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(54) Admixture for a hydraulic composition

(57) This invention provides a liquid admixture for a hydraulic composition, which is excellent in shelf stability and capable of endowing a hydraulic composition with excellent fluidity and fluidity retention without being influenced by variations in hydraulic powders of cement etc. Is provided a method of improving fluidity retention of a hydraulic composition, comprising adding, to a hydraulic slurry comprising water and a hydraulic powder and having a sulfate ion concentration of 2,500 to 40,000 mg/kg in the aqueous solution thereof, (1) at least one polycarboxylic acid-based dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is higher than 30 % by weight and (2) at least one polycarboxylic acid-based dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is not higher than 30 % by weight.

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Description

Technical Field

[0001] This invention relates to a method of improving fluidity retention of a hydraulic composition or an admixture for a hydraulic composition. This invention relates in particular to an admixture for a hydraulic composition which is excellent in shelf stability and capable of endowing a hydraulic composition for cement pastes, mortar and concrete or the like with excellent fluidity and fluidity retention without being influenced by variations in hydraulic powders of cement etc.

Prior Arts

[0002] As cement admixtures such as a high-performance water-reducing agent, those based on polycarboxylic acids are known, but the performance of polycarboxylic acid-based dispersants is known to be varied depending on the concentration of sulfate ions in hydraulic slurry. The concentration of sulfate ions in a hydraulic slurry is varied depending on the type of cement etc., so that when the type of cement is changed, the dispersants may fail to exhibit their initial desired effect. To solve this problem, JP-A 2000-327385 discloses a dispersant with less variation in performance against variation in sulfate ions. In the reference the water-reducing performance is improved to a certain extent, but the problem of variation in fluidity retention has not been completely solved.

[0003] On one hand, JP-A 11-60305 and JP-A 9-67153 disclose techniques of improving fluidity retention by both a polyalkylene glycol ester monomer/carboxylic acid monomer copolymer and at least one kind of unsaturated carboxylic acid-based homopolymer or copolymer.

[0004] The polycarboxylic acid-based polymer can, even in an acid form, be used directly as a dispersant for cement. But from the viewpoint of inhibiting acid hydrolysis of esters or corrosion of material of a tank or the like, the polymer is often used in a salt form after neutralization by an alkali. For handling etc., the polymer is preferably in the form of an aqueous solution.

[0005] Each of the above-mentioned two copolymers, when used at an solid concentration of 10 weight-% or more as usual, is in the form of a homogeneous aqueous solution, but the two are mixed for use, the mixture may be separated after being left for a predetermined time, thus making it sometimes necessary to add the two copolymers separately to cement in order to provide a stable performance. In the case of the mixed product rendered highly viscous to suppress the above-mentioned separation, their solution is so highly viscous as to be poor in dropping at the time of dosing, thus suffering from varying performance attributable to errors in dosing. When the polymers different in the content of carboxyl groups are mixed, there arises a difference in solubility between the polymers, which would sometimes cause phase separation, so there is a demand for polymers excellent in shelf stability even in the form of an aqueous solution.

Disclosure of invention

[0006] The object of this invention is to provide a method of improving fluidity retention of a hydraulic composition or a liquid admixture for a hydraulic composition. The invention is excellent in shelf stability and handling and capable of exhibiting dispersibility and dispersion retention stably even if the type of hydraulic powders of cement etc. is changed.

[0007] The invention provides a method of improving fluidity retention of a hydraulic composition, comprising adding, to a hydraulic slurry comprising water and a hydraulic powder and having a sulfate ion concentration of 2,500 to 40,000 mg/kg in the aqueous solution thereof, (1) at least one polycarboxylic acid-based dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is higher than 30 % by weight and (2) at least one polycarboxylic acid-based dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is not higher than 30 % by weight.

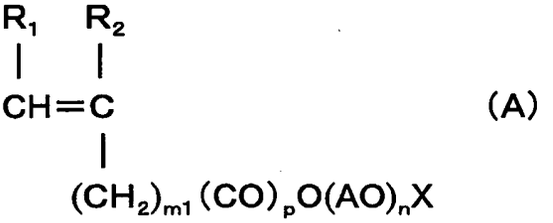
[0008] It is preferable in the method that the sulfate ion concentration is 6,000 to 40,000 mg/kg.

[0009] This invention then relates to an admixture for a hydraulic composition which is in the form of a homogeneous aqueous solution, wherein a 5-fold (ratio by weight) dilution (dilution to 5 times as much an amount as the initial) of the admixture with water has an electric conductivity of not higher than 45 mS/cm at 25°C, said admixture comprising at least one kind of a polycarboxylic acid-based dispersant (1) comprising a polymer wherein the ratio of carboxylic acid monomers is higher than 30 % by weight and at least one kind of a polycarboxylic acid-based dispersant (2) comprising a polymer wherein the ratio of carboxylic acid monomers is not higher than 30 % by weight.

[0010] It is preferable in the method that (1) the polycarboxylic acid-based dispersant is selected from 1) and (2) the polycarboxylic acid-based dispersant is selected from 2):

1) dispersants comprising a water-soluble salt of a homopolymer of an unsaturated carboxylic acid selected from an unsaturated monocarboxylic acid and an unsaturated dicarboxylic acid or of a copolymer of two or more of the unsaturated carboxylic acids,

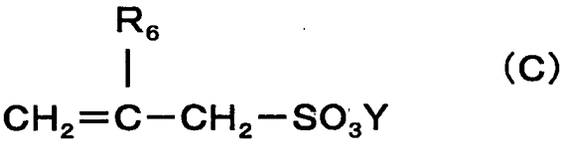
2) dispersants comprising a copolymer obtained by polymerizing a monomer (a) represented by formula (A) :



(A)

wherein R_1 and R_2 each represents a hydrogen atom or a methyl group, m1 is a number of 0 to 2, p is 0 or 1, AO is a C_{2-4} oxyalkylene group, n is a number of 2 to 300 and X represents a hydrogen atom or a C_{1-22} alkyl group;
with at least one monomer (b) selected from compounds represented by formulae (B) and (C):

(B)



(C)

wherein R_3 to R_5 are the same as or different from one another and each represent a hydrogen atom, a methyl group or $(CH_2)_{m2}COOM_2$, R_6 represents a hydrogen atom or a methyl group, M_1, M_2 and Y are the same as or different from one another and each represent a hydrogen atom, an alkali metal, an alkaline earth metal, ammonium, an alkylammonium or a substituted alkylammonium, an amine salt or a substituted amine salt and m2 is a number of 0 to 2.

[0011] The invention provides an admixture for a hydraulic composition comprising a homogeneous mixed liquid comprising the polycarboxylic acid-based dispersant (1) described above and the polycarboxylic acid-based dispersant (2) described above.

[0012] The admixture is preferred to have the total solid of the polycarboxylic acid-based dispersant (1) and the polycarboxylic acid-based dispersant (2) in the range of 10 to 40 percent by weight. The admixture is then preferred to have the weight ratio [(1)/(2)] of the polycarboxylic acid-based dispersant (1) to the polycarboxylic acid-based dispersant (2) in the range of 3/97 to 40/60.

