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(54) **MANUFACTURING PROCESS FOR A DECORATIVE SHEET**

(57) This invention refers to a manufacturing process for a high-performance resin-saturated decorative foil, designed for surface lining, both outdoors and indoors. The decorative foil can be used as a decorative lining for

HPL-High-Pressure Laminate-panels and CPL-Continuous-Pressure Laminate-panels, as well as to be adhered to any flat or curved 2D surface.

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Description

Technical field

[0001] This invention refers to a manufacturing process for a high-performance resin-saturated decorative foil, designed for surface lining, both outdoors and indoors. The decorative foil can be used as a decorative lining for HPL-High-Pressure Laminate-panels and CPL-Continuous-Pressure Laminate-panels, as well as to be adhered to any flat or curved 2D surface.

State of the art

[0002] High-pressure laminate-HPL-panels and continuous-pressure laminate-CPL-panels are examples of panels made up of different materials that are used in applications requiring scratch resistance, wear resistance, resistance to chemical attacks or to acts of vandalism of any kind, and that furthermore have the particularity of maintaining colour fastness. To achieve these specific features, surfaces consisting of decorative panels and coatings impregnated with modified melamine resins capable to meet the required properties for each case are described in the state of the art

[0003] Melamine impregnated papers have a limited resistance to acid attacks and, specifically, are not very appropriate to be used in outdoor applications. This problem is described and partially solved in document US 4 927 572, describing a method to produce a decorative panel, comprising the following steps: providing an underlay; applying to such underlay a decorative layer; applying to said decorative layer a liquid coating, essentially consisting of a radiation-polymerizable mixture; applying radiation to create a radiation-polymerized layer on said decorative layer; and thermopressing said underlay, said decorative layer, and said radiation-polymerized layer together, under conditions of elevated temperature and pressure, such that a scratch resistance of at least about 1.5 Newton is achieved.

[0004] Furthermore, document EP 1 631 454 B1 describes a decorative panel comprising a decorative layer on one or both surfaces of a carrier layer, wherein said decorative layer comprises a substrate layer and a surface layer, the substrate layer being a printed paper and the surface layer being a synthetic resin comprising one or more radiation-curable components, and an adhesion layer is present between the carrier layer and the decorative layer, which adhesion layer is in contact with the substrate layer characterized in that a transparent layer is present between the substrate layer and the surface layer, consisting of a synthetic resin comprising radiation-curable components selected from the group of unsaturated, (meth) acrylates.

[0005] Document EP 2 406 086 B1 describes a manufacturing procedure for a decorative paper and a decorative panel using a water-based resin to impregnate the substrate.

[0006] More specifically, this document describes a procedure comprising the following steps: providing a paper; impregnating the paper with a first, actinic radiation-curable resin; subjecting the paper obtained from the previous step to a drying step; applying a second actinic radiation curable resin to the dried paper obtained from the previous step; and curing the resulting paper from the previous step to obtain the resin-impregnated decorative paper, characterized by an initial drying process with a residual moisture < 5%, calculated on the basis of the weight obtained after the drying step.

[0007] Document EP 2 574 476 B1 is also relevant, describing a production procedure for a decorative film comprising a resin-impregnated substrate paper as well as one or more top layers. The procedure comprises the following steps: providing a resin-impregnated substrate paper; printing the substrate paper with an ink composition using inkjet technology; subjecting the previously printed substrate paper to a drying and/or curing treatment; applying at least one transparent top layer to the paper resulting from the previous step; and curing the paper from the previous step. A further feature of this procedure is that the degree of impregnation of the resin-impregnated substrate paper used in the first step is 30%-60%, based on the dry weight of the substrate paper used as a base. The resin present in the substrate paper comprises reactive groups, and the resin extends throughout the entire thickness of the substrate paper.

[0008] The processes described in the state of the art improve-generally speaking-the features of melamine resin impregnated panels, although some limitations are still observed in terms of: insufficient adhesion between layers, insufficient internal cohesion of the paper, insufficient impermeability of the decorative paper, difficulty to come up with a flat product, premature expiration of the decorative foil before even being used, difficulty for a stable processing of the product, insufficient resistance to atmospheric conditions, high risk of permeable porosity or areas of unsaturated paper, dependence on external adhesive layers to ensure paper saturation, as well as the impossibility to reduce or remove the content or the dependence, as an adhesive, on resins containing formaldehyde. One of the purposes of this invention is to solve those problems with the manufacturing process and the resulting panel described in the claims attached to this descriptive report.

