(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 August 2013 (08.08.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/113152 A1

(51) **International Patent Classification**:
C04B 28/00 (2006.01) ***C04B 28/14*** (2006.01)

(21) **International Application Number**:
PCT/CN2012/070794

(22) **International Filing Date**:
31 January 2012 (31.01.2012)

(25) **Filing Language**: English

(26) **Publication Language**: English

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2013/113152 A1

(54) **Title**: VINYL ACETATE-ETHYLENE COPOLYMER EMULSION AND POLYMER CEMENT WATERPROOF COMPOSITION BASED ON THE SAME

(57) **Abstract**: The present invention relates to a vinyl acetate-ethylene copolymer emulsion and a polymer cement waterproof composition based on the same. More specifically, the present invention relates to a vinyl acetate-ethylene copolymer emulsion based cement waterproof composition with high filler loading. The present invention also relates to processes for preparing the vinyl acetate-ethylene copolymer emulsion and the polymer cement waterproof composition, and uses thereof.

Vinyl acetate-ethylene copolymer emulsion and polymer cement waterproof composition based on the same

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a vinyl acetate-ethylene copolymer emulsion and a polymer cement waterproof composition based on the same. More specifically, the present invention relates to a vinyl acetate-ethylene copolymer emulsion based cement waterproof composition with high filler loading. The present invention also relates to processes for preparing the vinyl acetate-ethylene copolymer emulsion and the polymer cement waterproof composition, and uses thereof.

2. Description of the Related Art

[0002] Polymer cement waterproof composition is flexible waterproof slurry which is prepared by using cement and fine aggregate as main components, polymer and additives etc. as modifiers in suitable ratio. Typically, the polymer cement waterproof composition should have a relative high weight ratio of solid part to liquid part, normally about 2.7:1 to 4:1. Anti-water permeability and bonding strength of a polymer cement waterproof composition are the main factors for the end users when choosing suitable polymer cement waterproof composition.

[0003] Currently, the polymer cement waterproof composition is dominated by styrene acrylic emulsion. However, there are several shortcomings when using styrene acrylic emulsion in waterproof slurry: (a) the waterproof slurry thus obtained is odorous, while a more environmentally friendly and easily applied product is required by the market; (b) the storage life of waterproof slurry obtained by mixing styrene acrylic emulsion with cement is short, typically less than about 45 minutes, while a longer storage life product is required in the on-site application; and (c) the price of styrene acrylic emulsion is increasing in the last two years for the reason that the cost of raw materials increases and the supply of raw materials is unstable. Therefore the manufactures are seeking for a cheaper alternative for the styrene acrylic emulsion.

[0004] CN1998111098 discloses a waterproof glue. However, said waterproof glue has a lower solid/liquid weight ratio of about 1:1, which is far less than 2.7:1 to 4:1 as required in waterproof slurry field.

[0005] CN200610015818 discloses a two components water-proof paint for roofing which is based on polyacrylic emulsion and vinyl acetate-ethylene

emulsion. The two components water-proof paint is not targeted for mixing with cement, and uses polyacrylic emulsion as essential component.

[0006] CN200610165204 discloses a vinyl acetate-ethylene copolymer emulsion. However, the vinyl acetate-ethylene copolymer emulsion is used as adhesive for wood processing and package, not for waterproof application during construction by mixing with cement.

[0007] KR200928065A discloses a polymer-modified mortar composition used for waterproof coating during construction which is based on ethylene vinyl acetate copolymer and/or styrene acrylic copolymer. The polymer-modified mortar composition has a low solid/liquid weight ratio, and is not used for mixing with cement.

[0008] Traditional vinyl acetate-ethylene copolymer emulsion cannot be used in polymer cement waterproof composition because the fact that the waterproof slurry made from traditional vinyl acetate-ethylene copolymer emulsion has high consistency therefore cannot be applied, such as brush coated or roll coated, under such high solid/liquid weight ratio as mentioned above.

[0009] Therefore, a need still exists for cheaper polymer cement waterproof composition that has one or more of the following properties: high solid/liquid weight ratio; excellent anti-water permeability and bonding strength; unodorous smell; good workability; and long-time storage stability.

BRIEF SUMMARY OF THE INVENTION

[0010] It has been surprisingly found by the present inventors that, by using a combination of specific amounts of surfactant and polymeric protective colloid, a vinyl acetate-ethylene copolymer emulsion and a polymer cement waterproof composition based on the same with high filler loading are obtained.

[0011] The polymer cement waterproof composition of the present invention has excellent anti-permissive pressure, bonding strength, workability and long-time storage stability, while the preparation cost thereof is decreased as compared to traditional styrene acrylic emulsion based cement composition.

[0012] As compared to traditional vinyl acetate-ethylene copolymer emulsion, the inventive vinyl acetate-ethylene copolymer emulsion has the following advantages: high filler loading, low production cost, unodorous smell, good workability, high bonding strength and long-time storage stability.

[0013] Thus, one object of the present invention is to provide a vinyl acetate-ethylene copolymer emulsion.

[0014] Another object of the present invention is to provide a process for preparing said vinyl acetate-ethylene copolymer emulsion.

[0015] Still another object of the present invention is to provide a use of the vinyl acetate-ethylene copolymer emulsion for polymer cement waterproof composition.

[0016] Furthermore, one object of the present invention is to provide a high filler loaded polymer cement waterproof composition.

[0017] Another object of the present invention is to provide a process for preparing said high filler loaded polymer cement waterproof composition.

[0018] Still another object of the present invention is to provide a use of the high filler loaded polymer cement waterproof composition.

DETAILED DESCRIPTION OF THE INVENTION

[0019] For the purposes of this description, unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the description and claims are to be understood as being modified in all instances by the term “about”. Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following description and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0020] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific Examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0021] It is noted that, as used in this description and the appended claims, the singular forms “a”, “an” and “the” include plural referents unless expressly and unequivocally limited to one referent.

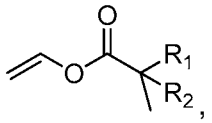
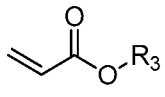
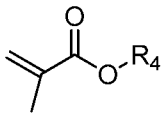
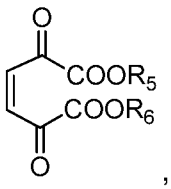
[0022] According to one aspect of the present invention, a vinyl acetate-ethylene copolymer-based emulsion for polymer cement waterproof composition is provided, wherein the copolymer comprises, based on the total weight of the copolymer:

(1) about 70-95pphm (parts by weight / 100 parts by weight of monomers used for preparing the emulsion), preferably about 75-90 pphm of a moiety derived from vinyl acetate;

(2) about 5-30pphm, preferably about 10-20 pphm of a moiety derived from ethylene; and

(3) about 0-10pphm, preferably about 0-5 pphm of a moiety derived from other comonomers or functional monomers,

wherein the copolymer-based emulsion is formed by emulsion polymerization of the monomers in the presence of about 1-5pphm of a surfactant and about 0-3pphm of a polymeric protective colloid as emulsifier / protective colloid.