[0013] The above shown admixture preferably satisfies any one of the following conditions (a) to (f):

(a) the total amount (hereinafter referred to as solids content) of the polycarboxylic acid-based dispersants (1) and (2) in the admixture for a hydraulic composition is more than 30 to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.15 or less,
(b) the solids content is more than 20 to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.4 or less,
(c) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(d) the solids content is more than 30 to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 0.25,
(e) the solids content is more than 20 to 30 weight-%, and the dispersants are neutralized with triethanolamine,

and the degree of neutralization thereof is 1 or less, and
(f) the solids content is 20 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less.

[0014] The invention provides a process for preparing an admixture for a hydraulic composition, being homogeneous and having a pH of 4 to 9, comprising adding an alkali to an aqueous solution comprising the polycarboxylic acid-based dispersant (1) described above and the polycarboxylic acid-based dispersant (2) described above in the total solid of 10 to 40 percent by weight.

[0015] The invention moreover provides a method of improving fluidity retention of a hydraulic composition, comprising adding, to a hydraulic slurry comprising water and a hydraulic powder and having a sulfate ion concentration of 2,500 to 40,000 mg/kg in the aqueous solution thereof, an oxycarboxylic acid and a polycarboxylic acid-based dispersant (2) comprising a polymer wherein the ratio of carboxylic acid monomers is not higher than 30 % by weight.

[0016] As used herein, the phrase "in the form of a homogeneous aqueous solution" refers to a state free of liquid or solid separation, precipitation, flotation, etc. when observed with naked eyes. Any part of the solution are estimated as equivalent to other parts in view of the chemical organization thereof. The admixture for a hydraulic composition in this invention is in the form of a homogenious aqueous solution particularly preferably after storage at 20°C for 1 month after preparation.

[0017] The phrase "ratio of carboxylic acid monomers" means the ratio by weight of unsaturated carboxylic acids to the total monomers used in producing the polymer. When the monomer is a salt, the weight of its corresponding acid is calculated, and in the case of a structure for example an anhydride such as maleic anhydride, the weight of the anhydride is calculated.

[0018] Further, this invention relates to a hydraulic composition comprising the invented admixture for a hydraulic composition added to water- and hydraulic powder-containing hydraulic slurry having a sulfate ion concentration of 2,500 to 40,000 mg/kg(ppm) in its aqueous solution.

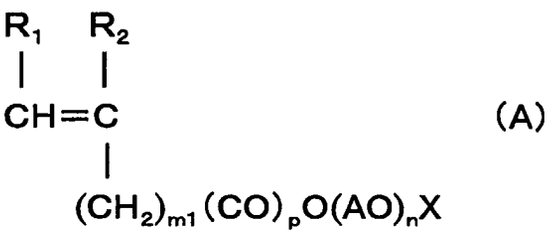
[0019] In this invention, the dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is higher than 30 % by weight is used in combination with the dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is not higher than 30 % by weight, whereby the performance of the hydraulic composition is inhibited from being varied due to a change in sulfate ions in hydraulic slurry, and further the electric conductivity of a 5-fold (ratio by weight) dilution, with water, of the admixture comprising two kinds of dispersants mixed therein is regulated to be not higher than 45 mS/cm at 25°C, whereby a homogeneous admixture excellent in shelf stability and handling is achieved.

[0020] In the method of improving fluidity retention and the admixture for a hydraulic composition according to this invention, two kinds of dispersants, that is, dispersants (1) and (2), are used. Then two or more kinds of one or both of the dispersants can also be used. In this case, dispersant polymers different in e.g. average molecular weight or salt are regarded as different dispersants even if they are identical in the type of used monomer. Further, copolymers different in e.g. copolymerization molar ratio are regarded as different dispersants even if they are identical in combination of monomers. As the indicator to determine whether dispersants are identical or not, mention is made of the type of monomer, weight-average molecular weight, molar ratio of monomers, etc.

[0021] In place of the dispersant (I), alternatively, an oxycarboxylic acid or a salt threof may be used.

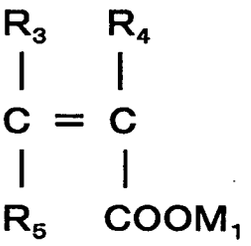
[0022] Preferably, the polycarboxylic acid-based dispersant (1) used in this invention is selected from the following 1), and the polycarboxylic acid-based dispersant (2) is selected from the following 2):

1) dispersants (referred to collectively as dispersant (1a)) comprising a water-soluble salt of a homopolymer of an unsaturated carboxylic acid selected from an unsaturated monocarboxylic acid and an unsaturated dicarboxylic acid or of a copolymer of two or more kinds of such unsaturated carboxylic acids, and
2) dispersants (referred to collectively as dispersant (2a)) comprising a copolymer obtained by polymerizing a monomer (a) represented by formula (A) with at least one monomer (b) selected from compounds represented by the formulae (B) and (C) :

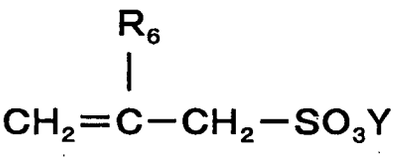


(A)

wherein R_1 and R_2 each represents a hydrogen atom or a methyl group, m1 is a number of 0 to 2, p is 0 or 1, AO is a C_{2-4} oxyalkylene group, n is a number of 2 to 300 and X represents a hydrogen atom or a C_{1-22} alkyl group.



(B)



(C)

wherein R_3 to R_5 are the same as or different from one another and each represent a hydrogen atom, a methyl group or $(CH_2)_{m2}COOM_2$, R_6 represents a hydrogen atom or a methyl group, M_1, M_2 and Y are the same as or different from one another and each represent a hydrogen atom, an alkali metal, an alkaline earth metal, ammonium, an alkylammonium or a substituted alkylammonium, an amine salt or substituted amine salt, and m2 is a number of 0 to 2.

<Dispersant (1a)>

[0023] The dispersant (1a) is a water-soluble salt of a homopolymer of an unsaturated carboxylic acid selected from an unsaturated monocarboxylic acid and an unsaturated dicarboxylic acid or of a copolymer of two or more kinds of such unsaturated carboxylic acids, and the unsaturated monocarboxylic acid includes acrylic acid, methacrylic acid, and the like, the unsaturated dicarboxylic acid includes maleic acid, fumaric acid, itaconic acid, and the like, and the water-soluble salt thereof includes alkali salts. Examples thereof include homopolymers such as sodium polyacrylate, sodium polymethacrylate, sodium polymaleate, copolymers such as acrylic acid-sodium maleate. In the copolymer as the dispersant (1a), the ratio of the unsaturated monocarboxylic acid and the unsaturated dicarboxylic acid is higher than 30 weight-%, preferably 40 to 100 weight-%, more preferably 50 to 100 weight-%.