Explanation of the invention

[0009] An object of this invention is a manufacturing procedure for a decorative foil. The procedure according to the invention allows to saturate a foil with a waterless resin, which in a non-limitative way, can be cured through ultraviolet radiation and/or electron beam, presenting superior mechanical properties in terms of paper traction in a direction perpendicular to the plane of its surface, also known as internal bond strength-or 'Z-Strength'-and that, in turn, despite the fact it can have a high crosslink

density, has no shrinking issues derived from the high level of crosslinking, which curls the product and strongly complicate its application. This object is achieved through the procedure in claim 1. The dependent claims contain details of particular and/or preferred embodiments for the invention.

[0010] More specifically, this invention describes a procedure comprising the execution of the following:

- a first step of providing a substrate;
- a second step of sealing one of the sides of the substrate with a first resin;
- a third step of drying and/or curing the sealed side with the first resin;
- a fourth step of impregnating the substrate with a waterless resin containing radiation-curable functional groups on the side of the substrate opposite to the side sealed with the first resin;
- a fifth step of curing the by-product resulting from the previous steps;
- a sixth step of applying one or several layers of a resin or resins to one of the two sides of the by-product resulting from the previous steps, with at least one resin containing radiation-curable functional groups; and
- a seventh step of drying and/or curing the foil resulting from all the above steps.

[0011] In an embodiment of the invention, the process execution is sequential, in the stated order. However, there can be execution sequences of the procedure in other practical embodiments of the invention, including but not limited to, adding intermediate steps or duplicating steps.

[0012] In this invention, the difference between *sealing with resin* (second step) and impregnating with resin (fourth step) must be highlighted. *Impregnating with resin*, in this descriptive report, means applying as much resin as the substrate can take, until the said substrate is *saturated* with the applied resin (i.e. "stuffed" with this resin). Instead, *sealing with resin* means generating a superficial resin membrane or layer that makes the substrate impermeable, so that the impregnation resin will not soak through, at least temporarily.

[0013] Additionally, in this invention a distinction is made between *drying* and *curing* the resin, since these cannot be technical equivalents. In a drying process, a solvent is extracted by evaporation, whereas when curing, a polymerization reaction is performed. Therefore, according to this descriptive report, the radiation-curing process, in a non-limitative way, entails both ultraviolet radiation processes and media and electron beam radiation processes and media, since both techniques, well known by the field experts, are sources of radiating energy.

[0014] In light of the above, in the context of this invention, *radiation-curable resins* mean any resins that polymerize when exposed to a source of radiation, including

but not limited to, ultraviolet radiation sources or electron beams.

[0015] In this invention, two forms of inertization are used. One of them involves generating an inert atmosphere-the most common way is using high-purity nitrogen in order to reduce the presence of oxygen in the air in contact with the resin. The other one, which we refer to as physical inerting, is accomplished by excluding the presence of oxygen from a surface by generating a physical barrier between the surface and the oxygen contained in the air. This can be achieved through direct contact-in a non-limitative way-of the resin with a film, or a flat or cylindrical surface with the surface of the resin, thus preventing the presence of oxygen. An example would be to put in contact the resin with a BOPET film, so that the uncured resin is not in contact with oxygen.

[0016] In this invention, a partially oxygen-enriched atmosphere is that in which surface curing is significantly inhibited due to the presence of oxygen. In systems in which radiation-curable components have been selected from the unsaturated acrylate and methacrylate group, the surface inhibition phenomenon is observed from values beyond 200 ppm of oxygen.

[0017] Thanks to the procedure and product described in this technical report, a good level of adhesion is obtained, which is mutual and durable between the different layers of the decorative foil, and at the same time, with the support, in order to achieve this, one or several chemical reaction mechanisms can be used in all of them to ensure crosslinking and permanent covalent chemical bonding. The impregnation of the substrate can be colourless or pigmented, with the particularity that it can be formulated to attain a certain resistance to different adverse weather conditions. Particularly, the impregnation of the substrate can be formulated to show high colour stability in spite of its exposure to ultraviolet radiation. Consequently, even a previously printed substrate can be impregnated, minimizing the effects of the degradation caused by exposure to sun radiation.

