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(54) Title: COMPOSITION AND METHOD FOR PRODUCING PRE-IMPREGNATED DECORATIVE BASE PAPER COMPRISING BIOPOLYMER NANOPARTICLES

(57) Abstract: A pre-impregnated decorative base paper for decorative coating materials, comprising biopolymer nanoparticles.

Composition and Method for Producing Pre-impregnated Decorative Base Paper Comprising Biopolymer Nanoparticles

The present invention relates to a pre-impregnated decorative base paper, also referred to as "prepreg" or "prip", and decorative coating materials obtainable therefrom.

Decorative papers in general are used to cover surfaces in furniture manufacturing and in interior fitting.

There exists two categories of decorative papers, namely on the one hand papers for high pressure laminates (HPL) or low pressure laminates (LPL), and on the other hand pre-impregnated papers for foil applications.

Papers for HPL or LPL are decorative papers that are made on a paper machine, printed, and impregnated off-line.

High pressure laminates are laminates which are formed by pressing together several impregnated papers stacked on top of one another. In general, such high pressure laminates are constituted by an uppermost transparent overlay which produces surface resistance, the resin-impregnated decorative paper and one or more impregnated phenolic resin-Kraft papers. The underlay is, for example, particle board or wood chipboard, or even plywood.

In case of low pressure laminates, the decorative paper impregnated with synthetic resin is pressed directly onto an underlay, for example particle board, using low pressure.

In HPL or LPL, the resin content of the impregnated paper is relatively high, about the same weight of resin as paper, and the resin is of use to the adhesion between the impregnated papers or on the underlay.

Prepregs should be distinguished from these impregnated papers for HPL or LPL, because the paper is resin impregnated on line on the paper machine, then printed and lacquered.

In pre-impregnated papers, the resin content is not as high as in impregnated papers for HPL or LPL, and a glue must be used to make the paper adhere to the underlay.

The impregnation of papers to make pre-impregnated papers is carried out on both faces of the paper in a symmetrical manner. The top face is the one that will be printed and lacquered and the bottom face is the one that will be glued to the underlay.

A good lacquering requires that the lacquer remains mostly at the surface of the paper to obtain a smooth and glossy surface.

On the contrary, gluing requires that the glue penetrates into the paper more deeply to achieve high resistance against delamination.

Generally speaking, to get a good lacquer hold out, a closed surface is desirable and to get a good gluability, an open structure is desirable.

5 Pre-impregnates must accordingly meet these specific two opposite requirements in a satisfactory manner. This is typically achieved by using a pre-impregnating composition that has a latex copolymer component and a water soluble component.

10 In addition, pre-impregnates should preferably satisfy other properties desirable for decorative papers in general, which include high opacity to improve covering of the underlay, uniform sheet formation and grammage of the sheet for uniform resin uptake, high light-fastness, high purity and uniformity of colour for good reproducibility of the pattern to be printed, high wet strength for a smooth impregnation procedure, an appropriate absorbency in order to obtain the required degree of resin saturation, and dry strength, which is important in rewinding operations in the paper machine and for printing in the printing machine, good
15 internal bond, good printability and the paper must not fray during processing steps such as sawing or drilling.

An example of a pre-impregnated decorative base paper is disclosed in US 8 349 464 B2. It comprises a base paper that is impregnated with an impregnating resin comprising at least one polymer latex and a solution of thermally or oxidatively degraded
20 starch with a specific molecular weight distribution and a polydispersity index M_w/M_n of 6 to 23.

Other pre-impregnated decorative base papers are disclosed in EP 0 648 248 B1, in which the impregnating composition comprises a dispersion of styrene-ethyl acrylate-butyl acrylate copolymer and an aqueous composition of a binder chosen from polyvinyl alcohol (PVOH), polyvinyl acetate (PVAc), gelatin and starch. A preferred composition comprises
25 50 parts by weight of a polyvinyl alcohol solution at between 5 to 15% and 50 parts by weight of a styrene-ethyl acrylate-butyl acrylate copolymer dispersion.

