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(21) International Application Number: PCT/US98/07017 (22) International Filing Date: 7 April 1998 (07.04.98) (30) Priority Data: 60/042,710 7 April 1997 (07.04.97) US 09/052,482 31 March 1998 (31.03.98) US (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US). (72) Inventors: SHARMA, Mahendra, Kumar; 2600 Brighton Court, Kingsport, TN 37660 (US). GARRITY, Richard, Irving; 2216 Glenwood Street, Kingsport, TN 37664 (US). (74) Agent: GRAVES, Bernard, J., Jr.; P.O. Box 511, Kingsport, TN 37662-5075 (US).		(81) Designated States: DE, JP. Published <i>With international search report.</i>
(54) Title: WATERBORNE SEALER FOR POROUS STRUCTURAL MATERIALS (57) Abstract The present invention relates to sealer compositions containing acrylic polymer dispersions used to treat porous surfaces such as concrete, brick, masonry, and wood, to provide protection from water penetration. The waterborne sealer provides flexible, continuous and fast drying films when applied to porous substrates. This coated film provides for easy cleaning of coated porous articles and also serves to render such articles substantially impervious to water penetration.		

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TITLE OF THE INVENTION

WATERBORNE SEALER FOR POROUS STRUCTURAL MATERIALS

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CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit under 35 USC § 119 of U.S. Provisional Application Serial No. 60/042,710 filed on April 7, 1997.

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FIELD OF THE INVENTION

The present invention relates to sealer compositions containing acrylic
15 polymer dispersions and more particularly, to waterborne sealers used to treat
porous surfaces to provide protection from water penetration. The waterborne
sealers provide flexible, continuous and fast drying films when applied to porous
substrates. This coated film provides for easy cleaning of coated porous substrates.
The invention further relates to methods for applying waterborne sealers to porous
20 substrates.

BACKGROUND OF THE INVENTION

Porous substrates such as brick, concrete, masonry and wood are very prone
25 to damage from weather, especially on exposure to water. To prevent penetration of
water into these rigid structural materials, it is desirable to coat these objects with
waterproofing and/or sealing formulated products. Several products have been
developed for waterproofing and sealing rigid objects.

U.S. Patent No. 5,482,737 discloses a method of waterproofing and sealing
30 a rigid structural material using a styrene polymeric film cast from an organic
solvent. The coating may be reapplied to imperfections and damaged areas to repair
the continuous film. The coating composition requires solvent use to cast a film.

- 2 -

U.S. Patent 5,496,615 discloses a waterproofing membrane with a carrier layer having a non-bituminous pressure-adhesive waterproofing adhesive, a protective layer coated on the non-bituminous adhesive, and a second waterproofing adhesive layer on the other face of the carrier to permit adherence of the membrane to a cementitious surface and to permit concrete to be cast against the non-bituminous layer.

U.S. Patent No. 5,527,853 discloses a shelf stable fast-cure aqueous coating. The coating contains an anionically stabilized latex, a polyfunctional amine and a volatile base in an amount sufficient to deprotonate the conjugate acid of an amine.

U.S. Patent No. 5,527,931 discloses organosilane compounds used for treating porous substrates to render them repellant to water-based and oil-based challenges.

U.S. Patent No. 5,037,873 discloses aqueous silane emulsion compositions containing hydrolyzable silanes, water thickening agents, water and optional buffers, biocides and water beading additives.

U.S. Patent No. 5,346,943 discloses a water-based wax-free stable emulsion composition useful as a water sealer for wood, concrete and porous materials. The water-based sealer composition forms a non-drying film that is water-repellent, flexible, self-sealing and allows passage of water vapor. The water-based composition contains less than 400 grams per liter of volatile organic compounds.

U.S. Patent No. 5,258,424 discloses an aqueous coating composition containing an acrylic resin emulsion and hydrophilic microparticles. The coating composition is storage stable and capable of forming a coating with moisture permeability, water resistance, flexibility and durability.