[0023] In some non-limiting embodiments of the present invention, the monomers used in emulsion polymerization can be composed of about 70-95pphm of vinyl acetate, about 5-30pphm of ethylene and about 0-10pphm of other comonomers or functional monomers. Examples of other comonomers or functional monomers suitable for the present invention include, but not limited to, one or more selected from the group of: vinyl esters of polyacid; acrylates; methacrylates; maleate esters; vinyl chloride; , wherein each of R_1 and R_2 is hydrogen or alkyl group, provided that the total carbon atom number of R_1 and R_2 is from 0 to 14; , wherein R_3 is hydrogen or alkyl group with 1 to 16 carbon atom(s); , wherein R_4 is hydrogen or alkyl group with 1 to 16 carbon atom(s); , wherein each of R_5 and R_6 is alkyl group with 1 to 16 carbon atom(s); acrylic acid; methacrylic acid; maleic acid; maleic anhydride; fumaric acid; crotonic acid; itaconic acid; sodium vinylsulfonate; mono-sodium 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propylsulfonate; methacrylate ethyl trimethyl ammonium chloride; acrylamide; hydroxymethylacrylamide; hydroxyethylacrylamide; hydroxypropylacrylamide ; vinyltrimethoxysilane; vinyltriethoxysilane; vinyltri(2-methoxyethoxy)silane; methylacryloxypropyltrimethoxysilane; ethylene glycol acrylate; propylene glycol acrylate; glycidyl acrylate; diallyl maleate; diallyl phthalate; triallyl cyanurate; allyl methacrylate; ethylene glycol dimethylacrylate; pentaerythritol triacrylate; pentaerythritol tetraacrylate; or mixtures thereof.

[0024] In some non-limiting embodiments of the present invention, said surfactant can be selected from anionic surfactants, nonionic surfactants or combination thereof.

[0025] Examples of anionic surfactants suitable for the present invention include, but not limited to: alkylsulfates, alkylsulfonates, alkyl benzenesulfonates, alkyl polyoxyethylene ether sulfates, alkylpolyoxyethylene-propylene ether sulfates, sodium fatty alcohol succinic acid mono ester sulfonates, disodium fatty alcohol polyoxyethylene ether sulfosuccinates, disodium fatty alcohol polyoxyethylene-propylene ether sulfosuccinates, alkylpolyoxyethylene phosphates, alkylpolyoxyethylene-propylene phosphates and alkali metal salts of fatty acids. Specific examples of anionic surfactants suitable for the present invention include, but not limited to: sodium dodecylbenzene sulfonate, sodium dodecylsulfonate, sodium dodecylsulfate, disodium dodecyldiphenylether sulfonate, octadecyl sulfosuccinic acid and sodium dioctylsulfosuccinate.

[0026] Examples of nonionic surfactants suitable for the present invention include, but not limited to: linear alkyl alcohol polyoxyethylene ethers, linear alkyl alcohol polyoxyethylene-propylene ethers, branched alkyl alcohol polyoxyethylene ethers, branched alkyl alcohol polyoxyethylene-propylene ethers, fatty acid polyoxyethylenemonoesters, fatty acid polyoxyethylene-propylenemonoesters. Specific examples of nonionic surfactants suitable for the present invention include, but not limited to: isometric tridecyl alcohol polyoxyethylene monoether, cetyl alcohol polyoxyethylenemonoether, octadecyl alcohol polyoxyethylenemonoether a-lauroyl-w-Hydroxylpolyoxyethylene, etc., wherein the EO numbers of polyoxyethylene section are chosen according to the desired HLB value of the surfactant, typically in the range of about 20 to 40.

[0027] In some non-limiting embodiments of the present invention, the surfactant can be used in an amount of about 1-5 pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm.

[0028] In some non-limiting embodiments of the present invention, the said polymeric protective colloid can be selected from partially hydrolyzed polyvinyl alcohols, cellulose ethers and polyvinyl pyrrolidone. Specific examples of polymeric protective colloids suitable for the present invention include, but not limited to: polyvinyl alcohols having a degree of alcoholysis of about 75 to 95% and a degree of polymerization of about 200 to 4000, most preferably polyvinyl alcohols having a degree of alcoholysis of about 80 to 90% and a degree of polymerization of about 200 to 4000. Cellulose ethers as polymeric protective colloid suitable for the present invention include, but not limited to, hydroxymethyl cellulose ether, hydroxyl ethylcellulose ether and hydroxypropyl cellulose ether. In some non-limiting embodiments of the present invention, the polymeric protective colloid can be used in an amount of about 0-3 pphm, preferably about 0-1 pphm.

[0029] According to one aspect of the present invention, a polymer cement waterproof composition comprising a liquid part and a solid part is provided, characterized in that said liquid part comprises:

(a) a vinyl acetate-ethylene copolymer-based emulsion, wherein the copolymer comprises, based on the total weight of the copolymer:

(1) about 70-95pphm (parts by weight / 100 parts by weight of monomers used for preparing the emulsion), preferably about 75-90 pphm of a moiety derived from vinyl acetate;

(2) about 5-30pphm, preferably about 10-20 pphm of a moiety derived from ethylene; and

(3) about 0-10pphm, preferably about 0-5 pphm of a moiety derived from other comonomers or functional monomers,

wherein the copolymer-based emulsion is formed by emulsion polymerization of the monomers in the presence of about 1-5pphm of a surfactant and about 0-3pphm of a polymeric protective colloid as emulsifier / protective colloid,

(b) additional water.

[0030] The vinyl acetate-ethylene copolymer emulsion based cement waterproof composition comprises the liquid part and the solid part. In some non-limiting embodiments of the present invention, the weight ratio of solid part to liquid part is about 2.7:1 to 4:1, preferably about 2.7:1 to 3.3:1.

[0031] In some non-limiting embodiments of the present invention, the liquid part mainly comprises about 30 to 70% by weight of a vinyl acetate-ethylene copolymer-based emulsion and other common additives, such as wetting dispersing agents, preservatives, defoamers, etc..

[0032] Examples of wetting dispersing agents suitable for the present invention may include, but not limited to, sodium, potassium and ammonium salts-based dispersing agents containing acrylic group(s), or mixtures thereof. As specific examples, wetting dispersing agents commercially available under trade name Hydropalat 5040, SN5027, SN5029, SN5468, Hypropalat3204, Hydropalat3275, can be mentioned. Preferably, wetting dispersing agents such as Hydropalat5040 can be added in an amount of about 0 to 1%, preferably about 0.2 to 0.4%, based on the total weight of the composition.

[0033] Examples of preservatives suitable for the present invention may include, but not limited to MIT, BIT, CMIT, bronopol, or mixtures thereof. As specific examples, preservatives commercially available under trade name Rocima 562, ATICIDE MBS, ATICIDE RS, Kathlon LXE, Rocima 523 can be mentioned. Preferably, preservatives such as Kathlon LXE can be added in an amount of

about 0 to 1%, preferably about 0.1 to 0.2%, based on the total weight of the composition.

