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### (54) A DECORATIVE SHEET AND METHOD FOR MANUFACTURING

(57) In a first aspect, the present invention provides a method of manufacturing a decorative sheet comprising the steps of:

- Providing a carrier sheet,
- Impregnating the carrier sheet with a curable impregnation resin,
- providing a curable coating on the top surface of the impregnated carrier sheet, partially curing said curable coating and structuring its top surface, while leaving the curable impregnation resin at least partially uncured.

Further, a method for manufacturing a decorative panel comprising the step of manufacturing a decorative layer using the above method and adhering said decorative layer as a decorative top layer to a substrate is

provided as well.

In a second aspect, the present invention provides a decorative sheet comprising:

- a carrier sheet impregnated with a curable impregnation resin,
- a curable coating on the top surface of the impregnated carrier sheet, characterized in that said curable coating is partially cured and having a structured top surface, and that the curable impregnation resin is at least partially uncured.

Further, the present invention provides a decorative panel comprising a substrate and a decorative top layer comprising a decorative sheet as described above.

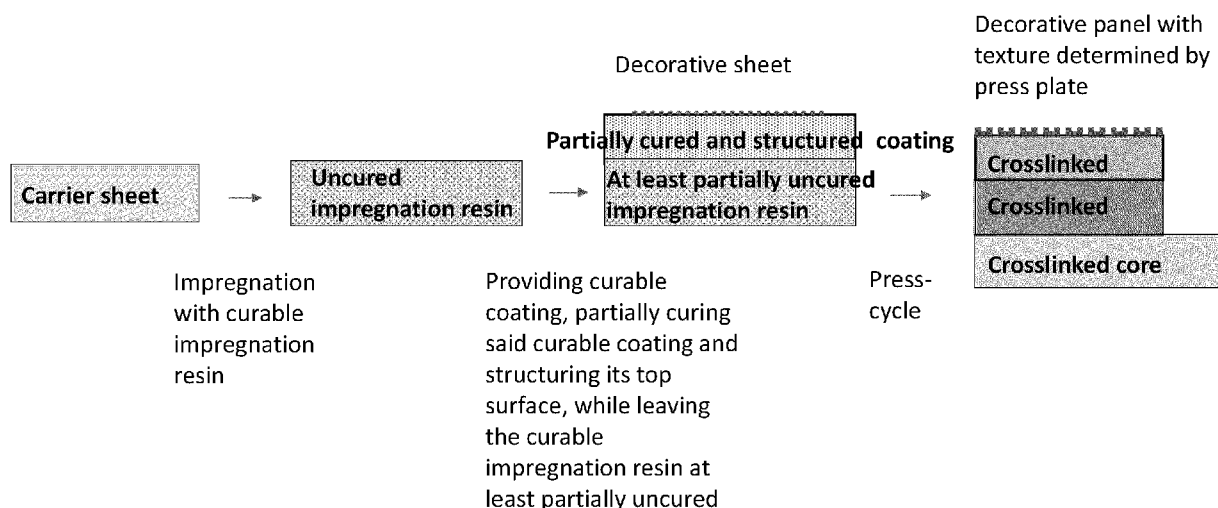


FIG 2

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## Description

### TECHNICAL FIELD

[0001] The present invention generally relates to decorative sheets, in particular decorative sheets being used as top layer of decorative panels, such as flooring panels, laminates, furniture panels, wall panels, worktops, cast panels etc.

[0002] In addition, the present invention relates to a method for manufacturing such decorative sheets and panels.

### BACKGROUND

[0003] Decorative panels, such as flooring panels, laminates, furniture panels, wall panels, etc. coated with simulated versions of materials such as wood and natural stone are commonly used today, in particular where a less expensive material is desired. Obviously, these panels have to be sufficiently resistant against abrasion, indentation, chemicals and moisture.

[0004] Such decorative panels substantially consist of a substrate such as MDF or HDF (Medium or High Density Fiberboard) or particle board and a decorative sheet provided thereon. The decorative sheets bear a printed decorative motif or pattern representing an image of different kinds of wood or natural stone such as marble or granite, and one or more finishing layers (so called top coating) to protect the decorative motif.