[0024] The weight-average molecular weight of the copolymer as the dispersant (1a) (polyethylene oxide-equivalent molecular weight determined by gel permeation chromatography) is preferably 500 to 100,000, more preferably 1, 000 to 50, 000, from the viewpoint of dispersibility and viscosity.

<Dispersant (2a)>

[0025] The copolymer as the dispersant (2a) is a water-soluble vinyl copolymer having an oxyalkylene group. The monomer (a) represented by the formula (A) used in production of the copolymer as the dispersant (2a) is preferably an ester of (meth)acrylic acid or (half)ester of maleic acid with an alkyl-terminated polyalkylene glycol such as methoxy polyethylene glycol, methoxy polypropylene glycol, methoxy polybutylene glycol, or ethoxy polyethylene polypropylene glycol, or an ether of (meth)allyl alcohol with the alkyl-terminated polyalkylene glycol, or an adduct having ethylene oxide (hereinafter referred to as EO) or propylene oxide (hereinafter referred to as PO) added to (meth)acrylic acid, maleic acid or (meth) allyl alcohol. R_1 is preferably a hydrogen atom, p is preferably 1, and m1 is preferably 0. It is more preferably an ester of (meth)acrylic acid with an alkoxy polyethylene glycol, in particular methoxy polyethylene glycol. EO, PO or butyleneoxide (BO) may be used for AO. X is preferably a hydrogen or a C_{1-4} alkyl group.

[0026] The average number of polyalkylene glycol molecules added, i.e. "n" in the formula (A), is 2 to 300, preferably 5 to 200, particularly preferably 20 to 150 from the viewpoint of dispersibility and fluidity retention (slump retention). In the copolymers different in AO, for example those containing EO and PO, the mode of addition thereof is not particularly limited, and any of random addition, block addition and alternate addition can be used.

[0027] The monomer represented by the formula (B) includes acrylic acid, methacrylic acid, crotonic acid, and metal

salts thereof. As the unsaturated dicarboxylic acid monomer, use is made of maleic anhydride, maleic acid, itaconic anhydride, itaconic acid, citraconic anhydride, citraconic acid or fumaric acid, or an alkali metal salt, alkaline earth metal salt, ammonium salt, amine salt or substituted amine salt thereof.

[0028] As the monomer represented by the formula (C), use is made of allylsulfonic acid or methallylsulfonic acid, or an alkali metal salt, alkaline earth metal salt, ammonium salt, amine salt, substituted amine salt thereof, or the like.

[0029] From the viewpoint of dispersibility, fluidization, fluidity retention and separation resistance, the mole ratio of the monomer (a) to the monomer (b) as the reaction units constituting the copolymer as the dispersant (2a), that is, the monomer (a) /the monomer (b), is preferably 1/100 to 10000/100, more preferably 1/100 to 200/100, especially 1/100 to 100/100. In the dispersant (2a), however, the ratio of carboxylic acid monomers as monomers represented by the formula (B) should be 30 weight-% or less. The ratio of the unsaturated carboxylic acid monomers charged is preferably 3 to 30 weight-% and simultaneously 50 to 99 mol-%, more preferably 5 to 25 weight-% and simultaneously 60 to 95 mol-%.

[0030] The copolymer as the dispersant (2a) can be produced in a known method. The method includes, for example, solvent polymerization methods in JP-A 59-162163, JP-B 2-11542, JP-B 2-7901, JP-B 2-7897 and the like.

[0031] The solvent used in the solvent polymerization method includes water, methyl alcohol, ethyl alcohol, isopropyl alcohol, benzene, toluene, xylene, cyclohexane, n-hexane, aliphatic hydrocarbons, ethyl acetate, acetone, methyl ethyl ketone, etc. In consideration of handling and reaction facilities, water and primary to quaternary alcohols are preferable.

[0032] As an aqueous polymerization initiator, a water-soluble initiator such as an ammonium or alkali metal persulfate or hydrogen peroxide is used. For solvent polymerization using a non-aqueous solvent, benzoyl peroxide, lauroyl peroxide or the like is used as the polymerization initiator.

[0033] An accelerator such as sodium hydrogen sulfite, mercaptoethanol or an amine compound can also be used in combination with the polymerization initiator, and the polymerization initiator or the accelerator can be suitably selected for use.

[0034] The weight-average molecular weight of the copolymer as the dispersant (2a) (polyethylene oxide-equivalent molecular weight determined by gel permeation chromatography) is preferably 1,000 to 500,000, more preferably 3,000 to 150,000, from the viewpoint of dispersibility and fluidity retention(slump retention).

[0035] Further, the copolymer as the dispersant (2a) may be reacted with other copolymerizable monomers in such a range that the effect of this invention is not deteriorated. Example of such monomers include acrylonitrile, acrylate, acrylamide, methacrylamide, styrene, styrenesulfonic acid, etc.

[0036] In this invention, two or more kinds of the dispersant (2a) are preferably simultaneously used. In this case, those different in n (AO chain length) in the formula (A), those different in the copolymerization molar ratio of the monomers and those different in the monomers of the formula (B) are preferable. In particular, two or more kinds of copolymers different in n by 10 or more in the formula (A) are preferably contained. For example, one of the copolymers is produced from the monomer (a) wherein n = 2 to 100, preferably 2 to 50, more preferably 5 to 20, and the other from the monomer (a) wherein n = 20 to 300, preferably 50 to 200, more preferably 100 to 150, provided that the two kinds of monomers are different in n by 10 or more.

[0037] The two or more kinds of dispersants are selected preferably from those wherein the ratio of unsaturated carboxylic acid monomers charged is preferably 3 to 30 weight-% and simultaneously 50 to 99 mole-%, more preferably from those wherein the ratio of unsaturated carboxylic acid monomers charged is 5 to 25 weight-% and simultaneously 60 to 95 mole-%.

[0038] The oxycarboxylic acid to use in the invention preferably has 2 to 20 carbon atoms, more preferably 2 to 10. It preferably includes 1 to 8 carboxylic groups, in particular 1 to 3. A salt of an oxycarboxylic acid may be used. For example it may include gluconic acid, glucoheptonic acid, galactonic acid, citric acid, tartaric acid, malic acid, glycolic acid, lactic acid, α-oxybutyric acid, lactobionic acid or a salt thereof. The salt may include an inorganic salt such as sodium salt or potassium salt or an organic salt. Gluconic acid, glucoheptonic acid or a salt thereof, in particular sodium salt, is preferable from the viewpoint of dispersion of cement.

<Admixture for hydraulic composition>

[0039] The admixture for a hydraulic composition according to this invention is in the form of an aqueous solution, and the electric conductivity of a 5-fold (ratio by weight) dilution of the admixture with water is not higher than 45 mS/cm, preferably not higher than 40 mS/cm, more preferably not higher than 35 mS/cm. The lower limit of the electric conductivity is 0 mS/cm. This electric conductivity was measured at 25°C by a conductivity meter (HORIBA DS-15).