[0034] Examples of defoamers suitable for the present invention may include, but not limited to mineral oil, silicon based oil, or mixtures thereof. As specific examples, defoamers commercially available under trade name Foamaster 111, Foamaster NXZ, SN470, SN1370, SN1390, can be mentioned. Preferably, defoamers such as SN1370 can be added in an amount of about 0 to 1%, preferably about 0.1 to 0.3%, based on the total weight of the composition.

[0035] In some non-limiting embodiments of the present invention, besides the water contained in the copolymer-based emulsion, additional water may be added to the liquid part of the inventive cement waterproof composition. The said additional water may be added in an amount of about 30 to 70%, preferably about 40 to 60%, based on the total weight of liquid part.

[0036] In some non-limiting embodiments of the present invention, the liquid part essentially consists of vinyl acetate-ethylene copolymer-based emulsion, additional water and other common additives. In some non-limiting embodiments of the present invention, the liquid part does not comprise other polymers.

[0037] In some non-limiting embodiments of the present invention, the solid part mainly comprises hydraulic cement, filler and regular powder additives.

[0038] Examples of cements suitable for the present invention may include, but not limited to various kinds of portland cements, aluminate cements, sulphoaluminate cements, ferroaluminate cements, fluoaluminate cements, cements having volcanic ash, potential hydraulic materials or other active materials as the main components, or mixtures thereof. Preferably, for example, ordinary portland cement 42.5 can be added in an amount of about 30 to 60%, preferably about 40 to 60%, based on the total weight of the composition.

[0039] Examples of fillers suitable for the present invention may include, but not limited to: particulate fillers prepared by mining and processing of natural minerals as raw materials, such as river (sea) sands, silica, silicates, carbonates and carbides; or some kinds of industrial active fillers commonly used in cement products, such fly ash, slag, volcanic ash, mineral powder, silica fume, etc.. Preferably, for example, 70-40 mesh quartz sand can be added in an amount of about 30 to 70%, preferably about 40 to 60%, based on the total weight of the solid part.

[0040] Examples of powder additives suitable for the present invention may include, but not limited to those commonly used in cement products, such as defoamers, water reducing agents, etch.. In some non-limiting embodiments of the present invention, the powder additives can be added in an amount of about 0 to 2%, based on the total weight of the composition.

[0041] In a preferable embodiment of the present invention, the conventional additives added to the aqueous phase include those known in the art which are useful in the emulsion polymerization system or improve the stability or pot life of the final emulsion. For example, those additives can be redox reaction promoter, pH adjusting agents, defoamers, fungicides, chelating agents, and the like.

[0042] In some non-limiting embodiments of the present invention, the emulsion polymerization is conducted in the presence of a redox initiator. The oxidizing agent and reducing agent used to make up of the redox initiator include, but not limited to water soluble oxidizing agents and reducing agents known in the art. Examples of oxidizing agents and reducing agents suitable for the present invention may include, but not limited to, ammonium persulfate, sodium persulfate, potassium persulfate, hydrogen peroxide, tert-butyl peroxide, sodium formaldehyde-sulfoxylate, disodium 2-hydroxyl-2-sulfinatoacetate, ascorbic acid, erythorbic acid, sodium bisulfite, sodium sulfite, sodium metabisulfite, etc.. Typically, the oxidizing agent and reducing agent can be each added in an amount of about 0.05 to 5 pphm.

[0043] According to another aspect of the present invention, a process for preparing the vinyl acetate-ethylene copolymer-based emulsion is provided, said process comprises emulsion polymerizing a monomeric composition comprising:

(1) about 70-95pphm of a moiety derived from vinyl acetate;

(2) about 5-30pphm of a moiety derived from ethylene; and

(3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

in the presence of about 1-5pphm of a surfactant and about 0-3pphm of a polymeric protective colloid as emulsifier / protective colloid.

[0044] According to another aspect of the present invention, a process for preparing the polymer cement waterproof composition is provided, said process comprises

(a) forming an ethylene-vinyl acetate copolymer-based emulsion by emulsion polymerizing a monomeric composition comprising:

(1) about 70-95pphm of a moiety derived from vinyl acetate;

(2) about 5-30pphm of a moiety derived from ethylene; and

(3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

in the presence of about 1-5pphm of a surfactant and about 0-3pphm of a polymeric protective colloid as emulsifier / protective colloid;

(b) mixing said ethylene-vinyl acetate copolymer-based emulsion with additional water to form a liquid part;

(c) mixing said liquid part and a solid part to form the polymer cement waterproof composition.

[0045] The vinyl acetate-ethylene copolymer-based emulsion can be obtained by emulsion polymerization of vinyl acetate, ethylene and other comonomers or functional monomers, in the presence of a surfactant and a polymeric protective colloid as emulsion system. The emulsion generally can have a solid content of about 40 to 70%. The emulsion polymerization process is well known in the art. In a preferable embodiment of the present invention, the emulsion may be obtained by the following steps: forming an aqueous phase by adding surfactant and protective colloid, as emulsifier, and other conventional additives into water; feeding the aqueous phase to a reactor under slow stirring; evacuating the reactor under vacuum and purging with nitrogen at least three times for removing any air; raising the temperature of the reactor to about 40-70°C, then increasing the speed of stirring, adding to the reactor part of the vinyl acetate monomer or mixture of the vinyl acetate monomer and the other comonomers or functional monomers, together with part of ethylene gas; after the pressure of the reactor becomes constant, adding dropwise oxidizing agent and reducing agent, as redox initiator, so that polymerization takes place, with increasing of temperature; adding remaining monomers when the temperature of the reactor reaches a predetermined value, about 50-90°C, until the consumption of the monomers. The temperature of the reactor was controlled at about 50-90°C during the emulsion polymerization process. After completion of polymerization, the reactor is cooled to selected temperature, about 50-70°C, and the polymerization product therein was transferred to a post-treatment reactor, while the unreacted ethylene gas was discharged as exhaust gas. Subsequently, certain amount of oxidizing agent and reducing agent were added to the post-treatment reactor, to reduce the amount of residual monomers by further initiating the polymerization of residual monomers. Alternatively, the amount of residual monomers can be further reduced by extraction of water vapor. Finally, the emulsion parameters of the copolymer-based emulsion thus obtained can be adjusted by feeding with additional water and/or other conventional additives. The emulsion thus obtained can have a solid content of about 40 to 70%, most commonly about 50 to 60%.

[0046] In some non-limiting embodiments of the present invention, a vinyl acetate-ethylene copolymer-based emulsion was obtained according to the above mentioned formulation and process, and the vinyl acetate-ethylene copolymer-based emulsion thus obtained can be used to formulate the polymer cement waterproof composition.

