

WATERPROOFING STRUCTURES FORMED FROM
WATER PENETRABLE CONSTRUCTION MATERIALS

The present invention relates to compositions and methods useful for waterproofing or dampproofing various
5 water-penetrable materials used in building construction and other civil engineering projects. The invented compositions are aqueous compositions including polymer latices useful as waterproofing agent pretreatments. The invented methods use these new aqueous pretreatment compositions as a component in
10 a system to reduce water penetration through construction materials. The invention also includes packages including waterproofing agents and these new pretreatment compositions and structures to which these new pretreatment compositions and a waterproofing agent have been applied.

15 Various materials used in building construction and other civil engineering projects such as roads and bridges are susceptible to water penetration resulting either from their inherent properties or imperfections such as cracks or pores. Reducing or eliminating water penetration through
20 structures formed of these materials often is desirable such as for below-grade building walls, and may be critical in certain structures such as those housing expensive electrical equipment or tunnels moving vehicular or pedestrian traffic under bodies of water. Available waterproofing agents
25 include ethylene propylene diene

monomer (EPDM) sheets, polyvinyl chloride sheets, Bentonite panels, built-up asphalt systems, coal tar-based, and other asphalt-based compositions. Asphalt-based compositions are preferred; most preferred are preformed, flexible sheet-like laminates of support film(s) and bituminous layer(s) (waterproofing laminates) such as described in U.S. Patent Nos. 3,741,856; 3,853,682; and 3,900,102. Bituthene^(R) brand of waterproofing membrane is an example of preferred, commercially available asphalt-based waterproofing agents.

Many currently available waterproofing agents are very effective when applied correctly. For example, when using waterproofing laminates as a waterproofing agent on structures contaminated by dirt, dust, or efflorescence current practice requires that a pretreatment be applied to the structure before application of the waterproofing laminate. Most pretreatments commercially available are based upon volatile organic compounds and usually contain high levels of these compounds as solvents. Known aqueous pretreatments, such as asphalt emulsions, have not been used widely because of poor water immersion resistance and freeze/thaw resistance. Consequently, use of most commercially available pretreatments is fraught with disadvantages including the need to exercise great care to avoid fire hazard and atmospheric release of volatile organic compounds, or risk of failure resulting from poor water immersion resistance or poor low temperature applicability.

Therefore, despite use of waterproofing agents that require pretreatment, such as waterproofing laminates, for many years, there has been and remains a need for pretreatment compositions which eliminate use of volatile organic compounds without sacrificing the strength and duration of the bond between the waterproofing agent and structure and which can be applied when ambient temperatures are significantly below the freezing point of water.

Acrylic latex formulations including about 27 wt. % latex solids and about 9 wt. % 2-butoxyethanol, about 4 wt. % 2-(2-ethoxyethoxy) ethanol, and about 1 wt. % dibutyl phthalate are known for use as lacquers. These formulations may have freezing points at or below 0°C (32°F) but are not useful as waterproofing agent pretreatments at or below -4°C (25°F).

U.S. Patent No. 4,897,313 describes use of water-based acrylic latex compositions as waterproofing agent pretreatments. These pretreatment compositions overcome many of the disadvantages of other known aqueous pretreatments but cannot be used at temperatures at or below -4°C (25°F).

U.S. Patent No. 3,940,540 to Schmidt teaches built-up roofing employing precoated felts inhibited from slipping by use of bituminous emulsions to bind the felts. A minor amount of compatible latex is incorporated into the emulsion to increase the adhesion of bonded felts.

U.S. Patent No. 4,172,830 to Rosenberg et al. is one of many examples of references disclosing sheet-like flexible materials used for waterproofing.

U.S. Patent No. 4,362,586 to Uffner et al. describes use of polyamide resins as primers for highway repairs using asphaltic membranes.

U.S. Patent No. 4,731,399 discloses extending certain latices by addition of up to about 40% by weight of an emulsion of asphalt, bitumen, or coal tar. The extended latices are said to be useful in adhering scrim to carpet or in manufacture of attached foamed carpet backing.

U.S. Patent No. 4,597,817 to Larsen describes processes for preparation of a water-impervious surface coating on a substrate which comprises applying to the substrate an aqueous bitumen emulsion containing, in part, 5 to 55% by weight of an acrylic prepolymer.

U.S. Patent No. 4,544,690 to Ladish discloses an aqueous rubberized coal tar emulsion composition suitable for coating and sealing bituminous substrates containing asphalt in which the coal tar emulsion includes water admixed with a small amount of carboxylated butadiene/styrene/acid copolymer latex having a particular particle size.

U.S. Patent No. 4,104,211 to Keene et al. describes pipe sealants made from an aqueous emulsion of non-cationic asphalt and rubber.

U.S. Patent No. 4,176,102 to Favata teaches sealant asphaltic emulsion compositions having 20 - 50 parts by volume of a copolymer prepared by copolymerization of a vinyl acetate monomer with an organic acid.

U.S. Patent No. 4,619,166 to DeFatis teaches a mortar for waterproofing and protective coverings used in building and road construction wherein the mortar includes a mixture of an acrylic emulsion and finely ground clay which has been baked at a temperature range between 600°C and 1,400°C.