[0018] This resistance to ultraviolet radiation is not just important for outdoor applications, but this property is also gaining significance in surfaces for medical and hospital use, given that UV radiation disinfection is increasingly frequent.

[0019] Additionally, this invention allows for the decorative foil integrating the panel to be completely saturated with non-hygroscopic resins, so that it is impermeable before adhering it to the support, irrespective of any external agent. In the case of HPL or CPL panels, there is no dependence on the resins of the supports to which it is pressed, or on the pressure and temperature process as such. Furthermore, in case it is adhered by means of an external adhesive, the impermeability of the decorative foil is not dependent on the adhesives used.

[0020] The above property is particularly important. It has been observed that dependence on the transfer of resin or external adhesive involves a process that is very difficult to control, since the external resin has to be able

to flow, and at the same time, be able to draw the air that stays trapped in the substrate. Moreover, it has been confirmed that it is hard to ensure no area is left unsaturated, which in terms of outdoor applications can drive humidity to soak in and end up deteriorating the foil. The complexity to check whether any area has been left unsaturated makes it extremely hard to detect such an effect before its application, when it may already be too late. It must also be noted that in applications dependent on the resin or adhesive flowing thorough the substrate, it is difficult to obtain a covalent chemical adhesion, in which case the substrate and the resin might present delamination issues.

[0021] The decorative foil in the invention also retains its adhesion capacity, even in adverse conditions, such as those inherent to transport and storage. Therefore, the resins usually applied in the state of the art, such as melamine-formaldehyde and phenol-formaldehyde or similar substances, show a limited level of stability, since they are resins with a slowed-down yet not inhibited chemical reaction. Unlike these, in this invention, the resins used to ensure adhesion do not engage in slow chemical reactions, so that their stability and full adhesion are guaranteed for a much longer period-extending the life of the product with no gradual reduction of adhesion due to aging of the decorative foil, before it is even used.

[0022] Finally, the decorative foil in the invention can be used in a HPL or CPL panel, or a 2D flat or curved element covered with Finish-Foil, and has the particularity that it can be printed on using traditional techniques or else digital printing, after being impregnated with resin, under the invention procedure described.

Preferred embodiment of the invention and examples

[0023] As stated above, this invention describes a manufacturing procedure for a decorative foil, as well as the resulting product and its application in different types of panels, comprising the execution of the following:

- a first step of providing a substrate;
- a second step of sealing one of the sides of the substrate with a first resin;
- a third step of drying and/or curing the sealed side with the first resin;
- a fourth step of impregnating the substrate with a waterless resin containing radiation-curable functional groups on the side of the substrate opposite to the side sealed with the first resin;
- a fifth step of curing the by-product resulting from the previous steps;
- a sixth step of applying one or several layers of a resin or resins to one of the two sides of the by-product resulting from the previous steps, with at least one resin containing radiation-curable functional groups; and
- a seventh step of drying and/or curing the foil result-

ing from all the above steps.

[0024] Next, an analysis will be carried out of the different practical embodiments for the invention, as well as practical examples illustrating, in a non-limitative way, the procedure of the claims contained in this descriptive report. The reference throughout this technical report to «an embodiment» means that a characteristic, structure, or particular feature described in regard to the embodiment is included in at least one embodiment of this invention. Therefore, the occurrence of the phrase «an embodiment» in several spots throughout this descriptive report is not necessarily referred to the same embodiment, but it is just an explanatory non-limitative reference. Furthermore, several embodiments and examples of this invention can be referenced in this document, together with alternatives for the different components thereof. Such embodiments, examples, and alternatives should not be interpreted as de facto equivalents between them, but as stand-alone embodiments of this invention. Moreover, the characteristics, structures or features described herein can be combined in any appropriate way in one or more embodiments. In this description, numerous specific details are supplied to provide a comprehensive understanding of the embodiments of the invention. However, any expert in the field will acknowledge that the invention can be implemented without one or more of these specific details, or with other methods, components, materials, or additional steps in the process.

[0025] Some practical non-limitative embodiments are described below as to how the different steps of the procedure for this invention can be implemented in practice. As stated, these embodiments are merely practical examples and cannot be combined together. At the same time, unless otherwise indicated, all percentages and weights of the resins given in the following examples are referred to their dry content.