[0047] In a preferable embodiment of the present invention, the polymer cement waterproof composition may be obtained by the following steps: forming an liquid part by adding required additives, including defoamers, preservatives and dispersing agent etc., and then the polymer emulsion to certain amount of water under a stirring rate of about 300rpm for about 5 minutes; forming a solid part by mixing certain amount of cement, filler and some additives under stirring until a uniform mixture was obtained; mixing the liquid part and solid part in specific ratio under stirring to get a homogeneous polymer cement waterproof composition.

[0048] The anti-water permeability of the inventive polymer cement waterproof composition was tested according to anti water permeability test of Chinese Standard GB 23440-2009 after curing 7 days. However, the anti-water permeability test cannot be carried out on the polymer cement waterproof composition which was prepared by conventional vinyl acetate-ethylene copolymer-based emulsion in similar weight ratio of liquid part to liquid part, since such polymer cement waterproof composition has a high consistency, therefore cannot be applied and tested.

[0049] The bonding strength of the inventive polymer cement waterproof composition was tested according to Part 7.6.3.1 of Chinese Standard GB23445-2009 after curing 7 days. However, the bonding strength test cannot be carried out on the polymer cement waterproof composition which was prepared by conventional vinyl acetate-ethylene copolymer-based emulsion in similar weight ratio of liquid part to liquid part, since such polymer cement waterproof composition has a high consistency, therefore cannot be applied and tested.

[0050] The required anti-permissive pressure and bonding strength of the polymer cement waterproof composition can be varied according to specific application. Typically, the required anti-permissive pressure of the polymer cement waterproof composition is equal to or greater than 0.5MPa, and the required bonding strength of the polymer cement waterproof composition is equal to or greater than 0.7MPa.

[0051] The following Examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the Examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

EXAMPLES

[0052] Unless indicated to the contrary, all parts and percentages are by weight.

TEST

[0053] The anti-water permeability of the inventive polymer cement waterproof composition was tested according to anti water permeability test of Chinese Standard GB 23440-2009 after curing 7 days.

[0054] The bonding strength of the inventive polymer cement waterproof composition was tested according to Part 7.6.3.1 of Chinese Standard GB23445-2009 after curing 7 days.

Example 1

[0055] A vinyl acetate-ethylene copolymer-based emulsion (Emulsion 1) was prepared using the following formulation.

Charge I (aqueous phase)	
deionized water	3379.95 g
Disponil A3065 (Cognis, a.i. 65%)	238.47 g
polyvinyl alcohol (Celvol 504 from Sekisui company, alcohoysis degree: 88%, a.i. 29%)	37.12 g
sodium dodecylbenzene sulfonate (a.i. 24%)	118.85 g
sodium vinylsulfonate (a.i. 30%)	89.7 g
disodium 2-hydroxy-2-sulfinatoacetate	1.08 g
Charge II (monomers)	
vinyl acetate	4814.28 g
vinyl silane	22.07 g
ethylene	567.81 g
Charge III (oxidizing agent and reducing agent)	
sodium persulfate	7.53 g
water	198.6 g
disodium 2-hydroxy-2-sulfinatoacetate	4.31 g
water	220.67 g

Charge IV (post-treatment agents)

water	149.62 g
t-butyl peroxide (70%)	3.08 g
sodium metabisulfite	1.08 g

[0056] To a 10L reactor was added the aqueous phase under stirring (300 rpm). The reactor was evacuated and purged with nitrogen for three times to remove residual air. The stirring speed was then increased to 600 rpm. 242 g of a mixture of vinyl acetate and vinyl silane and 22 g reducing agent solution were added within 10 mins. The pressure of the reactor was raised to 40 bars by feeding ethylene gas. The reactor was heated to 55 °C and equilibrated for 5 mins. The oxidizing agent solution and the rest of reducing agent solution were added for 270 mins. In the meantime, the temperature of the reactor was adjusted to 70 °C within 15 mins. When the temperature of the reactor reached 57 °C, the remaining mixture of vinyl acetate and vinyl silane was added within 200 mins. When the temperature of the reactor reached 70 °C, the remaining ethylene gas was fed to maintain the maximum pressure of the reactor below 55 bars.

[0057] After completion of adding the mixture of vinyl acetate and vinyl silane, the temperature of the reactor was raised from 70 °C to 85 °C within 15 mins and maintained for 10 to 30 mins. The reactor was then cooled to 60 °C. The obtained emulsion was transferred to post-treatment reactor.

[0058] The post-treatment reactor was stirred at a speed of 200 rpm. The solution of sodium metabisulfite was added within 15 mins. Then, the solution of *t*-butyl peroxide was added within 10 mins. The post-treatment reactor was cooled to 40 °C.

[0059] The obtained vinyl acetate-ethylene copolymer-based emulsion (Emulsion 1) has the following properties:

ratio of vinyl acetate/ethylene/sodium vinyl sulfonate/vinyl silane	89.5/10.5/0.5/0.41
polyvinyl alcohol content	0.2 pphm
surfactant content	3.4 pphm
solid content	54.2% by weight
pH	5.2
viscosity (BVF, 20 rpm)	220 mPa.s
particle size (D90)	250 nm

Example 2

[0060] A vinyl acetate-ethylene copolymer-based emulsion (Emulsion 2) was prepared using the following formulation.

Charge I (aqueous phase)	
deionized water	3303.25 g
Disponil AFX 3070 (a.i. 70%)	222.42 g
polyvinyl alcohol (Celvol 523 from Sekisui company, alcohoysis degree: 88%, a.i. 15%)	211.05 g
sodium dodecylsulfonate (a.i. 15%)	186.83g
sodium vinylsulfonate (a.i. 30%)	76.12g
Charge II (monomers)	
vinyl acetate	4525.42 g
vinyl silane	11.42 g
ethylene	664.27 g
glycidyl acrylate	57.09 g
Charge III (oxidizing agent and reducing agent)	
sodium persulfate	13.49 g
water	202.4 g
disodium 2-hydroxy-2-sulfinatoacetate	5.19 g
water	223.16 g
Charge IV (post-treatment agents)	
water	193.57 g
t-butyl peroxide (70%)	4.52 g
Sodium metabisulfite	3.17 g

[0061] To a 10L reactor was added the aqueous phase under stirring (300 rpm). The reactor was evacuated and purged with nitrogen for three times to remove residual air. The stirring speed was then increased to 600 rpm. A mixture of 351.3 g vinyl acetate, 0.57 g vinyl silane and 2.85 g glycidyl acrylate and 22.8 g reducing agent solution were added within 10 mins. 93.4 g ethylene gas was fed into the reactor. In the meantime, the reactor was heated to 50 °C and equilibrated for 5 mins. The oxidizing agent solution and the rest of reducing agent solution were added for 265 mins. When the temperature of the reactor reached 52 °C, the remaining mixture of vinyl acetate, vinyl silane and glycidyl acrylate was added.