Starch is a complex carbohydrate polymer which is insoluble in water in its native form. It must be solubilized to act as a binder in pre-impregnated paper applications. It can
30 be in its high molecular weight native form (but then gels at very low concentrations), or preferably in modified form where the molecular weight is typically significantly reduced. A common example is ethylated starches, which contain a certain low level of hydroxyethyl functionalities and resultant modified starches have much reduced molecular weights. Many

other modified starches are known, including phosphate, acid-thinned, and thermally modified starches. These native and modified starches must be cooked in order to provide a soluble starch solution. Some highly modified or pregelatinized (used in food applications) starches may be at least partially cold soluble, while most commercial modified starches must be cooked to provide a starch solution. Starch is often found in the fruit, seeds, or tubers of plants. The four major resources for starch production are corn, potatoes, wheat, and rice.

Starch is a mix of two polymeric carbohydrates (polysaccharides) called amylose and amylopectin.

The relative content of amylose and amylopectin varies between species.

Fragmented starch is described in EP 1 360 209 B1.

US 6,677,386 discloses a process for producing biopolymer nanoparticles, in which the biopolymer is plasticized using shear forces, a crosslinking agent preferably being added during the processing. After said processing, the biopolymer nanoparticles can be dispersed in an aqueous medium to a concentration between 4 and 40 wt. %. This results in biopolymer nanoparticles which are typically characterized by an average particle size of less than 400 nm. In one embodiment of this '386 invention, the biopolymer is starch. Some uses of the nanoparticles of U.S. Pat. No. 6 677 386 can be found in: (i) U.S. Pat. No. 7,160,420 which describes the use of the biopolymer nanoparticles as a wet-end additive in papermaking pulp slurry, or applied to the surface of the paper as a surface sizing agent; (ii) U.S. Pat. No. 6,825,252 which describes the use of the biopolymer nanoparticles in a binder in a pigmented paper coating composition; (iii) U.S. Pat. No. 6,921,430 which describes the use of the biopolymer nanoparticles in environmentally friendly adhesives; and (iv) U.S. Patent Application Publication No. 2004/0241382 which describes the use of the biopolymer nanoparticles in an adhesive for producing corrugated board.

There exists a need to further improve pre-impregnated decorative base papers in order to lower the amount of synthetic resin in the impregnating composition, preferably while keeping good printability, good lacquering, good gluability and other desired properties, or to avoid the need for a water soluble binder, or both.

The invention aims at satisfying this need as a result of a pre-impregnated decorative base paper for decorative coating materials, comprising biopolymer based nanoparticles.

A new pre-impregnated decorative base paper described herein is obtained by impregnating a decorative base paper with an impregnating composition, which is a latex

comprising 1) petroleum based polymer particles, and 2) biopolymer nanoparticles. The petroleum based polymer is selected from the group consisting of latex polymers including but not limited to styrene copolymers, styrene acrylate copolymers, styrene butyl acrylate copolymers, styrene butyl acrylate acrylonitrile copolymers, and vinyl acrylic copolymers, and mixtures thereof. The biopolymer nanoparticles are preferably selected from those of the 6,677,386 patent and related publications as described above. The biopolymer nanoparticles are optionally characterized by one or more attributes, such as low-viscosity high-solids dispersion in water, having a dominant size range less than 400 nm, having a polydispersity index (M_w/M_n) of less than or equal to 2 as determined by gel permeation chromatography (GPC), or having a molecular weight of 1,000,000 Da or more. In some embodiments of the present invention, the biopolymer is starch. GPC analysis was conducted using a PL220 GPC system equipped with a differential refractometer and light scattering detector (measures light scattering at 90° and 15°). The GPC was equipped with the following columns (in series): 1 guard column, 1 High MW mixed column (separation range 500 Da-10,000,000 Da) Agilent PLgel 10 μ m Mixed B. The mobile phase was 0.05 M LiBr in DMSO at 70 °C. For system calibration, the differential refractometer and light scattering detectors were calibrated using a Pullulan 110K standard purchased from American Polymer Standards. Data was collected and analyzed using Cirrus Multi software version 3.4.1. Percent Below “X”K was calculated as: ($\sum$ concentration response less than “X”K from LogM fit / $\sum$ concentration response of recovered sample) x 100%. The following sample preparation protocol was used: Samples were dissolved in the mobile phase at a concentration of 1.0 mg/mL, heated overnight at 65 °C, filtered over a 0.45 micron Teflon membrane filter, and 100 μ L injections were made in triplicate for each sample. For analysis, molecular weight calculations were based on $dn/dc = 0.066$, the literature value for amylopectin in DMSO.