[0005] Typically, the top surface, usually a condensation resin based top layer, is provided with a structure (i.e. a surface texture, profile, or topography) which gives the panel particular aesthetic and haptic characteristics making the decorative panel more realistic.

[0006] As is commonly known in the art of the manufacturing of such decorative panels, melamine-based hot press processes are widely used.

[0007] Typically, in a first step a (printed) decorative paper is impregnated with melamine formaldehyde (subsequently referred to as melamine) dissolved in water. Due to its very good price/performance level melamine is the most widely spread surface material for the medium to high quality surface materials used in the wood-based panel industry for interior applications. Melamine shows both good mechanical resistance (scratch- and wear resistance) and chemical resistance (resistance against common household chemical substances).

[0008] The impregnated paper is then passed through driers to evaporate the excessive amount of water and create a precuring of the melamine resin, resulting in a dry to the touch, stackable or rewindable impregnated paper with a resin content between 50 and 300% of the dry paper weight.

[0009] These impregnated papers are then further processed in hot presses operating at temperatures between 100-220°C and pressures between 20-120 kg/cm<sup>2</sup>. During pressing, the melamine resin will shortly

liquify and flow, adapting to the surface structure and gloss level of the mold it is pressed against. While being under pressure and at the elevated temperatures in the mold the melamine resin is cured to the desired level and surface structure, necessary for its intended use in the decorative industry.

[0010] However, the use of melamine in hot press processes for decorative sheet manufacturing faces several disadvantages, such as:

- Melamine based surfaces contain formaldehyde, a potentially carcinogenic product.
- The impregnation process uses a lot of energy for the evaporation of the water and precuring of the melamine formaldehyde resin.
- High visibility of fingerprints on melamine surface in combination with all gloss levels.
- The colour intensity of melamine surfaces decreases when the roughness of the surface increases - and the gloss level decreases - or when an overlay is used to achieve sufficient abrasion resistance, with the surface taking on a milky appearance. This effect is strongest with a matt black surface.
- A melamine based surface feels cold to the touch.
- Melamine surfaces are susceptible to degradation and discoloration when exposed to the elements, and are therefore not suitable as a long-lasting surface for exterior applications
- Melamine surfaces have poorer acoustic characteristics in flooring materials compared to other surfacing technologies as used in LVT, SPC or coated wood-based panels.
- Soft touch haptics are hard to achieve in combination with melamine resin.

[0011] In an attempt to overcome the above disadvantages, while seeking to use the relatively simple and traditional hot press processing, melamine was replaced most commonly by (meth)acrylates or unsaturated polyester-based impregnation resins. Examples thereof are WO2010/104380 and US9033486 using aqueous acrylic impregnation (Trespa).

[0012] A remaining problem however is that the above-mentioned state of the art methods still use the same impregnation technology as used in traditional melamine impregnation, which requires high amounts of energy for evaporation of water and pre(curing) of the impregnation resin.

[0013] Considering the above, it is a general objective of the present invention to provide a decorative sheet and a method of manufacturing which is not melamine-based, and which enables the use of less energy consuming impregnation methods, combined with the relatively simple hot press curing and structuring of the final surface as used in traditional melamine based processing..

[0014] Another general objective of the present invention is to produce decorative sheets having a high quality final cured top surface showing a minimum amount or

even zero defects.

## SUMMARY

**[0015]** In a first aspect, the present invention provides a method of manufacturing a decorative sheet comprising the steps of:

- Providing a carrier sheet,
- Impregnating the carrier sheet with a curable impregnation resin,
- providing a curable coating on the top surface of the impregnated carrier sheet, partially curing said curable coating and structuring its top surface, while leaving the curable impregnation resin at least partially uncured.

**[0016]** Further, a method for manufacturing a decorative panel comprising the step of manufacturing a decorative layer using the above method and adhering said decorative layer as a decorative top layer to a substrate is provided as well.