The reactor was maintained for 240 mins. The temperature of the reactor was adjusted to 65 °C within 15 mins. The reaction temperature was controlled at 65 °C during the whole polymerization process. When the temperature of the reactor reached 60°C, the remaining ethylene gas was fed within 150 mins and maintained the maximum pressure of the reactor below 55 bar.

[0062] After completion of adding the redox solution, the reactor was then cooled from 65 °C to 55 °C. The obtained emulsion was transferred to post-treatment reactor. The post-treatment reactor was stirred at a speed of 200 rpm, and the temperature was set to 50 °C. The solution of sodium metabisulfite was added within 10 mins. Then, the solution of *t*-butyl peroxide was added within 10 mins. The post-treatment reactor was stirred at a speed of 200 rpm for another 30mins at a temperature of 50°C.

[0063] The obtained vinyl acetate-ethylene copolymer-based emulsion (Emulsion 2) has the following properties:

ratio of vinyl acetate/ethylene/sodium vinyl sulfonate/vinyl silane/glycidyl acrylate	87.2/12.8/0.44/0.22/1.1
polyvinyl alcohol content	0.6 pphm
surfactant content	3.5 pphm
solid content	54.6% by weight
pH	4.9
viscosity (BVF, 20 rpm)	2950 mPa.s
particle size (D90)	290 nm

Example 3

[0064] A vinyl acetate-ethylene copolymer-based emulsion (Emulsion 3) was prepared using the following formulation.

Charge I (aqueous phase)

deionized water	2642.02 g
Disponil A3065 (Cognis, a.i. 65%)	238.47 g
polyvinyl alcohol (Celvol 504 from Sekisui company, alcohoysis degree: 88%, a.i. 29%)	445.4 g
sodium dodecylbenzene sulfonate (a.i. 24%)	448.5 g
sodium vinylsulfonate (a.i. 30%)	89.7 g
disodium 2-hydroxy-2-sulfinatoacetate	1.08 g

Charge II (monomers)	
vinyl acetate	4814.28 g
vinyl silane	80.7 g
ethylene	567.81 g
Charge III (oxidizing agent and reducing agent)	
sodium persulfate	7.53 g
water	198.6 g
disodium 2-hydroxy-2-sulfinatoacetate	4.31 g
water	220.67 g
Charge IV (post-treatment agents)	
water	149.62 g
t-butyl peroxide (70%)	3.08 g
sodium metabisulfite	1.08 g

[0065] To a 10L reactor was added the aqueous phase under stirring (300 rpm). The reactor was evacuated and purged with nitrogen for three times to remove residual air. The stirring speed was then increased to 600 rpm. 245 g of a mixture of vinyl acetate and vinyl silane and 22 g reducing agent solution were added within 10 mins. The pressure of the reactor was raised to 40 bars by feeding ethylene gas. The reactor was heated to 55 °C and equilibrated for 5 mins. The oxidizing agent solution and the rest of reducing agent solution were added for 270 mins. In the meantime, the temperature of the reactor was adjusted to 70 °C within 15 mins. When the temperature of the reactor reached 57 °C, the remaining mixture of vinyl acetate and vinyl silane was added within 200 mins. When the temperature of the reactor reached 70 °C, the remaining ethylene gas was fed to maintain the maximum pressure of the reactor below 55 bars.

[0066] After completion of adding the mixture of vinyl acetate and vinyl silane, the temperature of the reactor was raised from 70 °C to 85 °C within 15 mins and maintained for 10 to 30 mins. The reactor was then cooled to 60 °C. The obtained emulsion was transferred to post-treatment reactor.

[0067] The post-treatment reactor was stirred at a speed of 200 rpm. The solution of sodium metabisulfite was added within 15 mins. Then, the solution of *t*-butyl peroxide was added within 10 mins. The post-treatment reactor was cooled to 40 °C.

[0068] The obtained vinyl acetate-ethylene copolymer-based emulsion (Emulsion 3) has the following properties:

ratio of vinyl acetate/ethylene/ sodium vinyl sulfonate/vinyl silane	89.5/10.5/0.5/1.5
polyvinyl alcohol content	2.4 pphm
surfactant content	4.9 pphm
solid content	52.9% by weight
pH	5.2
viscosity (BVF, 20 rpm)	860 mPa.s
particle size (D90)	267 nm

Example 4

[0069] A vinyl acetate-ethylene copolymer-based emulsion (Emulsion 4) was prepared using the following formulation.

Charge I (aqueous phase)	
deionized water	3032.9 g
Disponil A3065 (Cognis, a.i. 65%)	238.47 g
polyvinyl alcohol (Celvol 504 from Sekisui company, alcohoysis degree: 88%, a.i. 29%)	222.72 g
sodium dodecylbenzene sulfonate (a.i. 24%)	280.3 g
sodium vinylsulfonate (a.i. 30%)	89.7 g
disodium 2-hydroxy-2-sulfinatoacetate	1.08 g
Charge II (monomers)	
vinyl acetate	4814.28 g
vinyl silane	40.4 g
ethylene	567.81 g
Charge III (oxidizing agent and reducing agent)	
sodium persulfate	7.53 g
water	198.6 g
disodium 2-hydroxy-2-sulfinatoacetate	4.31 g

water	220.67 g

Charge IV (post-treatment agents)

water	149.62 g
t-butyl peroxide (70%)	3.08 g
sodium metabisulfite	1.08 g

[0070] To a 10L reactor was added the aqueous phase under stirring (300 rpm). The reactor was evacuated and purged with nitrogen for three times to remove residual air. The stirring speed was then increased to 600 rpm. 243 g of a mixture of vinyl acetate and vinyl silane and 22 g reducing agent solution were added within 10 mins. The pressure of the reactor was raised to 40 bars by feeding ethylene gas. The reactor was heated to 55 °C and equilibrated for 5 mins. The oxidizing agent solution and the rest of reducing agent solution were added for 270 mins. In the meantime, the temperature of the reactor was adjusted to 70 °C within 15 mins. When the temperature of the reactor reached 57 °C, the remaining mixture of vinyl acetate and vinyl silane was added within 200 mins. When the temperature of the reactor reached 70 °C, the remaining ethylene gas was fed to maintain the maximum pressure of the reactor below 55 bars.

[0071] After completion of adding the mixture of vinyl acetate and vinyl silane, the temperature of the reactor was raised from 70 °C to 85 °C within 15 mins and maintained for 10 to 30 mins. The reactor was then cooled to 60 °C. The obtained emulsion was transferred to post-treatment reactor.

[0072] The post-treatment reactor was stirred at a speed of 200 rpm. The solution of sodium metabisulfite was added within 15 mins. Then, the solution of *t*-butyl peroxide was added within 10 mins. The post-treatment reactor was cooled to 40 °C.

