

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

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

09 January 2020 (09.01.2020)



(10) International Publication Number

WO 2020/006691 A1

(51) International Patent Classification:

C09J 131/04 (2006.01) C08L 33/26 (2006.01)
C09J 11/06 (2006.01) C09J 123/08 (2006.01)
D04H 1/587 (2012.01) C08F 218/08 (2006.01)
D04H 1/64 (2012.01) C09J 133/26 (2006.01)
A61F 13/15 (2006.01)

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, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/CN2018/094427

Published:

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

(22) International Filing Date:

04 July 2018 (04.07.2018)

(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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,

(54) Title: AQUEOUS POLYMER DISPERSION

(57) Abstract: A single-package polymer aqueous dispersion which has good adhesion after heating, has the advantages of long-term storage under room temperature conditions and good viscosity stability. The single-package polymer aqueous dispersion is particularly suitable for the bonding between a fiber textile material and a polymer foam material, and has high wet adhesion strength and excellent water resistance.



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Aqueous Polymer Dispersion

Field of the Invention

The present invention relates to an aqueous polymer dispersion and use thereof for interfacial bonding between polymeric porous materials.

Background of the Invention

Commercial VINNAPAS® 192 CGN is a self-crosslinking aqueous polymer dispersion based on ethylene-vinyl acetate. This product can be crosslinked at 150°C for bonding in the production of nonwovens. The recommended use of the product is: prior to use, adding 1% catalyst (based on the solids content of VINNAPAS® 192 CGN) to the product and mix well. The catalyst is generally formulated as a 10% aqueous solution. Among the commonly used are ammonium chloride, citric acid and sodium bisulfate. If the time for mixing VINNAPAS® 192 CGN with the catalyst is too long and exceeds thirty minutes under room temperature, the mixture will gel, leading to a significantly increased viscosity that renders it unusable.

CN102650094A discloses a non-woven fibrous structure where the fibers are consolidated by crosslinking a binder based on an ethylene-vinyl acetate polymer emulsion. The binder contains 1 to 5 wt% organic acidulant (based on the total weight of comonomers), such as oxalic, succinic adipic, glutaric, tartaric and citric acids, and crosslinkable functional monomers such as N-methylol amide derived from acrylic acid and methacrylic acid. The organic acidulant is a mono- or polycarboxylic acid having from about 2 to about 12 carbon atoms and a pKa value of from about 2 to 7 in water. The patent also indicates that the organic acidulant can promote premature crosslinking of the copolymer of the binder and ultimately destabilize the latex binder composition. Therefore, the organic acidulant should be added in preferably within several hours, typically within 5 hours, or more preferably within 2 hours, before the latex binder composition is contacted with the non-woven fibrous structure.

US4,449,978 discloses a VAE emulsion containing NMA. This VAE emulsion is a system stabilized by an alkylphenol polyoxyethylene ether surfactant. Among them, Run 9-15 contained a buffer system of sodium acetate and acetic acid, and adjusted the pH

of the VAE emulsion to be approximately 4.4. After Preparation Run 9-15 was completed, no additional ammonium chloride was added.

Summary of the Invention

The prior art adhesive products have the shortcomings of onsite preparation and short-term storage.

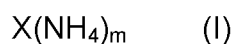
The present invention obtains a single-package polymer aqueous dispersion which has good adhesion after heating, has the advantages of long-term storage under room temperature conditions and good viscosity stability. The single-package polymer aqueous dispersion is particularly suitable for the bonding between a fiber textile material and a polymer foam material, and has high wet bond strength and excellent water resistance.

In present invention, we would like to provide an aqueous polymer dispersion, wherein the said polymer is obtained by the polymerization of a composition comprising Components A and B:

A – one or more monomers, selected from the group consisting of C1-C15 vinyl alkyl carbonates having unbranched or branched chains, vinyl aromatics, olefins, diolefins and haloethene compounds; and

B - crosslinkable comonomers, comprising crosslinkable N-methylol groups or their derivatives which are etherified with C1-C6 alkanols, preferably N-methylol amide derived from acrylic acid and methacrylic acid, more preferably one, or a combination, of N-methylolacrylamide and N-(N-butoxymethyl)acrylamide;

and wherein it also contains Component C, an ammonium salt having the following formula (I):



where m is a positive integer, preferably selected from among 1, 2 and 3, and

X represents organic or inorganic acid radicals,

wherein the organic or inorganic acids formed from X and hydrogen ions have a primary pK_a of less than 4.74, preferably less than or equal to 3.5 and greater than or equal to 1, as measured at 25°C and 1 atm, in 1 mol/L aqueous solution

the pH value of the resultant aqueous dispersion is adjusted to greater than or equal to 4.7 and less than or equal to 8, preferably greater than or equal to 4.7 and less than

or equal to 5.5, more preferably greater than or equal to 5 and less than or equal to 5.5; pH value analyzed by Mettler Toledo S220 SevenCompact pH/Ion according to its Instruction book.