Pre-impregnated decorative base papers according to the invention may be lower cost, easier to prepare or provide for more environmentally responsible alternatives to produce because the presence of the biopolymer based nanoparticles in the impregnating composition, which allows one to reduce the amount of a petroleum based polymer latex binder in the impregnating composition or the amount of a water soluble or petroleum based co-binder or both.

Surprisingly, the pre-impregnated papers made in accordance with the invention meet satisfactorily two very different and normally opposing requirements for good gluability and good lacquering, whilst maintaining good internal cohesion. Also very unexpectedly, at

least some pre-impregnated papers made in accordance with the invention satisfactorily meet all quality requirements even when the soluble binder component such as PVOH is eliminated. Relative to the preferred formulation in EP0648248, the optional partial petroleum based latex binder replacement with the biopolymer nanoparticles, combined with the total replacement of the PVOH binder, produces unexpected results especially given that PVOH is known to have more than twice the binding strength of the petroleum based latex binder.

The dry weight ratio of biopolymer nanoparticles to petroleum based polymer(s) is preferably in the range of 20:80 to 80:20, more preferably 40:60 to 70:30.

Furthermore, exemplary embodiments of the invention show good stiffness resulting from the inclusion of the biopolymer nanoparticles. Improved stiffness is particularly advantageous for laminates in sheets and not in rolls.

During the process, the risk of accumulation of dirt build-up is reduced after drying of the impregnation composition, because of the biopolymer nanoparticle content of the impregnation composition. This is another significant and totally unanticipated optional advantage of the present invention.

Biopolymer nanoparticles.

The nanoparticles are made from a biopolymers including but not limited to starch that may be native starch, or modified starch, proteins, other biobased materials, or mixtures thereof.

The biopolymer nanoparticles are preferably produced by a reactive extrusion process as described in US 6,677,386 and US 2011042841.

In one preferred embodiment of the present invention, the biopolymer is starch. The starch is preferably native starch. The starch may be previously modified, e.g. with cationic groups, carboxymethyl groups, by acylation, phosphorylation, hydroxyalkylation, oxidation and the like. Mixtures of starches may be used, or mixtures of starch with other biopolymers, those containing at least 50% starch being preferred. Especially preferred is high-amylopectin starch such as low-amylose starch, i.e. starch having a content of at least 75%, especially at least 90% of amylopectin, such as waxy starch.

The starch may be selected from tuber and root starches, as well as corn starches, tuber flour, root flour and corn flour. The tuber or root starch may be selected from the group consisting of potato starch and tapioca starch. The starch may be selected from the group consisting of maize starch and wheat starch.

The average size D_{50} in number of the biopolymer nanoparticles is preferably less or equal than 1000 nm, more preferably less than or equal to 400 nm as measured by Nanoparticle Tracking Analysis (NTA). NTA was performed using a *NanoSight LM20* unit equipped with a microscope, a digital camera, a blue laser and *NanoSight NTA 2.3* software.