SUMMARY OF THE INVENTION

The present invention provides waterborne acrylic polymer dispersions useful in water sealing and protecting porous substrates by forming a coherent, continuous and flexible coating film on substrates such as wood, concrete, road,

- 3 -

road marking, and masonry structural materials. Alternatively, the compositions of the present invention may be dispersed in the porous substrates during their manufacture, thereby rendering such substrates substantially impervious to water penetration.

- 5 The invention further provides methods for water sealing and protecting porous substrates by forming a coherent, continuous and flexible coating film on wood, concrete, road, road marking, and masonry structural materials.

DETAILED DESCRIPTION OF THE INVENTION

- 10 The present invention provides a waterborne acrylic polymer dispersion comprising:

- (a) an acrylic copolymer prepared from methyl methacrylate and butyl acrylate monomers in a ratio of from 45:55 to 60:40 of methyl methacrylate to
15 butyl acrylate, wherein the glass transition temperature (T_g) of the acrylic copolymer is from 0 °C to 30 °C;

- (b) at least one surfactant, wherein said surfactant has a molecular weight of less than 850; and

- (c) water in the amount of 35 to 90 weight percent;

- 20 wherein the waterborne acrylic copolymer dispersion has about 30 to about 60 weight percent solids content, based on the total weight of the dispersion, said solids having a particle size of about 50 to about 350 nm.

- The polymers above, in addition to other polymers are useful in coating porous substrates and, in particular, masonry building materials and structures such
25 as cement, concrete blocks, bricks, and mortar. The dispersions can be used as a coating composition or can be admixed with the materials as they are prepared. For example, the dispersions can be admixed with mortar used in building a brick wall or structure.

- 4 -

Thus, the present invention provides porous substrate comprising a surface having a continuous transparent coating thereon, said coating derived from a waterborne acrylic polymer dispersion comprising:

(a) an acrylic polymer prepared from acrylate monomers having the formula $\text{CH}_2=\text{C}(\text{R}_2)\text{COOR}_1$, wherein R_1 and R_2 are independently selected from C_1 to C_4 straight or branched chain alkyl groups, and R_2 may be hydrogen; wherein the glass transition temperature (T_g) of the acrylic copolymer is from 0°C to 30°C ;

(b) at least one surfactant;

(c) 35 to 90 weight percent water;

wherein the waterborne acrylic polymer dispersions have about 30 to about 60 weight percent solids content based on the total weight of the dispersion and a particle size of about 50 to about 350 nm.

As a further aspect of the invention, there is provided a method for waterproofing a porous surface which comprises:

(I) applying a waterborne acrylic polymer dispersion comprising:

(a) an acrylic copolymer prepared from acrylate monomers having the formula $\text{CH}_2=\text{C}(\text{R}_2)\text{COOR}_1$, wherein R_1 and R_2 are independently selected from C_1 to C_4 straight or branched chain alkyl groups, and R_2 may also be hydrogen; wherein the glass transition temperature (T_g) of the acrylic copolymer is from 0°C to 30°C ;

(b) at least one surfactant, wherein said surfactant has a molecular weight of less than 850; and

(c) water in the amount of 35 to 90 weight percent;

wherein the waterborne acrylic copolymer dispersion has about 30 to about 60 weight percent solids content, based on the total weight of the dispersion, said solids having a particle size of about 50 to about 350 nm; and

(II) allowing said composition to dry to form a continuous film.

- 5 -

Also, as noted above, the dispersions may be utilized in the production of such masonry products, to improve their resistance to the penetration of water.

Accordingly, as a further aspect of the invention, there is provided a masonry product or structure having dispersed therein, during its manufacture or use, a

5 waterborne acrylic polymer dispersion comprising:

(a) an acrylic polymer prepared from acrylate monomers having the formula $\text{CH}_2=\text{C}(\text{R}_2)\text{COOR}_1$, wherein R_1 and R_2 are independently selected from C_1 to C_4 straight or branched chain alkyl groups, and R_2 may be hydrogen; wherein the glass transition temperature (T_g) of the acrylic copolymer is from

10 0 °C to 30 °C;

(b) at least one surfactant;

(c) 35 to 90 weight percent water;

wherein the waterborne acrylic polymer dispersions have about 30 to about 60 weight percent solids content based on the total weight of the dispersion and a
15 particle size of about 50 to about 350 nm.

