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(71) Applicant: **DSM IP Assets B.V.**
6411 TE Heerlen (NL)

(72) Inventor: **van Benthem, Rudolfus Antonius
Theodorus Maria**
6141 BR Limbricht (NL)

(74) Representative: **van Tol-Koutstaal, Charlotte A.**
DSM Intellectual Property
Office Geleen
P.O. Box 9
6160 MA Geleen (NL)

(54) **Coated substrate**

(57) The invention relates to a method to coat a substrate with a melamine-formaldehyde resin comprising the following steps:

- a) Applying a layer of powdery melamine-formaldehyde A resin to a substrate,
- b) Melting the melamine-formaldehyde resin by IR- or NIR- radiation,
- c) Optionally applying an ink, dye solution or pigment dispersion to the with molten melamine-formaldehyde resin coated substrate,
- d) Optionally applying a layer of melamine-formaldehyde resin B to the coated substrate from step b) or c),
- e) Optionally heating the coated substrate from the

previous steps in a laminating press for a certain amount of time,

f) Increasing the pressure in the laminating press and keeping the laminate under pressure for a certain amount of time.

The invention also relates to the coated substrate and its use.

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Description

[0001] The invention relates to a method to coat a substrate with a melamine-formaldehyde resin so as to obtain good mechanical properties of the final coating. Good mechanical properties are for example required when the coated substrate is afterwards subjected to post-forming. The invention also relates to the coated substrate with good mechanical properties, appearance and durability, to the melamine-formaldehyde resin and to the melamine.

[0002] In US-3.730.828 a post-formable substrate is coated with a decorative barrier sheet consisting of ordinary α -cellulose wood fibre impregnated with a fully cured, unplasticized melamine-formaldehyde resin with a narrow range for the mole ratio between the formaldehyde and the melamine. A laminate is prepared by assembling various layers of kraft paper and a top, barrier, sheet with the unplasticized melamine-formaldehyde resin. All these carrier layers are formed into a laminate by placing the stacked layers in a laminating press under high pressure and at high temperatures during a certain amount of time. A disadvantage of the obtained laminates is that they cannot be bent into complex shapes along two (or more) mutually intersecting axis without breaking and/or cracking.

[0003] In WO 99/13000, a laminar prepreg is described which prepreg comprises one or more layers of a laminar carrier that is impregnated with an as yet uncured resin. The carrier is a laminar porous polymer. The laminar porous polymer may be a non-woven laminar polymer, a laminar open polymer foam or a microporous membrane. The laminar porous polymer is impregnated with the resin upon which drying is necessary at a temperature between 100 and 160 °C. The so obtained carrier is stacked after drying. The prepreg can subsequently be processed into a shaped final product by first deforming the prepreg and then curing the shaped intermediate product at elevated temperature or by combining the deformation and the curing step in one step. A disadvantage of the prepreg according to WO 99/13000 is that the laminar prepreg comprises at least two components that first must be obtained in separate steps: a laminar porous polymer and an (at the prepreg stage) uncured resin.

[0004] In WO00/53666 a prepreg is described that contains one or more layers of a porous carrier sheet, which porous carrier sheet has been impregnated with an as yet uncured resin, the carrier containing a meltable polymer mixed with cellulose or regenerated cellulose or mixtures there from. In WO 00/53667 a prepreg is described that contains one or more layers of a porous carrier sheet, which porous carrier sheet has been impregnated with an as yet uncured resin, the carrier being a porous carrier on the basis of wholly or partly regenerated cellulose. In WO 00/53688 a prepreg is described that contains one or more layers of a porous carrier sheet, which porous carrier sheet contains at least one

fibrous cellulose ester. A disadvantage of these systems that are based on a porous polymer as a carrier and an (at the prepreg stage) uncured resin is that at least two components are necessary in the initial stages of the prepreg stage.

[0005] It is an object of the invention to overcome the above-mentioned disadvantages and to make available a method to coat a substrate with a melamine-formaldehyde resin which is less complicated than the methods in the prior art and still results in a coated substrate with good mechanical properties.

[0006] The object is reached by a method that comprises the following steps:

- a. Applying a layer of powdery melamine-formaldehyde A resin to a substrate,
- b. Melting the melamine-formaldehyde resin by IR- or NIR- radiation,
- c. Optionally applying an ink, dye solution or pigment dispersion to the with molten melamine-formaldehyde resin coated substrate,
- d. Optionally applying a layer of melamine-formaldehyde resin B to the coated substrate from step b) or c),
- e. Optionally heating the coated substrate from the previous steps in a laminating press for a certain amount of time,
- f. Increasing the pressure in the laminating press and keeping the laminate under pressure for a certain amount of time.