[0040] The Admixture for a hydraulic composition according to the invention is a homogeneous mixed liquid including the polycarboxylic acid dispersant (1) and the polycarboxylic acid dispersant (2). The homogeneous mixed liquid means no separation observed by eyes in two or more phases of dispersants, being in the form of a solution or an emulsion. Any part of the solution are estimated as equivalent to other parts in view of the chemical organization thereof.

[0041] By selecting a neutralizing agent or a neutralization degree or controlling the salt concentration of the admix-

ture in terms of the electric conductivity in this invention, a suitable total solid of the polycarboxylic acid dispersant (1) and the polycarboxylic acid dispersant (2) (solid content) of the composition mixture may be determined and the admixture can exhibit dispersibility and fluidity retention performance stably against a change in the type of hydraulic powders of cement etc., and is excellent in shelf stability and handling. Such working mechanism is estimated as follows: That is, the dispersant (1) is adsorbed rapidly onto the surface of cement, to relieve the influence of sulfate ions eluted from the powder, and simultaneously the concentration of the residual dispersant (2) is secured thereby imparting a given dispersion retention. The dispersants (1) and (2) are dissolved homogeniously, thus stably exhibiting the desired performance. In the invention, it is considered that oxycarboxylic acid functions in the same way as the dispersant (1).

[0042] The admixture for a hydraulic composition according to this invention comprises the dispersants (1) and (2) in an amount of preferably 10 to 40 weight-% in total, more preferably 15 to 35 weight-%, still more preferably 20 to 30 weight-% (in terms of solids content). Even in this range, a stable aqueous solution can be obtained.

[0043] in the admixture for a hydraulic composition according to this invention, the weight ratio of the dispersant (1) to (2), (dispersant (1) to dispersant (2)), is preferably 3/97 to 40/60, more preferably 5/95 to 30/70, in particular 10/90 to 20/80.

[0044] The admixture for a hydraulic composition according to this invention comprises oxycarboxylic acid or a salt thereof and the dispersant (2) in an amount of preferably 10 to 40 weight-% in total, more preferably 15 to 35 weight-%, still more preferably 20 to 30 weight-% (in terms of solids content). Even in this range, a stable aqueous solution can be obtained.

[0045] In the admixture for a hydraulic composition according to this invention, the weight ratio of oxycarboxylic acid or a salt thereof to the dispersant (2), (oxycarboxylic acid or a salt thereof to the dispersant (2)), is preferably 3/97 to 60/40, more preferably 5/95 to 50/50, in particular 10/90 to 40/60.

[0046] The pH value at 20°C of the admixture for a hydraulic composition according to this invention is preferably 4 to 9, particularly 5 to 8 from the viewpoint of hyrolysis of esters which are included in a dispersant of the admixture or prevention of corrosion of material of a storage tank or the like.

[0047] To achieve the electric conductivity upon dilution, mention is made of a method wherein the dispersants (1a) and (2a) are simultaneously used and the solids-content concentration of the two is regulated in the range of 10 to 40 weight-%, especially 15 to 35 weight-%, particularly 20 to 30 weight-%. As another method, mention is made of a method of controlling the degree of neutralization with an acid or an alkali.

[0048] The acid used for controlling the degree of neutralization includes acetic acid, hydrochloric acid, sulfuric acid, and the like, and the alkali therefor includes potassium hydroxide, sodium hydroxide and triethanolamine. From the viewpoint of reducing the salt concentration in the admixture for a hydraulic composition, the acid dispersant is preferably neutralized with an alkali. In particular, neutralization with triethanolamine is preferable to achieve homogeneousness even at a high degree of neutralization.

[0049] The process for producing the admixture for a hydraulic composition according to this invention includes, for example, a process wherein the polycarboxylic acid-based dispersants (1) and (2) are used to prepare an aqueous solution containing the dispersants (1) and (2) in an amount of 10 to 40 % by weight in the total solid, and then an alkali is added thereto under stirring to prepare a homogenious solution with a pH value of 4 to 9. The dispersants (1) and (2) may be preferably used in the form of the polycarboxylic acid-based dispersants.

[0050] The admixture for a hydraulic composition according to this invention includes those admixtures satisfying any one of the following conditions (a) to (f):

(a) the total amount (hereinafter referred to as solids content) of the polycarboxylic acid-based dispersants (1) and (2) in the admixture for a hydraulic composition is more than 30 to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.15 or less,

(b) the solids content is more than 20 to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.4 or less,

(c) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,

(d) the solids content is more than 30 to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 0.25,

(e) the solids content is more than 20 to 30 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less, and

(f) the solids content is 20 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less.

More preferably, the ratio by weight of the polycarboxylic acid-based dispersant (1) to the polycarboxylic acid-based dispersant (2) [polycarboxylic acid-based dispersant (1)/polycarboxylic acid-based dispersant (2)] is 30/70 to 1/99, and the following conditions (g) or (h) are met:

(g) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (1) is 65 (exclusive) to 100 weight-%, and any one of the following (g-1) to (g-3) is met:

(g-1) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 20 (exclusive) to 30 (exclusive) weight-%, and any one of the following (g-1-1) to (g-1-5) is further met:

(g-1-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.35 or less,
(g-1-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.7 or less,
(g-1-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(g-1-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(g-1-5) the solids content is 30 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less,

(g-2) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 10 (exclusive) to 20 weight-%, and any one of the following (g-2-1) to (g-2-5) is further satisfied:

(g-2-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.25 or less,
(g-2-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.5 or less,
(g-2-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(g-2-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(g-2-5) the solids content is 30 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less,

(g-3) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 10 weight-% or less, and any one of the following (g-3-1) to (g-3-6) is further met:

(g-3-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.15 or less,
(g-3-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.4 or less,
(g-3-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(g-3-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 0.25 or less,
(g-3-5) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(g-3-6) the solids content is 20 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less,

(h) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (1) is 30 to 65 weight-%, and any one of the following (h-1) to (h-3) is further met:

(h-1) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 20 (exclusive) to 30 weight-%, and any one of the following (h-1-1) to (h-1-5) is further met:

(h-1-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.45 or less,
(h-1-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(h-1-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium

hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1.5 or less,
(h-1-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(h-1-5) the solids content is 30 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less,

(h-2) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 10 (exclusive) to 20 weight-%, and any one of the following (h-2-1) to (h-2-5) is further met:

(h-2-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.40 or less,
(h-2-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.75 or less,
(h-2-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(h-2-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(h-2-5) the solids content is 30 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less,

(h-3) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 10 weight-% or less, and any one of the following (h-3-1) to (h-3-6) is further met:

(h-3-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.25 or less,
(h-3-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.6 or less,
(h-3-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(h-3-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 0.25 or less,
(h-3-5) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(h-3-6) the solids content is 20 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less.