A first step-providing a substrate;

[0026] In a practical non-limitative embodiment of the first step, a cellulose-based paper-a foil-is provided, with a weight between 25 g/m² and 200 g/m², preferably comprised between 50 g/m² and 140 g/m², more preferably between 60 g/m² and 120 g/m². Furthermore, the paper foil can contain pigments and/or mineral fillers in its mass and/or surface decorative effects obtained through traditional and/or digital printing known in the state of the art. This paper is thus configured as a substrate for all other resin layers that will be successively applied under the invention procedure. In a practical embodiment, cellulose-based paper is used, but other types of materials can also be used, like for instance a non-woven textile-in which case, this will have a weight comprised between 5 g/m² and 100 g/m², preferably between 10 g/m² and 60 g/m², more preferably between 15 g/m² and 50 g/m²

A second step-sealing one of the sides of the substrate with a first resin

[0027] Next, the substrate is sealed on one of its sides with a first resin. The amount of resin should be enough to impermeabilize one of the sides of the substrate, thus holding back liquid resins that will be applied on the opposite side in successive steps of the invention procedure. In a particular embodiment, the layer of such first resin used as a sealant contains oligomers, monomers, adhesion-promoting additives, rheology modifiers, crosslinking reagents capable of acting as chemical crosslinking agents to ensure anchoring with adjacent sides, or any combination of the above. As previously stated, it is particularly important to highlight that in this second step there is no *impregnation*, that is to say, the first resin does not completely *fill* the interior of the substrate, but an impermeabilizing layer is generated so that all other liquid resins applied in subsequent steps do not soak through the substrate.

[0028] In a particular embodiment to produce HPL panels, a first water-based resin is used, either physically dryable and/or radiation-curable, appropriately diluted to adjust its viscosity and, consequently, its penetration power within the paper. To adjust its viscosity and its thixotropy, amorphous silica can be used as a thickening agent. This first resin used in this embodiment example allows for good sealing, enabling impermeabilization thanks to the surface membrane obtained on one of the sides of the substrate, which in this practical example is a decorative paper foil. The said impermeabilizing layer is configured to hold back infiltrations of the liquid resins that will be successively applied on the opposite side of the substrate or paper. The amount of this first sealing resin is comprised between 1 and 30 g/m², preferably between 2 and 25 g/m², and more preferably between 5 and 20 g/m². Moreover, blocked isocyanate up to 20% of the dry weight of the first resin has been considered advisable, preferably below 15%, and more preferably between 5 and 10% of the dry weight. It is also advisable to include a dispersion of blocked isocyanate with a rated unblocking temperature over 110°C, in particular with a rated unblocking temperature at or above 130°C.

[0029] The first sealing resin described for this HPL panel example presents chemical functionalities configured for proper crosslinking, extending covalent bonds with both adjacent layers in the finished product (i.e., adjoining layers to the finished decorative foil under the invention procedure), even if they do not share the same crosslinking chemical nature, thus establishing a connection between chemical groups not spontaneously reacting between themselves.

[0030] Additionally, given that the underlying substrate where the foil in this example is applied is a Kraft paper impregnated with phenol-formaldehyde resin, such resin reacts by cross-linking with the blocked isocyanate available in the sealing layer during the high temperature and pressure pressing step to obtain the decorative board or

finished product where the paper resulting from the invention procedure is applied.

[0031] In another particular embodiment to produce a *Finish-Foil*, a sealing layer is applied which is also adhesive, and for that purpose contains a physically dried vinyl resin or vinyl-acrylic resin, including blocked isocyanates. In this way, the foil resulting from the invention procedure can be adhered by means of pressure and temperature, with no need to add other external adhesives. In this application, a sealing layer with a weight between 1 and 80 g/m² is applied, preferably between 20 and 60 g/m², more preferably between 25 and 55 g/m², depending mostly on the support on which it will be adhered; however, the amount penetrating the substrate will still be between 1 and 30 g/m², preferably between 1 and 25 g/m², and more preferably between 1 and 15 g/m².

A third step-drying and/or curing the sealed side with the first resin

[0032] The substrate containing a sealed layer with the first resin is dried and/or cured in a third step, immediately afterward. This drying and/or curing process is selected in a non-limitative way-between: curing by ultraviolet radiation, by electron beam, curing by polymerization thermal initiators, curing by exposure to moisture, curing by oxidation, thermal curing, physical drying of water, drying by solvent removal or a combination of any of the above processes. In case thermolabile components are added, such as blocked isocyanates, to obtain a subsequent covalent chemical reaction with the adjacent layer(s), the drying and/or curing technique applied will be adjusted so that there is no premature reaction.