U.S. Patent No. 4,151,025 to Jacobs describes use of volatile organic solvent-based primers with laminated waterproofing membranes.

The present invention relates to methods useful for attaching waterproofing agents to water-penetrable constructions materials, compositions useful in these methods, and structures resulting from use of these methods. More specifically, the present invention relates to using compositions including styrene-butadiene rubber latex, styrene-butadiene-styrene rubber latex, natural rubber latex, polybutadiene latex, polychloroprene latex, polyvinyl acetate latex, and/or nitrile latex in application of waterproofing agents to buildings and other civil engineering structures. The present invention includes water-based latex compositions useful in waterproofing construction materials at temperatures at or below about -4°C (25°F) and for other applications in which aqueous latex compositions are used at these temperatures.

Optimal waterproofing of structures such as buildings, bridges, roads, and tunnels requires bonds between the structure and waterproofing agent which endure essentially for the life of the structure. These enduring bonds even are important in applications such as subterranean basements, where the backfill holds the waterproofing agent in place, to prevent migration along the surface of the structure of water which may enter through damaged areas of the waterproofing agent. To achieve enduring bonds between structures and asphalt or coal tar-based waterproofing agents, pretreatments usually are applied prior to application of the waterproofing agent. All the waterproofing agent pretreatments in current widespread use have high levels of volatile

organic compounds, usually as solvents, and thus present potential fire hazards and sources of atmospheric release of volatile organic compounds.

The present invention resides in the discovery that
5 when used as waterproofing agent pretreatments aqueous mixtures of styrene-butadiene rubber (SBR) latex, styrene-butadiene-styrene rubber (SBS) latex, natural rubber latex, polybutadiene latex, polychloroprene latex, polyvinyl acetate latex, and/or nitrile latex facilitate formation of strong
10 and enduring bonds between waterproofing agents and the structure to which they are applied; the bonds are generally sufficiently strong and enduring to secure the waterproofing agent to the structure essentially for the life of the structure. The latices used in the aqueous-based
15 pretreatments of the invented methods have the following characteristics:

Preferred SBR latices include styrene:butadiene polymers having styrene:butadiene ratios of from 1:99 to 60:40, more preferred are SBR latices having
20 styrene:butadiene ratios of from about 20:80 to about 40:60. Stabilizers such as fatty acid surfactants or mixed acid surfactants are necessary ingredients in these latices.

Preferred SBS latices include styrene:butadiene polymers of number average molecular weights from about
25 100,000 to 2,000,000 having styrene:butadiene ratios of from about 10:90 to 40:60. Components in these latices include

cationic, anionic, or nonionic surfactants and, optionally, tackifiers such as rosin esters. Preferred natural rubber and polybutadiene latices have a minimum weight average molecular weight of 50,000 and may contain some gel.

Generally, any SBR latex, SBS latex, natural rubber latex, polybutadiene latex, polychloroprene latex, polyvinyl acetate latex, and/or nitrile latex which, when used as a waterproofing agent pretreatment, provides bonds sufficiently strong and enduring to secure the waterproofing agent to the structure essentially for the life of the structure are used in this invention. Persons skilled in the art readily are able to select from SBR, SBS, natural rubber, polybutadiene, polychloroprene latex, polyvinyl acetate, or nitrile latices those which are operable in this invention. The Examples 20 and 21 Test procedures are examples of tests representing important performance criteria which are useful to determine whether latex-containing compositions are useful as waterproofing agent pretreatments.

The invented aqueous pretreatments and those used in the invented methods include one or more of the above latices in 1-70% by weight of solids, preferably 3-35% by weight of solids. Optional ingredients in these pretreatments include tackifiers such as emulsions of rosin esters or emulsions of hydrocarbon resins; antifungicides such as formaldehyde, oxazolidine-heterocyclic amine, 2-[(hydroxymethyl)-amino]ethanol, or benzisothiazolin-3-one; thickeners such as cellulosic polymers, polyacrylic acid, or associative urethane; and cationic, or anionic, or nonionic surfactants. Asphalt emulsions, preferably in amounts of about 5 to about 20%, also are optional ingredients in the invented pretreatments. To help prevent mold, mildew growth and rust formation, if stored in ferrous metal containers, the pH of the invented pretreatments optionally is adjusted to about 8 to 9 by, for example, addition of ammonium hydroxide. Another optional ingredient is a freeze/thaw stabilizing agent such as ethylene glycol or propylene

glycol. These are added at low levels (in comparison to freezing point depressing agents), for example about 1 to 3 wt. % of total formulation. These agents prevent coalescence (in the package) of pretreatments which freeze and thaw.

Preferred invented aqueous pretreatments are those which have a freezing point significantly below 0°C (32°F), preferably at least as low as -4°C (25°F). More preferred are aqueous pretreatments having a freezing point at or below -7°C (20°F). Surprisingly, it was discovered that various agents known to be useful as freezing point depressants in other applications also can be added to aqueous-based latex compositions in amounts sufficient to reduce the freezing point to at least about -4°C (25°F) without significantly affecting the utility of these compositions as waterproofing agent pretreatment compositions. Using standard techniques persons skilled in the art readily are able to determine such amounts.