**[0017]** In a second aspect, the present invention provides a decorative sheet comprising:

- a carrier sheet, said carrier sheet impregnated with a curable impregnation resin,
- a curable coating on the top surface of the impregnated carrier sheet, characterized in that said curable coating is partially cured and having a structured top surface, and that the curable impregnation resin is at least partially uncured.

**[0018]** Further, the present invention provides a decorative panel comprising a substrate and a decorative top layer comprising a decorative sheet as described throughout this text.

## BRIEF DESCRIPTION OF DRAWINGS:

**[0019]** FIG 1 schematically illustrates a method of the prior art as described in WO2010/104380 and US9033486.

**[0020]** FIG 2 schematically illustrates an embodiment of a method for manufacturing a decorative sheet in accordance with the present invention.

## DETAILED DESCRIPTION

**[0021]** Upon seeking to reduce the energy consumption of the impregnation step in producing decorative panels, the inventors surprisingly found that, in case a carrier sheet was impregnated with a non-melamine-based curable impregnation resin, then followed by a curable coating on top of the impregnated carrier sheet, finally followed by a traditional hot press cycle, the decorative sheet in many cases showed glossy spots and/or defects in the final cured surface after the hot press cycle.

**[0022]** In addition, the inventors now found that, by partially curing the curable coating and structuring its top surface before the press-cycle while leaving the non-melamine-based impregnation resin underneath the partially cured coating at least partially uncured, decorative sheets are produced which, in subsequent hot press processing, appear not to lead to glossy spots and/or defects in the final cured top surface after such press cycle regardless of the texture imparted during the pressing step.

**[0023]** Therefore, in a first aspect as illustrated in FIG 2, the present invention provides a method of manufacturing a decorative sheet comprising the steps of:

- Providing a carrier sheet,
- Impregnating the carrier sheet with a curable impregnation resin,
- providing a curable coating on the top surface of the impregnated carrier sheet, partially curing said curable coating and structuring its top surface, while leaving the curable impregnation resin at least partially uncured.

**[0024]** Without being bound by any theory, the cause of the glossy spots/defects in the cured surface seems to lie in air entrapment during the hot press processing. During hot press processing, air entrapment between the top coating and the mold should be avoided. However, avoiding this air entrapment appears to be difficult as soon as the mold exhibits a more pronounced depth of its structures. Also, the direction of the structures and especially the combination of different directions of the structures in the mold play a significant role.

**[0025]** Surprisingly, the inventors found that the above-described problem can be avoided if the surface of the partially cured curable coating is sufficiently structured.

**[0026]** Again without bound by any theory, structuring potentially creates channels for the air to escape during the pressure build-up while pressing the decorative sheet against the mold.

**[0027]** The impregnation resin may be any of type of resin suitable for impregnation of a carrier sheet in the context of the present invention, in particular free-radical polymerization-based resins, preferably acrylate- or methacrylate-based resins, and even more preferably acrylic or methacrylic resins of the following groups: epoxy (meth)acrylates, silicone (meth)acrylates, polyether (meth)acrylates, polyester (meth)acrylate, urethane (meth)acrylates, and amino (meth)acrylates.

**[0028]** Dual-cure resins can be used as well, e.g. blends of free-radical resins with other types of resins, such as condensation curing resins (e.g. amino resins), isocyanate/polyol-based (i.e. polyurethane) resins, or epoxy resins.

**[0029]** In an embodiment of the present invention, impregnation resin may be applied at the bottom or at the top surface of the carrier sheet, or both.

**[0030]** The curable impregnation resin may be applied by

any suitable technique. However preferably, the curable impregnation resin is applied by a coating process or a printing process, such as for example rotogravure coating, screen-printing, roller coating, or slot-die coating. The advantage thereof is reduced energy consumption compared to conventional impregnation which includes evaporation of water. Another advantage is that same coating and printing technology as used for coating can be used.