Particularly preferably, the ratio by weight of the polycarboxylic acid-based dispersant (1) to the polycarboxylic acid-based dispersant (2) [polycarboxylic acid-based dispersant (1)/polycarboxylic acid-based dispersant (2)] is 15/85 to 1/99, and the following conditions (i) or (j) are met:
(i) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (1) is 65 (exclusive) to 100 weight-%, and any one of the following (i-1) to (i-3) is further satisfied:

(i-1) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 20 (exclusive) to 30 weight-%, and any one of the following (i-1-1) to (i-1-5) is further met:

(i-1-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.45 or less,
(i-1-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.8 or less,
(i-1-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(i-1-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(i-1-5) the solids content is 30 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less,

(i-2) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 10 (exclusive) to 20 weight-%, and any one of the following (i-2-1) to (i-2-5) is further met:

(i-2-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.35 or less,
(i-2-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.6 or less,
(i-2-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(i-2-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(i-2-5) the solids content is 30 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less,

(i-3) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 10 weight-% or less, and any one of the following (i-3-1) to (i-3-6) is further met:

(i-3-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.25 or less,
(i-3-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.5 or less,
(i-3-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(i-3-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 0.35 or less,
(i-3-5) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(i-3-6) the solids content is 20 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less,

(j) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (1) is 30 to 65 weight-%, and any one of the following (j-1) to (j-3) is further met:

(j-1) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 20 (exclusive) to 30 weight-%, and any one of the following (j-1-1) to (j-1-6) is further met:

(j-1-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.55 or less,
(j-1-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(j-1-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1.5 or less,
(j-1-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(j-1-5) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(j-1-6) the solids content is 20 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less,

(j-2) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 10 (exclusive) to 20 weight-%, and any one of the following (j-2-1) to (j-2-5) is further met:

(j-2-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.5 or less,
(j-2-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.85 or less,
(j-2-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(j-2-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(j-2-5) the solids content is 30 weight-% or less, and the dispersants are neutralized with triethanolamine,

and the degree of neutralization thereof is 1.5 or less,

(j-3) the ratio of carboxylic acid monomers in the polycarboxylic acid-based dispersant (2) is 10 weight-% or less, and any one of the following (j-3-1) to (j-3-6) is further met:

(j-3-1) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.35 or less,
(j-3-2) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.7 or less,
(j-3-3) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(j-3-4) the solids content is 30 (exclusive) to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 0.35 or less,
(j-3-5) the solids content is 20 (exclusive) to 30 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less,
(j-3-6) the solids content is 20 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less.

[0051] The admixture for a hydraulic composition according to this invention is added to hydraulic slurry preferably in such an amount that the total amount of the dispersant (1) or an oxycarboxylic acid (salt), and the dispersant (2) is 0.05 to 3.0 weight-%, particularly 0.1 to 0.5 weight-% relative to hydraulic powders.

[0052] When the dispersants (1a) and (2a) are simultaneously used, the compounding ratio of the two, that is, the dispersant (1a) /the disper (2a), is in the range of preferably 0.1/99.9 to 99/1 (weight ratio of solids content), more preferably 1/99 to 50/50, still more preferably 5/95 to 30/70, from the viewpoint of fluidity retention (slump retention) , in addition to achievement of the electric conductivity in the diluted products.

[0053] When the admixture for a hydraulic composition according to this invention comprises the dispersants (1a) and (2a), the admixture is added to a hydraulic slurry, that is, a hydraulic composition including no dispersant of the admixture, preferably in such an amount that the total amount of the dispersants (1a) and (2a) may be 0.05 to 3.0 weight-%, particularly 0.1 to 0.5 weight-% in terms of solids content relative to hydraulic powders.

[0054] Further, when the admixture for a hydraulic composition according to this invention comprises the dispersants (1a) and (2a), a mixture prepared by compounding the dispersants (1a) and (2a) may be added, or the two may be added separately, and there is no limit to the way to add the two.

[0055] The admixture for a hydraulic composition according to this invention may be used in combination with other dispersants. In this case the requirement for electric conductivity upon dilution may be preferably met. The dispersants may be those used generally as admixtures for concrete and may be preferably a high-range water-reducing agents (superplasticizer) or a water-reducing agents(plasticizer), such as a naphthalene sulfonate-formaldehyde condensate, a melamine sulfonate-formamide condensate, refined ligninsulfonic acid or a salt thereof, polystyrene sulfonate, cement dispersants having a phenol skeleton (for example, a formaldehyde co-condensate of phenolsulfonic acid with another copolymerizable monomer) and cement dispersants based on anilinesulfonic acid (for example, a formaldehyde co-condensate of anilinesulfonic acid with another copolymerizable monomer).

[0056] The admixture for a hydraulic composition according to this invention may be used for a hydraulic composition of cement for civil engineering, building, precast concrete products or the like. The hydraulic composition is not specified. Cement may be preferably normal portland cement, high-early strength portland cement, ultra high-early strength portland cement or CEMI listed in (Categorized in) European Standard EN197-1 or the like. A hydraulic powder such as blast furnace slag, fly ash or silica fume or a non-hydraulic lime stone powder etc. may be contained. In addition, silica fume cement or blast furnace slag blended cement, CEMII, CEMIII, CEMIV or CEMV, listed in(categorized in) European Standard EN197-1, may be used.

[0057] The admixture for a hydraulic composition according to this invention can be used in combination with known additives (materials). Examples of such additives include an AE agent, an AE water-reducing agent(plasticizer), a fluidizing agent, a high-range water reducing agent(superplasticizer), a retardant, a high-early-strength agent, an accelerator, a foaming agent, a water-retaining agent, a thickener, a waterproofing agent, a defoaming agent, a water-soluble polymer, various surfactants, siliceous sand, high-furnace slag, fly ash, silica fume etc.

<hydraulic composition>

[0058] The admixture for a hydraulic composition according to this invention is added to various a hydraulic composition constituting hydraulic powder-containing cement pastes, mortar and concrete, and the kind of the hydraulic composition is not limited. The weight ratio of water to hydraulic powder(W/C) is preferably 0.7 or less, more preferably 0.6

or less, specially preferably 0.55 or less.

[0059] In particular, this invention provides a hydraulic composition comprising the invented admixture for a hydraulic composition added to water- and hydraulic powder-containing hydraulic slurry having a sulfate ion concentration of 2,500 to 40,000 mg/kg (ppm) in an aqueous solution thereof. In this hydraulic slurry, the concentration of sulfate ions in the aqueous solution is preferably 4,000 mg/kg (ppm) or more, more preferably 6,000 mg/kg (ppm) or more, still more preferably 7,000 mg/kg (ppm) or more.

[0060] The concentration of sulfate ions in the aqueous solution is preferably 6,000 to 40,000 mg/kg (ppm), still more preferably 7,000 to 40,000 mg/kg (ppm).

[0061] The invention may be preferably applied to a hydraulic slurry in which an amount of sulfate ion eluted from cement is 10 μmol or more per 1 g of cement, more preferably 25 μmol or more.