A fourth step-impregnating the substrate with a waterless resin containing radiation-curable functional groups on the side of the substrate opposite to the side sealed with the first resin

[0033] After drying and/or curing the first resin sealing one of the sides of the substrate, the opposite side of the paper to the side sealed with the first resin is impregnated with a waterless resin, with an amount enough to saturate the substrate through impregnation. The invention process allows for that impregnation resin to be a resin without formaldehyde. The membrane formed by the first resin on one of its sides, as stated, impermeabilizes that side of the substrate, so that the second resin does not exude and is in contact with the support and conveyance surfaces in the product manufacturing line, thus preventing contamination of the product and staining of the parts in contact. This waterless resin can be in different embodiments-a transparent resin or a pigmented resin.

[0034] The sealing membrane formed with the first resin allows for the application on the opposite side of the substrate of an impregnation resin which despite the possibility of being a resin without water, solvents, or formal-

dehyde, could be a low molecular weight resin, with a high density of functional groups and a very low viscosity. Thus, the substrate may be quickly saturated by extracting all the air therein, even if it was impregnated only through just one side. All of this without the problems arising from such impregnation soaking through to the opposite side, obtaining a substrate with a sealing layer that can also have chemical reactivity and different properties from those of the impregnation.

[0035] This waterless resin incorporated in the substrate during the fourth step of the procedure ensures crosslinking by covalent bonds with the adjacent layers of the finished final product, as well as full saturation of the substrate, which prevents subsequent infiltrations of moisture—particularly critical in outdoor applications exposed to adverse weather conditions.

[0036] The waterless resin applied in this fourth step can contain, in a non-limitative way, and in different practical embodiments, a mixture of oligomers, monomers, additives with properties suitable to obtaining covalent-type interfacial crosslinking with adjacent layers, as well as pigments, fillers nanoparticles, rheology modifiers, moisturizing agents, compatibilizers, ultraviolet radiation absorbers, light stabilizers, flame retardants, polymerization thermal initiators and/or any combination of the above.

[0037] In order to obtain a strong network of crosslinked polymers in the body of the substrate, the waterless resin applied in the fourth step can contain, in a non-limitative way, methacrylic and acrylic monomers and/or oligomers with a global functionality preferably over 2. Different monofunctional and polyfunctional monomers capable of generating a network will be combined, where polyfunctional flexibilizing oligomers and/or chain extenders, capable of altering the flexibility of the product, are optionally included.

[0038] Optionally, an oligomer or mixtures of oligomers can be used, which can contain combinations of epoxy acrylate, preferably polyester acrylate, more preferably urethane acrylate and/or their corresponding methacrylates as oligomeric precursors, together with acrylate monomers and their corresponding mono- and polyfunctional-methacrylates. All of them can also incorporate a hydroxylated functionality (-OH) and/or free or blocked isocyanate functionality (-N=C=O). Acrylate oligomers can also be used, as well as their corresponding methacrylates containing functionality and/or ethoxylated melamine groups in their chain.

[0039] In a particular embodiment, in a non-limitative way, acrylate monofunctional monomers with a hydroxylated terminal group (-OH) are added to the mixture, e. g., 4-Hydroxybutyl acrylate (4-HBA), 2-Hydroxypropyl acrylate (HPA), 2-Hydroxyethyl acrylate (HEA), Carboxyethyl acrylate (CEA), as well as their corresponding methacrylates.

[0040] In another particular embodiment, just an HDDA monomer-hexanediol diacrylate monomer bifunctional-is used, showing an exceptionally high ability to

penetrate the paper structure, which allows to easily draw out the air trapped between the cellulose fibres, giving the compound a high degree of saturation. In another embodiment, for papers with transparent finishing, ultraviolet-absorbing additives can be used, as well as light stabilizers and/or metal pigments and/or iridescent pigments (synthetic micas). Finally, in another embodiment, the second resin can include amorphous silica as a thickening agent, configured to adjust viscosity and provide the mixture with a thixotropic behaviour.

A fifth step-curing the by-product resulting from the previous steps

[0041] Next, the invention procedure advocates curing, at least partially, the by-product resulting from the execution of steps one to four, in order to obtain a curing that will even allow to wind the paper if necessary and, at the same time, ensuring chemical anchor points and reactivity to connect adjacent layers in the coating.