Waterborne acrylic polymer dispersions used in the present invention can be formed using a wide range of monomers. In preparing these waterborne acrylic polymer dispersions, polymerization may be carried out in conventional ways using
20 appropriate amounts of a monomer and/or mixture of monomers, surfactants, polymerization initiators, chain transfer agents and aqueous medium.

Preferred monomer compositions in the acrylic polymer contain methyl methacrylate (MMA)/butyl acrylate (BA) in a ratio ranging from 45/55 to 60/40. The glass transition temperature (T_g) of the acrylic polymers used in the sealer
25 formulation is in the range of 0 °C to 30 °C, preferably 5 to 25°C. Polymers With a $T_g < 0$ °C form a sticky film, and polymer with $T_g > 30$ °C require plasticizers to form clear films. The waterborne acrylic polymer dispersions of the present invention completely eliminate the need for plasticizers to formulate coherent, transparent, continuous and glossy films which act as barriers to water penetration
30 when applied to porous substrates.

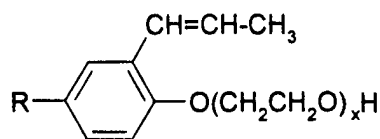
- 6 -

Surfactants used in polymerizing acrylic monomers may be water soluble or dispersible surfactants, preferably with a hydrophilic-lipophilic balance (HLB) value greater than 7.0. The amount of surfactant used as an emulsifying ingredient in the present invention is preferably in the range of 0.01 to 1.0 wt %, more
5 preferably 0.05 to 0.5 wt % based on total weight of the acrylic emulsion latex. The surfactant should provide small latex size particles with minimum incorporation of surfactant. Examples of useful surfactants include, but are not limited to, ionic and nonionic surfactants such as alkyl polyglycol ethers including ethoxylation products of lauryl, oleyl, and stearyl alcohols; alkyl phenol polyglycol
10 ethers such as ethoxylation products of octyl-or nonylphenol, diisopropyl phenol, triisopropyl phenol; alkali metal ammonium salts of alkyl, aryl or alkylaryl sulfonates, sulfates, phosphates, and the like, including sodium lauryl sulfate, sodium octylphenol glycol ether sulfate, sodium dodecylbenzene sulfonate, sodium lauryldiglycol sulfate, ammonium tritertiarybutyl phenol, penta- and octa-glycol
15 sulfonates, sulfosuccinate salts such as disodium ethoxylated nonylphenol half ester of sulfosuccinic acid, disodium n-octyldecyl sulfosuccinate, sodium dioctyl sulfosuccinate, and the like.

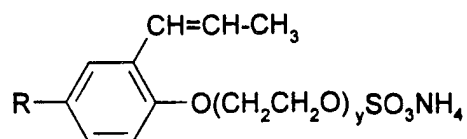
The surfactant may also be reactive anionic or nonionic surfactants possessing styrene or allyl groups. Examples of useful surfactants include surface
20 active monomers sold by PPG Industries, Inc., under the trademark SAM 181, 183, 184, and 211 which are anionic sulfates or sulfonates and SAM 185-187 which are nonionic. Other reactive surfactants include those sold by Daiichi Kogyo Seiyaku under the trademark AQUARON. Examples of AQUARON surfactants includes compounds of the formulae

25

- 7 -



and



wherein R is a C₁-C₁₂ alkyl group and x and y are integers of from 1 to 5. Other reactive surfactants include the sodium alkyl allyl sulfosuccinate sold by Henkel,
 5 under the trademark TREMLF-40. The incorporation of large amount of surfactant into the acrylic polymer dispersion is deleterious to water sealing and protecting hard surfaces.

