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(54) Crosslinkable creping adhesives

Vernetzbare Kreppklebmittel

Adhésifs de crépage réticulables

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(73) Proprietor: **JAMES RIVER CORPORATION OF
VIRGINIA
Richmond, VA 23217 (US)**

(72) Inventors:
• **Hollenberg, David Henry
Neenah, Wisconsin 54956 (US)**
• **Collins, Stephen Risley
Neenah, Wisconsin 54956 (US)**
• **Van Luu, Phuong
Appleton, Wisconsin 54914 (US)**

(74) Representative: **Cropp, John Anthony David et al
London, WC1X 8AL (GB)**

(56) References cited:
EP-A- 0 340 020 **US-A- 4 063 995**
US-A- 4 883 564

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Description

This invention relates to creping fibrous webs.

In the manufacture of tissue and towel products, a common step is the creping of the product. This creping is done to provide desired aesthetic and performance properties to the product. Many of the aesthetic properties of tissue and towel products rely more upon the perceptions of the consumer than on properties that can be measured quantitatively. Such things as softness, and perceived bulk are not easily quantified, but have significant impacts on consumer acceptance. Since many of the properties of tissue and towel products are controlled or are at least influenced by the creping process, it is of interest to develop methods for controlling the creping process. Although the creping process is not well understood, it is known that changes in the process can result in significant changes in the product properties. A need exists to provide a method for influencing the creping process by allowing the control of the adhesion of the tissue or towel substrate to the surface from which it is creped, most usually large cylindrical dryers known in the industry as Yankee dryers.

Obtaining and maintaining adhesion of tissue and towel products to Yankee dryers is an important factor in determining crepe quality. Inadequate adhesion results in poor or non-existing creping, whereas excessive adhesion may result in poor sheet quality and operational difficulties. Traditionally, creping adhesives alone or in combination with release agents have been applied either to the sheet or to the surface of the dryer in order to provide the appropriate adhesion to produce the desired crepe.

Various types of creping adhesives have been used to adhere fibrous webs to dryer surfaces such as Yankee dryers. Prior art creping adhesives rely upon combinations of self-crosslinkable soft polymers having a T_g of less than 10°C with a non-film forming hard polymer emulsion having a T_g greater than 50°C (US-A-4,886,579) or thermoset resins (US-A-4,528,316 and US-A-4,501,640). The ability to control the mechanical properties of the polymers, as well as the adhesion and release of the fibrous web from the Yankee dryer, is limited when using these types of creping adhesives.

SUMMARY OF THE INVENTION

The present invention provides an improved creping adhesive which provides the ability to readily control T_g and adhesion and which can be more easily removed from dryer surfaces. Thus, the adhesive can provide high adhesion of a fibrous web to a dryer surface with low "friction", i.e., the fibrous web can be easily removed from the dryer surface. This can be accomplished while at the same time reducing or inhibiting corrosion of the dryer surface.

The essence of the present invention is that the adhesion properties of specific types of polymers can be systematically changed by varying the amount of crosslinking that may occur when the polymer is dried onto the surface of a Yankee dryer. Because crosslink density influences the mechanical properties (i.e., modulus, brittleness, T_g), this permits the adjustment of adhesion/release of the fibrous substrate onto the surface of the dryer. The nature of the polymers and types of crosslinkers used permits the incorporation of anti-corrosion components in the formulations of the present invention. This can have significant benefits in that corrosion of dryer surfaces can be a major problem in some tissue and towel mills.

The method of the present invention includes the steps of providing to the interface of a fibrous web and a heated support drying surface for the fibrous web a creping adhesive which contains a non-self-crosslinkable material and a crosslinking agent which is a crosslinker for the non-self-crosslinkable material and removing the fibrous web from the support surface by creping. The process preferably includes the steps of providing to the interface of a fibrous web and a drying surface a creping adhesive which contains a polymer or oligomer having functional groups which can be crosslinked by ionic crosslinking and an ionic crosslinking agent which contains metal cations having a valence of three or more and removing the fibrous web from the drying surface with a creping blade to thereby crepe the fibrous web.

The invention also provides a creping adhesive, comprising:
 polymer, oligomer or mixture thereof having functional groups which can be crosslinked by cations;
 an amount of metal cations having a valence of three or more effective to provide crosslinking when creping a fibrous web from a heated dryer surface by means of the creping adhesive; and
 an aqueous solvent or diluent for said polymer, oligomer or mixture thereof.