The pK_a in the present invention represents the ability of an acid to dissociate hydrogen ions and refers to the negative logarithm of the acid dissociation constant K_a , i.e.:

$$pK_a = -\log_{10} K_a$$

the pK_a of common organic or inorganic acids can be obtained from LANGE'S HANDBOOK OF CHEMISTRY Science Press 1991 1st edition. For example, the primary pK_a of some organic or inorganic acids are listed in the following table 1:

Source: Table 5-7 and Table 5-8 Proton transfer reaction in above handbook.

Table 1

Citric acid	3.128
Acetic Acid	4.76
Hydrochloric acid	-6.1
Oxalic acid	1.27
Benzenesulfonic acid	0.7
Tartaric acid	3.04

The primary pK_a of these acids refers to the value when an organic acid or an inorganic acid loses the first hydrogen ion; if an organic or inorganic acid has multiple hydrogen ions, the value when it loses the second hydrogen ion is the secondary pK_a .

The aqueous dispersion as mentioned above, it is a single package product.

The aqueous dispersion as mentioned above, wherein the content of alkyl alcohol polyoxyethylene ethers and/or alkylphenol polyoxyethylene ethers and or polyoxyethylene ether-polyoxypropylene ethers is lower than 1wt%; preferably lower than 0.1wt%; based on the total weight of monomers of Component A.

The aqueous dispersion as mentioned above, wherein the content of PVOH is greater than 2.5wt%; preferably greater than or equal to 2.5wt% and lower than or equal

to 5wt%; preferably greater than or equal to 3wt% and lower than or equal to 5wt%; based on the total weight of monomers of Component A.

The aqueous dispersion as mentioned above, wherein the organic or inorganic acids formed from X and hydrogen ions have a boiling point of greater than or equal to 120°C, preferably greater than or equal to 150°C, as measured at 25°C and 1 atm.

The aqueous dispersion as mentioned above, wherein the ammonium salt according to formula (I) have a solubility in water of greater than or equal to 30 g/L, preferably greater than or equal to 50 g/L, as measured at 25°C and 1 atm.

The aqueous dispersion as mentioned above, wherein Component C is an ammonium salt of organic acids and/or ammonium salt of an inorganic acid,

wherein the organic acids are acidic organic compounds having from 2 to 8 carbon atoms and containing a carboxyl group (-COOH) and a sulfonyl group (-SO₃H);

preference is given to the organic acids containing a carboxyl group (-COOH), and greater preference is given to one, or a combination, of mono-, di- and tri-carboxylic acids; or

preference is given to the organic acids containing a sulfonyl group (-SO₃H), and greater preference is given to one, or a combination, of p-toluenesulfonic, benzenesulfonic and methanesulfonic acids;

the ammonium salt of organic acids is one or more preferably selected from among ammonium citrate, ammonium oxalate, ammonium tartrate, ammonium p-toluenesulfonate, ammonium succinate, ammonium adipate and ammonium glutarate;

the ammonium salt of organic acids is one or more further preferably selected from among ammonium citrate, ammonium oxalate, ammonium tartrate and ammonium p-toluenesulfonate; further preferably one or more selected from among ammonium citrate, ammonium oxalate, ammonium tartrate;

the inorganic acid is an acidic inorganic compound;

the inorganic acid is one or more selected from among sulfuric, hydrochloric and phosphoric acids;

The ammonium salt of the inorganic acid is one or more preferably selected from among ammonium chloride and ammonium hydrogen sulfate.

The aqueous dispersion as mentioned above, further comprising a buffer solution.

The aqueous dispersion as mentioned above, further comprising Component F1, a buffer solution containing sodium acetate and acetic acid.

The aqueous dispersion as mentioned above, further comprising Component F2, a buffer solution containing sodium dihydrogen phosphate and disodium hydrogen phosphate.

The aqueous dispersion as mentioned above, wherein the amount of vinyl acetate and ethylene in Component A is greater than or equal to 90 wt%, preferably greater than or equal to 95 wt%, more preferably greater than or equal to 98 wt%, based on the total weight of monomers of Component A.

The aqueous dispersion as mentioned above, wherein the monomers of Component A are vinyl acetate and ethylene.

The aqueous dispersions as mentioned above, wherein the amount of the ammonium salt as Component C is between 0.1 and 5 wt%, preferably between 0.5 and 3 wt%, based on the total weight of monomers of Component A.

The aqueous dispersions as mentioned above, wherein the amount of the crosslinkable comonomer as Component B is between 0.1 and 5 wt%, preferably between 0.5 and 3 wt%, based on the total weight of monomers of Component A.

The aqueous dispersion as mentioned above, further comprising other comonomers as Component D, which is one or more selected from among acrylic acid and acrylamide.

The aqueous dispersion as mentioned above, wherein the aqueous polymer dispersion is an emulsion having a Brookfield viscosity between 5,000 and 12,000 mPa·s, preferably between 7,000 and 10,000 mPa·s, as measured according to the ST-2 Brookfield viscosity test method and having a rate of change in Brookfield viscosity of less than 100 wt%, preferably less than 30%, more preferably less than 10%, after 60 days of storage at 23°C; preferably a rate of change in Brookfield viscosity of less than 100 wt%, after 14 days of storage at 50°C.