[0062] As the method of measuring the concentration of sulfate ions, a method of centrifuging the hydraulic slurry and measuring the concentration in the separated aqueous solution may be used. The centrifugation for obtaining the separated aqueous solution may be carried out under the conditions of 3000 rpm (with an arm radius of 17 cm) and 10 minutes.

[0063] Using the supernatant water obtained by this centrifugation, the concentration of sulfate ions was determined by ion chromatography (unit: Dionex DX-120; column: AS9-HS4; eluents: 5 mmol/L aqueous sodium bicarbonate, 12 mmol/L aqueous sodium carbonate; suppressor: 25 mmol/L aqueous sulfuric acid; detection: electric conductivity).

[0064] According to this invention, there can be obtained a liquid admixture for a hydraulic composition, which is capable of endowing a hydraulic composition with excellent fluidity and fluidity retention and simultaneously exhibiting this effect stably without being influenced by its storage period.

EXAMPLE

[0065] As the concrete composition, Composition 1 or 2 in Table 1 was used. As the admixture, dispersant (1) in Table 2 and dispersant (2) in Table 3 were compounded and combined as shown in Table 4, and a neutralizing agent shown in Table 4 was added thereto to prepare a liquid admixture (balance: water) whose 5-fold dilution has the electric conductivity (determined under the conditions described above) shown in Table 4. The dispersion retention and shelf stability of the resulting admixture were evaluated in the following manner. The results are shown in Table 4.

(i) Dispersion retention

[0066] The hydroric materials in Table 1 were mixed (63 rpm, 120 seconds) in a mortar mixer, to prepare mortar. During this preparation, the dosage of the admixture was adjusted to obtain the mortar flow in the range of 220 mm ± 10 mm without tapping. The mortar flow value was measured just after mixing (F_0) and 90 minutes later (F_{90}). In terms of the percentage [(F_{90}/F_0) × 100] thereof to the initial flow value (F_0), the degree of dispersion retention (%) was calculated. The degree of dispersion retention thus determined was evaluated according to the following criteria:

ⓞ : The degree of dispersion retention is 90% or more.
○: The degree of dispersion retention is 80 to less than 90%.
Δ: The degree of dispersion retention is 70 to less than 80%.
×: The degree of dispersion retention is less than 70%.

(ii) Shelf stability

[0067] The admixture in Table 4 was stored at 20°C for 1 month and then observed for its outer appearance, and when it was homogenious, "○" was given, while it was separated, "×" was given. The evaluation "○" means that the admixture is maintained in the form of a single-phase homogeneous aqueous solution.

Table 1

	W/C	Mixture proportions				Sulfate ion concentration
		W(g)	C		S (g)	
			(g)	Type		
Composition1	0.45	360	800	CamentA	1500	7000 mg/kg
Composition2	0.45	360	800	CementB	1500	15000mg/kg

Table 1 (continued)

	W/C	Mixture proportions				Sulfate ion concentration
		W(g)	C		S (g)	
			(g)	Type		

CementA: Normal Portland cement(Taiheiyo) (specific gravity 3.14, B.V.3400)

Cement B : Normal Portland cement (Lafarge) (specific gravity 3.14, B.V.3620)

S:Kimitsu Pit sand(F.M.2.42 S.G.2.63)

Sulfate ion concentration : The concentration of sulfate ions in the separated aqueous solution obtained by centrifugation under the conditions described in the description of the application.

Table 2

	Dispersant(1)No.						
	1	2	3	4	5	6	7
Monomer	Acrylic acid (100 mol-%)	Acrylic acid (100 mol-%)	Maleic anhydride /Acrylic acid= 60/40(mol-%)	Maleic anhydride /Acrylic acid= 70/30(mol-%)	Acrylic acid (100 mol-%)	Allyl alcohol EO_5 /Maleic anhydride= 25/75(mol-%)	Methanol EO_9· methacrylic acid monoester/methacrylic acid= 25/75(mol-%)
Molecular weight	9000	13000	10000	18000	10000	5000	20000
Solid content (weight-%)	45	48	40	50	46	50	40
Ratio of carboxylic acid monomers (weight-%)	100	100	100	100	100	51.4	34.2

Table 3

		Formulation	Mw	Ratio of carboxylic acid monomers (weight-%)
Dispersant(2)No.	b-1	Methanol EO_{115}・methacryrate／acrylic acid Na salt＝14.8／85.2(molar ratio, hereinafter the same)	75000	7.4
	b-2	Methanol EO_{50}・methacryrate／acrylic acid Na salt＝20.1／79.9	59000	13
	b-3	Methanol EO_{25}・methacryrate／acrylic acid Na salt＝25.7／74.3	28000	17.2
	b-4	Methanol EO_{31}・methacryrate／methacrylic acid Na salt／methallyl sulfonic acid Na salt ＝27.2／63.3／9.5	45000	11.7
	b-5	Polyoxyethylene(EO_{33})monoallyl monomethyl ether ／maleic acid Na salt＝35／65	30000	10.7*
	b-6	Methanol EO_{115}・methacryrate／methacrylic acid Na salt／methyl acrylate＝5／40／55	52000	10.1
	b-7	The copolymer obtained in Production Example 1	—	13.9
	b-8	Methanol EO_9・methacryrate／methacrylic acid Na salt＝42.1／57.9	42000	19.3

* Regarding maleic acid Na salt, the ratio of carboxylic acid monomers was calculated as maleic anhydride. .

[0068] In the table, EO is an oxyethylene group, and its assigned number is average polymerization degree. Mw is weight-average molecular weight. b-7 is a product obtained in Production Example 1 below.

Production Example 1

(1) Monomers

[0069] A copolymer was produced from the following monomers by the process described below.

- A-1: Methoxy polyethylene glycol monomethacrylate (number of added ethylene oxide molecules on average = 9; weight-average molecular weight, 496)
- A-2 : Methoxy polyethylene glycol monomethacrylate (number of added ethylene oxide molecules on average =

120; weight-average molecular weight, 5380)

- B-1 : methacrylic acid

(2) Production of the copolymer (dispersant b-7)

[0070] Water, 1107 parts by weight, was introduced into a glass reaction vessel and then heated up to 70°C in a nitrogen atmosphere. Then, 3 solutions, that is, a monomer mixture (1) consisting of 179 parts by weight of the monomer A-1, 343 parts by weight of the monomer A-2, 101 parts by weight of the monomer B-1 and 281 parts by weight of water, 41.0 parts by weight of 10% aqueous 2-mercaptoethanol, and 36.5 parts by weight of 10% aqueous ammonium persulfate, were simultaneously dropped thereto over 55 minutes and subjected to copolymerization reaction, and then 3 solutions, that is, a monomer mixture (2) consisting of 76 parts by weight of the monomer A-1, 124 parts by weight of the monomer A-2, 25.7 parts by weight of the monomer B-1 and 103 parts by weight of water, 12.0 parts by weight of 10% aqueous 2-mercaptoethanol, and 10.8 parts by weight of 10% aqueous ammonium persulfate, were simultaneously dropped over 20 minutes to the above reaction system and subjected to copolymerization reaction, and further 3 solutions, that is, a monomer mixture (3) consisting of 62 parts by weight of the monomer A-1, 94 parts by weight of the monomer A-2, 15 parts by weight of the monomer B-1 and 78 parts by weight of water, 18 parts by weight of 10% aqueous 2-mercaptoethanol, and 7.2 parts by weight of 10% aqueous ammonium persulfate, were simultaneously dropped thereto over 15 minutes thereto and subjected to copolymerization reaction, and the reaction was carried out in this manner for 90 minutes in total. After dropping was finished, the reaction solution was aged at the same temperature for 1 hour, and 27.3 parts by weight of 10% aqueous ammonium persulfate was dropped thereto over 10 minutes, and the reaction solution was aged at 70°C for 2 hours to complete the polymerization reaction. Further, the reaction solution was neutralized with 59 parts by weight of 48% aqueous sodium hydroxide to give the copolymer.