BRIEF DESCRIPTION OF THE DRAWING

The sole drawing Figure is a schematic illustration of a Yankee dryer to which a tissue web is presented, dried, creped and then wound into a soft roll.

DETAILED DESCRIPTION OF THE INVENTION

The drawing Figure illustrates the conventional steps in formation of a tissue paper web suitable for use as a facial tissue. This conventional process includes the steps of preforming a fibrous web, applying a creping adhesive to the

surface of a Yankee dryer, applying the fibrous web to the surface of the Yankee dryer having the creping adhesive on the external surface thereof, removing the fibrous web from the Yankee dryer by use of a creping blade and winding the dried fibrous web onto a roll. Alternatively, the creping adhesive can be applied to the surface of the fibrous web that will contact the dryer, before the fibrous web is presented to the dryer.

5 Referring to the drawing Figure, this represents one of a number of possible configurations used in processing tissue products. In this particular arrangement, the transfer and impression fabric designated at 1 carries the formed, dewatered web 2 around turning roll 3 to the nip between press roll 4 and Yankee dryer 5. The fabric, web and dryer move in the directions indicated by the arrows. The entry of the web to the dryer is well around the roll from creping blade 6 which, as schematically indicated, crepes the traveling web from the dryer as indicated at 7. The creped web 7 exiting from the
10 dryer is wound into a soft creped tissue roll 8. To adhere the nascent web 2 to the surface of the dryer, a spray 9 of adhesive is applied to the surface ahead of the nip between the press roll 4 and Yankee 5. Alternately, the spray may be applied to the traveling web 2 directly as shown at 9'. Suitable apparatus for use with the present invention are disclosed in US-A-4,304,625 and US-A-4,064,213.

This illustration does not incorporate all the possible configurations used in presenting a nascent web to a Yankee
15 dryer. It is used only to describe how the adhesive of the present invention can be used to promote adhesion and thereby influence the crepe of the product. The present invention can be used with all other known processes that rely upon creping the web from a dryer surface. In the same manner, the method of application of the adhesive to the surface of the dryer or the web is not restricted to spray applications, although these are generally the simplest method for adhesive application.

20 The present invention is useful for the preparation of fibrous webs which are creped to increase the thickness of the web and to provide texture to the web. The invention is particularly useful in the preparation of final products such as facial tissue, toilet tissue, paper towels and the like. The fibrous web can be formed from various types of wood pulp based fibers which are used to make the above products such as hardwood kraft fibers, softwood kraft fibers, hardwood sulfite fibers, softwood sulfite fibers, high yield fibers such as chemi-thermo-mechanical pulps (CTMP), thermomechanical pulps (TMP) or refiner mechanical pulps (RMP). Furnishes used may also contain or be totally comprised of recycled
25 fibers (i.e., secondary fibers). The fibrous web, prior to application to the Yankee dryer, usually has a water content of 40 to 80 wt. %, more preferably 50 to 70 wt. %. At the creping stage, the fibrous web usually has a water content of less than 7 wt. %, preferably less than 5 wt. %. The final product, after creping and drying, has a base weight of 7 to 80 pounds per ream.

30 The creping operation itself can be conducted under conventional conditions except that the creping adhesive of the present invention is substituted for a conventional creping adhesive.

The non-self-crosslinkable material of the present invention may be a polymer or oligomer which contains crosslinkable functional groups. Exemplary crosslinkable functional groups include hydroxyl, carboxyl, sulfonate, sulfate, phosphate and other functional groups containing active hydrogens and mixtures thereof.

35 Examples of hydroxylated polymers and oligomers that can be used in the process include polysaccharides and oligosaccharides such as starch, modified starches, partially hydrolyzed or oxidized starches, alginic acid, carageenans, water soluble derivatives of cellulose, dextrans, maltodextrins, and naturally occurring water soluble polysaccharides. Other useful hydroxylated polymers include polyvinyl alcohols, partially hydrolyzed polyvinyl acetates, and ethylenevinyl alcohols.