[0073] The obtained vinyl acetate-ethylene copolymer-based emulsion (Emulsion 4) has the following properties:

ratio of vinyl acetate/ethylene/ sodium vinyl sulfonate/vinyl silane	89.5/10.5/0.5/0.75
polyvinyl alcohol content	1.2 pphm
surfactant content	4.2 pphm
solid content	53.2% by weight
pH	5.2
viscosity (BVF, 20 rpm)	288 mPa.s

particle size (D90)	177 nm

Example 5

[0074] 0.2 g SN1370 defoamers and 0.1g Kathon LXE were added to 49.7g water to get a solution which was stirred at a speed of 400rpm for 2mins. 50g vinyl acetate-ethylene copolymer-based emulsion from Example 1 (Emulsion 1) was added to the solution, which was then stirred at a speed of 400rpm for 5mins. A homogeneous liquid part for polymer cement waterproof composition was obtained.

[0075] 220g ordinary portland cement 42.5, 176g 70-140 mesh quartz sand and 4g F10 water reducing agents were minxed and stirred for about 20 mins. A homogeneous solid part for polymer cement waterproof composition was obtained.

[0076] The liquid part and solid part were thoroughly mixed to get a polymer cement waterproof composition. Table 1 below shows the composition and the testing results of anti-water permeability and bonding strength properties of this polymer cement waterproof composition.

Example 6

[0077] 0.2 g SN1370 defoamers and 0.1g Kathon LXE were added in 59.7g water to get a solution which was stirred at a speed of 400rpm for 2mins. 40g vinyl acetate-ethylene copolymer-based emulsion from Example 1 (Emulsion 1) was added in the solution, which was then stirred at a speed of 400rpm for 5mins. A homogeneous liquid part for polymer cement waterproof composition was obtained.

[0078] 220g ordinary portland cement 42.5, 176g 70-140 mesh quartz sand and 4g F10 water reducing agents were minxed and stirred for about 20 mins. A homogeneous solid part for polymer cement waterproof composition was obtained.

[0079] The liquid part and solid part were thoroughly mixed to get a polymer cement waterproof composition. Table 1 below shows the composition and the testing results of anti-water permeability and bonding strength properties of this polymer cement waterproof composition.

Example 7

[0080] 0.2 g SN1370 defoamers and 0.1g Kathon LXE were added in 49.7g water to get a solution which was stirred at a speed of 400rpm for 2mins. 50g vinyl acetate-ethylene copolymer-based emulsion from Example 2 (Emulsion 2) was added in the solution, which was then stirred at a speed of 400rpm for 5mins. A

homogeneous liquid part for polymer cement waterproof composition was obtained.

[0081] 220g ordinary portland cement 42.5, 176g 70-140 mesh quartz sand and 4g F10 water reducing agents were minxed and stirred for about 20 mins. A homogeneous solid part for polymer cement waterproof composition was obtained.

[0082] The liquid part and solid part were thoroughly mixed to get a polymer cement waterproof composition. Table 1 below shows the composition and the testing results of anti-water permeability and bonding strength properties of this polymer cement waterproof composition.

Comparative Example 1

[0083] 0.2 g SN1370 defoamers and 0.1g Kathon LXE were added in 59.7g water to get a solution which was stirred at a speed of 400rpm for 2mins. 40g commercially available vinyl acetate-ethylene copolymer-based emulsion (Comparative Emulsion 1, containing 4.5 pphm polymeric protective colloid and 0.4 pphm surfactant) was added in the solution, which was then stirred at a speed of 400rpm for 5mins. A homogeneous liquid part for polymer cement waterproof composition was obtained.

[0084] 220g ordinary portland cement 42.5, 176g 70-140 mesh quartz sand and 4g F10 water reducing agents were minxed and stirred for about 20 mins. A homogeneous solid part for polymer cement waterproof composition was obtained.

[0085] The liquid part and solid part were thoroughly mixed to get a polymer cement waterproof composition. Table 1 below shows the composition and the testing results of anti-water permeability and bonding strength properties of this comparative polymer cement waterproof composition.

Table 1

	Formulation	Ex.5	Ex.6	Ex.7	Comp. Ex.10
Liquid part	Emulsion 1	50	40		
	Emulsion 2			50	
	commercially available Comparative Emulsion 1				40
	SN1370 defoamers	0.2	0.2	0.2	0.2
	Preservatives, Kathon LXE	0.1	0.1	0.1	0.1
	Water	49.7	59.7	49.7	59.7
	Total	100	100	100	100
Solid part	ordinary portland cement 42.5	220	220	220	220
	quartz sand, 70-140 mesh	176	176	176	176
	F10 water reducing agents	4	4	4	4
	Total	400	400	400	400
	Liquid part: Solid part	1:4	1:4	1:4	1:4
Properties	Parameters				
	Workability	Applicable	Applicable	Applicable	Cannot be stirred or coated
	Workability after 3 hours	Applicable	Applicable	Applicable	NA
Anti-permissive pressure/MPa	7d, standard condition	>1.0	>0.6	>1.0	NA
bonding strength /MPa	7d, standard condition	1.4	1.0	1.3	NA

[0086] Analysis:

[0087] The applicability of the polymer cement waterproof compositions prepared by Emulsion 1 (Examples 5 and 6) are both good. The anti-permissive pressure and bonding strength of cement slurry with lower emulsion content (Example 6) are slightly decreased respectively as compared to those of cement slurry with higher emulsion content (Example 5).

[0088] When Emulsion 1 and Emulsion 2 are used in the same amount, the properties of polymer cement waterproof composition prepared by Emulsion 1

(Example 5) are similar to those of the polymer cement waterproof composition prepared by Emulsion 2 (Example 7).

[0089] The data of Comparative Example 1 shows that the polymer cement composition prepared by commercially available vinyl acetate-ethylene copolymer-based emulsion (i.e. Comparative Emulsion 1) cannot be stirred or coated, therefore cannot be applied in practice.

[0090] Storage stability test of liquid part:

[0091] The liquid part made in each of Examples 5 to 10 was sampled and divided into two aliquots respectively. The two aliquots of the same sample were loaded into two 200 ml clean graduates respectively, which was then sealed by aluminum foil and rubber band. One graduate was transferred into an oven under 40°C, the other graduate was moved to laboratory environment at 23°C. The stratification result of each aliquot of sample was observed according to the intervals as listed in Table 2.

[0092] The results showed that, no stratification was observed in the liquid parts made by Emulsion 1 or Emulsion 2 (Examples 5 to 7), regardless stored in oven under 40°C or under laboratory environment, which means the storage stability of these liquid parts were excellent. However, the liquid part sample made by commercially available vinyl acetate-ethylene copolymer-based emulsion (Comparative Example 1) stratified both in oven under 40°C or laboratory environment, which means that this liquid part sample is unsuitable for long-time storage.

