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(54) **Starch binder composition for fiber mats.**

(57) A starch binder composition for fiber mats is disclosed which comprises a starch, a starch crosslinking agent, an anti-wicking agent and preferably a polymer strength additive. When the starch binder composition is applied to a fiber mat, e.g. a polyester fiber mat, the treated mat exhibits less stretching, shrinkage and wicking than is common with conventional latex binder systems. The starch binder composition can also be used on glass mats as a partial or total replacement for conventional urea-formaldehyde resin binders with the treated mat exhibiting improved dry, wet and hot wet tensile strength when compared to a urea formaldehyde resin binder containing a conventional acrylic latex.

Description

STARCH BINDER COMPOSITION FOR FIBER MATS

This invention relates to a binder composition for fiber mats, in particular to a starch based binder composition. Various products are prepared by forming a mat of fibers which then have a binder applied to coat or impregnate the fiber mat. Typical fibers include polyester fibers, glass fibers, polypropylene fibers, cellulose fibers or other nonwoven fiber materials.

Polyester fibers are often dry laid to form a mat which is then fed through a pad bath to apply a binder. After drying and curing, the polyester mat is fed through a hot asphalt bath to apply a coating of asphalt. Due to the high temperature of the asphalt bath, untreated polyester mat will stretch resulting in a decrease in the width of the mat. Application of a binder will lessen that stretch and lessen the shrinkage of the mat width. Conventional binder systems comprise acrylic or vinyl acrylic latex emulsions. However, these conventional latex systems have exhibited an unacceptable level of stretching and wicking and generally contain formaldehyde-based crosslinking agents.

Fiberglass roofing mats have been conventionally treated with a urea-formaldehyde resin binder which can typically contain about 10 to 20% acrylic latex. However, it is desirable to improve the dry, wet and hot wet tensile strength of these systems and/or partially or fully replace the urea-formaldehyde resin in the binder.

An object of this invention is to provide a starch based binder composition which when applied to a fiber mat, dried and cured reduces the level of stretching and wicking.

Another object of this invention is to provide a starch based binder composition with desirable dry, wet and hot wet tensile strength when applied to a fiber mat.

A still further object of this invention is to provide a binder composition which can eliminate or reduce the use of formaldehyde-based crosslinking agents and urea-formaldehyde resins.

Briefly, a starch binder composition is provided for fiber mats which comprises a starch, a starch crosslinking agent, an anti-wicking agent and preferably a polymer strength additive. The starch binder composition when applied to a fiber mat, dried and cured reduces the stretching and wicking of the mat, particularly when the mat is to be subsequently coated and provides improved dry, wet and hot wet tensile strength. The bound fiber mats can be subsequently coated, for example, with an asphalt or resin depending upon the end use.

The binder composition of this invention is a starch based system. The starch can be any one of a variety of starches with the starch preferably being chosen to provide a high solids binder composition while maintaining a workable viscosity. The starch may be from corn, wheat, potato, waxy maize or sorghum and may be treated by any one of a variety of known methods, e.g. the starch may be gelatinized, enzyme converted, acid modified and oxidized; or starch esters, starch ethers, starch acetates, as well as starch derivatives such as cyclodextrins or maltodextrins can be used. While the starch may be used in a granular ungelatinized form, preferably it is first gelatinized. Preferred starches include maltodextrins, acid modified, enzyme converted, oxidized and ethoxylated starches. Preferably the starches are chosen to be able to formulate a high solids aqueous binder composition, i.e. greater than 25% solids, and preferably the starch will provide a viscosity of less than 500cps when measured at room temperature and at a solids level of 35% on a Brookfield viscometer having a #3 spindle at 100rpm. In a preferred embodiment, the starch chosen is a low molecular weight starch, i.e. having a molecular weight of less than 7200 daltons, to obtain the high solids and desired viscosity. For added strength it is desirable to add to the low molecular weight starch up to 20% by weight of a high molecular weight starch, i.e. having a molecular weight of greater than 7200 daltons. Various blends of starches or starch derivatives may best exhibit improved strength with the desired high solids and workable viscosity.