40 Examples of carboxylated polymers useful in this invention include homopolymers of acrylic and methacrylic acids, acrylic acid/methacrylic acid copolymers, partially hydrolyzed polyacrylamides and polymethylacrylamides, carboxylated polymers and copolymers obtained by polymerization or copolymerization of acrylic, methacrylic, maleic, itaconic, fumaric, crotonic, and other ethylenically unsaturated acids with suitable ethylenically unsaturated monomers. Suitable carboxylated polymers and copolymers can also be obtained through polymerization or copolymerization of unsaturated
45 anhydrides such as maleic or itaconic anhydrides with suitable unsaturated monomers followed by hydrolysis.

Examples of sulfonate containing polymers are those derived from polymerization or suitable copolymerization of unsaturated sulfonic acids such as styrene sulfonic acid, 2-vinyl-3-bromo benzenesulfonic acid, 2-allyl-benzenesulfonic acid, vinyl phenylmethane-sulfonic acid, ethylene sulfonic acid, phenylethylene sulfonic acid, 2-sulfo-vinylfurane, 2-sulfo-5-allylfurane and 1-phenylethylene sulfonic acid.

50 Examples of phosphate containing polymers include homopolymers or copolymers of unsaturated monomers containing a phosphoric acid moiety such as methacryloxy phosphate. Sulfated polymers useful in the invention may be derived from treatment of hydroxylated or unsaturated polymers with either sulfuric acid or sulfur trioxide/H₂SO₄ mixtures.

55 Polymers containing more than one type of functional group can also be used in this invention. Oxidized starches, carboxymethyl celluloses, potato starches, sulfated polyvinyl alcohols, gelatin, casein, protein as well as sulfated and phosphated derivatives of celluloses or starches could all find application in this invention.

Although in certain instances, some of the polymers containing more than one functional group could conceivably crosslink, e.g., internal esterification of a carboxylated cellulose, the present invention is drawn to rely upon the ability to finely control the level of crosslinking through addition of an appropriate amount of crosslinking agent. In addition to

having crosslinkable functional groups, the polymer or oligomer should be water-soluble, water dispersible or capable of being formed into a water-based emulsion. The polymer or oligomer is preferably water soluble.

The non-self-crosslinkable material should be present in the creping adhesive in an amount sufficient to provide the desired results in the creping operation. If it is intended to spray the creping adhesive onto the surface of Yankee dryer, the creping adhesive should have a viscosity low enough to be easily sprayed yet high enough to provide a sufficient amount of adhesion. If the creping adhesive will be sprayed onto the surface of the Yankee dryer, the content of polymer, oligomer or mixture thereof will probably be about 0.01 to 0.5, preferably 0.03 to 0.2 % by weight based on the total weight of the adhesive. The solids content is constituted primarily by the polymer or oligomer, i.e., the crosslinkable material and the crosslinker.

Various types of crosslinking agents may be used in accordance with the present invention. Preferred crosslinking agents are ionic crosslinking agents which provide ionic crosslinking between functional groups of polymers. An added benefit of ionic crosslinking is that it is reversible at high pH. This is in contrast with many other crosslinking resins that have been used as adhesives that are thermoset resins. The reversibility of the crosslinking provides the flexibility to remove excess amounts of material that may have built up on dryer surfaces as a result of machine operational problems. For example, if it is desired to remove built up adhesives, the adhesive can be treated with a basic solution, which preferably is an aqueous basic solution having a non-volatile base dissolved therein. As the water evaporates, the pH of the solution will rise causing the crosslinks to hydrolyze thereby allowing easier removal of the built up layer(s) of polymer from the machine.

Metal cations with a valency of 3 or more, and more preferably 4 or more may be used as crosslinking agents. Exemplary cations are Fe^{+3} , Cr^{+4} , Cr^{+6} , Ti^{+4} , Zr^{+4} , etc. Zirconium has been found to be a particularly useful crosslinking agent because it is capable of crosslinking hydroxylated polymers as well as the more acidic carboxylated and sulfonated polymers.

Although zirconium compound cations are the preferred crosslinkers, it has been found that mixtures of zirconium and aluminium ions are effective in providing crosslinking of complex polymers containing more than one type of functional group. For example, aluminium will crosslink carboxyl and sulfonate groups. Mixtures of polymers, for example, polyvinyl alcohol and polyacrylamides (partially hydrolyzed) can be effectively crosslinked using mixtures of aluminium and zirconium ions.