Aqueous-based latex compositions are useful as waterproofing agent pretreatments only if after application and drying they allow for formation of a sufficiently strong and enduring bond between the subsequently applied waterproofing agent and structure being waterproofed. It was expected that addition of freezing point depressing agents to aqueous-based latex compositions in amounts sufficient to reduce the freezing point to about -4°C (25°F) would render such compositions unsuitable for use as waterproofing agent pretreatment compositions. Butoxypropanol, 10.4%, in a composition containing 28.4% SBR latex solids and 61.2% water is an example of a known freezing point depressing agent found not to be useful in aqueous-based latex waterproofing agent pretreatment compositions.

Various freezing point depressing agents were discovered to be useful in aqueous-based latex waterproofing agent pretreatment compositions having freezing points at or below -4°C (25°F). Latices useful in freezing point depressing agent-containing compositions are latices in which the latex polymer plus absorbed freezing point depressing agent has a minimum film forming temperature at or below -4°C (25°F). Freezing point depressing agents useful in this invention are agents which have:

- (1) infinite water solubility;
- (2) do not coagulate latex during preparation of a composition; and
- (3) have a vapor pressure at 25°C that is not more than about one-half the vapor pressure of water.

Preferred freezing point depressing agents are those which have a solubility parameter (cal./gm^3)^{1/2} that is about 2 or more units greater than the solubility parameter for the latex being used. Preferred freezing point depressing agents include C_2 to C_5 alkyl diols such as ethylene glycol, propylene glycol, and butane diol; N-methyl pyrrolidinone; and dimethyl formamide. Other useful freezing point depressing agents are methoxyethanol and methoxypropanol. Persons skilled in the art can determine useful freezing point depressing agents using well known techniques.

Example 20 provides data supporting the unexpected utility of these compositions as waterproofing agent pretreatments.

The preferred invented waterproofing agent pretreatment compositions include about 10 to about 65 wt. % latex solids, about 4 to about 33 wt. % freezing point depressing agent, and about 17 to about 80 wt. % water and may include other optional components. More preferred invented waterproofing agent pretreatment compositions include about 10 to about 53 wt. % latex

solids, about 9 to about 33 wt. % freezing point
depressing agent, and about 23 to about 80 wt. % water or
about 16 to about 53 wt. % latex solids, about 9 to about
26 wt. % freezing point depressing agent, and about 23 to
5 about 75 wt. % water. Most preferred are compositions
containing about 20 wt. % latex solids and about 12 wt. %
freezing point depressing agent. All pretreatment
formulations should be prepared such that the ratio of
freezing point depressing agent to latex solids is less
10 than or equal to about 1 and the ratio of freezing point
depressing agent to water is greater than or equal to
about 0.12 but less than or equal to about 1. All wt.
percentages of latex, freezing point depressing agent, and
water are determined exclusive of any other components
15 which may be included in the pretreatment composition.
Compositions including higher concentrations of latex
solids and freezing point depressing agents which are
intended for dilution prior to use are within the above
ranges if the diluted form is within these ranges.

20 The invented waterproofing agent pretreatment
compositions also may include styrene maleic anhydride
copolymer having a molecular weight of about 2,000 (SMA)
and ammonia. Preferred compositions including SMA and
ammonia have about 2 wt. % SMA and 0.4 wt. % ammonia.

25 As used in the specification and claims a
waterproofing agent pretreatment(s) is a composition used
as a surface conditioner or a composition used as a
primer. A surface conditioner composition is applied to a
structure surface to adhere dust and other contaminants to
30 the surface thereby enhancing the mechanical integrity of
the surface. Primers are compositions applied to
structure surfaces which may perform the functions of
surface conditioners. In addition primers also promote
good initial adhesion of the waterproofing agent by

filling in voids in microscopically rough structure surfaces thereby providing a smoother surface that is more receptive for bonding. Because of this characteristic the preferred waterproofing agent, a pressure sensitive adhesive waterproofing laminate, need not be as deformable to make good contact with a primed surface as would be the case for a conditioned surface. Also a primer layer because of its greater thickness than a conditioner layer generally is tacky. Tackiness also aids in promoting good initial adhesion. Primer compositions generally have a higher solids content than surface conditioner compositions.

In the invented methods, waterproofing materials based on coal tar or asphalt are used, asphalt-based waterproofing materials are preferred. Especially preferred are waterproofing materials constructed of preformed, flexible sheet-like laminates of support films and bituminous layers which shall be referred as waterproofing laminates. Various waterproofing laminates are commercially available. Bituthene^(R) brand waterproofing membranes are preferred commercially available waterproofing laminates.

Various civil engineering structures including, for example, buildings, bridges, roads, and tunnels, are made waterproof using the present invention. As used herein, making a structure "waterproof" means reducing or eliminating the ability of water to penetrate the structure. The present invention is used to make waterproof structures constructed of materials which are water-penetrable either inherently or as a result of imperfections such as cracks or pores. The types of water-penetrable construction materials with which the present invention is used include wood, brick, stone, blended cements, pozzolanic cements, or concrete, preferably Portland cement concrete.