A starch crosslinking agent is added to the binder composition for the purpose of crosslinking the starch. Various crosslinking agents which are commonly used to crosslink starch may be used including, but not limited to, urea formaldehyde resins, melamine formaldehyde resins, acetone formaldehyde resins, glyoxal, blocked glyoxal resins (e.g. glyoxal blocked with polyols, glycols or cyclic urea) or various metal salts including ammonium zirconium carbonate. A preferred crosslinking agent is the blocked glyoxal resin, as is disclosed in U.S. Patent No. 4695606, particularly the cyclic urea glyoxal condensation product disclosed therein. Generally, the crosslinking agent is added at a level of 1 to 15% based on the dry weight of the starch, preferably about 5 to 10%.

In a preferred embodiment, to provide a binder composition which provides a desired level of dry, wet and hot wet tensile strength to the bound fiber mat, a polymer strength additive is added to the starch binder composition. Generally, the polymer strength additive is added at a level less than 50% by dry weight of the starch, preferably up to 10% by dry weight of the starch. Various polymers may be chosen which provide the desired additive strength to the resultant bound fibrous mat. Suitable polymers include polyvinyl alcohol and homopolymers or copolymers of acrylamide. The polymer can be a copolymer of acrylamide and either acrylic acid, methacrylic acid, vinyl acetate, vinyl pyrrolidone, sodium vinyl sulfonate, hydroxethyl acrylate, acrylonitrile, acrylic ester, methacrylic ester, cationic monomers, N-substituted acrylamide and N-substituted methacrylamide. A preferred polymer strength additive is either polyvinyl alcohol or a copolymer of acrylamide and methacrylic acid or both used together. Where wet tensile strength is important, such as in glass mat applications, a polyamine-polyamide epichlorohydrin reaction product may also be added.

An anti-wicking agent is added to prevent wicking in the fiber mat bound by the starch binder composition. Wicking is the capillary action which draws liquid through the fibrous mat and is generally considered undesirable in fiber mat applications. The anti-wicking agent is commonly referred to as a sizing agent or a water repellent and may be any agent which inhibits the capillary action of fluids in the bound fiber mat. The anti-wicking agent is often formulated as an emulsion consisting of a hydrophobic base, such as a wax, a melamine formaldehyde resin alkylated by fatty alcohols, alkyl ketene dimers, alkenyl succinic anhydrides, fluorochemicals, or silicone oils; and an emulsifying agent such as ethoxylated alkyl phenols, ethoxylated castor oils, ethoxylated fatty alcohols, ethoxylated fatty acids, sulfate esters, phosphate esters, quaternary ammonium salts, ethoxylated or propoxylated fatty alcohols or amine oxides. A preferred anti-wicking agent comprises a melamine-formaldehyde resin alkylated by fatty alcohols and a non-rewetting surfactant such as the amine oxide of dimethyl amino propyl lauramide. Another preferred anti-wicking agent is a neutralized solution of a styrene-maleic anhydride copolymer. Generally, the anti-wicking agent is added at a level of up to 40% by dry weight of the starch, preferably at a level of up to 10%.

Other ingredients may be added to the starch binder composition to enhance the properties and storage capabilities of the binder composition both before and after application to the fiber mat. Optionally, a latex such as a vinyl emulsion polymer or an acrylic emulsion polymer may be added to the bath formulation generally at levels up to 30% by dry weight of the starch. A surfactant may also be added to the starch binder composition to improve the stability of the emulsion mixture with preferred surfactants including an amide oxide of dimethyl amino propyl lauramide, amine oxide of dimethyl amino ethyl lauramide, ethoxylated fatty alcohol, ethoxylated fatty acid ester, propoxylated-ethoxylated fatty alcohols and ethoxylated alkyl phenol. Generally a surfactant will be added at a level of 0.001% to 5% by dry weight of the starch. Also desirable to include in the starch binder composition is biocide such as Kathon LX[®] by Rohm & Haas which is a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one to improve the storage shelf stability of the starch binder composition, generally at levels of up to 25ppm active ingredients of the finished starch-based product or a level recommended by the supplier to insure biocidal activity.