The aqueous dispersion as mentioned above, wherein the glass transition temperature (T_g) of the dried product of the aqueous polymer dispersion ranges from -2°C to 10°C, preferably from 0°C to 5°C as measured according to ST-1.

A method for preparing the aqueous dispersion as mentioned above, wherein after the emulsion polymerization of Components containing A and B is completed,

Component C and/or Component C aqueous solution is added to obtain the aqueous dispersion.

The aqueous dispersion as mentioned above, wherein after the emulsion polymerization of Components containing A and B is completed, the pH value of the emulsion is greater than or equal to 4.7 and less than or equal to 8, preferably greater than or equal to 4.7 and less than or equal to 5.5; preferably greater than or equal to 5 and less than or equal to 5.5.

The preparation method as mentioned above, wherein Component C is dissolved in water in advance.

The aqueous dispersion as mentioned above, wherein the pH value of the Component C aqueous solution is greater than or equal to 4.7 and less than or equal to 8, preferably greater than or equal to 4.7 and less than or equal to 5.5; preferably greater than or equal to 5 and less than or equal to 5.5 .

The preparation method as mentioned above, wherein after the emulsion polymerization of Components containing A and B is completed, Component C and/or Component C aqueous solution is added in when the system temperature is lower than or equal to 70°C, preferably lower than or equal to 40°C.

The preparation method as mentioned above, after the addition of Component C and/or Component C aqueous solution, the pH value of the resultant aqueous dispersion is adjusted to greater than or equal to 4.5 and less than or equal to 8, preferably greater than or equal to 4.5 and less than or equal to 5.5, preferably greater than or equal to 5 and less than or equal to 5.5

The preparation method as mentioned above, preferably using acetic acid and/or Sodium hydroxide as the pH adjuster.

Use of the aqueous dispersion as mentioned above for interfacial bonding between polymeric porous materials

wherein the interfacial bonding between polymeric porous materials is that between one type or more types of materials selected from among fiber textile materials and polymeric foamed materials, preferably that between one type or more types of materials selected from the group consisting of synthetic fiber textile materials, synthetic fiber non-woven materials, natural fiber textile materials, natural fiber non-woven materials, regenerated cellulose materials, ethylene-vinyl acetate (EVA) copolymer foams and

polyurethane (PU) foams, more preferably that between that PU foams and synthetic fiber textile materials, or between PU foams and natural fiber textile materials, or between EVA copolymer foams and synthetic fiber textile materials, or between EVA copolymer foams and natural fiber textile materials.

Use of the aqueous dispersion as mentioned above for structural bonding between textile materials and non-woven materials.

A composite structure for insoles, comprising an artificial fiber textile material and a polymeric foamed material, which are held in place by bonding with the aforesaid aqueous dispersion.

Composite products are obtained in such a way that polymeric porous materials are interfacially bonded. Some of them often come into contact with water during use, or frequently need to be cleaned. Use fields of these composites include, for example, shoe liners, shoe inserts and sportswear. Composite products with poor water resistance are prone to degumming in contact with water, that is, interface debonding, leading to a short service life.

According to the use as described above, the interfacial bonding between polymeric porous materials is preferably the lamination of an artificial fiber textile material onto a polymeric foamed material.

According to the use as described above, the interfacial bonding between polymeric porous materials is preferably that between polyester or acrylic or cotton textile materials and EVA copolymer foams.

According to the use as described above, the aqueous polymer dispersion is applied onto the surfaces of the polymeric porous materials to be bonded, the resulting product being exposed to a heat source for a period of time.

According to the use as described above, uses in carpet area are excluded. Most conventional carpets comprise a primary backing with yarn tufts in the form of cut or uncut loops extending upwardly from the backing to form a pile surface. In the case of tufted carpets, the yarn is inserted into a primary backing by tufting needles and a pre-coat or binder is applied thereto. In the case of non-tufted or bonded pile carpets, the fibers are embedded and actually held in place by the binder composition.

According to the use as described above, the interfacial bonding between polymeric porous materials does not include the production of polymeric porous materials themselves using a binder, which mainly refers to the bonding together of fibrous polymer materials less than 5 mm in diameter. For example, in the process of manufacturing non-woven, a binder is used to form non-woven fabrics by bonding together the fibrous materials such as wood pulp fibers, rayon, cottons, wools and acetate fibers; or in the process of paper making, a binder is used to form paper webs, papers or cardboards by bonding pulp fibers together.

According to the use as described above, the aqueous polymer dispersion is applied onto the surfaces of the polymeric porous materials to be bonded, the resulting product being exposed to a heat source, at between 150 and 200°C, for a period of time between 25 and 120 seconds to complete the drying step; or the aqueous polymer dispersion is applied onto the surfaces of the polymeric porous materials to be bonded, the resulting product being exposed to a heat source, at between 100 and 110°C, for a period of time between 20 and 30 minutes to complete the drying step.

