodine atom, or mixture thereof; and the molar ratio of hydrogen bonded to nitrogen of said amine compound to the epoxy group of said epoxy compound is from 50:50 to 75:25;

wherein said water-soluble polyamine is being functionalized using at least one functionalizing agent selected from the following compounds: halide compounds represented by structural formulae (E) and (F) below; sulfate compounds represented by structural formula (G) below; epoxy compounds

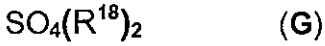
represented by structural formula (H) below; and dihalide compounds represented by formula (I) below



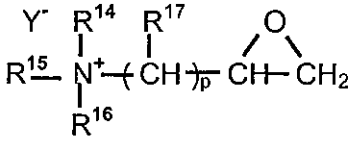
(E)



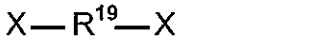
(F)



(G)



(H)



(I)

wherein R^{13} to R^{16} each independently represent an aliphatic or aromatic, saturated or unsaturated, C_1 to C_{16} alkyl group; R^{17} represents a hydrogen, C_1 to C_5 alkyl, hydroxyalkyl, alkylene or aryl group; R^{18} represents a C_1 to C_3 alkyl group; R^{19} represents a linear, branched or cyclic, C_1 to C_{10} alkylene or arylene group, "X" represents a chlorine, bromine, iodine atom, or mixtures thereof; "Y^-" represents a chloride, bromide, or iodide anion; and "p" represents an integer of 1 to 16; and

wherein the dry weight ratio of said polyamine to said functionalizing agent is from 99.5:0.5 to 75:25.

2. The method of claim 1 wherein said aggregates are selected from mortar aggregates, concrete aggregates, asphalt aggregates, and road base aggregates.

3. The method of claim 1 wherein said water-soluble functionalized polyamine is introduced to clay contained in a plurality of aggregates in an amount of 1% to 50% by weight based on dry weight of the clay contained in said aggregates.

4. The method of claim 1 wherein said water-soluble functionalized polyamine is introduced to clay contained in a plurality of aggregates in an amount of 2% to 25% by weight based on dry weight of the clay contained in said aggregates.

5. The method of claim 1 wherein said amine compound is represented by structural formula (A) and comprises an ammonia, methylamine, ethylamine, propylamine, dimethylamine, diethylamine, dipropylamine, methyl ethyl amine, methyl propyl amine, ethyl propyl amine, or mixture thereof.

6. The method of claim 5 wherein said amine compound is dimethylamine.

7. The method of claim 1 wherein said amine compound is represented by structural formula (B) and comprises ethylene diamine, 1,3-propylene diamine, 1,4-butylene diamine, 1,5-pentamethylene diamine, 1,6-hexamethylene diamine, or mixture thereof.

8. The method of claim 7 wherein said amine compound comprises ethylene diamine, hexamethylene diamine, or mixture thereof.

9. The method of claim 1 wherein said amine compound is represented by structural formula (C) and comprises diethylene triamine, triethylene tetramine, tetraethylene pentamine, or mixture thereof.

10. The method of claim 9 wherein said amine compound is tetraethylene pentamine.

11. The method of claim 1 wherein said amine compound is a mixture of dimethylamine and ethylene diamine in the molar ratio of 99.9:0.1 to 90:10.

12. The method of claim 1 wherein said amine compound is a mixture of dimethylamine and tetraethylene pentamine in the molar ratio of 99.9:0.1 to 92:8.

13. The method of claim 1 wherein said amine compound is reacted with an epoxy compound comprising epichlorohydrin, epibromohydrin, epiiodohydrin, or mixture thereof.

14. The method of claim 1 wherein said epoxy compound is epichlorohydrin.

15. The method of claim 1 wherein said water-soluble polyamine is functionalized using said halide compound represented by structural formula (E), said halide compound comprising methyl chloride, ethyl chloride, propyl chloride, allyl chloride, benzyl chloride, or mixture thereof.