According to the presently invented method for reducing water penetration through a structure, initially a pretreatment including one or more of the above latices is applied to a structure and allowed to dry. Thereafter, a waterproofing agent is affixed to the pretreatment-coated structure surface. Using the invented method, the pretreatment preferably is applied to a structure surface at a coverage rate of about 100-1200 sq. ft./gal., preferably about 100-400 sq. ft./gal. when used as a primer and 400-1,200 sq. ft./gal. when used as a surface conditioner. Other suitable coverage rates and film thicknesses are readily determined by persons skilled in the art.

Waterproofing laminates are the preferred waterproofing agents for use in the invented methods. Preferred waterproofing laminates have a bituminous layer comprised of about 29 - 60% by weight asphalt, about 25 - 55% by weight process oil, about 10-35%, preferably 16-35% by weight of a thermoplastic block polymer of styrene and butadiene monomers or random styrene and butadiene rubber polymers. As used herein, the weight percent of asphalt, process oil, and thermoplastic block polymer of butadiene and styrene is calculated based on the total of these components not including fillers, which may be included in amounts of up to 50%, preferably 10-20%, by weight of the total weight of asphalt, process oil, thermoplastic block polymer of butadiene and styrene, and filler, or any other components.

In more preferred waterproofing laminates the asphalt used has the following alumina separation (ASTM D4124) ranges and preferred ranges:

	<u>Range</u>	<u>Preferred Range</u>
Saturates	5 - 25%	8 - 15%
Naphthenic Aromatics	15 - 40%	32 - 40%
Polar Aromatics	30 - 50%	40 - 46%
Asphaltenes	5 - 30%	8 - 15%

Also, in the preferred waterproofing laminates the preferred process oil for use in the bituminous layer has the following clay gel separation (ASTM D-2007) ranges:

Saturates	10 - 30%
Polar Compounds	10 - 20%
Aromatics	50 - 85%
Asphaltenes	0 - 0.5%

Additionally, in the preferred waterproofing laminates preferred thermoplastic block polymers of styrene and butadiene monomers are mixtures of polymers having a butadiene:styrene ratio of about 70:30 and a block polystyrene content of about 30% (high molecular weight polymer) and polymers having a butadiene:styrene ratio of about 75:25 and a block polystyrene content of about 18% (low molecular weight polymer). More preferred are polymers in which the ratio of the low molecular weight polymer to the high molecular weight polymer is in the range of 5:1 to 1:1; most preferred are polymers wherein the ratio of low molecular weight polymer to high molecular weight polymer is about 3.8:1 or 2:1. In the preferred waterproofing laminates including random styrene and butadiene rubber polymers, the preferred styrene:butadiene ratio is in the range of 1:99 to 35:65, the most preferred range is 15:85 to 28:72.

In another aspect the present invention is a packa including an aqueous-based pretreatment including one or more of the above latices and a waterproofing laminate used in the presently invented methods. The invention also includes a structure to which has been attached a presently invented latex pretreatment and a coal tar or asphalt-base waterproofing agent used in the invented methods.

Contemplated equivalents of the present invention include methods for reducing water penetration through a structure that comprise using other aqueous pretreatments which include latices that are compatible with the waterproofing agent with which they are used and that produce strong and enduring bonds between waterproofing laminates and the structure to which they are applied. Other contemplated equivalents are aqueous-based latex compositions useful as waterproofing agent pretreatment compositions at temperatures below the freezing point of water. Equivalent compositions are determined by mixing a waterproofing agent-compatible latex and a freezing point depressing agent and testing as described herein to determine whether the composition facilitates formation of sufficiently strong and enduring bonds between the waterproofing agent and structure.

The following examples provide specific illustrations of the invention, but are not intended to limit the scope of the invention as described above and claimed below.

Example 1

SBR Latex Pretreatment

A waterproofing agent pretreatment composition was prepared from Butonal NS 175^(R) (BASF), an SBR latex

including a styrene:butadiene polymer having a styrene:butadiene ratio of 24:76 and fatty acid as a surfactant. This SBR latex (36.2% w/w) and water (63.8% w/w) were charged into a mixer and stirred until blended, approximately 5 minutes. This SBR latex pretreatment had 25% solids.

Example 2

SBR Latex Pretreatment

Using the process of Example 1 a SBR latex pretreatment was prepared except that the Butonal NS 175^(R) SBR latex and water each were added at 50% w/w to yield a pretreatment composition having 35% solids.

Example 3

SBR Latex Pretreatment

Using the process of Example 1 an SBR latex pretreatment was prepared from Butonal NS 175^(R) SBR latex (18.1% w/w), Aquatac-6025^(R) Arizona Chemical Co. (20.8% w/w), a hydrocarbon resin emulsion tackifying agent, and water (61.1% w/w). This pretreatment composition had 25% total solids.

Example 4

SBR Latex Pretreatment

Using the process of Example 1 an SBR latex pretreatment was prepared from Butonal NS 175^(R) SBR latex

SBR Latex Pretreatment

Using the process of Example 1 an SBR latex pretreatment was prepared from Butonal NS 175^(R) latex (27.2% w/w), Aquatac 6085 (10.4% w/w), a rosin ester resin emulsion tackifying agent, and water (62.2% w/w). This pretreatment composition had 25% total solids.

SBR Latex Pretreatment

An SBR latex pretreatment was prepared as in Example 5 except that Aquatac 6025^(R) (10.4% w/w), a hydrocarbon resin emulsion tackifying agent was used and yielded a pretreatment composition containing 25% solids.