The crosslinker will usually be added to the creping adhesive in the form of a water-soluble salt or water-soluble "complex" which provides cations upon dissolution in water. An example of one type of complex is ammonium zirconium carbonate.

The crosslinker should be present in the creping adhesive in an amount sufficient to provide changes in the mechanical properties of the polymer once the solution has been evaporated and the polymer crosslinked. As the level of crosslinking increases, the mechanical properties change with the crosslink density. Increased crosslinking generally will increase the T_g , increase the brittleness and provide different responses to mechanical stresses than uncrosslinked polymers. Obtaining the appropriate crosslink density will depend not only on the relative concentration of added crosslinker but also on the type of polymer employed, the functional groups present, and the molecular weight of the polymer. Early work demonstrated that, in general, as the molecular weight of the starting polymer increases, the amount of crosslinker necessary to provide particular levels of final properties (i.e., T_g , brittleness, etc.) decreases. A discussion concerning the relationship between T_g and crosslinking of polymers is contained in the article by Stutz et al, Journal of Polymer Science, 28, 1483-1498 (1990), the entire contents of which is hereby incorporated by reference.

For most of the polymers used in the present invention, the amount of crosslinker, i.e., the compound which provides the cations, necessary to promote improvements in adhesion is in the range of 0.5 to 10% by weight based on the weight of the polymer to be crosslinked. The ability to control the mechanical properties of crosslinked polymers by varying the amount of crosslinker is the essential part of the invention. It is believed that a key property influenced by crosslink density is the T_g . Since prior work has claimed that T_g does influence adhesive properties (see US-A-Patents 4,064,213; US-A-4,886,579; US-A-4,063,995; US-A-4,304,625), the ability to change or modify T_g through crosslink density offers an opportunity to control the adhesion and subsequent creping. The exact amount of crosslinker will depend upon the desired properties of the adhesive, the type of non-self-crosslinking material, and the molecular weight of the non-self-crosslinking material.

While the polymer and crosslinker are the major "active" ingredients of the present invention, other materials can be incorporated with beneficial results. Materials can be added to modify the mechanical properties of the crosslinked polymers. Some of these materials may actually be incorporated into the crosslinked polymer. Examples would include glycols (ethylene glycol, propylene glycol, etc.), polyethylene glycols, and other polyols (simple sugars and oligosaccharides). Other components can be added to modify interfacial phenomena such as surface tension or wetting of the adhesive solution. Nonionic surfactants such as the octyl phenoxy based Triton (Rohm & Haas, Inc.) surfactants or the Pluronic or Tetronic (BASF Corp.) surfactants can be incorporated in the present invention to improve surface spreading or wetting capabilities. Mineral oils or other low molecular weight hydrocarbon oils or waxes can be included to modify interfacial phenomena.

Finally, one additional class of materials can be added to the formulation. These are phosphate salts or salts of phosphate oligomers. Addition of these materials will provide some buffering capability as well as provide changes in the surface tension of the solution. The major purpose for inclusion is, however, the anti-corrosive properties of phosphates. While some of the other materials used in the formulations of the present invention provide anti-corrosive properties (most notably the zirconium containing crosslinkers), it is expected that the addition of phosphates to the formulation will enhance the overall anti-corrosive properties of the adhesive formulation. If phosphate is incorporated, it should be added in an amount of 5 to 15 wt. %, preferably 5 to 10 wt. % based on the total weight of the adhesive formulation.

The various components of the adhesive formulation, i.e., non-self-crosslinking polymer, crosslinking agent, polymer modifiers, surfactants, and anti-corrosive additives, will all be dissolved, dispersed, suspended, or emulsified in a liquid carrying fluid. This liquid will usually be a non-toxic solvent such as water.

The liquid component is usually present in an amount of 90 to 99.98 wt. %, preferably 99 to 99.9 wt. % based on the total weight of the creping adhesive. The pH of the adhesive when it is applied to the desired surface in the paper-making operation will usually be about 7.5 to 11. The solvent preferably consists essentially (or completely) of water. If other types of solvents are added, they are preferably added in small amounts.