16. The method of claim 15 wherein said halide compound comprises methyl chloride, benzyl chloride, or mixture thereof.

17. The method of claim 1 wherein said water-soluble polyamine is functionalized using said halide compound represented by structural formula (F), said halide compound comprising 3-chloro-2-hydroxypropyl trimethylammonium chloride, 3-chloro-2-hydroxypropyl lauryl dimethylammonium chloride, 3-chloro-2-hydroxypropyl dimethyl stearyl ammonium chloride, 3-chloro-2-hydroxypropyl dimethyl cocoalkylammonium chloride, or mixture thereof.

18. The method of claim 17 wherein said halide compound is 3-chloro-2-hydroxypropyl trimethylammonium chloride.

19. The method of claim 1 wherein said water-soluble polyamine is functionalized using a sulfate compound represented by structural formula (G), said sulfate compound comprising dimethyl sulfate, diethyl sulfate, methyl ethyl sulfate, methyl propyl sulfate, or mixture thereof.

20. The method of claim 19 wherein said sulfate compound is dimethyl sulfate.

21. The method of claim 1 wherein said water-soluble polyamine is functionalized using an epoxy compound represented by structural formula (H), said epoxy compound comprising glycidyl trimethylammonium chloride, glycidyl triethylammonium chloride, glycidyl dimethyl propylammonium chloride, glycidyl dimethylhexylammonium chloride, glycidyl dipropyldecylammonium bromide, glycidyl dimethyl laurylammonium chloride, or mixture thereof.

22. The method of claim 1 wherein said epoxy compound represented by structural formula (H) is glycidyl trimethylammonium chloride.

23. The method of claim 1 wherein said water-soluble polyamine is functionalized using a dihalide compound represented by structural formula (I), said dihalide compound comprising dichloroethane, dibromobutane, dichlorobenzene, 1-bromo-4-chlorobenzene, or mixture thereof.

24. The method of claim 23 wherein said dihalide compound is dichloroethane or 1-bromo-4-chlorobenzene.

25. The method of claim 1 wherein said weight ratio of said polyamine to said functionalizing agent is from 99:1 to 85:15.

26. The method of claim 25 wherein said weight ratio of said water-soluble polyamine to said functionalizing agent is from 99:1 to 90:10.

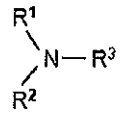
27. The method of claim 1 wherein said water-soluble functionalized polyamine has a Brookfield viscosity of 2 to 500 centipoise at 50 wt% aqueous solution as measured at 60 rpm and 25°C with a Brookfield Viscometer model DV-II+, spindle LV-1 .

28. An aggregate composition provided by the method of claim 1.

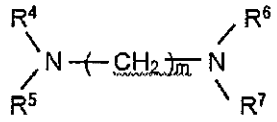
29. An aggregate composition comprising:

a plurality of clay-bearing aggregates selected from the group of natural and/or manufactured sand, crushed stone, crushed gravel, crushed rock, crushed shale, or mixtures thereof; and, in an amount of 0.1% to 100% by weight based on dry weight of the clay contained in said aggregates,

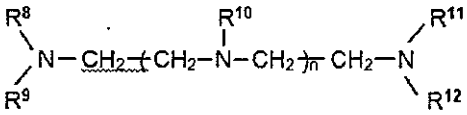
a water-soluble functionalized polyamine comprising a water-soluble polyamine formed by reacting at least one of the amine compounds represented by the structural formulae (A) through (C) below with an epoxy compound represented by the structural formula (D) below:



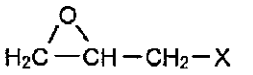
(A)



(B)



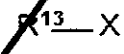
(C)



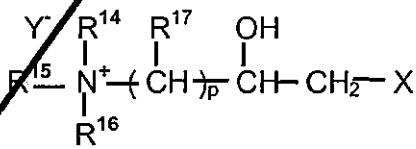
(D)

wherein R^1 to R^{12} each independently represent hydrogen or a C_1 to C_3 alkyl group; "m" and "n" each independently represent an integer of 1 to 6; "X" represents chlorine, bromine, iodine atom, or mixture thereof; and the molar ratio of hydrogen bonded to nitrogen of said amine compound to the epoxy group of said epoxy compound is from 50:50 to 75:25;

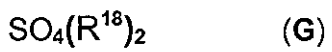
wherein said water-soluble polyamine is being functionalized using at least one functionalizing agent selected from the following compounds: halide compounds represented by structural formulae (E) and (F) below; sulfate compounds represented by structural formula (G) below; epoxy compounds represented by structural formula (H) below; and dihalide compounds represented by formula (I) below