SBR Latex Pretreatment

A waterproofing agent pretreatment composition was prepared according to the Example 1 procedure using Butonal NS 198^(R) (BASF), an SBR latex including styrene:butadiene polymer having a styrene:butadiene ratio of 24:76 and a fatty acid as a surfactant. This SBR latex (39.7% w/w) and water (60.3% w/w) were mixed to yield a pretreatment composition having 25% solids.

Example 8SBR Latex Pretreatment

5 Using the process of Example 7, an SBR latex
pretreatment was prepared except that the Butonal NS
198^(R) SBR latex and water each were added at 50% w/w to
yield a pretreatment composition having 32% solids.

Example 9SBR Latex Pretreatment

10 Using the process of Example 1 an SBR latex
15 pretreatment composition was prepared from Butonal NS
125^(R) (BASF, an SBR latex including a styrene:butadiene
polymer having a styrene:butadiene ratio of 31:69 and a
fatty acid as a surfactant. This SBR latex (35.4% w/w),
water (65.6% w/w), and ethylene glycol (2.5% w/w) were
20 mixed to yield a pretreatment composition containing 25%
solids.

Example 10SBR Latex Pretreatment

25 Using the process of Example 1 an SBR latex
pretreatment was prepared using Butonal NS 131^(R) (BASF)
an SBR latex including a styrene:butadiene polymer having
30 a styrene:butadiene ratio of 35:65 and a fatty acid as a
surfactant. This SBR latex (35.7% w/w), water (64.2% w/w)
and ethylene glycol (2.5% w/w) were mixed to yield a
pretreatment composition having 25% solids.

Example 11SBR Latex Pretreatment

5 Using the process of Example 1 an SBR latex
pretreatment was prepared from Pliolite LPF 6733^(R)
(Goodyear Tire and Rubber Co.) an SBR latex including a
styrene:butadiene polymer having a styrene:butadiene ratio
10 of 34:66 and a mixed acid surfactant. This SBR latex
(36.2% w/w), water (63.8% w/w), and ethylene glycol (2.5%
w/w) were mixed to yield a pretreatment composition having
25% solids.

Example 12SBR Latex Pretreatment

15 Using the process of Example 1 an SBR latex
pretreatment was prepared from Pliolite LPF 6738^(R)
20 (Goodyear Tire & Rubber Co.) an SBR latex including a
styrene:butadiene polymer having a styrene:butadiene ratio
of 29:71 and a mixed acid surfactant. This SBR latex
(36.2% w/w), water (63.8% w/w), and ethylene glycol (2.5%
w/w) were mixed to yield a pretreatment composition having
25 25% solids.

Example 13SBR Latex Pretreatment

30 Using the process of Example 1 an SBR latex
pretreatment was prepared from Pliolite LPF 5356, an SBR
latex including a styrene:butadiene polymer having a
styrene:butadiene ratio of 23.5:76.5 and a fatty acid

surfactant. This SBR latex (36.2% w/w), water (63.8% w/w), and ethylene glycol (2.5% w/w) were mixed to yield a pretreatment composition having 25% solids.

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Example 14

SBR Latex Pretreatment

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Using the process of Example 1 an SBR latex pretreatment was prepared except that the Polysar 275^(R) (BASF) SBR latex was added at 10% w/w and the pretreatment composition also contained 10% solids of asphalt emulsion (SS-1H, designating a slow setting grade with a residue penetration of 40-90 dmm, a hard grade) and 0.15% Carbopol 934^(R) (E. F. Goodrich) polyacrylic acid thickener. This pretreatment composition had 20% solids.

Example 15

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Natural Rubber Latex Pretreatment

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A waterproofing agent pretreatment composition was prepared from Hartex 103^(R) (Firestone Tire and Rubber Company) a natural rubber latex having the following chemical and/or physical characteristics: 62% solids, KOH number=0.55, and pH=9.8. This natural rubber latex (50.0% w/w) and water (50.0% w/w) were charged into a mixer and stirred until blended, approximately 5 minutes. This natural rubber pretreatment had 31% solids.

Example 16Polybutadiene Latex Pretreatment

5 A waterproofing agent pretreatment composition was
prepared from LPM 2374 ^(R) (Goodyear Tire and Rubber Co.)
a polybutadiene latex. This polybutadiene latex (41.7%
w/w) and water (58.3% w/w) were charged into a mixer and
10 stirred into a blended composition for approximately
5 minutes. This polybutadiene latex pretreatment had 25%
solids.

Example 17SBS Latex Pretreatment

15 A waterproofing agent pretreatment composition was
prepared from Kraton G 1657 ^(R) (Shell Oil Company), an SBS
block copolymer having a styrene:butadiene ratio of 30:70
20 and a rosin ester. The pretreatment composition was
prepared by emulsifying the SBS block copolymer and rosin
ester in water with an ionic surfactant in amounts
yielding a total solids content of 43%.

Example 18Polychloroprene Latex Pretreatment

25 A waterproofing agent pretreatment composition was
prepared from Despercoll C-84 ^(R) (Mobay), a
30 polychloroprene latex. This latex was diluted with water
to yield a composition having 28.4% latex solids and
blended for approximately 5 minutes.