According to the use as described above, the aqueous polymer dispersion is applied onto the surfaces of the polymeric porous materials to be bonded using a roll coater with a certain pressure, and simultaneously completing the drying step therein.

According to the use as described above, after the drying step is completed using the roll coater, no further hot press treatment is required.

According to the use as described above, the coat weight of the aqueous polymer dispersion is between 120 and 210 g/m².

When the viscosity of the aqueous polymer dispersion is too low, the coating roller takes up a small amount of glue during the production, leading to a poor bonding effect of the product; while the viscosity of the aqueous polymer dispersion is too high, the coating roller takes up a large amount of glue, leading to excessive coat weight in the product and high consumption of the aqueous polymer dispersion and thus to diseconomy.

Component A – one or more monomers, selected from the group consisting of C1-C15 vinyl alkyl carbonates having unbranched or branched chains, vinyl aromatics, olefins, diolefins and haloethene compounds;

Preferred C1-C15 vinyl alkyl carbonates having unbranched or branched chains are selected from the group of vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl laurate, 1-methylvinyl acetate, vinyl pivalate and vinyl esters of α -branched monocarboxylic acids having up to 10 carbon atoms, for example VeoVa9 or VeoVa10, wherein vinyl acetate is particularly preferred.

The said component A can also be polymerized to form copolymers of vinyl acetate and ethylene, or copolymers of vinyl acetate and ethylene and one or more other vinyl monomers, such as vinyl acetate-ethylene-acrylate copolymers and vinyl acetate-ethylene-vinyl chloride copolymers.

Component D. Suitable comonomers, i.e. methacrylates or acrylates, are the esters of unbranched or branched alcohols having 1 to 15 atoms, for example methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, propyl acrylate, propyl methacrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate and norbornyl acrylate, wherein preference is given to methyl acrylate, methyl methacrylate, n-butyl acrylate and 2-ethylhexyl acrylate.

The polymers are prepared by the solution polymerization process, emulsion polymerization process or suspension polymerization process, preferably by the emulsion polymerization process, in which the polymerization temperature is generally from 20°C to 100°C, preferably from 45°C to 80°C. The polymerization of gaseous monomers, such as ethylene, 1,3-butadiene or vinyl chloride, can also be carried out under a pressure of generally from 5 bar to 100 bar (abs.). The pH range desired for the polymerization, which is in general between 2.5 and 10, preferably 3 and 8, can be established in a known manner by acids, bases or customary buffer salts, such as alkali metal phosphates or alkali metal carbonates.

The polymerization is initiated by a water-soluble or monomer-soluble initiator or redox initiator combinations customary for emulsion polymerization or suspension polymerization. Examples of water-soluble initiators are the sodium, potassium and ammonium salts of peroxydisulfuric acid, hydrogen peroxide, t-butyl peroxide (e.g. t-butyl hydroperoxide), potassium peroxydisulfate, t-butyl peroxy-pivalate and azobisisobutyronitrile. These initiators are generally used in an amount of 0.01 to 3% by weight in each case based on the total dry weight of the monomers.

As redox initiators, use is made of combinations of the initiators above-mentioned in combination with reducing agents. Suitable reducing agents are the sulfites of alkali metals or of ammonium, the bisulfites of alkali metals or of ammonium, the derivatives of sulfoxylic acid of alkali metals or of ammonium, or sulfinates of alkali metals or of ammonium. The amount of said reducing agent is generally from 0.01 to 3 % by weight in each case based on the total dry weight of the monomers of Component A.

To control the molecular weight, regulating substances can be used during the polymerization. If regulators are used, they are usually employed in amounts of from 0.01 to 5.0% by weight, based on the total dry weight of the monomers of Component A, and are introduced separately or premixed with reaction components. Examples of such substances are n-dodecyl mercaptan, t-dodecyl mercaptan, mercaptopropionic acid, methyl mercaptopropionate, isopropanol and acetaldehyde.

Suitable protective colloids for the polymerization are polyvinyl alcohols; polyvinyl acetals; polyvinylpyrrolidones; polysaccharides in water-soluble form, e.g. starches (amylose and amylopectin), celluloses and their carboxymethyl, methyl, hydroxyethyl, hydroxypropyl derivatives, dextrans and cyclodextrins.

The polymerization can be carried out successively or continuously.

After conclusion of the polymerization, a post-polymerization can be carried out to remove residual monomers using known methods, in general by means of a post-polymerization initiated by a redox catalyst. Volatile residual monomers can also be removed by means of distillation, preferably under reduced pressure, and, if appropriate, with inert entrainer gases such as air, nitrogen or steam being passed through or over the polymerization mixture. The aqueous polymer dispersions obtainable in this way have a solids content of from 40 to 70% by weight.

Protective colloids (used as spray additives), defoamers and anti-caking agents can be added to the aqueous polymer dispersions herein for subsequent preparation of water-redispersible polymer powders by means of a traditional process: fluidized-bed drying, freeze drying or spray drying.