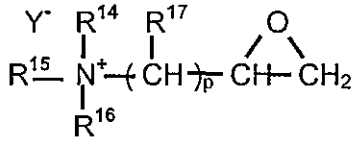
(E)



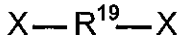
(F)



(G)



(H)



(I)

wherein R^{13} to R^{16} each independently represent an aliphatic or aromatic, saturated or unsaturated, C_1 to C_{16} alkyl group; R^{17} represents a hydrogen, C_1 to C_5 alkyl, hydroxyalkyl, alkylene or aryl group; R^{18} represents a C_1 to C_6 alkyl group; R^{19} represents a linear, branched or cyclic, C_1 to C_{10} alkylene or arylene group, "X" represents a chlorine, bromine, iodine atom, or mixtures thereof; "Y^-" represents a chloride, bromide, or iodide anion; and "p" represents an integer of 1 to 16; and

wherein the dry weight ratio of said polyamine to said functionalizing agent is from 99:1 to 75:25.

30. Method for modifying a hydratable cementitious composition comprising: combining a hydratable cement with said aggregate composition of claim 29.

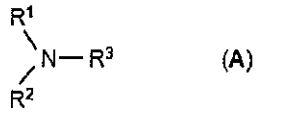
31. The method of claim 29 wherein said water-soluble functionalized polyamine is introduced to clay contained in a plurality of aggregates in an amount of 1% to 50% by weight based on dry weight of the clay contained in said aggregates.

32. The method of claim 29 wherein said water-soluble functionalized polyamine is introduced to clay contained in a plurality of aggregates in an amount of 2% to 25% by weight based on dry weight of the clay contained in said aggregates.

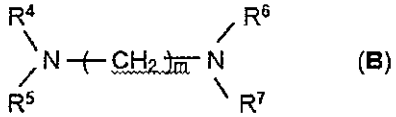
33. An admixture composition for modifying one or more properties of an aggregate or cementitious composition, comprising:

at least one chemical admixture selected from the group of water reducing agents, set retarders, set accelerators, defoamers, air entraining agents, surface active agents, and mixtures thereof; and

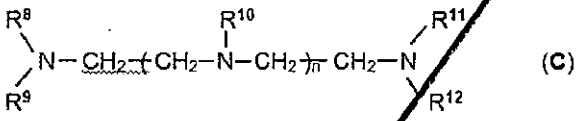
a water-soluble functionalized polyamine comprising a water-soluble polyamine formed by reacting at least one of the amine compounds represented by the structural formulae (A) through (C) below with an epoxy compound represented by the structural formula (D) below:



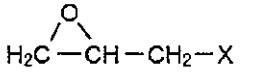
(A)



(B)



(C)

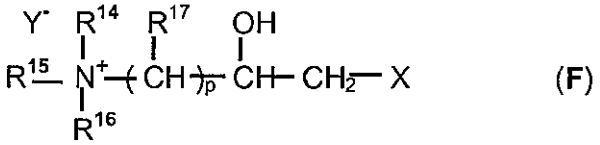


(D)

wherein R^1 to R^{12} each independently represent hydrogen or a C_1 to C_3 alkyl group; "m" and "n" each independently represent an integer of 1 to 6; "X" represents chlorine, bromine, iodine atom, or mixture thereof; and the molar ratio of hydrogen bonded to nitrogen of said amine compound to the epoxy group of said epoxy compound is from 50:50 to 75:25;

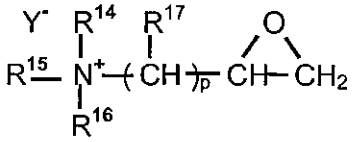
wherein said water-soluble polyamine is being functionalized using at least one functionalizing agent selected from the following compounds: halide compounds represented by structural formulae (E) and (F) below; sulfate compounds represented by structural formula (G) below; epoxy compounds represented by structural formula (H) below; and dihalide compounds represented by formula (I) below

$$R^{13}—X \qquad (E)$$



(F)

$$SO_4(R^{18})_2 \qquad (G)$$



(H)