5 The target concentration used for dispersions of samples was 0.01% (w/w). Typically a minimum 30-60s video clip was sufficient for sample analysis, but longer times may be used for increased accuracy. The NTA microscope provides a method of visualizing, tracking and analyzing a sampling of individual particles (as opposed to the typical averaged global response as, for example, in dynamic light scattering), by correlating their Brownian motion
10 (the actual speed of which relates to particle size, i.e. faster meaning smaller particles), and calculating their diffusion coefficient to provide the particle size and size distribution for that sampling of particles. The particles contained in the dispersion are visualized by the light they scatter when illuminated by the laser light source. The scattered light is captured by the digital camera, and the motion of each particle is tracked from frame to frame by the software.
15 The particle size (sphere equivalent hydrodynamic radius) is calculated by substituting the rate of particle movement via the Stokes-Einstein equation.

The molecular weight polydispersity index M_w/M_n of the nanoparticles is preferably less than or equal to 2 as determined by GPC. The average molecular weight of the biopolymer nanoparticles is preferably at least 1,000,000 Da.

20 To obtain the nanoparticles, a starch based material may be processed, preferably extruded, at a temperature of between 40°C and 200°C, for example between 100°C and 200°C, a crosslinking agent preferably being present during the processing, and the starch based material preferably being dissolved or dispersed in a hydroxylic solvent during the processing, the starch based material being submitted during the processing to shear forces
25 preferably corresponding to a mechanical energy input of at least 100J/g starch based material, more preferably at least 400 J/g, the starch based material preferably having a dry substance content during the processing of at least 50 % by weight. The crosslinking agent may be, for example, a dialdehyde or polyaldehyde, such as glyoxal. US 6,677,386, and US 2011042841, the contents of which are incorporated by reference, disclose a process to
30 produce biopolymer nanoparticles used in accordance with the invention.

Method for producing the pre-impregnated decorative base paper

A further object of the present invention is a method for producing the pre-impregnated decorative base paper of the invention, as defined above, comprising

impregnating a decorative base paper with an impregnating composition comprising a dispersion of biopolymer nanoparticles.

An exemplary impregnating composition has a relatively low viscosity and a relatively high solid content. An unexpected further advantage of this embodiment is a good
5 runnability on the decorative paper machine despite such high solid contents.

The decorative base paper preferably has before impregnation a Bendsten porosity ranging from 100 to 1500 mL/min, preferably 300 to 1000. The porosity is measured in accordance to NF ISO 5636-3.

The impregnating composition preferably is an aqueous composition, and
10 preferably comprises a petroleum based polymer latex binder and the biopolymer nanoparticles, the petroleum based polymer preferably being selected from the group consisting of latex polymers including but not limited to styrene copolymers, styrene acrylate copolymers, styrene butyl acrylate copolymers, styrene butyl acrylate acrylonitrile copolymers, and styrene acrylics derivate copolymers, and mixtures thereof, the weight ratio
15 dry of biopolymer nanoparticles to the petroleum based polymer(s) preferably being in the range of 20:80 to 80:20, most preferably 40:60 to 70:30

The impregnating solution preferably is obtained by mixing an aqueous dispersion of the biopolymer nanoparticles with a petroleum based polymer latex binder. The solid content of the biopolymer nanoparticles dispersion is preferably to 15 to 35% of the total
20 weight of said aqueous dispersion, most preferably to 25 to 35%, said aqueous dispersion preferably being prepared by adding 4 to 6% of urea by weight of the biopolymer nanoparticles.

The viscosity of the impregnating composition at 23 °C is preferably 150 mPa.s or less, preferably from about 40 to about 100 mPa.s at 25% solids measured with a Brookfield
25 Viscometer at 100 rpm and using spindle N° 2.

The dry solid contents of the impregnating composition ranges preferably from 20 to 40%, preferably from 25 to 35%.

The decorative base paper is treated with the impregnating composition such that the dry weight of the impregnating composition ranges from 10 to 25% of the weight of the
30 decorative base paper, preferably from about 15 to about 20%.