EXAMPLES

In the following Examples, the adhesive is prepared by dissolving the indicated ingredients in water in the amounts indicated. The creping adhesive is applied to a small hand sheet which is then applied to a hot oil-heated cylinder which can be rotated at a controlled speed. This small lab-sized piece of equipment is used to simulate a Yankee dryer. The drum is rotated until the sheet is virtually dry, and a creping blade is placed on the surface of the drum to crepe the sheet from the drum. During this creping, the torque necessary to bring about creping is measured. This measurement allows the calculation of a torque-adhesion relationship and provides indications of the lubrication and release characteristics of the coating adhesive. Torque, adhesion and polymer buildup/release observations and calculations are shown in Table

1. The properties of some of these products are shown in Table 2.

Table 1

Sample #	Combinations	AVG (Nm)	STD (Nm)	AVG (Nm)	STD (Nm)	T	t ₁	AVG (Nm)	STD (Nm)	t ₂	AVG (Nm)	STD (Nm)	(T-t ₂)	AVG (Nm)	STD (Nm)	(t ₂ -t ₁)
1*	3g ZrO ₂	3.24	0.29	5.84	0.44	0.44	5.32	0.38	0.52	0.32	2.08	0.19				
2*	3g PVA	3.07	0.10	4.88	0.08	0.08	2.78	0.06	2.10	0.11	-0.29	0.12				
3	3g PVA+1.5g ZrO ₂	3.43	0.25	6.24	0.20	0.20	3.58	0.19	2.66	0.18	0.15	0.17				
4*	3g PVA+1.5g Na ₃ PO ₄	3.56	0.07	4.45	0.21	0.21	2.38	0.09	2.07	0.17	-1.18	0.12				
5	.75g ZrO ₂ +1.5g Na ₃ PO ₄ +3g PVA	3.06	0.04	5.86	0.13	0.13	3.09	0.08	2.77	0.12	0.02	0.07				
6	3g PVA+.75g ZrO ₂	3.13	0.10	5.73	0.25	0.25	3.23	0.11	2.50	0.25	0.01	0.06				

* comparative

- t1 - torque on cylinder before application of adhesive and sample
- T - torque on cylinder during creping of sample (with adhesive) from cylinder
- t2 - torque on cylinder after removal of sample
- T-t2 - sample adhesion
- t2-t1 - Polymer buildup/release
- ZrO₂ - Ammonium zirconium carbonate or BaCote 20, Magnesium Electron Corp.
- PVA - Polyvinyl Alcohol - Airvol 540, Air Products Corp.
- Na₃PO₄ - trisodium phosphate - reagent grade.

The properties of some of these products are shown in Table 2.

Table 2

	Unit	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Wave Length	(μ m)	176.75	175.540	173.260	165.670	179.850
Crepe/Cm	(#)	56.045	56.678	58.745	59.445	55.468
% Void-Area	(%)	3.181	3.265	3.401	2.037	4.651
Basis Weight g/m^2 (lbs./R)		17.918 (11.009)	18.158 (11.156)	18.234 (11.203)	18.169 (11.163)	17.908 (11.003)
Caliper mm/1 sheet (.001in/8 sheets)		0.01323 (4.167)	0.01286 (4.050)	0.01316 (4.144)	0.01288 (4.056)	0.01321 (4.161)
Bulk	(cm^3/g)	5.907	5.666	5.773	5.671	5.902
Water ABS Rate	(Sec)	2.052	2.833	2.5	3.218	2.548
MD-Tensil	(G)	1483	1573	1446	1688	1549
CD-Tensil	(G)	796	885	788	888	809
Breaking Length	(Km)	0.795	0.852	0.768	0.884	0.820
MD- % Disp.	(%)	15.79	16.858	16.416	16.83	17.16
CD- % Disp.	(%)	2.943	2.871	2.924	2.702	2.863