$$X—R^{19}—X \qquad (I)$$

wherein R^{13} to R^{16} each independently represent an aliphatic or aromatic, saturated or unsaturated, C_1 to C_{16} alkyl group; R^{17} represents a hydrogen, C_1 to C_5 alkyl, hydroxyalkyl, alkylene or aryl group; R^{18} represents a C_1 to C_3 alkyl group; R^{19} represents a linear, branched or cyclic, C_2 to C_{10} alkylene or arylene group, "X" represents a chlorine, bromine, iodine atom, or mixtures thereof; "Y^-" represents a chloride, bromide, or iodide anion; and "p" represents an integer of 1 to 16; and

wherein the dry weight ratio of said polyamine to said functionalizing agent is from 99:1 to 75:25.

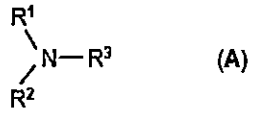
34. The admixture composition of claim 33 wherein said at least one chemical admixture is a water reducer selected from the group consisting of lignin sulfonate, naphthalene sulfonate formaldehyde condensate, melamine sulfonate formaldehyde condensate, polycarboxylate comb polymers which contain an alkylene oxide group, gluconate, and mixtures thereof.

35. A method for modifying a hydratable cementitious composition containing clay-bearing aggregates, comprising: introducing to clay-bearing aggregates the admixture composition of claim 33.

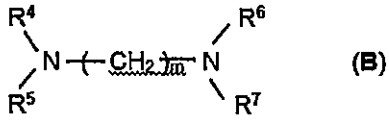
It is claimed:

1. A method for mitigating the effects of clay in aggregates, comprising:

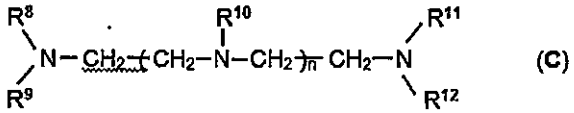
introducing to clay contained in a plurality of aggregates, in an amount of 0.1% to 100% by weight based on dry weight of the clay contained in said aggregates, a water-soluble functionalized polyamine comprising a water-soluble polyamine formed by reacting at least one of the amine compounds represented by the structural formulae (A) through (C) below with an epoxy compound represented by the structural formula (D) below:



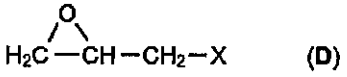
(A)



(B)



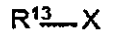
(C)



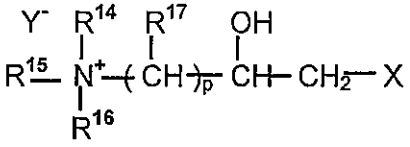
(D)

wherein R^1 to R^{12} each independently represent hydrogen or a C_1 to C_3 alkyl group; "m" and "n" each independently represent an integer of 1 to 6; "X" represents chlorine, bromine, iodine atom, or mixture thereof; and the molar ratio of hydrogen bonded to nitrogen of said amine compound to the epoxy group of said epoxy compound is from 50:50 to 75:25;

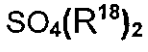
wherein said water-soluble polyamine is being functionalized using at least one functionalizing agent selected from the following compounds: halide compounds represented by structural formulae (E) and (F) below; sulfate compounds represented by structural formula (G) below; epoxy compounds represented by structural formula (H) below; and dihalide compounds represented by formula (I) below



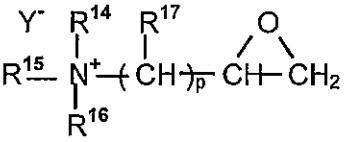
(E)



(F)



(G)



(H)



(I)

wherein R^{13} to R^{16} each independently represent a C_1 to C_{16} alkyl group; R^{17} represents a hydrogen, C_1 to C_5 alkyl, hydroxyalkyl, alkylene or aryl group; R^{18} represents a C_1 to C_3 alkyl group; R^{19} represents a linear, branched or cyclic, C_1 to C_{10} alkylene or arylene group, "X" represents a chlorine, bromine, iodine atom, or mixtures thereof; "Y-" represents a chloride, bromide, or iodide anion; and "p" represents an integer of 1 to 16; or the compound of formula (E) is allyl chloride or benzyl chloride, or the compound of formula (F) is 3-chloro-2-hydroxypropyl dimethyl stearyl ammonium chloride or 3-chloro-2-hydoxypropyl dimethyl cocoalkyl ammonium chloride and

wherein the dry weight ratio of said polyamine to said functionalizing agent is from 99.5:0.5 to 75:25.