To prepare the starch binder composition the various ingredients may be blended together in water. In one embodiment the starch crosslinking agent is maintained separate from the remainder of the binder composition until use is anticipated in order to extend the shelf stability. While the starch binder composition of this invention can be formulated at solid levels of anywhere from 3 to 50%, advantageously, a high solids starch binder composition can be formulated containing at least 25% solids. This high solids level can be achieved while maintaining a viscosity of below 500cps as measured on a Brookfield viscometer at room temperature having a #3 spindle at 100rpm. The starch binder composition may be coated and/or impregnated into the fiber mat, dried and cured by any known or conventional means available. Generally, the starch binder composition will be coated or impregnated onto or into the fiber mat at a level of about 10 to 30% by dry weight of the fiber mat and the coated and/or impregnated mat will be dried and cured generally at temperatures ranging from 80°C to 250°C for 0.25 to 8 minutes.

The foregoing examples are meant to illustrate this invention.

Example 1

Mat samples (9" x 12") of polyester fibers were impregnated in a pad bath containing either a latex binder (acrylic/N-methylol acrylamide copolymer emulsion) or starch based binders at 15% solids. Mat samples were padded to 145% wet pick-up to achieve an add-on level of 22% dry weight. Samples were dried and cured at 204°C (400°F) for 3.5 minutes. Samples were equilibrated at 180°C in the environmental chamber of an Instron Model 1130 instrument and tested for percent stretch at 5Kg and 8Kg. Samples were also tested for wicking by placing a strip of mat (15x5cm) vertically in 1 cm of blue-tinted water for 4 hours and measuring the rise of color. Results are shown in Table I. The viscosities of all the baths were less than 80cps when measured on a Brookfield RV Viscometer at room temperature with a #3 spindle at 100rpm.

Table I

5	Pad Bath Component, Parts Dry Basis	Sample Number				
		1	2	3	4	5
10	Conventional latex (acrylic/N-methylol acrylamide copolymer emulsion)	100				
15	Starch (maltodextrin m.w. 3600 daltons)		100	100	100	100
20	Starch Crosslinking Agent (cyclic urea-glyoxal condensate)			10		
25	Pad Bath Component, Parts Dry Basis	Sample Number				
		1	2	3	4	5
30	Starch Crosslinking Agent + 13% acrylamide- methacrylic acid copolymer				10	10
35	Anti-wicking Agent (Stearylated melamine - for- maldehyde sizing agent)					0.25
40	180°, % Stretch					
	5 Kg	4.1	2.7	1.7	1.5	1.9
	8 Kg	11.0	6.8	4.9	4.2	5.3
45	Wicking, mm	10	22	40	35	4

50 In Table I, a comparison of Samples #1 and #2 shows the benefit of a starch binder compared to a conventional system using a latex binder. The percent stretch for the starch binder is substantially less than the latex binder, although the wicking is worsened. Comparison of Sample #3 to Samples #1 and #2 shows the benefit of adding a starch crosslinking agent to the formulation. The stretching is substantially reduced in Sample #3, although there is substantial wicking. A comparison of Sample #4 to the previous samples shows the further improvement which was obtained by the addition of a small amount of acrylamide-methacrylic acid copolymer; however, wicking is still high. Comparing Sample #5 to the other samples show the benefit of adding a small amount of anti-wicking agent to the formulation. The percent stretch is about one-half the level found in a conventional latex system and there is a substantial reduction of wicking compared to the latex or other starch systems.

60 Example II

65 The samples in Table II demonstrate the usefulness of various starch crosslinking agents. The crosslinking agents used in this example include cyclic urea-glyoxal condensate, glycol-glyoxal condensate and melamine-formaldehyde resin. The binder was applied to a polyester mat and tested as detailed in Example I. In all three cases, the stretch is less than that seen with the conventional latex (acrylic/N-methylol acrylamide copolymer emulsion). The anti-wicking agent was deleted in these samples to better observe the performance

of the crosslinking agents.

Table II

Pad Bath Component, parts dry basis	Sample Number			
	6	7	8	9
Conventional latex (acrylic/N-methylol acrylamide)	100			
Starch (maltodextrin m.w. 3600 daltons)		100	100	100
Cyclic urea-glyoxal condensate + 13% acrylamide copolymer		10		
Glycol-glyoxal condensate + 13% acrylamide copolymer			10	
Melamine-formal- dehyde resin + 13% acrylamide copolymer				10
180° C, % Stretch				
5 Kg	5.2	2.0	1.9	1.7
8 Kg	13.2	5.7	5.2	3.3
Wicking, mm	2	30	25	10

Viscosity of all baths was less than 80cps measured as in Example I.