Inorganic and organic initiators may also be used during polymerization of the acrylic emulsion. Useful initiators include: ammonium persulfate, potassium
 10 persulfate, hydrogen peroxide, dibenzoyl peroxide, lauryl peroxide, ditertiary butyl peroxide, 2,2'-azobisisobutyronitrile, t-butylperoxide, t-butyl hydroperoxide, benzoyl peroxide, sodium formaldehyde sulfoxylate and the like. A preferred initiator is ammonium persulfate.

In preparing the acrylic polymer dispersion of the present invention, a 10 to
 15 30 weight percent portion of the acrylic emulsion may be heated to 40° to 95°C., preferably 50°C to 80°C., and an aqueous solution of initiator and any remaining emulsion slowly injected using separate pumps at different injection rates into the reaction mixture. The polymer dispersions form a clear film without additives such as solvents, plasticizers and coalescents.

20 However, optional additives may be incorporated in the acrylic polymer dispersions to enhance protection and film forming properties for water sealing applications. For example, wetting agents, leveling agents, defoaming agents, lubricants, ultraviolet light absorbing agents, preservatives, and antioxidants can be

- 8 -

included in the waterborne acrylic polymer dispersion. Examples of suitable additives include defoamers such as 2-ethylhexanol, hydrocarbon oil, silicone compounds, silicone emulsions, siloxane, fatty acid sulfonate, polyols, block polyol, glyceryl mono- and dioleate, petroleum oil, oleyl alcohols, ammoniac
5 fluorinated compound, glycols, pine oil, esters of vegetable oil fatty acids, polypropylene glycols, iso-eicosyl alcohol, 1-eicosanol, 1-docosanol, fatty acids; leveling agents such as acrylic resins, urea resins, melamine resins, cellulose acetobutyrate, dimethylpolysiloxanes, methylphenylpolysiloxane, organically modified polysiloxanes, and fluorocarbons; as well as mixtures of any two or more
10 of the above mentioned classes of compounds, or mixtures of two or more compounds from within a given class of compounds. Useful UV light absorbing agents can be those per se known in the art, such as TiO_2 .

The waterborne acrylic polymer dispersions of the present invention may be applied to any hard porous surface. Examples of suitable hard porous surfaces
15 include concrete, tile, wood, metal, ceramic and the like. The compositions provide porous surfaces with a flexible, glossy protective film. By varying the ratio of the monomers in the emulsion, acrylic dispersions with different polymer properties can be prepared.

20 Specific Examples

The following examples are meant to illustrate the present invention. Numerous modifications and variations are possible, and it is to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

25 Waterborne acrylic polymer dispersions were prepared by conventional methods as follows. An acrylic monomer or a mixture of monomers was emulsified in an aqueous solution of a surfactant (e.g. Abex EP-100, available from Rhone-Poulenc, Cranbury, NJ) using a mixing device (e.g. Ross Mixer). About 1/4 - 1/3 of the emulsion was poured in the reactor. The reactor contents were heated
30 to 50 - 85°C. At about 70°C, aqueous ammonium persulfate solution was pumped

- 9 -

in to the reactor over a period of 2 hours with continuous stirring. After pumping in catalyst, the reactor temperature was maintained at 70°C for an additional hour to complete polymerization. Polymer dispersions compositions of the waterborne acrylic prepared using this method are outlined in Table 1 and the following

5 abbreviations are used:

MMA	Methyl Methacrylate
BA	Butyl Acrylate
ST	Styrene
EHA	Ethylhexyl Acrylate

10

Table 1

Polymer	Monomer (Ratio)	Surfactant (Amount)	% Solid	Average particle size (NM)	Tg (°C)
A	MMA/BA (50/50)	Abex EP-100 (0.5%)	43.6	131.7	9.7-12.9
B	MMA/BA (55/45)	Abex EP-100 (0.5%)	38.0	173.7	17.0-19.5
C	MMA/BA (65/35)	Abex EP-100 (0.5%)	41.0	147.8	37.0-40.0
D	MMA/BA (40/60)	Abex EP-100 (0.5%)	39.5	138.5	15.0 - 10.0
E	ST/MMA/2 EHA (25/50/25)	Abex EP-100 (0.5%)	40.5	181.0	60.0 - 70.6
F	MMA/BA (50/50)	Sodium Lauryl Sulfate (0.5%)	41.2	141.5	10.5-12.8
G	MMA/BA (50/50)	Abex-EP-100 (0.25%)	40.8	171.3	9.0-13.2