2. The method of claim 1 wherein said aggregates are selected from mortar aggregates, concrete aggregates, asphalt aggregates, and road base aggregates.

3. The method of claim 1 wherein said water-soluble functionalized polyamine is introduced to clay contained in a plurality of aggregates in an amount of 1% to 50% by weight based on dry weight of the clay contained in said aggregates.

4. The method of claim 1 wherein said water-soluble functionalized polyamine is introduced to clay contained in a plurality of aggregates in an amount of 2% to 25% by weight based on dry weight of the clay contained in said aggregates.

5. The method of claim 1 wherein said amine compound is represented by structural formula (A) and comprises an ammonia, methylamine, ethylamine, propylamine, dimethylamine, diethylamine, dipropylamine, methyl ethyl amine, methyl propyl amine, ethyl propyl amine, or mixture thereof.

6. The method of claim 5 wherein said amine compound is dimethylamine.

7. The method of claim 1 wherein said amine compound is represented by structural formula (B) and comprises ethylene diamine, 1,3-propylene diamine, 1,4-butylene diamine, 1,5-pentamethylene diamine, 1,6-hexamethylene diamine, or mixture thereof.

8. The method of claim 7 wherein said amine compound comprises ethylene diamine, hexamethylene diamine, or mixture thereof.

9. The method of claim 1 wherein said amine compound is represented by structural formula (C) and comprises diethylene triamine, triethylene tetramine, tetraethylene pentamine, or mixture thereof.

10. The method of claim 9 wherein said amine compound is tetraethylene pentamine.

11. The method of claim 1 wherein said amine compound is a mixture of dimethylamine and ethylene diamine in the molar ratio of 99.9:0.1 to 90:10.

12. The method of claim 1 wherein said amine compound is a mixture of dimethylamine and tetraethylene pentamine in the molar ratio of 99.9:0.1 to 92:8.

13. The method of claim 1 wherein said amine compound is reacted with an epoxy compound comprising epichlorohydrin, epibromohydrin, epiiodohydrin, or mixture thereof.

14. The method of claim 1 wherein said epoxy compound is epichlorohydrin.

15. The method of claim 1 wherein said water-soluble polyamine is functionalized using said halide compound represented by structural formula (E), said halide compound comprising methyl chloride, ethyl chloride, propyl chloride, allyl chloride, benzyl chloride, or mixture thereof.

16. The method of claim 15 wherein said halide compound comprises methyl chloride, benzyl chloride, or mixture thereof.

17. The method of claim 1 wherein said water-soluble polyamine is functionalized using said halide compound represented by structural formula (F), said halide compound comprising 3-chloro-2-hydroxypropyl trimethylammonium chloride, 3-chloro-2-hydroxypropyl lauryl dimethylammonium chloride, 3-chloro-2-hydroxypropyl dimethyl stearyl ammonium chloride, 3-chloro-2-hydroxypropyl dimethyl cocoalkylammonium chloride, or mixture thereof.

18. The method of claim 17 wherein said halide compound is 3-chloro-2-hydroxypropyl trimethylammonium chloride.

19. The method of claim 1 wherein said water-soluble polyamine is functionalized using a sulfate compound represented by structural formula (G), said sulfate compound comprising dimethyl sulfate, diethyl sulfate, methyl ethyl sulfate, methyl propyl sulfate, or mixture thereof.

20. The method of claim 19 wherein said sulfate compound is dimethyl sulfate.

21. The method of claim 1 wherein said water-soluble polyamine is functionalized using an epoxy compound represented by structural formula (H), said epoxy compound comprising glycidyl trimethylammonium chloride, glycidyl triethylammonium chloride, glycidyl dimethyl propylammonium chloride, glycidyl dimethylhexylammonium chloride, glycidyl dipropyldecylammonium bromide, glycidyl dimethyl laurylammonium chloride, or mixture thereof.

22. The method of claim 1 wherein said epoxy compound represented by structural formula (H) is glycidyl trimethylammonium chloride.