Table 2

	Formulation	Ex. 5	Ex. 6	Ex. 7	Comp. Ex. 10
liquid part	Emulsion 1	50	40		
	Emulsion 2			50	
	commercially available Emulsion,				40
	commercially available Emulsion,				
	SN1370 defoamers	0.2	0.2	0.2	0.2
	dispersing agent, 5040	0.4	0.4	0.4	0.4
	Preservatives, Kathon LXE	0.1	0.1	0.1	0.1
	Water	49.3	59.3	49.3	59.3
	Total	100	100	100	100
laboratory environment	2 weeks	No stratification	No stratification	No stratification	Slight aqueous phase
	4 weeks	No stratification	No stratification	No stratification	aqueous phase, stratification
	6 weeks	No stratification	No stratification	No stratification	NA
	8 weeks	No stratification	No stratification	No stratification	NA
	10 weeks	No stratification	No stratification	No stratification	NA
	12 weeks	No stratification	No stratification	No stratification	NA
Oven, 40°C	2 weeks	No stratification	No stratification	No stratification	aqueous phase, stratification
	4 weeks	No stratification	No stratification	No stratification	NA
	6 weeks	No stratification	No stratification	No stratification	NA
	8 weeks	No stratification	No stratification	No stratification	NA
	10 weeks	No stratification	No stratification	No stratification	NA
	12 weeks	No stratification	No stratification	No stratification	NA

[0093] All of the methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While

the products and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A polymer cement waterproof composition, comprising a liquid part and a solid part, characterized in that said liquid part comprises:

(a) a vinyl acetate-ethylene copolymer-based emulsion, wherein the copolymer comprises, based on the total weight of the copolymer:

(1) about 70-95pphm of a moiety derived from vinyl acetate;

(2) about 5-30pphm of a moiety derived from ethylene; and

(3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

wherein the copolymer-based emulsion is formed by emulsion polymerization of the monomers in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-3pphm, preferably about 0-1 pphm of a polymeric protective colloid as emulsifier / protective colloid,

(b) additional water.

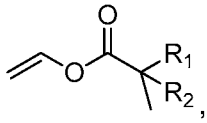
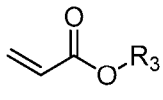
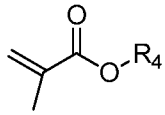
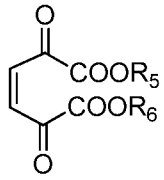
2. The polymer cement waterproof composition according to claim 1, wherein the surfactant is selected from anionic surfactants, nonionic surfactants or combination thereof.

3. The polymer cement waterproof composition according to claim 2, wherein the anionic surfactants are selected from alkylsulfates, alkylsulfonates, alkyl benzenesulfonates, alkyl polyoxyethylene ether sulfates, alkylpolyoxyethylene-propylene ether sulfates, sodium fatty alcohol succinic acid mono ester sulfonates, disodium fatty alcohol polyoxyethylene ether sulfosuccinates, disodium fatty alcohol polyoxyethylene-propylene ether sulfosuccinates, alkylpolyoxyethylene phosphates, alkylpolyoxyethylene-propylene phosphates and alkali metal salts of fatty acids, or mixtures thereof.

4. The polymer cement waterproof composition according to claim 2, wherein the nonionic surfactants are selected from linear alkyl alcohol polyoxyethylene ethers, linear alkyl alcohol polyoxyethylene-propylene ethers, branched alkyl alcohol polyoxyethylene ethers, branched alkyl alcohol polyoxyethylene-propylene ethers, fatty acid polyoxyethylenemonoesters, fatty acid polyoxyethylene-propylenemonoesters, or mixtures thereof.

5. The polymer cement waterproof composition according to claim 1, wherein the polymeric protective colloid is selected from partially hydrolyzed polyvinyl alcohols, cellulose ethers, polyvinyl pyrrolidone, or mixtures thereof.

6. The polymer cement waterproof composition according to claim 5, wherein the polyvinyl alcohol has a degree of alcoholysis of about 75 to 95% and a degree of polymerization of about 200 to 4000, preferably a degree of alcoholysis of about 80 to 90% and a degree of polymerization of about 200 to 4000.

7. The polymer cement waterproof composition according to claim 1, wherein other comonomers or functional monomers are selected from vinyl esters of polyacid; acrylates; methacrylates; maleate esters; vinyl chloride; , wherein each of R_1 and R_2 is hydrogen or alkyl group, provided that the total carbon atom number in R_1 and R_2 is from 0 to 14; , wherein R_3 is hydrogen or alkyl group with 1 to 16 carbon atom(s); , wherein R_4 is hydrogen or alkyl group with 1 to 16 carbon atom(s); , wherein each of R_5 and R_6 is alkyl group with 1 to 16 carbon atom(s); acrylic acid; methacrylic acid; maleic acid; maleic anhydride; fumaric acid; crotonic acid; itaconic acid; sodium vinylsulfonate; mono-sodium 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propylsulfonate; methacrylate ethyl trimethyl ammonium chloride; acrylamide; hydroxymethylacrylamide; hydroxyethylacrylamide; hydroxypropylacrylamide ; vinyltrimethoxysilane; vinyltriethoxysilane; vinyltri(2-methoxyethoxy)silane; methylacryloxypropyltrimethoxysilane; ethylene glycol acrylate; propylene glycol acrylate; glycidyl acrylate; diallyl maleate; diallyl phthalate; triallyl cyanurate; allyl methacrylate; ethylene glycol dimethylacrylate; pentaerythritol triacrylate; pentaerythritol tetraacrylate; or combinations thereof.

8. The polymer cement waterproof composition according to claim 1, wherein the solid part comprises hydraulic cement, filler and regular powder additives.

9. The polymer cement waterproof composition according to claim 8, wherein the hydraulic cement is selected from portland cements, aluminate cements, sulphoaluminate cements, ferroaluminate cements, fluoaluminate cements, cements having volcanic ash, potential hydraulic materials or other active materials as the main components, or mixtures thereof.

10. The polymer cement waterproof composition according to claim 1, wherein the

weight ratio of solid part to liquid part is about 2.7:1 to 4:1, preferably about 2.7:1 to 3.3:1.

11. A process for preparing the polymer cement waterproof composition according to any one of claims 1 to 10, said process comprises

(a) forming an ethylene-vinyl acetate copolymer-based emulsion by emulsion polymerizing a monomeric composition comprising:

(1) about 70-95pphm of a moiety derived from vinyl acetate;

(2) about 5-30pphm of a moiety derived from ethylene; and

(3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-3pphm, preferably about 0-1 pphm of a polymeric protective colloid as emulsifier / protective colloid.

(b) mixing said ethylene-vinyl acetate copolymer-based emulsion with additional water to form a liquid part;

(c) mixing said liquid part and a solid part to form the polymer cement waterproof composition.

12. A vinyl acetate-ethylene copolymer-based emulsion for polymer cement waterproof composition, wherein the copolymer comprises, based on the total weight of the copolymer:

(1) about 70-95pphm of a moiety derived from vinyl acetate;

(2) about 5-30pphm of a moiety derived from ethylene; and

(3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

wherein the copolymer-based emulsion is formed by emulsion polymerization of the monomers in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-3pphm, preferably about 0-1 pphm of a polymeric protective colloid as emulsifier / protective colloid.