- 10 -

Waterborne acrylic polymer dispersions may be prepared using different combinations of monomers. The glass transition temperature (T_g) of the polymer varied with the monomer ratio in the polymer. Waterborne polymers with T_g in the range of 0°C to 30°C are preferred for use as a sealer formulation. The waterborne acrylic polymer dispersions in Table 1 were used as sealer formulations in the following examples, which are intended to be exemplary of the invention.

EXAMPLE 1

A sealer formulation was prepared by adding with stirring, 5.0% TiO₂ aqueous dispersion (62.0 % solid) to the waterborne acrylic polymers (A) of Table I. The sealer was applied on a clean and dry cinder block with brush or spray systems, per se known in the art, to form a film. The film was dried at an ambient temperature. The film adhesion was excellent on the cinder block. The film formed had an excellent shine (gloss about 4-10 at 20° and 12-20 at 60°). Once the film was dried, water had no effect on the film.

EXAMPLE 2

Example 1 was repeated with the exception that a waterborne acrylic thickener was added to adjust viscosity in the range of 500 – 1,500 cps. The particular acrylic thickener used is Acrysol RM-825, available from Rohm and Haas, Philadelphia, PA., but any acrylic thickener known in the art may be used. The sealer was again applied, as in Example 1, on a dry cinder block. The drying time to touch was 5-8 minutes. The film adhesion was excellent. After drying the material and the film gloss was 4.5 at 20° and 15.2 at 60°.

EXAMPLE 3

Example 1 was repeated with the exception that 50% TiO₂ pigment was used instead of 5.0% in the sealer formulation. The film formation was excellent, on the dry cinder block surface. The film drying time to touch was 3-5 minutes. The gloss of the coating was about 2-6 at 20° and 14-20 at 60°.

- 11 -

EXAMPLE 4 – Comparative Example

Example 1 was repeated with the exception that the waterborne acrylic polymer E from Table 1 was used instead of Polymer A. Polymer E did not form a continuous and coherent film when applied to dry cinder block. The adhesion of the film was also poor. The Tg of polymer E was $> 30^{\circ}\text{C}$.

EXAMPLE 5

This example illustrates the comparison of the waterborne acrylic polymer dispersions of the present invention with a commercial product called "DRY LOCK," a latex based sealer commercially available from UGL, Scranton, PA.. The sealer of the present invention used for coating cinder block is described in Example 3. The cinder block was coated side-by-side with both the sealer of the present invention and DRYLOCK. The drying time to touch was 2 to 3 times longer for DRYLOCK as compared to the waterborne sealer of Example 3. The gloss of the dried film was 1.5 at 20° and 1.8 at 60° for DRY LOCK, and 4.5 at 20° and 16.5 at 60° using the waterborne sealer of the present invention.

EXAMPLE 6

The cinder block of Example 5 was used to test for water-resistance. The coated cinder block was completely immersed in a water bath for one week. The coated film of the present invention was tough with excellent adhesion to cinder block. The film formed using DRYLOCK lost gloss and appeared dull. The gloss for DRYLOCK film reduced to 1.2 at 20° from 1.5, whereas the waterborne sealer of the present invention had considerable high gloss (1.8-2.4 at 20°C) after immersing the cinder block in water for one week.

EXAMPLE 7

The outer surface of the cinder blocks was coated (3" x 3") with the sealer of Example 3. The sealer had 53.0 wt. % solid. The block was filled with water.