[0042] The curing method is selected in a non-limitative way-between: curing by electron beam, by ultraviolet radiation, curing by polymerization thermal initiators, curing by exposure to moisture, curing by oxidation, thermal curing, or a combination of any of the above processes.

[0043] Preferably, the foil resulting from the previous steps is cured by electron beam and/or by ultraviolet radiation, and more preferably, it is cured by electron beam-E.B-. In both cases, it can also be cured in a non-limitative way-by exposition to moisture, oxidation, thermal mechanisms, two-component resin polymerization, free and/or blocked isocyanate polymerization, to obtain interconnection by crosslinking all layers, thus ensuring interfacial adhesion, and to achieve curing of all the layer previously applied.

[0044] The issue of curling is one of the main problems with this kind of products, and it comes up when a layer of the foil shrinks in a different way to another, thus generating tensions which cause the foil to be unbalanced. This curling happens during drying and/or curing, and it does to a greater or lesser extent depending mainly on the resins used.

[0045] In an embodiment, curing is performed by electron beam. In this embodiment, even though high crosslink density resins are used in the impregnation, which may pose the issue of leading to strong curling, this is minimized thanks to the invention procedure, since by performing this partial curing of the substrate, without having yet applied the subsequent layers, we allow the substrate to shrink more freely. Therefore, by controlling uncured functional groups, we can control the remaining amount of shrinking, which can be adjusted to leave the desired shrinking to the following step or steps in the curing process.

[0046] In this embodiment, the said process allows for great control over one of the critical points since the curing can be adjusted to get a flat finished foil. In order to adjust curling in this embodiment, without compromising

adhesion with the adjacent layer or layers, it has been found that both the dose and the voltage can be adjusted, as well as the amount of oxygen on the surfaces. Thus, in an example using electron beam curing, the following is observed:

- With the dose, the number of electrons emitted by the device can be adjusted, so that we can control the amount of crosslinking on the surface whereby electrons penetrate. It is advisable to use a dose between 1 and 90 kGy.
- Voltage allows us to adjust the electron penetration curve, so that if voltage is in the low range, the penetration curve looks very steep, and the dose quickly decreases as the electrons go into the material. It is advisable to use a voltage between 80 and 300 kV.
- To obtain a chemically active surface, a partially oxygen-enriched inert atmosphere can be used. It can even be done without inerting, with oxygen partially or totally inhibiting surface curing on at least one of the two sides of the foil.

[0047] By adjusting these parameters, we can also adjust the remaining shrinkage, both in terms of amount and distribution. It is possible to have less polymerized surfaces, or even an asymmetric distribution, by adjusting the voltage and/or the oxygen level on the sides.

[0048] Surprisingly, and thanks to the process of the present invention, it was found that acrylic resins with high density of unsaturated groups can be used without an adverse curling effect, also minimizing the inherent fragility of strongly crosslinked systems. An even more surprising finding, after this electron beam curing, a high density of reactive groups may stay active on the surface, which may in turn even lead to a stoichiometric excess with regard to reactive groups in adjacent layers.

[0049] All of this allows for a substrate densely saturated with-optionally pigmentable-translucent resin, which displays high colour stability when being exposed to ultraviolet radiation. It also features a high level of crosslinking and internal cohesion, with a moderate adjustable degree of shrinking in the following step of the curing process. Tackiness can also be adjusted, so that it can be wound, easily printed and with a high availability of reactive groups on the contact surface with adjacent layers, which can ensure covalent anchoring.

[0050] In a variation of the previous particular embodiment, hydroxylated functional groups (-OH) and free isocyanate functional groups are added to the radiation-curing resin. In this application, curing is performed by an electron beam, just as in the previous embodiment, but it can be combined with a thermal curing process-before or after applying curing by radiation-to accelerate the reaction of free isocyanate, particularly on the surface, so that this will contribute to a tack-free surface, achieving such property with a minor surface curing process of the radiation-curing resin. This system allows for curing in an inert atmosphere with high oxygen content, or even

without inerting.

[0051] In another particular embodiment, thermal curing is performed in a substrate that has been previously impregnated with a resin consisting of radiation-curable functional groups, which go together with thermal initiators, as well as hydroxylated groups and free and/or blocked isocyanate. First, a thermal curing process of free and/or blocked isocyanates is performed, so that radiation-curing groups and-if desired-blocked isocyanate groups stay pending to react. Therefore, such groups will be able to create covalent bonds with adjacent layers.