13. The vinyl acetate-ethylene copolymer-based emulsion according to claim 12, wherein the surfactant is selected from anionic surfactants, nonionic surfactants or combination thereof.

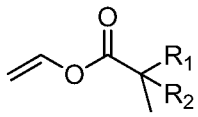
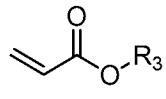
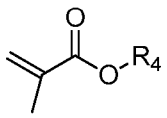
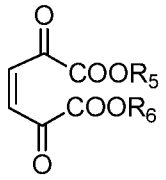
14. The vinyl acetate-ethylene copolymer-based emulsion according to claim 13, wherein the anionic surfactants are selected from alkylsulfates, alkylsulfonates, alkyl benzenesulfonates, alkyl polyoxyethylene ether sulfates, alkylpolyoxyethylene-propylene ether sulfates, sodium fatty alcohol succinic acid

mono ester sulfonates, disodium fatty alcohol polyoxyethylene ether sulfosuccinates, disodium fatty alcohol polyoxyethylene-propylene ether sulfosuccinates, alkylpolyoxyethylene phosphates, alkylpolyoxyethylene-propylene phosphates and alkali metal salts of fatty acids, or mixtures thereof.

15. The vinyl acetate-ethylene copolymer-based emulsion according to claim 13, wherein the nonionic surfactants are selected from linear alkyl alcohol polyoxyethylene ethers, linear alkyl alcohol polyoxyethylene-propylene ethers, branched alkyl alcohol polyoxyethylene ethers, branched alkyl alcohol polyoxyethylene-propylene ethers, fatty acid polyoxyethylenemonoesters, fatty acid polyoxyethylene-propylenemonoesters, or mixtures thereof.

16. The vinyl acetate-ethylene copolymer-based emulsion according to claim 12, wherein the polymeric protective colloid is selected from partially hydrolyzed polyvinyl alcohols, cellulose ethers, polyvinyl pyrrolidone, or mixtures thereof.

17. The vinyl acetate-ethylene copolymer-based emulsion according to claim 16, wherein the polyvinyl alcohol has a degree of alcoholysis of about 75 to 95% and a degree of polymerization of about 200 to 4000, preferably a degree of alcoholysis of about 80 to 90% and a degree of polymerization of about 200 to 4000.

18. The vinyl acetate-ethylene copolymer-based emulsion according to claim 12, wherein other comonomers or functional monomers are selected from vinyl esters of polyacid; acrylates; methacrylates; maleate esters; vinyl chloride; , wherein each of R_1 and R_2 is hydrogen or alkyl group, provided that the total carbon atom number in R_1 and R_2 is from 0 to 14; , wherein R_3 is hydrogen or alkyl group with 1 to 16 carbon atom(s); , wherein R_4 is hydrogen or alkyl group with 1 to 16 carbon atom(s); , wherein each of R_5 and R_6 is alkyl group with 1 to 16 carbon atom(s); acrylic acid; methacrylic acid; maleic acid; maleic anhydride; fumaric acid; crotonic acid; itaconic acid; sodium vinylsulfonate; mono-sodium 2-methyl-2-[(1-oxo-2-propenyl)amino]-1-propylsulfonate; methacrylate ethyl trimethyl ammonium chloride; acrylamide; hydroxymethylacrylamide;

hydroxyethylacrylamide; hydroxypropylacrylamide ; vinyltrimethoxysilane; vinyltriethoxysilane; vinyltri(2-methoxyethoxy)silane; methylacryloxypropyltrimethoxysilane; ethylene glycol acrylate; propylene glycol acrylate; glycidyl acrylate; diallyl maleate; diallyl phthalate; triallyl cyanurate; allyl methacrylate; ethylene glycol dimethylacrylate; pentaerythritol triacrylate; pentaerythritol tetraacrylate; or combinations thereof.

19. The vinyl acetate-ethylene copolymer-based emulsion according to claim 12, wherein the copolymer-based emulsion has a solid content of about 40 to 70% by weight, based on the total weight of the emulsion.

20. A process for preparing the vinyl acetate-ethylene copolymer-based emulsion according to any one of claims 12 to 19, said process comprises emulsion polymerizing a monomeric composition comprising:

(1) about 70-95pphm of a moiety derived from vinyl acetate;

(2) about 5-30pphm of a moiety derived from ethylene; and

(3) about 0-10pphm of a moiety derived from other comonomers or functional monomers,

in the presence of about 1-5pphm, preferably about 2-5 pphm, more preferably about 2-4 pphm of a surfactant and about 0-3pphm, preferably about 0-1 pphm of a polymeric protective colloid as emulsifier / protective colloid.

21. The process according to claim 20, wherein the emulsion polymerization is carried out in the presence of a redox initiator.

22. The process according to claim 21, wherein the initiator is selected from ammonium persulfate, sodium persulfate, potassium persulfate, hydrogen peroxide, tert-butyl peroxide, sodium formaldehyde-sulfoxylate, disodium 2-hydroxyl-2-sulfinatoacetate, ascorbic acid, erythorbic acid, sodium bisulfite, sodium sulfite, sodium metabisulfite, or mixtures thereof.

23. Use of the vinyl acetate-ethylene copolymer-based emulsion according to any one of claims 12 to 19 or obtainable by the process according to any one of claims 20 to 22 in polymer cement waterproof composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/070794

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C04B28/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI,EPODOC,CNKI,CNPAT: cement, EVA, vinyl, acetate, ethylene, solid, liquid, ratio, content, high

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN102167551 A(CAI, Haijun) 31 Aug. 2011(31.08.2011) claims	1-11,23
X	CN101200518 A (CHINA PETROLEUM NATURAL GAS GROUP CORP. et al)	12-22
Y	18 Jun. 2008 (18.06.2008) claims, page7 lines 1-4	1-11,23
A	CN1248601A(LI, Hai) 29 Mar. 2000 (29.03.2000) claims	1-23

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

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

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

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 Oct. 2012 (18.10.2012)	**22 Nov. 2012 (22.11.2012)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer JIN, Hua Telephone No. (86-10)82246661

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/070794

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN101333403A(CHINA BUILDING MATERIALS ACADEMY) 31 Dec. 2008(31.12.2008) claims	1-23
A	CN102173728A(BEIJING ORIENTAL YUHONG WATERPROOF TECH.) 07 Sep. 2011(07.09.2011)claims	1-23

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2012/070794

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN102167551 A	31.08.2011	None	
CN101200518 A	18.06.2008	CN100526348C	12.08.2009
CN1248601A	29.03.2000	None	
CN101333403A	31.12.2008	CN101333403B	20.04.2011
CN102173728A	07.09.2011	None	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/070794

A. CLASSIFICATION OF SUBJECT MATTER

C04B28/00 (2006.01) i
C04B28/14 (2006.01) i