23. The method of claim 1 wherein said water-soluble polyamine is functionalized using a dihalide compound represented by structural formula (I), said dihalide compound comprising dichloroethane, dibromobutane, dichlorobenzene, 1-bromo-4-chlorobenzene, or mixture thereof.

24. The method of claim 23 wherein said dihalide compound is dichloroethane or 1-bromo-4-chlorobenzene.

25. The method of claim 1 wherein said weight ratio of said polyamine to said functionalizing agent is from 99:1 to 85:15.

26. The method of claim 25 wherein said weight ratio of said water-soluble polyamine to said functionalizing agent is from 99:1 to 90:10.

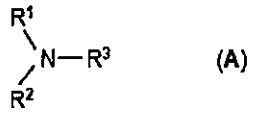
27. The method of claim 1 wherein said water-soluble functionalized polyamine has a Brookfield viscosity of 2 to 500 centipoise at 50 wt% aqueous solution as measured at 60 rpm and 25°C with a Brookfield Viscometer model DV-II+, spindle LV-1 .

28. An aggregate composition comprising:

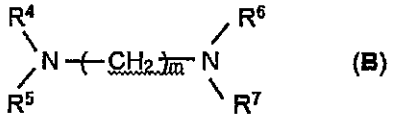
a plurality of clay-bearing aggregates selected from the group of natural and/or manufactured sand, crushed stone, crushed gravel, crushed rock, crushed shale, or

mixtures thereof; and, in an amount of 0.1% to 100% by weight based on dry weight of the clay contained in said aggregates,

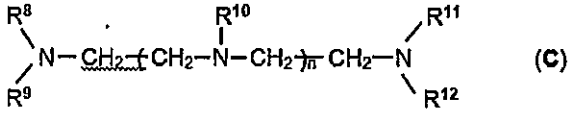
a water-soluble functionalized polyamine comprising a water-soluble polyamine formed by reacting at least one of the amine compounds represented by the structural formulae (A) through (C) below with an epoxy compound represented by the structural formula (D) below:



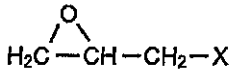
(A)



(B)



(C)



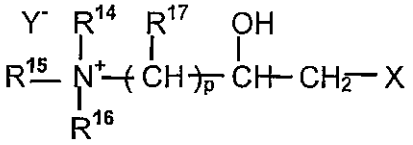
(D)

wherein R^1 to R^{12} each independently represent hydrogen or a C_1 to C_3 alkyl group; "m" and "n" each independently represent an integer of 1 to 6; "X" represents chlorine, bromine, iodine atom, or mixture thereof; and the molar ratio of hydrogen bonded to nitrogen of said amine compound to the epoxy group of said epoxy compound is from 50:50 to 75:25;

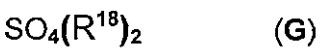
wherein said water-soluble polyamine is being functionalized using at least one functionalizing agent selected from the following compounds: halide compounds represented by structural formulae (E) and (F) below; sulfate compounds represented by structural formula (G) below; epoxy compounds represented by structural formula (H) below; and dihalide compounds represented by formula (I) below



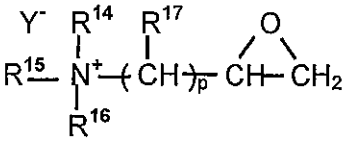
(E)



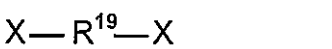
(F)



(G)



(H)



(I)

wherein R^{13} to R^{16} each independently represent a C_1 to C_{16} alkyl group; R^{17} represents a hydrogen, C_1 to C_5 alkyl, hydroxyalkyl, alkylene or aryl group; R^{18} represents a C_1 to C_3 alkyl group; R^{19} represents a linear, branched or cyclic, C_1 to C_{10} alkylene or arylene group, "X" represents a chlorine, bromine, iodine atom, or mixtures thereof; "Y^-" represents a chloride, bromide, or iodide anion; and "p" represents an integer of 1 to 16; or the compound of formula (E) is allyl chloride or benzyl chloride, or the compound of formula (F) is 3-chloro-2-hydroxypropyl dimethyl stearyl ammonium chloride or 3-chloro-2-hydoxypropyl dimethyl cocoalkyl ammonium chloride and

wherein the dry weight ratio of said polyamine to said functionalizing agent is from 99:1 to 75:25.