[0007] The method according to the invention makes it superfluous to install a separate drying section for the impregnated porous polymer. Therefore the space and apparatus necessary for the process of coating a substrate can be reduced compared to the prior art. Additionally as no drying of the impregnated porous polymer at increased temperatures is necessary in the present invention the method is advantageous from an economical and ecological point of view. Another advantage of the method according to the invention is that separate stacking of the various layers is not necessary anymore. A further advantage of the method according to the present invention is that the melamine-formaldehyde coating is applied directly onto the substrate that needs to be coated for further use, as for example worktops cupboards and fronts of kitchen cupboards. In this method a separate "prepreg stage" is absent.

[0008] In step a) of the method according to the invention a melamine-formaldehyde resin in powder form is applied onto the surface of the substrate so as to form a layer. With powder is here and hereinafter meant a solid consisting of small particles generally with a particle size smaller than 250 μm , preferably below 100 μm . With very large particles an even distribution over the surface of the substrate is difficult, further the resolution of the applied pattern that is formed by the ink, dye solution or pigment dispersion in step c) is worse than

when smaller particles are used. The thickness of the layer is not particularly critical and can be chosen between wide ranges, for example between 20 and 500 μm . A preferred layer has a thickness between 50 and 250 μm . A balance should be found between a thick layer that is advantageous for hiding imperfections in the substrate surface, and a thin layer that is more advantageous for post-forming. It is known to the man skilled in the art how powders can be obtained from melamine-formaldehyde resins. Reference can for example be made to "Kunststoff Handbuch, 10-Duroplaste" by W. Becker, D. Braun, 1988 Carl Hanser Verlag; more specifically to the chapter "Melaminharze", page 41 and further.

[0009] With melamine-formaldehyde resin A is meant a resin with as main building blocks melamine and formaldehyde. The melamine-formaldehyde resin in A can additionally contain other building blocks, for example urea and flexibilizers as for example diethylene glycol and sugars.

[0010] The melamine-formaldehyde resin that is used in step a) should have a glass transition temperature (T_g) high enough to be stable at room temperature as a powder for an extended period of time. In case the T_g is not high enough the resin particles will coagulate and the powder will lose its form and stability. Suitable values for the T_g are at least 30 $^{\circ}\text{C}$, preferably 40 $^{\circ}\text{C}$, with more preference between 60 and 90 $^{\circ}\text{C}$. The T_g should be below the temperature at which steps e) and/or f) in the method are performed; as when the T_g is higher than the temperature in step e) the resin will not melt and thus it will not flow. Generally the T_g should therefore be below 140 $^{\circ}\text{C}$, preferably lower than 120 $^{\circ}\text{C}$.

[0011] The melamine-formaldehyde resin A should advantageously be able to form a non-porous layer after heating and curing in step f) so as to prevent diffraction of light by included components as for example water or air. Diffraction would lead to a "blurred" pattern. This requirement can advantageously be reached by a formaldehyde-melamine ratio in the resin A between 1 and 3 (on mol basis). Optionally the melamine-formaldehyde resin A can be partially crosslinked before it is applied onto the substrate. Depending on the precise composition of the melamine-formaldehyde resin A, the rate of pre-crosslinking is determined by the ability to flow. When the pre-crosslinking has proceeded too far, the resin A will not flow sufficiently and it will be impossible to remove all included components such as for example air by pressing. The man skilled in the art can easily determine the desired rate of pre-crosslinking.

[0012] The resin A in step a) can additionally contain a pigment. In that case the coating that is finally obtained has a more or less uniform colour, with no special recognizable pattern. In case that such a uniform coloured layer is required the optional steps c) and d) can be left out but it may still be desirable to add in step d) a transparent topcoat layer on top of layer A to obtain a better appearance and durability. When a décor pattern in the

coating is desired steps c) and d) are required.

[0013] The resin should display such a combination of properties that the resin after the melting in step b) forms a porous layer. When melting the resin particles, they flow towards each other. Depending on the circumstances during the flow phase, and given enough time, the molten particles will finally touch each other completely, thereby giving rise to a non-porous layer. However for the optional step c) it is necessary to have a layer that is still porous to some level. To keep the layer porous, the temperature during the flow-phase shouldn't be too high when the time for the flow phase is moderate. When the time available for flowing is only short, the temperature should be higher. Therefore a balance should be found between these parameters that determine the amount of flow. The man skilled in the art can easily determine the suitable conditions by routine experimentation.