Example 19Polyvinyl Acetate Latex Pretreatment

5 A waterproofing agent pretreatment composition was prepared from Daraweld C^(R) (W. R. Grace & Co.-Conn.), a polyvinyl acetate latex. This latex was diluted with water to yield a composition having 28.4% latex solids and blended for approximately 5 minutes.

Example 20Pretreatments Including Freezing Point Depressing Agent

15 Table I shows results of testing aqueous-based waterproofing agent pretreatment compositions including latex solids 28.4 wt. %, freezing point depressing agent 10.4%, and water. In compositions containing SMA and ammonia, SMA 2.0 wt. % and ammonia 0.4 wt. % replaced an
20 equivalent amount of water.

 Compositions not including SMA and ammonia were prepared by mixing the water with the freezing point depressing agent and then adding the water/freezing point depressing agent mixture to the latex dropwise with
25 stirring.

 Compositions including SMA and ammonia were prepared by mixing water with ammonium hydroxide solution. SMA (SMA 3000, Atochem, Inc., M.W. = 1900) was stirred into the mixture and the mixture then was stirred until the
30 SMA was dissolved. Then the SMA/ammonia/water mixture was added dropwise to the latex mixture while stirring. Thereafter, the freezing point depressing agent was added dropwise to the mixture with stirring.

The adhesion test procedure consists of coating a pretreatment composition onto a cast concrete block at a coverage rate of approximately $9.82\text{m}^2/\text{l}$ (400 sq. ft./gal). The coated block then is force air dried at room temperature for about two hours. Next, an about 76.2-152.4mm (3" by 6") sample of waterproofing laminate is applied to the block and quickly rolled four times with a thirty-pound roller. After aging for one day at room temperature adhesion is measured using an Instron^(R) mechanical tester (tensile testing machine) using a peeloff angle of 90° and a crosshead speed of 50.8mm (2") per minute.

TABLE I

	<u>Latex</u>	<u>Freezing Point Depressing Agent</u>	<u>SMA/NH₃</u>	<u>Bond Strength kg/m (lb/in)</u>
5	SBR (Butonal ^{NS} 175(R))	None	-	185.7 (10.4)
		None	Yes	-
		Ethylene Glycol	-	67.9 (3.8)
		Ethylene Glycol	Yes	241.1 (13.5)
10		Propylene Glycol	-	160.7 (9.0)
		Propylene Glycol	Yes	257.2 (14.4)
		DMF	-	210.7 (11.8)
		DMF	Yes	207.2 (11.6)
15		N-methyl Pyrrolidinone	-	139.3 (7.8)
		N-methyl Pyrrolidinone	Yes	196.5 (11.0)
		Butanediol	-	142.9 (8.0)
		Butanediol	Yes	275.0 (15.4)
20		Methoxyethanol	-	242.9 (13.6)
		Methoxyethanol	Yes	250.0 (14.0)
		Methoxypropanol	-	225.0 (12.6)
		Methoxypropanol	Yes	264.3 (14.8)
25	Chloroprene (Dispercoll C-84(R))	None	-	83.9 (4.7)
		Ethylene Glycol	-	100.0 (5.6)
		Propylene Glycol	-	112.5 (6.3)
		Butanediol	-	64.3 (3.6)
30		DMF	-	66.1 (3.7)

Example 21Slow Peel Testing

The following procedure was used for slow peel testing. The waterproofing laminate used in this testing has a rubberized asphalt layer including asphalt, thermoplastic block polymers of styrene and butadiene, and process oil and a support film of crosslaminated polyethylene. The control pretreatment is a commercially available composition containing about 12% styrene:butadiene block copolymer and 12% Nevchem-140^(R) (alkylated aromatic nonsaponifiable petroleum hydrocarbon resin with a softening point of about 140°C) in xylene.

According to the test procedure a concrete block initially is sprayed with a pretreatment composition at a target coverage range of 9.82-12.3m²/l (400-500 sq. ft. per gallon). Then the pretreatment composition is allowed to dry for approximately about 2 hours, and a 76.2-152.4mm (3" by 6") sample of waterproofing laminate is applied and quickly rolled four times with a 13.5kg (30-pound) roller. Next, a 100 g weight is attached to a tab along one of the short sides of the waterproofing laminate and the waterproofing laminate is placed in a vertical position with the weighted side elevated. Waterproofing laminate displacement as a function of time is monitored.

Table II shows test results of the latex pretreatment compositions of the previous examples. Also tested as described in this example, but not shown in the Table, were several pretreatment compositions in which the latex was carboxylated SBR latex pretreatment compositions and acrylic pretreatment compositions had greater than 152.4mm (6 inches) movement after 5 days.