Table 4

		Cement admixtures							Shelf stability	Composition1		Composition2	
		Dispersant (1)	Dispersant (2)	(1)/(2) (weight ratio)	(1)+(2) (solid content by weight-%)	Neutralizing agent	pH (20°C)	Electric conductivity of 5-fold dilution (mS/cm)		Dosage** (weight-%)	Fluidity retention	Dosage** (weight-%)	Fluidity retention
Example	1	1	b-1	20/80	20	NaOH	5.3	33.8	○	0.75	◎	0.75	◎
	2	2	b-2	30/70	25	Triethanolamine	7.9	31.3	○	0.96	◎	0.96	◎
	3	3	b-3	10/90	25	KOH	5.5	28.8	○	0.56	◎	0.6	○~◎
	4	4	b-4	5/95	25	NaOH	—*	30.2	○	0.44	◎	0.48	○
	5	1	b-5	15/85	30	NaOH	—	36.8	○	0.5	◎	0.5	◎
	6	1	b-6	20/80	20	NaOH	—	32.2	○	0.75	◎	0.75	◎
	7	1	b-7	10/90	20	NaOH	—	31.2	○	0.7	◎	0.7	○~◎
	8	1	b-1/b-8 =50/50 (weight ratio)	20/80	20	NaOH	5.3	34.5	○	0.75	◎	0.75	◎
	9	6	b-1/b-8 =50/50 (weight ratio)	30/70	25	NaOH	—	32.5	○	0.55	◎	0.6	○
	10	7	b-1	25/75	25	NaOH	—	25.6	○	0.5	◎	0.62	○~△
	11	1	b-8	20/80	30	NaOH	5.8	46.2	×	0.5	◎	0.5	◎
	12	5	b-1	20/80	25	NaOH	6.5	48.6	×	0.6	◎	0.6	◎
Comparative example	1	-	b-1	0/100	25	NaOH	—	25.3	○	0.48	○	0.6	×
	2	1	-	100/0	25	NaOH	—	49.7	○	0.8	×	0.8	×
	3	—	b-1/b-8 =60/40 (weight ratio)	0/100	25	—	—	21	○	0.45	○	0.55	△~×

* In pH, "-" means "not measured".

** The compounding amount means the weight-% of the cement admixture based on cement.

[0071] It is shown in Example 1 to 12, that the admixture including the dispersants (1) and (2), is provided with a good fluidity retention. The invention is therefore provided with a constant retention regardless changed concentrations of sulfate ion eluting from cement.

[0072] In Example 11 and 12 an excess neutralization caused an insufficient stability of the product. It is noted in Comparative Example 2 using the dispersant 1 only that the dispersion was initially realized, but coagulation happened immediately. No fluidity retention was accordingly obtained. It is noted in Comparative Example 1 and 3 using the dispersant 2 only that a good fluidity retention was found in the composition 1, but a bad fluidity retention was found in the composition 2 using cement including a large amount of eluted sulfate ion. Combination of No. 1 as the dispersant (1) with (b-1) and (b-2) as the dispersant (2) was evaluated in view of pH and stability, changing a solid concentration (concentration by the total solid of the dispersants (1) and (2)), a neutralizing agent and a neutralization degree. Sodium hydroxide(NaOH), potassium hydroxide(KOH) or triethanolamine (TEA) was used as the neutralizing agent. Test results are shown in Table 5.

[0073] Using an oxycarboxylic acid (sodium gluconate) as the dispersant (1), shelf stability and dispersion retention were evaluated with concrete composition 3 or 4 shown in Table 6. The dispersant (2) neutralized with sodium hydroxide at the neutralization degree of 0.7 and sodium oxycarboxylic acid were used. Test results are shown in Table 7.

Table 5

Dispersant		Compounding ratio by weight		Solid content (weight-%)	Neutralizing agent	Neutralizatio n degree	pH	Shelf stability
Dispersant(1)	Dispersant(2)	Dispersant(1)	Dispersant(2)					
1	b-1	30	70	20	NaOH	0.35	5.4	×
						0.3	5.2	○
1	b-1	30	70	30	NaOH	0.2	4.9	×
						0.15	4.7	○
1	b-1	30	70	40	NaOH	0.1	4.9	×
						0.5	4.6	○
1	b-5	30	70	20	NaOH	0.4	5.9	×
						0.35	5.6	○
1	b-5	30	70	30	NaOH	0.25	5.1	×
						0.2	4.9	○
1	b-5	30	70	40	NaOH	0.15	4.8	×
						0.1	4.6	○
1	b-1	30	70	20	KOH	0.4	5.7	×
						0.35	5.5	○
1	b-1	30	70	30	KOH	0.2	5	×
						0.15	4.8	○
1	b-1	30	70	40	KOH	0.1	4.7	×
						0.5	4.5	○
1	b-5	30	70	20	KOH	0.5	6.9	×
						0.45	6.7	○
1	b-5	30	70	30	KOH	0.25	5.2	×
						0.2	5	○
1	b-5	30	70	40	KOH	0.15	4.9	×
						0.1	4.7	○

Table 5 (continued)

Dispersant		Compounding ratio by weight		Solid content (weight-%)	Neutralizing agent	Neutralizatio n degree	pH	Shelf stability
Dispersant(1)	Dispersant(2)	Dispersant(1)	Dispersant(2)					
1	b-1	30	70	20	TEA	1	7.95	○
1	b-1	30	70	30	TEA	0.25	5.1	×
						0.2	4.9	○
1	b-1	30	70	40	TEA	0.2	5.1	×
						0.15	4.9	○
1	b-5	30	70	20	TEA	1	8.1	○
1	b-5	30	70	30	TEA	1	8.2	○
1	b-5	30	70	40	TEA	0.2	5	×
						0.15	4.8	○
1	b-1	10	90	30	NaOH	0.25	5.1	×
						0.2	4.9	○
1	b-1	10	90	30	KOH	03	5.3	×
						0.25	5.1	○
1	b-1	10	90	30	TEA	0.4	5.6	×
						0.35	5.4	○
1	b-5	10	90	30	NaOH	0.3	5.6	×
						0.25	5.4	○
1	b-5	10	90	30	KOH	0.3	5.7	×
						0.25	5.5	○
1	b-5	10	90	30	TEA	0.83	8.09	○
NaOH; Sodium hydroxide,KOH;Potassium hydroxide,TEA; Triethnolamine								