An optional first step-printing decorative designs

[0052] Optionally, the procedure implements a decorative design printing step on any of the sides of the by-product resulting from the execution of steps one to five. In a special embodiment, a digital printer is used, and the printed image is partially cured by means of ultraviolet radiation and/or an electron beam. When partially curing, the image is fixed on the decorative foil, but at the same time, we keep active a part of surface reactive groups so that they can establish covalent bonds with the subsequent layer, i.e. with the layer formed by the radiation-curable resin upon radiation in the sixth step.

A sixth step-applying one or several layers of a resin or resins to one of the two sides of the by-product resulting from the previous steps, with at least one resin containing radiation-curable functional groups

[0053] In this sixth step, one or several resin or resins are applied-i.e., it could be one single type of resin or several types of stratified resins-, at least one of which contains radiation-curable functional groups. They can also cure-in a non-limitative way-by exposure to moisture, oxidation, thermal mechanisms, two-component resin polymerization, blocked isocyanate polymerization or other types of radiation other than ultraviolet or electron beam, on any of the two sides of the surface of the by-product resulting from the execution of steps one to five-and optionally the decorative design printing step as well-with a thickness between 10 and 300 μm .

[0054] The resin or resins used in this sixth step may contain-in a non-limitative way-a mixture of oligomers, monomers, additives with functionalities suitable to obtain interfacial crosslinking with the adjacent layer, as well as fillers to improve mechanical scratch hardness and abrasion resistance, nanoparticles, short fibres, pigments, rheology modifiers, moisturizing agents, surface tension modifiers, sun radiation protective additives, antioxidants, antivandalism additives (for instance, antigrffiti), antifouling additives, antimicrobial agents, flame retardants, infrared radiation reflective additives, antistatic additives, anti-fingerprints additives or any possible combination of the above.

[0055] In a particular embodiment, radiation-curable

components have been selected from the unsaturated acrylate and methacrylate group. In another particular embodiment, such radiation-curable components are formed by an epoxy acrylate oligomer, preferably an acrylate polyester oligomer, and particularly an urethane acrylate oligomer or the corresponding methacrylate oligomers, such as polymers capable of radiation polymerization, and if appropriate, diluted with mono- and/or polyfunctional acrylate monomer and/or their corresponding methacrylates. In another particular embodiment to increase colour stability when being exposed to ultraviolet radiation, the prepolymer is an aliphatic urethane acrylate oligomer, that has been duly diluted with a 1,6-hexanediol diacrylate monomer-HDDA.

[0056] In a particular embodiment of this step, it is advisable to apply none, one, or several layers of the aforementioned resins on a second paper or foil-optionally equipped with a surface treatment with release effect resin. The foil-in a non-limitative way-can be made of biaxially-oriented polyethylene terephthalate-BOPET-or biaxially-oriented paraffin thermoplastic resin, particularly BOPP, with a thickness between 19 and 90 μm , more advisably with a thickness between 20 and 50 μm . By means of mechanical coupling through calendering, the sides of both foils are placed in contact-on one hand this second foil and on the other hand the side of the foil on which one or several layers of resin are applied, as previously described.

An optional second step-applying one or several layers of adhesion-promoting and/or adhesive resin or resins

[0057] Optionally, the invention procedure comprises the application of one or several layers of a *resin or resins that promote adhesion and/or serve as an adhesive*, on the opposite side of the one where the layer or layers in the sixth step have been or will be applied. Subsequently, if necessary, a drying and/or curing step may be applied, selected-in a non-limitative way-between: curing by ultraviolet radiation, by electron beam radiation, curing by polymerization thermal initiators, curing by exposure to moisture, curing by oxidation, physical drying of water, drying by solvent removal or a combination of any of the above processes.

[0058] In an embodiment to produce HPL, a water-based physical drying and/or radiation-curable resin are used. The amount of this first sealing resin is comprised between 1 and 30 g/m^2 , preferably between 2 g/m^2 and 25 g/m^2 , and more preferably between 2 g/m^2 and 10 g/m^2 . Moreover, it has been deemed advisable to include blocked isocyanate up to 10% of the dry weight of the first resin. In this embodiment, it is advisable for blocked isocyanate to have with a rated unblocking temperature over 110°C, in particular with a rated unblocking temperature at or above 130°C.