Table II

Displacement [mm (in.)] with time (days)

Pretreatment Composition	1	2	3	5	6	8	9	10	12	16
Control		27.9 (1.1)	27.9 (1.1)		33.02 (1.3)			45.72 (1.8)		45.72 (1.8)
Example 1	0				3.05 (.12)			22.86 (.9)		
Example 2	1.27 (.05)			1.27 (.05)	2.54 (.1)	2.54 (.1)				
Example 3	1.52 (.06)	7.87 (.31)		12.7 (.5)			15.75 (.62)		35.56 (.14)	
Example 4	0	4.83 (.19)		7.87 (.31)			7.87 (.31)		14.22 (.56)	
Example 5	0	3.05 (.12)		6.35 (.25)			6.35 (.25)		9.65 (.38)	
Example 6	0	3.05 (.12)		6.35 (.25)			6.35 (.25)		9.65 (.38)	
Example 7	1.52 (.06)	1.52 (.06)		3.18 (.125)			6.35 (.25)		6.35 (.25)	
Example 8	3.81 (.15)				12.7 (.5)					
Example 9	1.52 (.06)	1.52 (.06)	6.35 (.25)		6.35 (.25)			9.40 (.37)		11.18 (.44)
Example 10	0.76 (.03)	1.52 (.06)	4.06 (.16)		4.06 (.16)			6.35 (.25)		6.35 (.25)
Example 11	6.35 (.25)	6.35 (.25)	9.40 (.37)		9.40 (.37)			23.88 (.94)		33.02 (1.3)
Example 12	3.05 (.12)	6.35 (.25)	6.35 (.25)		11.18 (.44)			19.05 (.75)		38.10 (1.5)
Example 13	4.83 (.19)	4.83 (.19)	9.40 (.37)		11.18 (.44)			20.57 (.81)		35.56 (1.4)
Example 14	0.76 (.03)	1.52 (.06)				25.4 (1.0*)		44.45 (1.75)		152.4 (6**)
Example 15	0	0			152.4 (6+)					
Example 16		0		2.29 (.09)			29.21 (1.15)		33.02 (1.3)	
Example 17	12.7 (.5)	14.2 (.56)			50.8 (2.0)				152.4 (6+)	

* 7-day data

** 18-day data

26.

Example 22Water Immersion Testing

Samples for testing were prepared by spraying a concrete block with a pretreatment at a target coverage range at about 9.82-12.3m² /l. (400-500 sq. ft./gallon). Then the pretreatment was allowed to dry for 2 hours and a 76.2-152.4mm (3" by 6") sample of waterproofing laminate, as used in Example 20, was applied and rolled four times with a 13.5kg (30-pound) roller. The samples were maintained for 1 day dry and then immersed in water for 28 days. Thereafter, adhesion was measured using an Instron^(R) mechanical tester (tensile testing machine) using a peeloff angle of 90° and a crosshead speed of 50.8mm (2") per minute. The data obtained is shown in Table III in which the control is an organic solvent-based primer containing solvent, SBS block copolymer, and hydrocarbon resin.

TABLE III

<u>Pretreatment Composition</u>	<u>Bond Strength kg/m (lb.in)</u>
Control	89.3 (5.0)
Example 1	85.7 (4.8)
Example 9	98.2 (5.5)
Example 10	80.4 (4.5)
Example 11	82.2 (4.6)
Example 12	96.4 (5.4)
Example 13	85.7 (4.8)
Example 14	50.0 (2.8)

Example 23Low Temperature Initial Adhesion

Prior to sample preparation all materials are equilibrated at 40°C (40°F). Then, in a 4°C (40°F) environment a concrete block is sprayed with a pretreatment composition at a target coverage range of about 9.82-12.3m²/l (400-500 sq. ft./gallon) and is allowed to dry for about 2 hours. Then, while continuing to work in a 4°C (40°F) environment a 76.2-152.4mm (3" by 6") sample of waterproofing laminate, as used in Example 20, is applied to the concrete block and quickly rolled with a 13.5kg (30-pound) roller. After maintaining the sample for one day at 4°C (40°F) adhesion is measured using an Instron^(R) mechanical tester (tensile measuring instrument) using a peeloff angle of 90° and a crosshead speed of 50.8mm (2") per minute. Test data is shown in Table IV in which the control is the same as in Example 22.

TABLE IV

<u>Pretreatment Composition</u>	<u>Bond Strength kg/m (lb/in)</u>
Control	30.36 (1.7)
Example 1	42.86 (2.4)
Example 9	37.51 (2.1)
Example 10	42.86 (2.4)
Example 11	57.15 (3.2)
Example 12	32.15 (1.8)
Example 13	25.00 (1.4)

WE CLAIM

1. A method for reducing water penetration through a structure which method comprises applying to the structure a waterproofing agent pretreatment composition which composition comprises SBR latex, SBS latex, natural rubber latex, polybutadiene latex, polychloroprene latex, polyvinyl acetate latex, nitrile latex, or a combination thereof which pretreatment composition is effective to produce long-lasting bonds between the structure and subsequently applied waterproofing agent; and

applying a waterproofing agent to the structure.

2. A method according to claim 1 in which the structure is a building or civil engineering structure.

3. A method according to claim 1 or 2 wherein the waterproofing agent is a waterproofing laminate.

4. A method according to claim 1, 2 or 3 wherein the waterproofing agent pretreatment composition further comprises an amount sufficient to reduce the pretreatment composition's freezing point to not above -4°C (25°F) of a freezing point depressing agent which has infinite water solubility, does not coagulate the latex during preparation, and has a vapor pressure at 25°C that is not more than about one-half the vapor pressure of water.