Sample Preparation and Test Method

Sample preparation and method ST-1 for glass transition temperature measurement:

sample a certain amount of the aqueous polymer dispersion and dry at 25°C overnight and then let stand in a vacuum oven at 40°C for 24 hours to obtain an dried polymer product.

Take 8-15 mg of the dry product and heat from -80°C to 100°C at a heating rate of 10K/min using NETZSCH F203 analyzer in a closed sample cell in protective nitrogen atmosphere, according to ISO11357-1 2014, to determine the glass transition temperature (T_g) of the dried polymer product.

Method ST-2 for viscosity inspection:

The viscosity of the sample is determined with a Brookfield RV/DV rotational viscometer according to GB/T 11175-2002 using spindle No. 4 at 20 rpm at 25°C.

Lab-scale sample preparation method for peeling strength test:

Cut a piece of polyester fabric and a piece of Polyurethane foam to size 20 × 15 cm in reference to the test method improved as per ISO11339-2010. Lay the Polyurethane foam on the glass, the upper and lower ends being fixed with 1.8cm wide 3M electrical tape. Spread the aqueous polymer dispersion over the foam using a doctor blade, scraped tight with a 300-μm scraper bar. Place the foam sample in an oven for heat treatment at 160°C for 30s before removing.

Spread another layer of aqueous polymer dispersion on the glass by a 300-μm scraper bar. The polyester fabric is layed on the glass, and pressed twice by a glass rod before removing.

Lay Polyurethane foam on the polyester fabric and press it twice with a 2-kg pressure roller. Place the fabric sample in an oven for heat treatment at 160°C for a while before removing. The dry fabric sample is prepared.

Method ST-4 for wet bonding strength test:

A dry fabric sample mentioned above is soaked in water at 25°C for 1 hour and then taken out. The resulting wet fabric is then tested for 180° peeling strength in reference to the method shown in Figure 1 of ISO11339-2010 on Shandong Labthink XLW (G)-PC smart electronic tensile tester. The wet sample, with its width remaining 25.4mm (1 inch), is vertically stretched for a distance of 40mm. The stretches up to 2mm at both the

beginning and end of the test are not taken into account. The stretching speed is 100mm/min.

Detailed Description of the Preferred Embodiments

The aqueous polymer dispersions in Examples and Comparative Examples were prepared according to the basic formulation in Table 2. The basic formulation in Table 2 contains the type of monomers, amount of monomers, type of protective colloid, initiator system, initial charge and subsequent feed of each raw material, and the like.

The amounts in the present invention are, unless otherwise specified, in parts by weight.

In Tables 2, unless otherwise specified, the part by weight of each raw material are calculated on the basis of 100 parts by weight of the vinyl acetate and ethylene monomers.

In Tables 2, the concentration of a solution is the weight of solute divided by the weight of solution, in the form of percent by weight.

Unless otherwise specified, pH value in present invention is analyzed by Mettler Toledo S220 SevenCompact pH/Ion according to its Instruction book.

NMA refers to N-Methylolacrylamide.

Ammonium citrate, sodium citrate, ammonium acetate, ammonium chloride, ammonium oxalate, ammonium p-toluenesulfonate, and ammonium tartrate are all commercially available products.

PVOH 04/88 20 wt% aqueous solution, having an alcoholysis degree of 88 wt%, 4 wt% aqueous solution of which has a viscosity of 4 mPa·s at 20°C according to DIN 53015, is prepared into a 20 wt% aqueous solution before use.

PVOH 25/88 10.3 wt% aqueous solution, having an alcoholysis degree of 88 wt%, 4 wt% aqueous solution of which has a viscosity of 25 mPa·s at 20°C according to DIN 53015, is prepared into a 10.3 wt% aqueous solution before use.

tBHP 10 wt% aqueous solution refers to t-butyl hydroperoxide, which is prepared into a 10 wt% aqueous solution before use.

FF6M 5 wt% aqueous solution refers to disodium hydroxysulfinoacetate (purchased from Brüggemann Chemical Incorporates), which is prepared into a 5 wt% aqueous solution before use.

FAS 1wt% aqueous solution refers to ferrous ammonium sulfate, which is prepared into a 1 wt% aqueous solution before use.

The raw materials primarily adjusted in Examples and Comparative Examples were referred to Table 2. The procedure was similar to that of Example 1.

Table 2

	Ex.1	C.Ex.2	C.Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	C.Ex.8
Vinyl acetate	82.8	82.8	82.8	82.8	82.8	82.8	82.8	82.8
Ethylene	17.2	17.2	17.2	17.2	17.2	17.2	17.2	17.2
NMA	1.53	1.53	1.53	1.53	1.53	1.53	1.53	1.53
Water	40.68	40.68	40.68	40.68	40.68	40.68	40.68	40.68
PVOH 04/88 20 wt% aqueous solution	4.83	4.83	4.83	4.83	4.83	4.83	4.83	4.83
PVOH 25/88 1 0.3 wt% aqueous solution	26.48	26.48	26.48	26.48	26.48	26.48	26.48	26.48
Sodium acetate	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Acetate	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42
FAS 1wt% aqueous solution	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
tBHP 10 wt% aqueous solution	4.24	4.24	4.24	4.24	4.24	4.24	4.24	4.24
FF6M 5 wt% aqueous solution	4.24	4.24	4.24	4.24	4.24	4.24	4.24	4.24