Claims

1. A method of creping a fibrous web, comprising:
 - 5 providing to the interface of a fibrous web and a heated support drying surface for the fibrous web a creping adhesive which contains a non-self-crosslinkable material and a crosslinking agent which is a crosslinker for the non-self-crosslinkable material; and
 - removing said fibrous web from said support surface by creping.
- 10 2. A method as claimed in claim 1 wherein the support surface is a drying surface and said fibrous web is removed from said drying surface by means of a creping blade.
3. The method of claim 2, wherein said drying surface is provided by a Yankee dryer.
- 15 4. The method of claim 2 or claim 3, wherein said creping adhesive is sprayed onto said drying surface prior to presentation of said fibrous web to said dryer surface.
- 20 5. A method as claimed in any one of claims 1 to 4 wherein said non-self-crosslinkable material comprises polymer, oligomer or mixture thereof having functional groups which can be crosslinked by ionic crosslinking and said crosslinking agent comprises an ionic crosslinking agent which contains metal cations having a valence of three or more.
- 25 6. The method of any one of claims 1 to 5, wherein said non-self-crosslinkable material comprises polymer, oligomer, or mixture thereof containing crosslinkable functional groups having active hydrogen atoms.
- 30 7. A method as claimed in claim 6 wherein said crosslinkable functional groups are selected from hydroxyl groups, carboxyl groups, sulfonate groups, sulfate groups, phosphate groups and mixtures thereof.
- 35 8. A method as claimed in any one of claims 1 to 7, wherein said non-self-crosslinkable material is selected from polysaccharides, oligosaccharides, polyvinyl alcohols, partially hydrolyzed polyvinyl acetates, ethylene vinyl alcohols, homopolymers of acrylic acid and methacrylic acid, acrylic acid/methacrylic acid copolymers, partially hydrolyzed polyacrylamides and polymethacrylamides, copolymers of acids selected from acrylic, methacrylic, maleic, itaconic, fumaric and crotonic acid with ethylenically unsaturated monomers, hydrolysed homopolymers and copolymers of unsaturated anhydrides, homopolymers and copolymers of unsaturated sulfonic acids, homopolymers and copolymers of unsaturated monomers containing phosphoric acid moieties, sulfated hydroxylated or unsaturated polymers, oxidised starches, carboxymethyl celluloses, potato starches, sulfated polyvinyl alcohols, gelatin, casein, protein and sulfated and phosphorylated derivatives of cellulose and starches.
- 40 9. The method of any one of claims 5 to 8, wherein said crosslinking agent comprises zirconium cations or a mixture of aluminium cations and zirconium cations.
10. The method of any one of claims 1 to 9, wherein said creping adhesive also contains a phosphate.
- 45 11. A creping adhesive, comprising:
 - polymer, oligomer or mixture thereof having functional groups which can be crosslinked by cations;
 - an amount of metal cations having a valence of three or more effective to provide crosslinking when creping a fibrous web from a heated dryer surface by means of the creping adhesive; and
 - an aqueous solvent or diluent for said polymer, oligomer or mixture thereof.
- 50 12. The adhesive of claim 11, wherein said polymer, oligomer or mixture thereof is present in an amount of about 0.01 to 0.5% by weight, based on the total weight of said adhesive.
13. The adhesive of claim 11 or claim 12 wherein a crosslinker is present in an amount of about 0.5 to 10% by weight based on the amount of the polymer to be crosslinked to provide said cations.
- 55 14. The adhesive of any one of claims 11 to 13, said adhesive containing a water soluble polymer selected from those specified in claim 8.
15. The adhesive of any one of claims 11 to 14 wherein said metal cations are selected from zirconium ions and mixtures thereof with aluminium ions.