[0014] The kind of substrate depends on the final use of the coated substrate and can be for example wood or wood-based material, paper, metal, glass or plastic. Examples of wood-based materials are MDF (Medium Density Fibreboard) or HDF (High Density Fibreboard), OSB (oriented strand board), particle board, plywood. The coated substrates can be used in a large number of applications, for example serving trays, washing-up basins, crockery, doors, kitchen worktops, furniture and wall panels, kitchen cupboards, window frames, laminated flooring.

[0015] In step b) of the method according to the invention the applied resin is being molten by IR- or NIR-radiation and can be chosen freely. It is preferred to use IR-radiation for thinner layers, for example 0-5 μm , NIR is preferably used for thicker layers for example up to 0.5 mm to ensure a favourable temperature profile across the layer thickness. The duration of the radiation depends on the intensity of the radiation and the characteristics of the resin to be molten. The duration and intensity of the radiation should be such that a coherent layer is obtained, that still has a maximum porosity. This can easily be determined by routine experimentation by the man skilled in the art.

[0016] In step c) a décor pattern is applied to the porous layer A. The coloured material for forming such a pattern can be an ink, or a dye solution in water, solvent or in a polymer, or a pigment dispersion in water, solvent or in a polymer. The coloured material can be a solid or a liquid and can be applied by any kind of imaging technique, such as off-set and roller printing, ink-jet printing, heat-transfer printing, toner printing etc as described in "Handbook of Imaging Materials" (Arthur S. Diamond ed., Marcel Dekker, 1991).

[0017] In step d) a layer of melamine-formaldehyde resin B is applied to the coated substrate obtained after step b) or c). The melamine-formaldehyde resin B can be a liquid or in powder form. It is preferred to use a powdery melamine-formaldehyde resin B as in the case that it is a liquid the risk exists that the liquid will

penetrate into the porous layer obtained after step b). The nature of the melamine-formaldehyde resin B can vary, depending on the required properties of the final coating. Preferably the resin B is in powderous form with a Tg in the same ranges as indicated for resin A, it preferably has a good flow at the temperature in steps e) and f) and cures into a transparent and scratch-resistant topcoat so as to make the underlying pattern visible, while also giving an excellent adhesion with the underlying layer by co-reaction in the final curing steps e) and f). In order to protect the underlying layer(s) from environmental influences and degradation, stabilizers for example Hindered Amine Light Stabilizers (HALS), and UV absorbers can be added to resin B. In addition, to ensure a better scratch resistance inorganic fillers for example clay, silica and corundum can be added to the resin. Preferably, for the purpose of maintaining the optical transparency, filler particles of less than 300 nanometer are used.

[0018] Subsequently the coated substrate from step d) is heated in a laminating press for a certain amount of time. The absolute duration is not critical. Time and temperature are interdependent, it means that the result obtained counts but that the result can be obtained either by a high temperature and a relatively short time or by a somewhat lower temperature and a longer time. For example the time can vary between 1 and 3 minutes and the temperature can then vary between 100 and 140 °C. The balance between time and temperature should be chosen so as to result in a level of cure to give acceptable properties regarding the gloss and Kiron test for laminates.

[0019] Advantageously the layers A and B are pre-cured with heat before applying pressure. This pre-curing is done to prevent flow and absorption of the molten resin into the substrate, under the influence of pressure, which would blur the image. For this purpose, the laminating press can for example be pre-heated before the coated substrate is fed to it. Alternatively the coated substrate can be pre-treated in a separate step so as to result in a partially cured coating. Both alternatives result in a better resolution of the pattern when a pigment, ink or dye is used in step c). It has also been found that the pre-heating or pre-treating results in a better topcoat.

[0020] In step f) the pre-cured coated substrate is subjected to increased pressure and kept under pressure for a certain amount of time. The time and pressure are as generally used in the field of laminates.

[0021] The invention also relates to the melamine-formaldehyde coated substrate that is obtained with the method according to the invention. It has good mechanical properties. Depending on its further use, requirements need to be met in view of for example scratch resistance, flexibility, durability, chemical resistance, abrasion resistance, cold check (that means the crack resistance at a sharp temperature change). Depending on its final use some of the above-mentioned properties

are more important than others. Also depending on its further use of the coated substrate, requirements need sometimes to be met in regard of its appearance.

[0022] The melamine-formaldehyde coated substrate that is obtained according to the invention shows improved adhesion between the coating layer and the substrate compared to the prior art laminates in which first a prepreg is made where after the prepreg is pressed onto the substrate.

[0023] The invention further relates to the use of the melamine-formaldehyde coated substrate that is obtained according to the method of the invention in a post-forming process without structural damage to the coating.

[0024] The invention also relates to the use of a melamine-formaldehyde resin with a formaldehyde to melamine ratio between 1-3 (on mol basis) in a method according to the invention.