29. Method for modifying a hydratable cementitious composition comprising: combining a hydratable cement with said aggregate composition of claim 28.

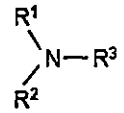
30. The method of claim 28 wherein said water-soluble functionalized polyamine is introduced to clay contained in a plurality of aggregates in an amount of 1% to 50% by weight based on dry weight of the clay contained in said aggregates.

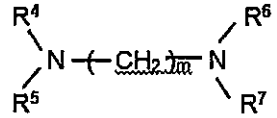
31. The method of claim 28 wherein said water-soluble functionalized polyamine is introduced to clay contained in a plurality of aggregates in an amount of 2% to 25% by weight based on dry weight of the clay contained in said aggregates.

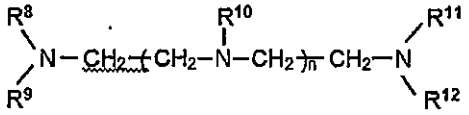
32. An admixture composition for modifying one or more properties of an aggregate or cementitious composition, comprising:

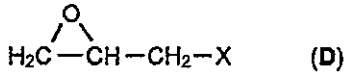
a water reducer selected from the group consisting of lignin sulfonate, naphthalene sulfonate formaldehyde condensate, melamine sulfonate formaldehyde condensate, polycarboxylate comb polymers which contain an alkylene oxide group, gluconate, and mixtures thereof; and

a water-soluble functionalized polyamine comprising a water-soluble polyamine formed by reacting at least one of the amine compounds represented by the structural formulae (A) through (C) below with an epoxy compound represented by the structural formula (D) below:


(A)


(B)

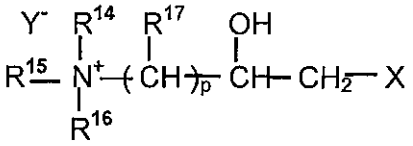

(C)


(D)

wherein R^1 to R^{12} each independently represent hydrogen or a C_1 to C_3 alkyl group; "m" and "n" each independently represent an integer of 1 to 6; "X" represents chlorine, bromine, iodine atom, or mixture thereof; and the molar ratio of hydrogen bonded to nitrogen of said amine compound to the epoxy group of said epoxy compound is from 50:50 to 75:25;

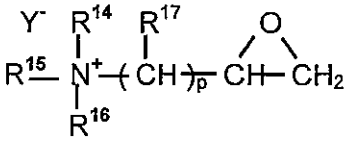
wherein said water-soluble polyamine is being functionalized using at least one functionalizing agent selected from the following compounds: halide compounds represented by structural formulae (E) and (F) below; sulfate compounds represented by structural formula (G) below; epoxy compounds represented by structural formula (H) below; and dihalide compounds represented by formula (I) below

$$R^{13}—X \qquad \textbf{(E)}$$



(F)

$$SO_4(R^{18})_2 \qquad \textbf{(G)}$$



(H)

$$X—R^{19}—X \qquad \textbf{(I)}$$

wherein R^{13} to R^{16} each independently represent a C_1 to C_{16} alkyl group; R^{17} represents a hydrogen, C_1 to C_5 alkyl, hydroxyalkyl, alkylene or aryl group; R^{18} represents a C_1 to C_3 alkyl group; R^{19} represents a linear, branched or cyclic, C_1 to C_{10} alkylene or arylene group, "X" represents a chlorine, bromine, iodine atom, or mixtures thereof; "Y^-" represents a chloride, bromide, or iodide anion; and "p" represents an integer of 1 to 16; or the compound of formula (E) is allyl chloride or benzyl chloride, or the compound of formula (F) is 3-chloro-2-hydroxypropyl dimethyl

stearyl ammonium chloride or 3-chloro-2-hydoxypropyl dimethyl cocoalkyl ammonium chloride and

wherein the dry weight ratio of said polyamine to said functionalizing agent is from 99:1 to 75:25.

33. A method for modifying a hydratable cementitious composition containing clay-bearing aggregates, comprising: introducing to clay-bearing aggregates the admixture composition of claim 32.