Patentansprüche

1. Verfahren zum Kreppen eines faserigen Gewebes, bei dem man die Grenzfläche zwischen einem faserigen Gewebe und einer erwärmten Trägeroberfläche zum Trocknen des faserigen Gewebes mit einem Kreppklebemittel versieht, das ein nicht selbstvernetzbares Material und ein vernetzendes Mittel enthält, welches ein Vernetzungsmittel für das nicht selbstvernetzbar darstellt, und das faserige Gewebe durch Kreppen von der Trägeroberfläche entfernt.
2. Verfahren nach Anspruch 1, bei dem die Trägeroberfläche eine Oberfläche zum Trocknen ist und das faserige Gewebe mittels einer Kreppklinge von der Oberfläche zum Trocknen entfernt wird.
3. Verfahren nach Anspruch 2, bei dem die Oberfläche zum Trocknen durch einen Glätzzylinder (Yankee dryer) zur Verfügung gestellt wird.
4. Verfahren nach Anspruch 2 oder 3, bei dem das Klebemittel zum Kreppen auf die Oberfläche zum Trocknen aufgesprüht wird, ehe man das faserige Gewebe auf die Oberfläche zum Trocknen aufbringt.
5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem das nicht selbstvernetzbar Material ein Polymer, Oligomer oder eine Mischung davon mit funktionellen Gruppen umfaßt, die durch ionisches Vernetzen vernetzt werden können, und das Vernetzungsmittel ein ionisches Vernetzungsmittel umfaßt, das Metallkationen mit einer Wertigkeit von 3 oder mehr enthält.
6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das nicht selbstvernetzbar Material ein Polymer, Oligomer oder eine Mischung davon umfaßt, das bzw. die vernetzbar funktionelle Gruppen mit aktiven Wasserstoffatomen enthält.
7. Verfahren nach Anspruch 6, bei dem die vernetzbaren funktionellen Gruppen aus Hydroxyl-, Carboxyl-, Sulfonat-, Sulfat- und Phosphatgruppen sowie deren Mischungen ausgewählt werden.
8. Verfahren nach einem der Ansprüche 1 bis 7, bei dem das nicht selbstvernetzbar Material aus Polysacchariden, Oligosacchariden, Polyvinylalkoholen, teilweise hydrolysierten Polyvinylacetaten, Ethylenvinylalkoholen, Homopolymeren von Acryl- und Methacrylsäure, Acryl-/Methacrylsäure-Copolymeren, teilweise hydrolysierten Polyacrylamiden und Polymethacrylamiden, Copolymeren von aus Acryl-, Methacryl-, Malein-, Itacon-, Fumar- und Crotonsäure ausgewählten Säuren mit ethylenisch ungesättigten Monomeren, hydrolysierten Homopolymeren und Copolymeren von ungesättigten Anhydriden, Homopolymeren und Copolymeren von ungesättigten Sulfonsäuren, Homopolymeren und Copolymeren von ungesättigten Monomeren, die Phosphorsäurekomponenten enthalten, sulfatierten hydroxylierten oder ungesättigten Polymeren, oxidierten Stärken, Carboxymethylcellulosen, Kartoffelstärken, sulfatierten Polyvinylalkoholen, Gelatine, Kasein, Protein und sulfatierten und phosphatierten Derivaten von Cellulose und Stärken ausgewählt ist.
9. Verfahren nach einem der Ansprüche 5 bis 8, bei dem das Vernetzungsmittel Zirconiumkationen oder eine Mischung aus Aluminium- und Zirconiumkationen umfaßt.
10. Verfahren nach einem der Ansprüche 1 bis 9, bei dem das Kreppklebemittel ebenfalls ein Phosphat enthält.
11. Kreppklebemittel, umfassend ein Polymer, Oligomer oder eine Mischung davon, das bzw. die durch Kationen vernetzbar funktionelle Gruppen aufweist; eine Menge an Metallkationen mit einer Wertigkeit von 3 oder mehr, die eine Vernetzung bewirkt, wenn ein faseriges Gewebe mittels des Kreppklebemittels von einer erhitzten Trockneroberfläche gekreppert wird, und ein wäßriges Lösungsmittel oder einen Verdünnner für das Polymer, Oligomer oder deren Mischung.
12. Klebemittel nach Anspruch 11, bei dem das Polymer, Oligomer oder deren Mischung in einer Menge von etwa 0,01 bis 0,5 Gew.-%, bezogen auf das Gesamtgewicht des Klebemittels, vorhanden ist.
13. Klebemittel nach Anspruch 11 oder 12, bei dem ein Vernetzungsmittel in einer Menge von etwa 0,5 bis 10 Gew.-%, bezogen auf die Menge des zu vernetzenden Polymeren, vorhanden ist, um die Kationen zur Verfügung zu stellen.

14. Klebemittel nach einem der Ansprüche 11 bis 13, das ein aus den in Anspruch 8 spezifizierten Polymeren ausgewähltes wasserlösliches Polymer enthält.

5 15. Klebemittel nach einem der Ansprüche 11 bis 14, bei dem die Metallkationen aus Zirconiumionen und Mischungen davon mit Aluminiumionen ausgewählt ist.