Ammonium citrate	1.19							/
Sodium citrate		1						/
Ammonium acetate			1					/

Ammonium chloride				1				/
Ammonium oxalate					1			/
Ammonium p-toluenesulfonate						1		/
Ammonium tartrate							1	/

* The amount of ethylene used in Table 2 refers to the amount of ethylene gas fed in each example

Example Ex.1

Step 1. A premix of 700g of deionized water, 114g of PVOH 04/88 20 wt% aqueous solution, 625g of PVOH 25/88 10.3wt%aqueous solution and 9g of sodium acetate was added into a 5-liter reactor. The premix was mixed well and its pH was adjusted to 5 with acetic acid before 7g of FAS was added.

The reactor was heated to 70°C, into which 1514g of vinyl acetate and 291g of ethylene were added, and the pressure in the reactor was maintained below 45 bar.

The temperature was raised to 70°C while 10 wt% t-butyl hydroperoxide aqueous solution and 5 wt% FF6M aqueous solution were added dropwisely with a pump to initiate reaction and the dropwise addition continued until the reaction was completed. After the initiation reaction, 440 g of vinyl acetate and a mixed solution of 144g of deionized water and 36 g of N-Methylolacrylamide were added.

Step 2. After reaction for 4 hours, the mixture was transferred to a degassing tank, where 1 g of mineral oil-based defoamer and 28 g of ammonium citrate (as aqueous solution) were added, and after degassing for 30 minutes, the aqueous polymer dispersion was obtained. The product's Tg is 0°C; solid content is 56wt%.

The other examples and comparative examples were prepared in the same manner as in Ex. 1, except that ammonium citrate was replaced with the corresponding other ammonium salts in Table 2.

Comparative Example C.Ex.0 was prepared in the same manner as in Ex. 1 and also contained 28 g of citric acid. However, after Step 2, acetic acid was additionally added to adjust the pH of aqueous polymer dispersion to 4.4.

Table 3.1

	Ex.1	C.Ex.2	C.Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	C.Ex.8	C.Ex.0
Initial									
pH value	5.35	5.42	5.01	4.70	4.97	4.80	5.00	5.00	4.40
Bookfield viscosity mPa.s	9640	7800	8520	8140	9100	9200	7600	8500	8200
after 60 days of storage at 23°C									
pH value	5.36	5.39	4.97	4.56	4.90	4.71	4.90	4.92	4.20
Brookfield viscosity mPa.s	9280	7200	9360	10420	9100	11380	7900	8600	Exceeding instrument range
Rate of change	-3.73%	-7.69%	9.86%	28.01%	0.00%	23.70%	1.04%	1.18%	/
Gel phenomenon	No	No	No	No	No	No	No	No	Gel

Test wet bonding strength as per ST-4 conditions after the products have been stored at 25°C for more than a week. Table 3.2 shows the performance test results of Examples 1, 4-7 and Comparative Examples 2, 3 and 8.

Table 3.2

	Ex.1	C.Ex.2	C.Ex.3	Ex.4	Ex.5	Ex.6	Ex.7	C.Ex.8
Time period within which the strength >6 N/inch (min)	<2	<10	10	<3	<2	<3	<3	10
Time period within which the strength >11 N/inch (min)	3	15	/	<3	<2	<3	<3	15
Time period within which the strength >17 N/inch (min)		/	/	/	3	7	15	/

Table 3.2 shows that three samples having a wet-bonding strength of greater than 11 N/inch in a short time (within 3 minutes) were obtained with Examples 1 and 4-7. In particular, by using the examples containing ammonium oxalate and ammonium p-toluenesulfonate, two samples having a wet bonding strength of more than 17 N/inch within 10 minutes, exhibiting particularly excellent performance. The wet-bond strength of these Examples was high and built up fast.

Comparative Example 2, which used sodium citrate, had a wet-bond strength and a build-up speed close to those of the blank C.Ex. 8, and was not effective.

In Comparative Example 3, due to ammonium acetate, the organic acid formed by acetate radicals and hydrogen ions had a primary pKa of 4.73, resulting in a poor wet-bond strength.

The stability of Example 1 of the present invention is shown in Table 4: the aqueous polymer dispersion containing ammonium citrate had very little change in viscosity without gelling when stored under higher temperature for a long period of time and could be used in actual applications.