5. A method according to claim 4 wherein the freezing point depressing agent has a solubility parameter that is at least 2 units $(\text{cal./gm}^3)^{\frac{1}{2}}$ greater than the latex selected.

6. A method according to any one of the preceding claims wherein the SBR latex includes styrene:butadiene polymers having styrene:butadiene ratios between about 1:99 and about 60:40 or the SBS latex includes
5 styrene:butadiene:styrene polymers having molecular weights between about 100,000 to about 2,000,000 and styrene:butadiene ratios of from about 10:90 to about 40:60.

7. A method according to claim 6 wherein the styrene:butadiene polymer has a styrene:butadiene ratio of
10 about 20:80 to about 40:60.

8. A method according to any one of claims 3 to 7 wherein the waterproofing laminate has a bituminous layer including about 29-54% by weight asphalt, about 25-55% by weight process oil, and about 10-35% by
15 weight of a thermoplastic block polymer of styrene and butadiene monomers or random styrene and butadiene rubber polymer.

9. A method according to any one of the preceding claims wherein the freezing point depressing agent
20 is propylene glycol or ethylene glycol.

10. A method according to claim 8 or 9 wherein the waterproofing laminate bituminous layer includes up to 50% filler based on weight of all bituminous layer components.

25 11. A method according to any one of claims 8, 9 or 10 wherein the bituminous layer includes 16-35% by weight

thermoplastic block polymer of styrene and butadiene monomers or random styrene and butadiene rubber polymer.

12. A method according to any one of claims 8 to 11 wherein the asphalt has the following alumina

5 separation (ASTM D-4124) ranges:

Saturates	5-25%
Naphthenic Aromatics	15-40%
Polar Aromatics	30-50%
Asphaltenes	5-30%

10 or the process oil has the following clay gel separation (ASTM D-2007) ranges:

Saturates	10-30%
Polar Compounds	10-20%
Aromatics	50-85%
15 Asphaltenes	0- 0.5%

13. A method according to any one of claims 8 to 12 wherein the asphalt has the following alumina separation (ASTM D-4124) range:

Saturates	8-15%
20 Naphthenic Aromatics	32-40%
Polar Aromatics	40-46%
Asphaltenes	8-15%

14. A method according to any one of claims 8 to 13 wherein the thermoplastic block polymer of styrene and
25 butadiene monomers are mixtures of polymers having a butadiene:styrene ratio of about 70:30 and a block

polystyrene content of about 30% and polymers having a butadiene:styrene content of about 75:25 and a block polystyrene content of about 18%.

15. A method according to any one of the
5 preceding claims wherein the waterproofing agent pretreatment includes asphalt emulsions in amounts of about 5 to about 20% by weight.

16. A method according to claim 1 substantially
as hereinbefore described in any one of the foregoing
10 Examples.

17. A package comprising a waterproofing agent
pretreatment composition; and

a waterproofing agent, the composition
and agent being as defined in any one of claims 1 to 16.

15 18. A package according to claim 16 wherein the waterproofing laminate has a bituminous layer including about 29-54% by weight asphalt, about 25-50% by weight process oil, and about 10-35% by weight of a thermoplastic block polymer of styrene and butadiene monomers or random styrene and
20 butadiene rubber polymer.

19. A package according to claim 17 substantially
as hereinbefore described.

20. A composition useful as a waterproofing agent
pretreatment at or below -4°C (25°F), when used in a method
25 according to any one of claims 1 to 16, comprising

a latex selected from the group consisting of
SBR latex, SBS latex, natural rubber latex, polybutadiene

latex, polychloroprene latex, polyvinyl acetate latex, and nitrile latex; and

a freezing point depressing agent in an amount sufficient to reduce the pretreatment composition
5 freezing point to not above about -4°C (25°F) which has infinite water solubility, does not coagulate the latex during preparation, and has a vapor pressure at 25°C that is not more than about one half the vapor pressure of water.

21. A composition according to claim 20 wherein
10 the freezing point depressing agent has a solubility parameter that is at least 2 units greater than the solubility parameter of the latex selected.

22. A composition according to claim 20 or 21 wherein the latex is an SBR latex or an SBS latex.

15 23. A composition according to claim 20, 21 or 22 wherein the freezing point depressing agent is ethylene glycol or propylene glycol.

24. A composition according to any one of claims 20 to 23 wherein the SBR latex includes
20 styrene:butadiene polymers having styrene: butadiene ratios between about 1:99 and about 60:40 and the SBS latex includes styrene:butadiene:styrene polymers having molecular weights between about 100,000 to about 2,000,000 and styrene:butadiene ratios of about 10:90 to about 40:60.

25 25. A composition according to claim 24 wherein the styrene:butadiene polymer has a styrene:butadiene ratio

of about 20:80 to about 40:60.

26. A composition according to claim 25 further comprising styrene maleic anhydride copolymer having a molecular weight of about 2,000 and ammonia.

5 27. A composition according to claim 24 including about 20 wt. % SBR latex solids, about 12 wt. % propylene glycol, about 2 wt. % styrene maleic anhydride copolymer having a molecular weight of about 2,000 and about 0.4 wt. % ammonia.

28. A composition according to claim 20
10 substantially as hereinbefore described.

29. A composition comprising a latex as defined in Claim 1 for use as a waterproofing agent pretreatment.