Example III

To further increase the tensile strength of the fiber mat bound with the starch binder composition, polyvinyl alcohol was added. The binder was applied to a polyester mat and tested as detailed in Example I with the results as shown in Table III. The tensile strength was also measured by placing a strip of the bound fiber mat in the Instron Model 1130 instrument.

Table III

5	Pad Bath Component, parts dry basis	Sample Number	
		10	11
10	Starch (maltodextrin m.w. 3600 daltons)	100	100
	Cyclic-urea- glyoxal condensate + 13% acrylamide copolymer	10	10
15	Polyvinyl alcohol	38.5	-
20	Tensile Kg 180°, % Stretch	22.1	18.8
25	5 Kg	2.7	2.0
	8 Kg	8.7	5.7

Viscosity of all pad baths were less than 80cps
measured as in Example I.

Example IV

A pad bath was prepared with the starch binder composition of Sample 5 of Example I at 25% solids and heated to 110°F (43°C). The room temperature viscosity of this bath was 125cps and at 100°F the viscosity was 90cps (Brookfield RV Viscometer, #3 spindle at 100rpm). A polyester mat was padded through 1 dip and 1 nip, then dried and cured for 3.5 minutes at 400°F (204°C). The sample was tested in the same manner as in previous examples with the following results:

40	Tensile Kg :	26.05
	180° C % Stretch:	
	5 Kg	1.60
	8 Kg	5.20
45	Wicking mm :	12

Example V

A starch was modified with a starch crosslinking agent by adding to a 1 liter round bottomed flask fitted with a mechanical stirrer, thermometer and condenser 445.2g of water, 6 grams of an 18% acrylamide-methacrylic acid copolymer, 6g of a 45% cyclic urea-glyoxal condensate, 0.5g of an ammonia-hydrolyzed styrene-maleic anhydride copolymer sizing agent and 240g of a low molecular weight acid modified starch (maltodextrin, m.w. 3600 daltons). This mixture was heated to 90°C for 30 minutes, then cooled to 35°C. the tan suspension was slightly foamy, which was remedied by adding four drops of a commercial defoamer, and ten drops of biocide to inhibit mold formation. This produced a starch binder suitable for use with a urea-formaldehyde resin, an acrylamide copolymer and a wet-strength agent for binding a glass mat.

Example VI

Example VI was similar to Example V in that a starch was modified with a starch crosslinking agent except that 4% of the low molecular weight starch was replaced by a high molecular weight starch (oxidized and ethoxylated potato starch), and 44g of a blocked glyoxal resin was used. After cooking for 30 minutes at 90°C,

the product was cooled to 40°C. To the product was then added 2.8g of an emulsified sizing agent consisting of a stearylated melamine resin and surfactants; and a biocide. This starch binder was suitable for use with a urea formaldehyde resin, an acrylamide copolymer and a wet strength agent for binding a glass mat.

Example VII

Sample 12 containing a mixture consisting of 25% of an 18% solution copolymer of acrylamide and methacrylic acid (72:28 mole ratio), 50% of the starch binder in Example VI and 25% of a 12.5% solution of a polyamide-polyamine-epichlorohydrin wet strength agent was prepared for use with a urea formaldehyde resin. Sample 13 contained a mixture similar to Sample 12 except that an 18% solution of a 10 mole% cationic polyacrylamide copolymer was used in lieu of the acrylamide-methacrylic acid copolymer. The products of Samples 12 and 13 were mixed to comprise 20% of the solids of a bath with a commercial urea formaldehyde resin which comprised 80% of the bath solids. A pad bath at 9% solids was prepared and used to pad Whatman filter paper. For controls, UF resin and a comparable mixture of acrylic latex and UF resin were used. The samples were dried and cured at 300°F (149°C) for 5 minutes resulting in an average add on of 20%. Dry, wet and hot wet tensile were measured on an Instron Model 1130 instrument. Results are shown in Table IV. Numbers reported are the average of 10 determinations. A second study was done with results shown in Table V. These samples were dried and cured 3.5 minutes at 400°F (204°C).