Table 4

Ex. 1	Initial status	14 days at 23°C	Rate of change	14 days at 50°C	Rate of change
Brookfield viscosity mPa.s	9640	9280	-3.7%	10400	7.9%
pH	5.35	5.36	0.2%	5.32	-0.6%

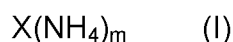
What is claimed is:

1. An aqueous polymer dispersion, wherein the said polymer is obtained by the polymerization of a composition comprising Components A and B:

A – one or more monomers, selected from the group consisting of C1-C15 vinyl alkyl carbonates having unbranched or branched chains, vinyl aromatics, olefins, diolefins and haloethene compounds; and

B - crosslinkable comonomers, comprising crosslinkable N-methylol groups or their derivatives which are etherified with C1-C6 alkanols, preferably N-methylol amide derived from acrylic acid and methacrylic acid, more preferably one, or a combination, of N-methylolacrylamide and N-(N-butoxymethyl)acrylamide;

and wherein it also contains Component C, an ammonium salt having the following formula (I):



where m is a positive integer, preferably selected from among 1, 2 and 3, and

X represents organic or inorganic acid radicals,

wherein the organic or inorganic acids formed from X and hydrogen ions have a primary pK_a of less than 4.74, preferably less than or equal to 3.5 and greater than or equal to 1, as measured at 25°C and 1 atm, in 1 mol/L aqueous solution

the pH value of the resultant aqueous dispersion is adjusted to greater than or equal to 4.7 and less than or equal to 8, preferably greater than or equal to 4.7 and less than or equal to 5.5, more preferably greater than or equal to 5 and less than or equal to 5.5; pH value analyzed by Mettler Toledo S220 SevenCompact pH/Ion according to its Instruction book.

2. The aqueous dispersion as mentioned in Claim 1, it is a single- package product.

3. The aqueous dispersion as mentioned in Claim 1 or 2, further comprising a buffer solution; preferable comprising Component F1 or F2, F1 is a buffer solution containing sodium acetate and acetic acid; F2 is a buffer solution containing sodium dihydrogen phosphate and disodium hydrogen phosphate.

4. The aqueous dispersion as mentioned in any of Claim 1-3, wherein Component C is an ammonium salt of organic acids and/or ammonium salt of an inorganic acid,

wherein the organic acids are acidic organic compounds having from 2 to 8 carbon atoms and containing a carboxyl group (-COOH) and a sulfonyl group (-SO₃H);

preference is given to the organic acids containing a carboxyl group (-COOH), and greater preference is given to one, or a combination, of mono-, di- and tri-carboxylic acids; or

preference is given to the organic acids containing a sulfonyl group (-SO₃H), and greater preference is given to one, or a combination, of p-toluenesulfonic, benzenesulfonic and methanesulfonic acids;

the ammonium salt of organic acids is one or more preferably selected from among ammonium citrate, ammonium oxalate, ammonium tartrate, ammonium p-toluenesulfonate, ammonium succinate, ammonium adipate and ammonium glutarate;

the ammonium salt of organic acids is one or more further preferably selected from among ammonium citrate, ammonium oxalate, ammonium tartrate and ammonium p-toluenesulfonate; further preferably one or more selected from among ammonium citrate, ammonium oxalate, ammonium tartrate;

the inorganic acid is an acidic inorganic compound;

the inorganic acid is one or more selected from among sulfuric, hydrochloric and phosphoric acids;

The ammonium salt of the inorganic acid is one or more preferably selected from among ammonium chloride and ammonium hydrogen sulfate.

5. The aqueous dispersion as mentioned in any of Claim 1-4, wherein the amount of vinyl acetate and ethylene in Component A is greater than or equal to 90 wt%, preferably greater than or equal to 95 wt%, more preferably greater than or equal to 98 wt%, based on the total weight of monomers of Component A.

6. The aqueous dispersions as mentioned in any of Claim 1-5, wherein the amount of the ammonium salt as Component C is between 0.1 and 5 wt%, preferably between 0.5 and 3 wt%, based on the total weight of monomers of Component A.

7. The aqueous dispersions as mentioned in any of Claim 1-6, wherein the amount of the crosslinkable comonomer as Component B is between 0.1 and 5 wt%, preferably between 0.5 and 3 wt%, based on the total weight of monomers of Component A.

8. The aqueous dispersion as mentioned in any of Claim 1-7, wherein the aqueous polymer dispersion is an emulsion having a Brookfield viscosity between 5,000 and 12,000 mPa·s, preferably between 7,000 and 10,000 mPa·s, as measured according to the ST-2 Brookfield viscosity test method and having a rate of change in Brookfield viscosity of less than 100 wt%, preferably less than 30%, more preferably less than 10%, after 60 days of storage at 23°C; preferably a rate of change in Brookfield viscosity of less than 100 wt%, after 14 days of storage at 50°C.

9. The aqueous dispersion as mentioned in any of Claim 1-8, wherein the glass transition temperature (T_g) of the dried product of the aqueous polymer dispersion ranges from -2°C to 10°C, preferably from 0°C to 5°C as measured according to ST-1.

10. A method for preparing the aqueous dispersion as mentioned in any of Claim 1-9, wherein after the emulsion polymerization of Components containing A and B is completed, Component C and/or Component C aqueous solution is added to obtain the aqueous dispersion.