Table 6

	W/C	Mixture proportions				Sulfate ion concent ration(mg/kg)
		W	C		S (g)	
			(g)	Type		
Composi tion3	0.45	360	800	Cement C	1500	6000
Composi tion4	0.45	360	800	Cement D	1500	18000
Cement C : Normal Portland cement (Taiheiyo) Cement D : Normal Portland cement (Norcem)						

Table 7

	Cement admixture				Shelf stability	Composition3		Composition4	
	Oxycarbonic acid	Dispersant (2)	Oxycarboxylic acid/(2) weight ratio	Oxycarboxylic acid+(2) solid content by weight		dosage (weight-%)	Fluidity retention	doage (weight-%)	Fluidity retention
Example	Gluconio acid Na	b-1/b-8	20/(48/32)	25%	○	0.48	◎	0.504	◎
Comparative example	-	b-1/b-8	0/(60/40)	25%	○	0.48	○	0.504	×

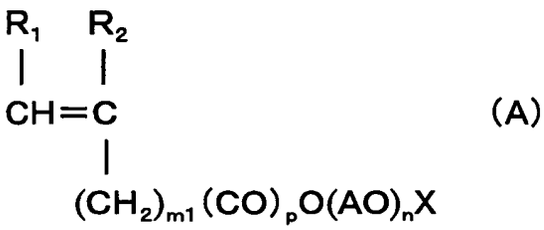
Claims

1. A method of improving fluidity retention of a hydraulic composition, comprising adding, to a hydraulic slurry comprising water and a hydraulic powder and having a sulfate ion concentration of 2,500 to 40,000 mg/kg in the aqueous solution thereof, (1) at least one polycarboxylic acid-based dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is higher than 30 % by weight and (2) at least one polycarboxylic acid-based dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is not higher than 30 % by weight.

2. The method according to Claim 1, in which the sulfate ion concentration is 6,000 to 40,000 mg/kg.

3. The method according to Claim 1, in which (1) the polycarboxylic acid-based dispersant is selected from 1) and (2) the polycarboxylic acid-based dispersant is selected from 2):

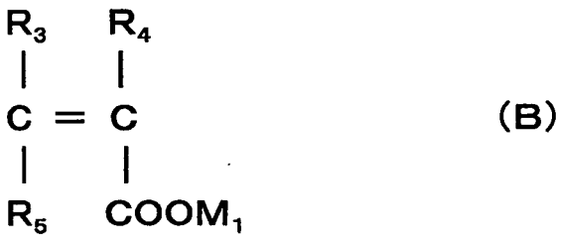
   1) dispersants comprising a water-soluble salt of a homopolymer of an unsaturated carboxylic acid selected from an unsaturated monocarboxylic acid and an unsaturated dicarboxylic acid or of a copolymer of two or more of the unsaturated carboxylic acids,
   2) dispersants comprising a copolymer obtained by polymerizing a monomer (a) represented by formula (A) :



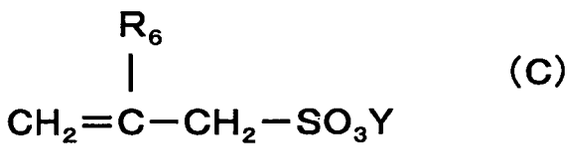
(A)

   wherein R_1 and R_2 each represents a hydrogen atom or a methyl group, m1 is a number of 0 to 2, p is 0 or 1, AO is a C_{2-4} oxyalkylene group, n is a number of 2 to 300 and X represents a hydrogen atom or a C_{1-22} alkyl group;

   with at least one monomer (b) selected from compounds represented by formulae (B) and (C):



(B)



(C)

   wherein R_3 to R_5 are the same as or different from one another and each represent a hydrogen atom, a methyl group or $(CH_2)_{m2}COOM_2$, R_6 represents a hydrogen atom or a methyl group, M_1, M_2 and Y are the same as or different from one another and each represent a hydrogen atom, an alkali metal, an alkaline earth metal, ammonium, an alkylammonium or a substituted alkylammonium, an amine salt or a substituted amine salt and m2 is a

number of 0 to 2.

4. An admixture for a hydraulic composition comprising a homogeneous mixed liquid comprising the polycarboxylic acid-based dispersant (1) described in Claim 1 and the polycarboxylic acid-based dispersant (2) described in Claim 1.

5. The admixture according to Claim 4, in which the total solid of the polycarboxylic acid-based dispersant (1) and the polycarboxylic acid-based dispersant (2) is 10 to 40 percent by weight in the admixture.

6. The admixture according to Claim 4 or 5, in which the weight ratio [(1)/(2)] of the polycarboxylic acid-based dispersant (1) to the polycarboxylic acid-based dispersant (2) is 3/97 to 40/60.

7. The admixture according to any of Claims 4 to 6, satisfying any one of the following conditions (a) to (f):

(a) the total amount (hereinafter referred to as solids content) of the polycarboxylic acid-based dispersants (1) and (2) in the admixture for a hydraulic composition is more than 30 to 40 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.15 or less,
(b) the solids content is more than 20 to 30 weight-%, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 0.4 or less,
(c) the solids content is 20 weight-% or less, and the dispersants are neutralized with potassium hydroxide or sodium hydroxide, and the degree of neutralization thereof is 1 or less,
(d) the solids content is more than 30 to 40 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 0.25,
(e) the solids content is more than 20 to 30 weight-%, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1 or less, and
(f) the solids content is 20 weight-% or less, and the dispersants are neutralized with triethanolamine, and the degree of neutralization thereof is 1.5 or less.

8. A process for preparing an admixture for a hydraulic composition, being homogeneous and having a pH of 4 to 9, comprising adding an alkali to an aqueous solution comprising the polycarboxylic acid-based dispersant (1) described in Claim 1 and the polycarboxylic acid-based dispersant (2) described in Claim 1 in the total solid of 10 to 40 percent by weight.

9. An admixture for a hydraulic composition (1), comprising at least one polycarboxylic acid-based dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is higher than 30 % by weight and (2) at least one polycarboxylic acid-based dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is not higher than 30 % by weight and being in the form of a homogenious aqueous solution, wherein a 5-fold (ratio by weight) dilution of the admixture with water has an electric conductivity of not higher than 45 mS/cm at 25°C.

10. A method of improving fluidity retention of a hydraulic composition, comprising adding, to a hydraulic slurry comprising water and a hydraulic powder and having a sulfate ion concentration of 2,500 to 40,000 mg/kg in the aqueous solution thereof, an oxycarboxylic acid and (2) a polycarboxylic acid-based dispersant comprising a polymer wherein the ratio of carboxylic acid monomers is not higher than 30 % by weight.