**[0031]** Preferably, the impregnation resin is in a liquid stage during the process of complete impregnation of the carrier sheet, which can vary from a few seconds till several days, depending on the viscosity and type of the resin and carrier sheet used, and more preferably during the process of partial curing and structuring of the curable coating. The final for its use intended level and evenness of impregnation throughout the carrier sheet is not necessarily obtained in-line with the machine used for impregnation, but can be achieved afterwards while wound on the roll. In the context of the present invention, liquid stage is understood as uncured, or at least partially uncured whereby a portion of the reactive double bonds have reacted, but the resin is still able to flow, either at room temperature or at a specific (process) temperature.

**[0032]** In a preferred embodiment, the impregnation resin remains in its uncured stage after the full impregnation cycle as described above, or even more preferably after the partial curing and structuring of the curable coating, is completed, such that crosslinking is initiated by downstream processing (eg. The press cycle).

**[0033]** Coating the carrier sheet with curable coating may be done by any known coating technique known in the art, such as roll, rotogravure, slotdie, commabar, screen printing, or curtain coating.

**[0034]** In the context of the present invention, it is understood that partially curing the curable coating comprises curing the curable coating to a precured stage adapted to enable the precured coating to flow during a subsequent pressing step, i.e. the precured coating is in a solid state at room temperature, (e.g. to enable it to withstand winding and unwinding) but is still able to flow under suitable process conditions such as applied in the press-cycle, i.e. at elevated temperature and elevated pressure, typically between 100°C and 230°C, more typically between 120°C and 210°C, and between 5 bar and 100 bar, more typically between 20 bar and 70 bar.

**[0035]** In an embodiment of the present invention, partially curing and structuring the curable coating comprises curing against a textured precuring mold, optionally under elevated pressure and/or temperature. A typical pressure applied may be between 2-100 kg/cm<sup>2</sup>. A typical temperature applied may be between 20 and 180°C.

**[0036]** Alternatively, partially curing and structuring the curable coating comprises irradiating by ultraviolet (UV) light. In this case the curable coating may be exposed to a curing wavelength range from at least part of the UV

spectrum between 150nm and 450nm. Preferably, multi-step irradiation is applied wherein in a first irradiation step a wavelength between 150 and 250 nm is applied, preferably by excimer irradiation, and wherein in a second step a wavelength between 250 and 450 nm is applied, or optionally by electron beam irradiation.

**[0037]** In this multi-step irradiation process, even more than 2 irradiation steps can be applied, as curing is dependent on a combination of a number of variables, including but not limited to substrate (type and/or thickness); coating formulation (photoinitiator type and/or concentration, additives, pigments etc); coating thickness; ink formulation (pigment type and/or concentration); ink thickness; lamp (type, age, dosage); distance between lamp and coating; exposure time (line speed, number of lamps).

**[0038]** In still another alternative embodiment, structuring the curable coating comprises brushing or embossing of the partially cured coating.

**[0039]** Optionally, the method may comprise printing a decorative ink (pattern or plain color) on at least part of the carrier sheet. Such printing a decorative ink pattern or plain color may be done by any technique including, but not limited to analogue printing, rotogravure printing or screen printing, or by digital printing methods as well, such as inkjet printing.

**[0040]** In an embodiment of the method in accordance with the present invention, the carrier sheet may be selected from paper based (impregnated or not impregnated) materials, film or foil-based materials, acrylic plastic based materials including PMMA/ABS, thermoplastic based materials including PP, PE, PVC, PET and the like, non-woven based materials, or glass fiber based materials, or any combination thereof.

**[0041]** In an embodiment, the carrier sheet is at least partially UV light irradiation transparent, in which case optionally the curable coating may be precured by irradiation through the carrier sheet.

**[0042]** In a further embodiment as illustrated in FIG 2, the method may further comprise providing a core layer at the bottom surface of the impregnated carrier sheet, curing the curable impregnation resin and further curing the partially cured coating by pressing in a textured mold at elevated temperature, thereby altering the coating's partially cured surface structure into a final surface texture.