- 12 -

A water pump was used to run water continuously through in-let and out-let while keeping the cinder block filled with water. The block was sealed at top to maintain 3 atmospheric pressure inside the block. It was noticed that the coated film provides 100% sealing to water, whereas water was coming out through uncoated portions of the cinder block. This demonstrates that the sealing formulation of the present invention had excellent water-residence (sealing) to the cinder blocks.

EXAMPLE 8

Example 7 was repeated with the exception that waterborne acrylic polymer G was used instead of Polymer A. The clear coat was formed on cinder block and dried. The water was continuously run for 24 hours. The water was completely sealed within the coated surface, while water was leaking through the uncoated cinder block. The clear film allowed visual examination of wetted areas under the coated film. The cinder surface was wet inside the coated film, but dry to touch on the outside. This example further illustrates that the waterborne sealer of the present invention exhibits excellent properties as a water barrier.

EXAMPLE 9

The acrylic dispersions disclosed in Table 1 were tested for freeze-thaw stability in the presence of propylene glycol at -23.0°C . The pH of the polymer dispersions was adjusted to about 2.65, 6.71 and 7.51 by adding aqueous solutions of sodium carbonate or sodium bicarbonate. The samples were placed in a freezer at -23.0°C for a 24 hour cycle. These samples were then removed from the freezer after 24 hours and allowed to thaw at an ambient temperature for 1-2 hours. After examination, the samples were again placed in the freezer for an additional 24 hours. These samples were examined after 5-cycles. Results indicate that the acrylic dispersions pass freeze-thaw stability test in the presence of 9.5 wt % propylene glycol. By "pass" is meant that the viscosity after the testing is essentially the same as before the testing.

- 13 -

EXAMPLE 10

Example 9 was repeated with the exception that the acrylic polymer
5 dispersion stability was examined at 50.0 °C instead of at -23.0 °C. The samples
were placed in an oven for 24 hours. Results indicate that there was no phase
separation, and the polymer dispersions were stable at 50.0 °C.

The invention has been described above in detail with particular reference
10 to preferred embodiments thereof, but it will be understood that variations and
modifications other than as specifically described herein can be effected within the
spirit and scope of the invention. The skilled artisan in possession of the present
disclosure will appreciate numerous uses for the aforementioned compositions.
Particularly envisioned uses include, but are not limited to: water-proofing, surface
15 protection and particularly salt-protection of roadways, bridges and other
infrastructures; antigraffiti coatings; color protection to concrete; floor surfaces (as
sealant, non-slip coatings, and the like); gap-filling, crack-filling, pit-filling, and the
like; sealers for driveways, sidewalks, porches, and the like; acid rain protection;
corrosion resistance coatings of pipes and bridges; and improved strength of aged
20 asphalt.

- 14 -

CLAIMS

We claim:

- 5 1. A waterborne acrylic polymer dispersion comprising:
 - (a) an acrylic copolymer prepared from methyl methacrylate and butyl acrylate monomers in a ratio of from 45:55 to 60:40 of methyl methacrylate to butyl acrylate, wherein the glass transition temperature (T_g) of the acrylic copolymer is from 0 °C to 30 °C;
 - 10 (b) at least one surfactant, wherein said surfactant has a molecular weight of less than 850; and
 - (c) water in the amount of 35 to 90 weight percent;wherein the waterborne acrylic copolymer dispersion has about 30 to about 60 weight percent solids content, based on the total weight of the dispersion, said
15 solids having a particle size of about 50 to about 350 nm.
2. The waterborne acrylic polymer dispersion of Claim 1, wherein said surfactant has a molecular weight of about 150 to 650.
- 20 3. The waterborne acrylic polymer dispersion of Claim 1, further comprising one or more thickeners in an amount sufficient to provide a dispersion having a viscosity of about 100 to about 5000 cps.
4. The waterborne acrylic polymer dispersion of Claim 1, wherein the glass
25 transition temperature (T_g) of the acrylic copolymer is from 5 °C to 25 °C.
5. A porous substrate comprising a surface having a continuous transparent coating thereon, said coating derived from a waterborne acrylic polymer dispersion comprising:

- 15 -

- (a) an acrylic polymer prepared from acrylate monomers having the formula $\text{CH}_2=\text{C}(\text{R}_2)\text{COOR}_1$, wherein R_1 and R_2 are independently selected from C_1 to C_4 straight or branched chain alkyl groups, and R_2 may be hydrogen; wherein the glass transition temperature (T_g) of the acrylic copolymer is from
- 5 0°C to 30°C ;
- (b) at least one surfactant;
- (c) 35 to 90 weight percent water;
- wherein the waterborne acrylic polymer dispersions have about 30 to about 60 weight percent solids content based on the total weight of the dispersion and a
- 10 particle size of about 50 to about 350 nm.
6. The porous substrate of Claim 5, wherein the surface is a hard, porous surface.
7. The porous substrate of Claim 5, wherein the surface comprises cement.
- 15 8. The porous substrate of Claim 5, wherein said porous substrate is a masonry structure.
9. The porous substrate of Claim 5, wherein said porous substrate is selected from
- 20 the group consisting of brick, cement, block, and mortar.
10. A method for waterproofing a porous surface which comprises:
- (I) applying a waterborne acrylic polymer dispersion comprising:
- (a) an acrylic copolymer prepared from acrylate monomers having the
- 25 formula $\text{CH}_2=\text{C}(\text{R}_2)\text{COOR}_1$, wherein R_1 and R_2 are independently selected from C_1 to C_4 straight or branched chain alkyl groups, and R_2 may also be hydrogen; wherein the glass transition temperature (T_g) of the acrylic copolymer is from 0°C to 30°C ;
- (b) at least one surfactant, wherein said surfactant has a molecular weight
- 30 of less than 850; and

- 16 -

(c) water in the amount of 35 to 90 weight percent;

wherein the waterborne acrylic copolymer dispersion has about 30 to about 60 weight percent solids content, based on the total weight of the dispersion, said solids having a particle size of about 50 to about 350 nm; and

5

(II) allowing said composition to dry to form a continuous film.

11. The method of Claim 10, further comprising the step of adding one or more thickeners to said dispersion in an amount sufficient to provide a viscosity of about
10 100 to 5000cps.

12. The method of Claim 10, wherein said acrylic copolymer is prepared from methyl methacrylate and butyl acrylate monomers in a ratio of from 45:55 to 60:40 of methyl methacrylate to butyl acrylate.

15

13. A masonry product or structure having dispersed therein, during its manufacture or use, a waterborne acrylic polymer dispersion comprising:

(a) an acrylic polymer prepared from acrylate monomers having the formula $\text{CH}_2=\text{C}(\text{R}_2)\text{COOR}_1$, wherein R_1 and R_2 are independently selected from
20 C_1 to C_4 straight or branched chain alkyl groups, and R_2 may be hydrogen; wherein the glass transition temperature (Tg) of the acrylic copolymer is from 0°C to 30°C ;

(b) at least one surfactant;

(c) 35 to 90 weight percent water;

25 wherein the waterborne acrylic polymer dispersions have about 30 to about 60 weight percent solids content based on the total weight of the dispersion and a particle size of about 50 to about 350 nm.

14. The masonry product or structure of Claim 13, wherein the surface is a hard,
30 porous surface.

- 17 -

15. The masonry product or structure of Claim 13, wherein the surface comprises cement.

5 16. The masonry product or structure of Claim 13, wherein said porous substrate is a masonry structure.

17. The masonry product or structure of Claim 13, wherein said porous substrate is selected from the group consisting of brick, cement, block, and mortar.

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18. The masonry product or structure of Claim 13, wherein said acrylic copolymer is prepared from methyl methacrylate and butyl acrylate monomers in a ratio of from 45:55 to 60:40 of methyl methacrylate to butyl acrylate.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/07017

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09D133/06 C04B41/48 C04B24/26 //C04B111/27

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 6 C04B C09D B27K

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 754 663 A (ROHM & HAAS) 22 January 1997 see claim 1 see page 8, line 14 - line 25 see examples; tables ---	1-18
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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