Revendications

- 10 1. Procédé de crêpage d'une nappe fibreuse, comprenant :
- la fourniture à l'interface d'une nappe fibreuse et d'une surface de séchage d'un support chauffé pour la nappe fibreuse, d'un adhésif de crêpage qui contient une matière non auto-réticulable et un agent de réticulation qui est un agent de réticulation pour la matière non auto-réticulable; et
- le détachement de cette nappe fibreuse de cette surface de support par crêpage.
- 15 2. Procédé suivant la revendication 1, dans lequel la surface de support est une surface de séchage et cette nappe fibreuse est détachée de cette surface de séchage avec une lame à crêper.
3. Procédé suivant la revendication 1, dans lequel cette surface de séchage est fournie par un appareil de séchage Yankee.
- 20 4. Procédé suivant les revendications 2 ou 3, dans lequel cet adhésif de crêpage est pulvérisé sur cette surface de séchage avant présentation de cette nappe fibreuse sur cette surface de sécheur.
- 25 5. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel cette matière non auto-réticulable comprend un polymère, un oligomère ou un mélange de ceux-ci ayant des groupes fonctionnels qui peuvent être réticulés par réticulation ionique et cet agent de réticulation comprend un agent de réticulation ionique qui contient des cations métalliques ayant une valence de trois ou plus.
- 30 6. Procédé suivant l'une quelconque des revendications 1 à 5, dans lequel cette matière non auto-réticulable comprend un polymère, un oligomère ou un mélange de ceux-ci contenant des groupes fonctionnels réticulables ayant des atomes d'hydrogène actifs.
- 35 7. Procédé suivant la revendication 6, dans lequel ces groupes fonctionnels réticulables sont choisis parmi des groupes hydroxy, des groupes carboxy, des groupes sulfonate, des groupes sulfate, des groupes phosphate et leurs mélanges.
- 40 8. Procédé suivant l'une quelconque des revendications 1 à 7, dans lequel cette matière non auto-réticulable est choisie parmi des polysaccharides, des oligosaccharides, des alcools polyvinyliques, des acétates de polyvinyle partiellement hydrolysés, des alcools éthylène vinyliques, des homopolymères d'acide acrylique et d'acide méthacrylique, des copolymères d'acide acrylique et d'acide méthacrylique, des polyacrylamides et des polyméthacrylamides partiellement hydrolysés, des copolymères d'acides choisis parmi les acides acrylique, méthacrylique, maléique, itaconique, fumarique et crotonique avec des monomères éthyléniquement insaturés, des homopolymères et des copolymères hydrolysés d'anhydrides insaturés, des homopolymères et des copolymères d'acides sulfoniques insaturés, des homopolymères et des copolymères de monomères insaturés contenant des parties acide phosphorique, des polymères sulfatés hydroxylés ou insaturés, des amidons oxydés, des carboxyméthyl celluloses, des amidons de pomme de terre, des alcools polyvinyliques sulfatés, une gélatine, une caséine, une protéine et des dérivés sulfatés et phosphatés de cellulose et d'amidons.
- 45 9. Procédé suivant l'une quelconque des revendications 5 à 8, dans lequel cet agent de réticulation comprend des cations zirconium ou un mélange de cations aluminium et de cations zirconium.
- 50 10. Procédé suivant l'une quelconque des revendications 1 à 9, dans lequel cet adhésif de crêpage contient aussi un phosphate.
- 55 11. Adhésif de crêpage, comprenant :
- un polymère, un oligomère ou un mélange de ceux-ci ayant des groupes fonctionnels qui peuvent être réticulés par des cations;
- une quantité de cations métalliques ayant une valence de trois ou plus, efficace pour fournir une réticulation lors du crêpage d'une nappe fibreuse à partir d'une surface de sécheur chauffée au moyen de l'adhésif de crêpage; et

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un diluant ou solvant aqueux pour ce polymère, cet oligomère ou leur mélange.

12. Adhésif suivant la revendication 11, dans lequel ce polymère, cet oligomère ou leur mélange est présent en une quantité d'environ 0,01 à 0,5% en poids par rapport au poids total de cet adhésif.

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13. Adhésif suivant les revendications 11 ou 12, dans lequel cet agent de réticulation est présent en une quantité d'environ 0,5 à 10% en poids par rapport à la quantité du polymère à réticuler pour fournir ces cations.

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14. Adhésif suivant l'une quelconque des revendications 11 à 13, cet adhésif contenant un polymère soluble dans l'eau choisi parmi ceux qui sont énumérés dans la revendication 8.

15. Adhésif suivant l'une quelconque des revendications 11 à 14, dans lequel ces cations métalliques sont choisis par des ions zirconium et leurs mélanges avec des ions aluminium.

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