**[0043]** In an embodiment of the present invention, the coating's partially cured surface texture and its final surface texture differ from each other in surface roughness and/or in specular reflection or gloss, and/or in top coating thickness, and/or in haptic properties, and/or in surface tension. More specifically, the textures may differ in shallowness or deepness, in higher gloss vs matt surfaces, in the presence of functional features such as light management structures, privacy film, optical gratings, antireflection surfaces, holographic surfaces, micro-fluidic devices, antimicrobial surfaces, brand protection, noise-absorbing/reducing, protective coatings. Option-

ally, one or more of these functional features may be aligned with the decorative motif as well.

**[0044]** The presses mainly used are discontinuous HPL, with a warm-up and cool-down cycle; continuous HPL/CPL presses, with or without cool down; and discontinuous hot short-cycle press, without warm-up or cool down.

**[0045]** In a second aspect, the present invention provides a decorative sheet comprising:

- a carrier sheet said carrier sheet impregnated with a curable impregnation resin,
- a curable coating on the top surface of the impregnated carrier sheet, characterized in that said curable coating is partially cured and having a structured top surface, and that the curable impregnation resin is at least partially uncured.

**[0046]** Typically, a decorative ink is located between the carrier sheet and the curable coating. However, in some embodiments, the decorative ink may be located at the rear side of the carrier sheet.

**[0047]** In accordance with the present invention, the partially cured coating is in a precured stage adapted to enable the precured coating to flow during a subsequent pressing step, i.e. the precured coating is in a solid state at room temperature, (e.g. to withstand winding and unwinding) but is still able to flow under suitable process conditions applied in the press-cycle.

**[0048]** In addition, the top surface of the partially cured coating is structured.

**[0049]** In the context of the present invention, structured is understood as the top surface of the partially cured curable coating being sufficiently textured to provide channels through which the majority of, or substantially all, air that is trapped between the partially cured curable coating and the mold can escape to the edges of the decorative sheet during a subsequent press cycle. Said channels may comprise all types of topography allowing air to flow towards the edges of the decorative sheet.

**[0050]** In an embodiment, said topography may have depths of at least 2 microns, and preferably at least 3 micron, and preferably between 4 and 20 microns, and more preferably between 4 and 10 microns.

**[0051]** In a preferred embodiment, the curable coating has at least a sufficiently structured top surface to decrease its glossiness compared to a non-structured top surface towards matte.

**[0052]** The partially cured curable coating may be any type of known curable coating suitable for finishing decorative sheets or panels.

**[0053]** In a particular embodiment of the present invention, the partially cured coating is selected for being curable by electron beam (EB), ultraviolet (UV) or visible light, as well as by heat pressing.

**[0054]** In an embodiment of the present invention, the curable coating materials may be a mix of components

with different curing mechanisms, such as free-radical polymerization-based resins similar to the impregnation resins mentioned above, thermally reactive coatings, or reactive poly-urethane based coating combined with UV curable acrylate-based components as main coating resin to achieve flow and curing in the hot press cycle.

**[0055]** The coating can also contain solvents, pigments, fillers and additives (eg. photo and thermal initiators, light stabilizers, matting agents).

**[0056]** In addition, the curable coating materials may comprise non-reactive components as well, such as dissolved acrylics and fillers.

**[0057]** In accordance with the present invention, the decorative sheet may further comprise a core layer at the bottom surface of the impregnated carrier sheet.

**[0058]** In an embodiment of the present invention, the carrier sheet may be selected from paper based (impregnated or not impregnated) materials film, foil or panel based materials, acrylic plastic based materials including PMMA/ABS, thermoplastic based materials including PP, PE, PVC, PET and the like, non-woven based materials, or glass fiber based materials, or any combination thereof. Optionally, the carrier sheet may bear a decorative ink (pattern or plain color).

**[0059]** The decorative sheet of the present invention may be applied as a final product. Final products may be, but not limited to wall paper, packaging or wrapping paper, nonwoven or plastic or glass fiber based fabrics, or any other type of decorative sheet. The decorative sheet may also be a panel. This panel may be glass or polymer based, and may be self-supporting.