A further object of the invention is a decorative coating material comprising the pre-impregnated decorative base paper of the invention, as described above, or produced by the method as described above.

Examples

The following examples serve to illustrate the invention and are not intended to limit the invention in any way. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description and the following examples and fall within the scope of the appended claims. Tests have been carried out to assess properties of pre-impregnated decorative base papers made in accordance with the invention, compared to comparative examples.

The lacquer used is the 5364.1 mixed with the hardener 9021.2 both of which were obtained from the company Plantag.

Control Example A

This pre-impregnated paper is made in accordance with the teaching of EP 0,648,248 B1 using an all-synthetic petroleum based binder system, including a main latex binder and a water soluble polyvinyl alcohol (PVOH) cobinder.

Control Example B.

This pre-impregnated paper is made in accordance with the teaching of US 8,349,464 with the starch referenced 07311 of the company CARGILL. The starch is prepared at 25% weight solid contents.

The dry weight ratio of starch/polymer latex in this example is 60:40.

Control Example C.

This pre-impregnated paper is made in accordance with the teaching of US 8,349,464 with the starch referenced 07325 supplied by the company CARGILL. The starch is prepared at 25% weight solid contents.

The dry weight ratio of starch/polymer latex in this example is 60:40.

Example 1 to 4.

Examples 1 to 4 are made in accordance with the invention, with respective ratios of 80:20, 60:40, 40:60 and 20:80 of biopolymer nanoparticles (supplied by the company EcoSynthetix Corporation) with respect to polymer latex. The aqueous latex dispersion of biopolymer nanoparticles is prepared at 35.7% weight solid contents.

For all the examples, the details of the impregnating compositions are given in the table below.

The proportions are weight proportions, unless specified otherwise.

The base paper is made from a fibrous composition of 100 % eucalyptus pulp or comprising at the most 20 % of long fibers of 58 gsm. The refining is about 30 °SR and is

adjusted so as to have a Bendsten porosity before impregnation of 100 to 1000 mL/min. Titanium dioxide is added up to 23 % ash content, and a wet resistance agent such as epichlorohydrine is added between 0.3% and 1% dry versus the base paper.

5 This base paper is treated on line, with the impregnating composition applied using a size press and then dried at 120 °C to a moisture level of 2.5%.

	<u>Control</u> <u>Example</u> <u>A</u>	<u>Control</u> <u>Example</u> <u>B</u>	<u>Control</u> <u>Example</u> <u>C</u>	Example 1	Example 2	Example 3	Example 4
Biobased Binder %	0%	60%	60%	80%	60%	40%	20%
Water	10,4	115,0	80,0	80,0	85,0	101,0	115,0
Cargill 07311		240,0					
Cargill 07325			240,0				
Biopolymer nanoparticles (1)				224,1	168,1	112,0	56,0
Polymer latex (2)	160	80,0	80,0	40,0	80,0	120,0	160,0
PVOH (3)	200						
Solid content	27,0	23,0	25,0	29,1	30,0	30,0	30,2
Viscosity 100trs (cps)	60	200	65	75	70	50	40
Pick up %/ treated paper	19,7	16,6	19,3	18,7	20,0	21,7	20,3
Bendtsen porosity (ml/min)	15	64	124	138	121	76	40
Internal bond SM (J/m²)	2400	1150	1200	1200	2200	2300	2400
Water cobb 1 min Top side / Back side (gsm)	13,8 / 14,7	20,7 / 21,2	18,9 / 19,7	31,0 / 33,7	23,7 / 25,2	17,6 / 18	13,5 / 14,3
Tesa test	1	5	3	3	1	1	1
Gloss 60° 8 gsm of lacquer (%)	29,4	28,3	27,1	28,4	27	29,1	29,8
Gluability	Poor	very good	very good	very good	very good	good	medium

(1) Starch nanoparticles, grade DuraBind™ 3356, were obtained from EcoSynthetix Corporation.