11. The aqueous dispersion as mentioned in Claim 10, wherein after the emulsion polymerization of Components containing A and B is completed, the pH value of the emulsion is greater than or equal to 4.7 and less than or equal to 8, preferably greater than or equal to 4.7 and less than or equal to 5.5; preferably greater than or equal to 5 and less than or equal to 5.5 .

12. The aqueous dispersion as mentioned in Claim 10 or 11, wherein the pH value of the Component C aqueous solution is greater than or equal to 4.7 and less than or equal to 8, preferably greater than or equal to 4.7 and less than or equal to 5.5; preferably greater than or equal to 5 and less than or equal to 5.5 .

13. The preparation method as mentioned in any of Claim 10-12, wherein after the emulsion polymerization of Components containing A and B is completed, Component C and/or Component C aqueous solution is added in when the system temperature is lower than or equal to 70°C, preferably lower than or equal to 40°C.

14. Use of the aqueous dispersion as mentioned in any of Claim 1-9 for interfacial bonding between polymeric porous materials,

wherein the interfacial bonding between polymeric porous materials is that between one type or more types of materials selected from among fiber textile materials and polymeric foamed materials, preferably that between one type or more types of materials selected from the group consisting of synthetic fiber textile materials, synthetic fiber non-woven materials, natural fiber textile materials, natural fiber non-woven materials, regenerated cellulose materials, ethylene-vinyl acetate (EVA) copolymer foams and polyurethane (PU) foams, more preferably that between that PU foams and synthetic fiber textile materials, or between PU foams and natural fiber textile materials, or between EVA copolymer foams and synthetic fiber textile materials, or between EVA copolymer foams and natural fiber textile materials.

15. A composite structure for insoles, comprising an artificial fiber textile material and a polymeric foamed material, which are held in place by bonding with the aforesaid aqueous dispersion in any of Claim 1-9.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/094427

A. CLASSIFICATION OF SUBJECT MATTER

C09J 131/04(2006.01)i; C09J 11/06(2006.01)i; D04H 1/587(2012.01)i; D04H 1/64(2012.01)i; A61F 13/15(2006.01)i; C08L 33/26(2006.01)i; C09J 123/08(2006.01)i; C08F 218/08(2006.01)i; C09J 133/26(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09J131/-; C09J11/-; D04H1/-; A61F13/-; C08L33/-; C08F218/-

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;EPODIC;STN:aqueous, binder, adhesive, fiber?, nowoven, emulsion, latex, acetate, ethylene, vinyl, VAE, +methylo, acrylamide, NMA, ammonium, citrate, 3458-72-8, 12125-02-9, 631-61-8

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012220968 A1 (CELANESE INTERNATIONAL CORPORATION) 30 August 2012 (2012-08-30) description, paragraphs [0014], [0032], [0037], [0046]	1-15
Y	US 2004063809 A1 (ROHM & HAAS CO.) 01 April 2004 (2004-04-01) description, paragraphs [0008]-[0010], [0045], [0056]	1-15
A	CN 104371605 A (CHINESE ACAD FORESTRY INST. CHEM. IND. FORE.) 25 February 2015 (2015-02-25) description, paragraphs [0005]-[0014]	1-15
A	US 2006118005 A1 (3M INNOVATIVE PROPERTIES CO.) 08 June 2006 (2006-06-08) description, paragraphs [0023]-[0032]	1-15
A	US 4449978 A (AIR PRODUCTS AND CHEMICALS INC.) 22 May 1984 (1984-05-22) abstract, description, column 2 lines 29-54	1-15

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

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 “O” document referring to an oral disclosure, use, exhibition or other means
 “P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
 “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
 “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
 “&” document member of the same patent family

Date of the actual completion of the international search

22 March 2019

Date of mailing of the international search report

08 April 2019

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2018/094427

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
US	2012220968	A1	30 August 2012	CN	102650094	A	29 August 2012
				CA	2766646	A1	28 August 2012
				JP	2012179355	A	20 September 2012
				US	8785714	B2	22 July 2014
				EP	2491910	A1	29 August 2012
				MX	2012002485	A	05 September 2012
				RU	2012106807	A	27 August 2013
				EP	2491910	B1	04 June 2014
US	2004063809	A1	01 April 2004	CN	1487042	A	07 April 2004
				CN	1283739	C	08 November 2006
CN	104371605	A	25 February 2015	None			
US	2006118005	A1	08 June 2006	CA	2590704	A1	15 June 2006
				CN	101076576	A	21 November 2007
				CN	101076576	B	13 February 2013
				KR	101228275	B1	30 January 2013
				EP	1819796	A2	22 August 2007
				MX	2007006585	A	22 April 2008
				CA	2590704	C	23 June 2015
				JP	2008523208	A	03 July 2008
				US	7851522	B2	14 December 2010
				KR	20070085845	A	27 August 2007
				WO	2006062713	A3	01 March 2007
				WO	2006062713	A2	15 June 2006
				US	4449978	A	22 May 1984
EP	0121864	A3	05 December 1984				
EP	0121864	A2	17 October 1984				
JP	S59187658	A	24 October 1984				
JP	S6244056	B2	18 September 1987				