**[0060]** Preferably, the decorative sheet of the present invention may be applied as an intermediate product for being adhered as a decorative top layer to any type of substrate for forming a final product. Such final product may be any type of panel such as flooring panels, wall panels, advertising panels, etc, or panels for assembling any type of furniture such as tables, kitchens, office desks, closets and the like. The substrate of any such final product may be wood based, glass based, stone based, carbon based, plastic based, metal based, mineral (eg. Gyproc) based, etc. Specific applications may be wooden plank look-alikes (flooring / sidings / decking / skirting boards /...), exterior furniture, high level finish foil, technical foil, acrylic décor, release film for texturing other surfaces (including recreational vehicles/caravan applications and textiles in the fashion industry), auto-motive parts for interior and exterior, molded parts or panels in general.

## EXAMPLE

**[0061]** A 80 g/m<sup>2</sup> black pigmented alpha-cellulose paper, often referred to as décor-paper was used as carrier sheet and impregnated using a gravure roller top and bottom side, resulting in a total resin weight of 30 g/m<sup>2</sup>.

**[0062]** The impregnation resin consists of

- 10-50 % of an acrylate monomer like DPGDA, HDDA, GPTA, ...
- 40-80 % of an polyester acrylate like Laromer PE9032, Sartomer CN2911 or Ebecryl 810,
- 0,5-4 % of an organic peroxide like MEKP or TBEC, or mixtures thereof
- 0-10 % of an organic solvent like ethanol, methanol, butylacetate,

**[0063]** The thus impregnated roll was wound and left to rest for 24 hours to allow full and uniform impregnation of the carrier sheet while being wound on a roll.

**[0064]** Then, the thus impregnated roll was coated with a UV-curable coating with following composition:

- 10-30 % of an acrylate monomer like HDDA, GPTA, PPTTA, TMPTA,
- 40-80 % of an aliphatic urethane acrylate like Laromer UA 9033 N, Ebecryl 5129, CN 9276, or mixtures thereof
- 0,5 - 4 % of a photoinitiator like Omnirad 819, Esacure KIP 160, omnipol TP or mixtures thereof
- 0,3- 2 % of an organic peroxide like MEKP, TBEC, Trigonox 22C50 or mixtures thereof
- 0-5 % of an amorphous silica like ED5, Acematt TS100
- 0-5% of release agents/slip aids like Tegorad 2700, Ebecryl 350, CN9800.

**[0065]** Said coating was applied with a meyer bar or slot-die on the impregnated paper with a weight ranging from 50 till 150 g/m<sup>2</sup>.

**[0066]** Subsequently, the liquid coating layer was irradiated with the UV-light from an 172 nm Excimer lamp while under nitrogen inert atmosphere, thereby creating a wrinkled surface topography with an average roughness of 8 micron, followed by partially curing with a LED-UV-light with a peak output of 16 Watt/cm at 395 nm at a speed of 20 m/min.

**[0067]** The thus impregnated, coated and pre-cured decorative sheet was then pressed against a matt-gloss structured press plate onto a MDF panel, incorporating a melamine impregnated sheet in-between the pre-cured decorative sheet and the MDF panel (for achieving adhesion) in a short-cycle press at a temperature of 180-200 C, pressure of 30-50 kg/cm<sup>2</sup> for 40-50 seconds, thereby obtaining a decorative panel having a decorative top surface with the structure and gloss level as defined by the press plate.

## Claims

1. A decorative sheet comprising:

- a carrier sheet impregnated with a curable impregnation resin,
- a curable coating on the top surface of the

impregnated carrier sheet,

**characterized in that** said curable coating is partially cured and having a structured top surface, and that the curable impregnation resin is at least partially uncured.

2. A decorative sheet according to claim 1, wherein the curable coating is selected for being curable by electron beam (EB), ultraviolet (UV) or visible light, as well as by heat pressing.

3. A decorative sheet according to claim 1, wherein the curable coating is curable at least partially via free-radical polymerization.

4. A decorative sheet according to claim 1, wherein the curable coating is at least sufficiently structured to decrease its glossiness towards matte.

5. A decorative sheet according to claim 1, further comprising a core layer at the bottom surface of the impregnated carrier sheet.