5 (2) Aqueous dispersion with 50% weight solid contents of a heat-crosslinking copolymer of n-butyl acrylate and styrene sold under reference Acronal S305D by the company BASF.

(3) Polyvinyl alcohol from the company KURARAY sold under reference Mowiol 4/98, with 10% weight solid contents.

Example 2 shows over Control Example B and C that with similar contents of polymer latex the internal bond is significantly improved.

Example 1 shows over Control Example B and C that with comparable internal
5 bond the amount of polymer latex can be significantly reduced.

Examples made in accordance with the invention show improved gluability with respect to Control Example A.

The examples made according to the invention also show acceptable viscosity for processing.

10 The tests show that the pre-impregnated decorative base paper in accordance with the invention exhibit good results for gluability, gloss and internal bond. What is quite surprising is to get an excellent compromise between the two opposing key properties of gluability and lacquer hold out, by using the biopolymer nanoparticles. Furthermore, equally
15 surprising is the high level of petroleum based latex binder replacement with the biopolymer nanoparticles, combined with the total elimination of the PVOH cobinder. This is totally unexpected especially given that PVOH is known to have more than twice the binding strength of the petroleum based latex binder. Furthermore, these results demonstrate that this performance is not achieved using water-soluble starches.

The invention is not limited to the disclosed embodiments. For example,
20 biopolymer nanoparticles other than those made in accordance with US 6677386 could be used.

CLAIMS

1. A pre-impregnated decorative base paper for decorative coating materials, comprising biopolymer nanoparticles.

5 2. The pre-impregnated decorative base paper of claim 1, wherein the pre-impregnated decorative base paper is obtained by impregnating a decorative base paper with an impregnating composition, comprising a petroleum based polymer latex binder and biopolymer nanoparticles.

3. The pre-impregnated base paper of claim 2, wherein the petroleum based latex
10 binder is selected from the group of styrene butyl acrylate copolymers, styrene butyl acrylate acrylonitrile copolymers, styrene acrylics derivate copolymers, and mixtures thereof.

4. The pre-impregnated decorative base paper of any of claims 1 to 3 wherein the biopolymer nanoparticles are made up of at least 50% starch.

5. The pre-impregnated decorative base paper according to any one of claims 2 to
15 4, wherein the weight ratio dry of biopolymer nanoparticles to petroleum based polymer(s) is in the range of 20:80 to 80:20, preferably 40:60 to 70:30.

6. The pre-impregnated decorative base paper of any one of claims 1 to 5, wherein the average size D_{50} in number of the biopolymer nanoparticles is less than or equal to 1000 nm as measured by Nanoparticle Tracking Analysis, and preferably wherein the
20 average size D_{50} in number of the biopolymer nanoparticles is less than or equal to 400 nm as measured by Nanoparticle Tracking Analysis.

7. The pre-impregnated decorative base paper of claims 1 to 6, including claim 4, wherein the starch is processed, preferably extruded, at a temperature of between 40°C and 200°C, a crosslinking agent being present during the processing, and the starch preferably
25 being dissolved or dispersed in a hydroxylic solvent during the processing, the starch being submitted during the processing to shear forces preferably corresponding to a mechanical energy input of at least 100J/g starch based material, the starch based material preferably having a dry substance content during the processing of at least 50 % by weight.

8. The pre-impregnated decorative base paper of any one of claims 1 to 7,
30 wherein the molecular weight polydispersity index M_w/M_n of the biopolymer nanoparticles is less than or equal to 2 as measured by Gel Permeation Chromatography, preferably with an average molecular weight of at least 1,000,000 Da.

9. The pre-impregnated decorative base paper of any one of claims 1 to 8, where the biopolymer nanoparticles comprise one or more types of starch, and preferably the starch comprises native corn starch, in particular native waxy corn starch, or wherein the starch comprises a tubular starch selected from the group consisting of potato and tapioca starch, or
5 wherein the starch comprises a chemically modified starch.