Table IV

Sample	Dry Ten- sile(Kg)	Wet Ten- sile(Kg)	Hot Wet Ten- sile(Kg)
UF resin	7.5	5.8	4.8
UF + latex	7.5	5.3	4.5
Sample 12	9.3	6.5	3.7
Sample 13	8.1	5.4	5.4

Table V

Sample	Dry Ten- sile(Kg)	Wet Ten- sile(Kg)	Hot Wet Ten- sile(Kg)
UF resin	8.7	6.2	4.6
UF + latex	8.2	5.8	5.3
Sample 12	10.0	6.2	4.7
Sample 13	9.1	4.5	3.9

Example VIII

Sample 13 of Example VII was mixed so as to comprise 20% of the solids of a pad bath, with a urea-formaldehyde resin comprising 80% of the solids. As a control, a similar bath was prepared in which an acrylic/N-methylol acrylamide latex comprised 20% of the solids. These binders were applied to fiberglass mat on a pilot-scale production machine, followed by normal drying and curing conditions. The results are in Table VI.

Table VI

	<u>Sample 13</u>	<u>Control</u>
5		
Dry Tensile (lb/3 in)		
Machine	135.6	125.2
Direction		
Cross	93.7	89.9
Direction		
10		
Wet Tensile (lb/3 in)		
Machine	83.0	79.7
Direction		
15		
Strength	61.2%	63.5%
Retention		
Tear, gm		
Machine	394	290
Direction		
20		
Cross	446	423
Direction		
Loss on	21.7	22.3
Ignition		
25		

Claims

1. A binder composition for fiber mats characterised in that the binder comprises starch, a starch crosslinking agent and an anti-wicking agent.

2. A binder composition according to claim 1 further comprising a polymer strength additive.

3. A binder composition according to claim 1 or claim 2 wherein the starch is chosen from the group consisting of maltodextrin, cyclodextrin, acid modified starch, enzyme converted starch, oxidized starch and ethoxylated starch.

4. A binder composition according to any preceding claim wherein the starch is a low molecular weight starch having a molecular weight of less than 7200 daltons.

5. A binder composition according to claim 4 further comprising a high molecular weight starch at up to 40% by weight of the low molecular weight starch, the high molecular weight starch having a molecular weight of greater than 7200 daltons.

6. A binder composition according to any preceding claim wherein the starch crosslinking agent is added at a level of about 1 to 15% by dry weight of the starch, and is chosen from the group consisting of urea-formaldehyde resin, malamine-formaldehyde resin, acetone-formaldehyde resin, glyoxal, blocked glyoxal resin and ammonium zirconium carbonate.

7. A binder composition according to claim 6 wherein the starch crosslinking agent is added at a level of about 5 to 10% by dry weight of the starch, and is chosen from the group consisting of a cyclic urea-glyoxal condensation product, a glyoxal and a polyol-glyoxal condensation product.

8. A binder composition according to claim 2 wherein the polymer strength additive is added at a level of up to 50% by dry weight of the starch, and is chosen from the group consisting of polyvinyl alcohol and a homopolymer or copolymer of acrylamide.

9. A binder composition according to claim 8 wherein the polymer strength additive is a copolymer of acrylamide and a monomer chosen from the group consisting of acrylic acid, methacrylic acid, vinyl acetate, vinyl pyrrolidone, sodium vinyl sulfonate, hydroxyethyl acrylate, acrylonitrile, acrylic ester, cationic monomer, methacrylic ester, N-substituted acrylamide and N-substituted methacrylamide.

10. A binder composition according to any preceding claim wherein the anti-wicking agent is added at a level of up to 4% by dry weight of the starch.

11. A binder composition according to any preceding claim further comprising a surfactant.

12. A binder composition according to any preceding claim further comprising a latex at a level of up to 30% by dry weight of the starch.

13. A binder composition according to any preceding claim composition has a solids level of 10 to 50% in water, and has a viscosity of no greater than 500cps when measured at room temperature.

14. Process for preparing a fiber mat comprising coating or impregnating a fiber mat with the binder composition according to any preceding claim and then drying and curing the mat.