6. A decorative panel comprising a substrate and a decorative top layer comprising the decorative sheet according to any of the above claims.

7. A method of manufacturing a decorative sheet comprising the steps of:

- Providing a carrier sheet,
- Impregnating the carrier sheet with a curable impregnation resin,
- providing a curable coating on the top surface of the impregnated carrier sheet,
- partially curing said curable coating and structuring its top surface, while leaving the curable impregnation resin at least partially uncured.

8. A method according to claim 7, wherein the curable impregnation resin is applied at the bottom and/or top surface of the carrier sheet by means of printing and/or coating.

9. A method according to claim 7, wherein partially curing the curable coating comprises curing the curable coating to a precured stage adapted to enable the precured coating to flow during a subsequent pressing step.

10. A method according to any of claims 7 to 9, wherein partially curing and structuring the curable coating comprises pressing in a textured precuring mold.

11. A method according to any of claims 7 to 9, wherein partially curing and structuring the curable coating comprises irradiating by excimer light followed by

electron beam (EB) irradiation or ultraviolet (UV) light.

12. A method according to any of claims 7 to 9, wherein structuring the curable coating comprises brushing or embossing. 5
13. A method according to any of claims 7 to 12, further comprising providing a core layer at the bottom surface of the impregnated carrier sheet, curing the curable impregnation resin and further curing the partially cured coating by pressing against a textured mold at elevated temperature, thereby altering the coating's partially cured surface structure into a final surface texture. 10 15
14. A method according to claim 13, wherein the final surface texture and the partially cured surface structure differ from each other in surface roughness and/or in specular reflection or gloss, and/or in haptic properties, and/or surface tension characteristics. 20
15. A method for manufacturing a decorative panel comprising the step of manufacturing a decorative layer using a method according to any of the claims 7 to 14, and adhering said decorative layer as a decorative top layer to a substrate. 25

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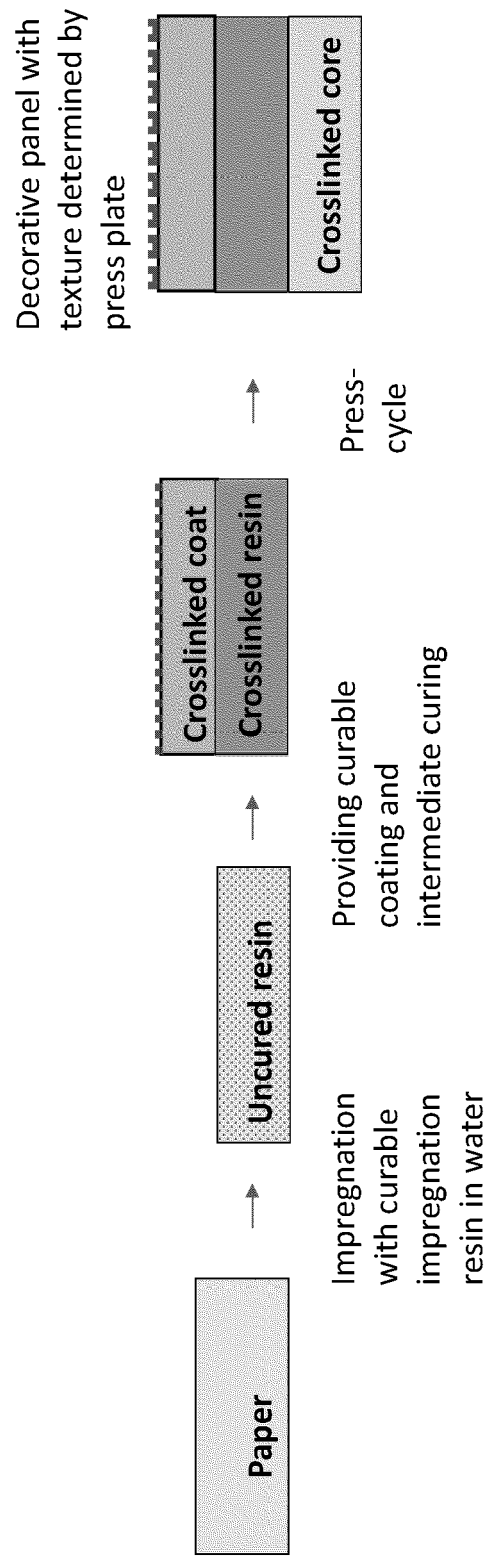