Claims

1. Method to coat a substrate with a melamine-formaldehyde resin comprising the following steps:

- a) Applying a layer of powderous melamine-formaldehyde A resin to a substrate,
- b) Melting the melamine-formaldehyde resin by IR- or NIR- radiation,
- c) Optionally applying an ink, dye solution or pigment dispersion to the with molten melamine-formaldehyde resin coated substrate,
- d) Optionally applying a layer of melamine-formaldehyde resin B to the coated substrate from step b) or c),
- e) Optionally heating the coated substrate from the previous steps in a laminating press for a certain amount of time,
- f) Increasing the pressure in the laminating press and keeping the laminate under pressure for a certain amount of time.

2. Melamine-formaldehyde coated substrate obtainable by the method according to claim 1.

3. Melamine-formaldehyde coated substrate with improved adhesion between the coating and the substrate.

4. Use of the melamine-formaldehyde coated substrate according to claim 2 or 3 in a post-forming process. Melamine-formaldehyde resin with a melamine to formaldehyde ratio between 2-3 (on mol basis).

5. Use of a melamine-formaldehyde resin with a melamine to formaldehyde ratio between 2-3, in a method according to claim 1.



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention EP 04 07 6083
shall be considered, for the purposes of subsequent
proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	GB 669 736 A (IND METAL PROTECTIVES INC) 9 April 1952 (1952-04-09) * the whole document *	2	B05D3/02 B05D3/12 B27N7/00
X	GB 1 024 126 A (WIGGINS TEAPE RES DEV; EDWARD BOTTLE) 30 March 1966 (1966-03-30) * the whole document *	2	
X	DATABASE WPI Section Ch, Week 200033 Derwent Publications Ltd., London, GB; Class A21, AN 2000-386110 XP002300367 & RU 2 135 352 C1 (OLIGO RES PRODN ENTERPRISE CO LTD) 27 August 1999 (1999-08-27) * abstract *	2	
A	DE 197 57 003 A (DIEFFENBACHER GMBH MASCHF ; GRIMM INTERNATIONAL TIMBER & P (DE)) 24 June 1999 (1999-06-24) * the whole document *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			B05D B27N
INCOMPLETE SEARCH			
The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims. Claims searched completely : Claims searched incompletely : Claims not searched : Reason for the limitation of the search: see sheet C			
Place of search		Date of completion of the search	Examiner
The Hague		13 October 2004	Brothier, J-A
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			

3

EPO FORM 1503 03.82 (P04C07)



Claim(s) searched incompletely:
1,2,4,5

Claim(s) not searched:
3

Reason for the limitation of the search:

Present claims 1-5 claim concern a process (use of a product made by that process and/or use of a product in the process) wherein the process has six steps a) ,b), c), d), e), f) in which steps c) d) and e) are optional. However step f) (not optional) is technically depending on e), therefore rendering unclear the fact that e) is optional. These claims lack clarity in the meaning of article 84 EPC. The search has therefore been carried out on the basis that step e) is not optional.

The scope of protection claimed in claim 2 is not limited by "obtainable by...", it therefore extends to all melamine-formaldehyde coated substrates. The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claim(s) may be said to define subject-matter for which protection might legitimately be sought (Article 84 EPC). For these reasons, a meaningful search over the whole breadth of the claim(s) is impossible. Consequently only a few documents relevant to the issue of novelty are cited.

Present claim 3 relate to a product defined by reference to a desirable characteristic or property, namely the improved adhesion between the coating and the substrate. The claims cover all products having this characteristic or property, whereas the application provides support within the meaning of Article 84 EPC and/or disclosure within the meaning of Article 83 EPC for only a very limited number of such products. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 84 EPC). An attempt is made to define the product by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, no search has been carried out for this claim.

The phrasing and lay out of claim 4 could lead to think that 2 claims were put together (numbering missing). This claim has been interpreted for reasons of clarity (article 84 EPC) as one single claim wherein the second sentence is describing the melamine-formaldehyde of the first sentence.

The "melamine to formaldehyde ratio between 2-3 (on mol basis)" in claim 4 and 5 is not supported by the description (article 83 EPC), on the contrary the description is supporting a " formaldehyde to melamine ratio between 1-3 (on mol basis)", leading to a lack of clarity (article 84 EPC) the search has however been carried out on the basis of the claims: "melamine to formaldehyde ratio between 2-3 (on mol basis)".

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

EP 04 07 6083

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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13-10-2004

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 669736	A	09-04-1952	BE 484300 A	
GB 1024126	A	30-03-1966	NONE	
RU 2135352	C1	27-08-1999	NONE	
DE 19757003	A	24-06-1999	DE 19757003 A1	24-06-1999