10. A method for producing the pre-impregnated decorative base paper of any one of the preceding claims, comprising impregnating a decorative base paper with an impregnating composition comprising a petroleum based latex and a dispersion of biopolymer nanoparticles.

10 11. The method of claim 10, the decorative base paper having before impregnation a Bendsten porosity ranging from 100 to 1500 mL/min, the decorative base paper preferably having before impregnation a Bendsten porosity ranging from 300 to 1000 mL/min.

12. The method of any one of claims 10 and 11, wherein the impregnating composition is preferably an aqueous composition, and comprises a petroleum based polymer
15 latex binder and biopolymer nanoparticles, the petroleum based polymer is selected from the group consisting of latex polymers including styrene copolymers, styrene acrylate copolymers, styrene butyl acrylate copolymers, styrene butyl acrylate acrylonitrile copolymers, and styrene acrylics derivate, and mixtures thereof, wherein the dry weight ratio of biopolymer nanoparticles to the petroleum based polymer(s) is preferably in the range of
20 20:80 to 80:20, and most preferably wherein the dry weight ratio of biopolymer nanoparticles to the petroleum based polymer(s) is in the range of 40:60 to 70:30,

the impregnating solution preferably being obtained by mixing an aqueous dispersion of the biopolymer nanoparticles with the petroleum based polymer latex binder, the solid content of the biopolymer nanoparticles dispersion is 15 to 35 % of the total weight of said
25 aqueous dispersion, said aqueous dispersion preferably being prepared by adding 4% to 6% of urea by weight of the biopolymer nanoparticles,

the impregnating solution more preferably being obtained by mixing an aqueous dispersion of the biopolymer nanoparticles with the petroleum based polymer latex binder, the solid content of the biopolymer nanoparticles dispersion is 25 to 35 % of the total weight of
30 said aqueous dispersion, said aqueous dispersion preferably being prepared by adding 4% to 6% of urea by weight of the biopolymer nanoparticles.

13. The method of any one of claims 10 to 12, the viscosity of the impregnating composition at 23 °C being 150 mPa.s or less, and preferably the viscosity of the impregnating composition at 23 °C being from 40 to about 100 mPa.s.

5 14. The method of any one of claims 10 to 13, wherein the dry solids contents of the impregnating composition ranges from 20 to 40 %, and preferably wherein the dry solids contents of the impregnating composition ranges from 25 to 35 %.

10 15. The method of any of claims 10 to 14, wherein the decorative base paper is treated with a quantity of the impregnating composition such that the dry weight of the impregnating composition ranges from 10 to 25 % of the weight of the decorative base paper, and preferably wherein the decorative base paper is treated with a quantity of the impregnating composition such that the dry weight of the impregnating composition ranges from 15 to 20 % of the weight of the decorative base paper.

15 16. A decorative coating material comprising the pre-impregnated decorative base paper of any of claims 1 to 9 or comprising the pre-impregnated decorative base paper produced by the method of any of the claims 10 to 15.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER INV. D21H27/26 B32B27/00 D21H17/35 D21H17/37 D21H19/58 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) D21H B32B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 825 252 B2 (HELBLING ANDRE MARCEL [CH] ET AL) 30 November 2004 (2004-11-30) cited in the application	1
Y	column 1, line 60 - column 2, line 16; claims	2

X	US 2012/263894 A1 (BLOEMBERGEN STEVEN [US]) 18 October 2012 (2012-10-18)	1-3
Y	paragraphs [0011], [0023], [0024], [0033], [0034]; claims	1-16

Y	US 8 916 027 B2 (WICHER MARTINA [DE]) 23 December 2014 (2014-12-23)	1-16
the whole document		

Y	EP 0 648 248 A1 (BUHL PAPIERFABRIKEN GMBH GEB [DE]) 19 April 1995 (1995-04-19)	1-16
cited in the application		
the whole document		

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
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Information on patent family members

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