FIG 1



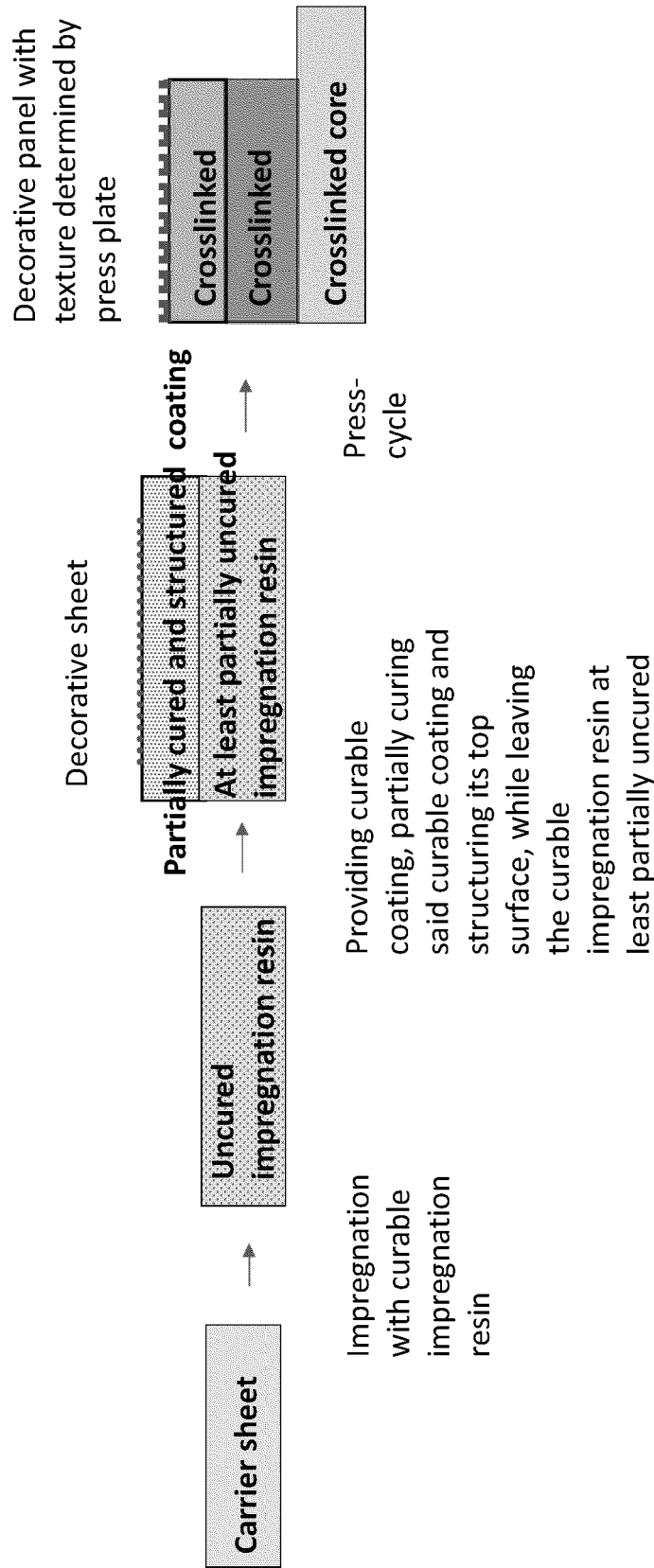


FIG 2



## EUROPEAN SEARCH REPORT

Application Number

EP 23 20 7724

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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			TECHNICAL FIELDS SEARCHED (IPC)
			B44C
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
Munich		21 March 2024	Björklund, Sofie
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)

# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**REFERENCES CITED IN THE DESCRIPTION**

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