[0059] In another particular embodiment to produce a Finish-Foil, an adhesive layer is applied containing a physically dried vinyl resin or vinyl-acrylic resin, including

blocked isocyanates. In this way, the foil resulting from the invention procedure can be adhered by means of pressure and temperature, with no need to add other adhesives. In this application, a layer of resin with a weight between 1 and 80 g/m^2 is applied, preferably between 20 and 60 g/m^2 , more preferably between 25 and 55 g/m^2

A seventh step-drying and/or curing the product resulting from all the above steps;

[0060] This drying and/or curing method is selected-in a non-limitative way-between: curing by electron beam, curing by ultraviolet radiation, curing by polymerization thermal initiators, curing by exposure to moisture, curing by oxidation, thermal curing, drying by solvent removal, or a combination of any of the above processes.

[0061] Preferably, the foil resulting from the previous steps-included, if the case may be, optional steps-is cured by electron beam and/or by ultraviolet radiation, and more preferably, it is cured by electron beam-E.B-. In both cases, it can also be cured-in a non-limitative way-by exposition to moisture, oxidation, thermal mechanisms, two-component resin polymerization, blocked isocyanate polymerization, in order to obtain interconnection through crosslinking of all layers, thus ensuring interfacial adhesion, and to achieve curing of all the layer previously applied.

[0062] In a particular embodiment, curing is performed by an electron beam, applying a dose between 1 and 90 kGy, preferably comprised between 10 kGy and 80 kGy, and more preferably between 20 and 60 kGy, at a voltage between 80 and 300 kV, preferably comprised between 100 and 300 kV, and more preferably between 150 and 300 kV. This is done in conditions of physical inertization, or else an inert atmosphere with oxygen content below 1000 ppm, preferably below 500 ppm, and more preferably below 200 ppm.

[0063] Having given a detailed explanation of the invention procedure, a series of non-limitative examples are described of several practical applications of the invention.

Example 1

[0064] A 70 g/m^2 decorative paper is used which is known in the state of the art, pigmented in mass, with decorative printing on the surface.

[0065] Secondly, it is sealed on the opposite side of the decorative print, by applying with a roller coater 7 g/m^2 -of dry content-of a water-based physical-drying urethane acrylate resin containing radiation-curable groups, to which a blocked isocyanate water-based dispersion is added, in a practical embodiment of the second step of the invention procedure.

[0066] In a non-limitative practical embodiment, this first resin consists of Lamberti ESACOTE® LX 101 dispersion with a solids content between 34% and 36%,

where Covestro Bayhydur BL2867 is incorporated-a water-based dispersion of blocked isocyanate with 38% reagent content, so that the dry proportion of the second product is 5% in regard to the solid content of the resin. The bifunctional monomer hexanediol diacrylate (HDDA) has been incorporated to the mixture in a proportion of 10%, based on the resin dry content.

[0067] The resulting by-product is subject to physical drying (third step of the invention) in a drying tunnel with hot-air jets at a temperature of 100°C, so as not to induce the reaction of the blocked isocyanate, which amounts to a non-limitative practical embodiment of the third step of the invention procedure.

[0068] Next, the fourth step is performed-impregnation through the opposite side of the substrate or paper-, which in a non-limitative way is applied with a roller coater, taking off the excess with a blade. For this purpose, 35 g/m² of a resin exclusively made up of a radiation-curable HDDA monomer are required, to which 1% of ultraviolet-absorber TINUVIN 400 is added, as well as 1% of light stabilizer HALS TINUVIN 292. This resin presents an extremely low viscosity and penetrates very easily, completely saturating the part of the substrate comprised between the surface and the sealing membrane resulting from the first resin.

[0069] Subsequently, the paper saturated in the previous steps with the first and second resins is exposed to an electron beam radiation, applying a 20 kGy, 200 kV dose on the impregnated side, with oxygen content of 500 ppm on the said side, and physical inertization on the sealing side.

[0070] In this non-limitative example, and after the steps described, the semielaborated product is wound up for further processing in subsequent steps.

[0071] On the previously prepared material, and on the opposite side to the one containing the first resin, a third layer is applied with 80 g/m² of urethane acrylate resin EBECRYL 284, adding 1% of TINUVIN 400 + 1% of light stabilizer HALS TINUVIN 292, and diluted with HDDA monomer to an application viscosity of 2000 mPa·s at 25°C, measured at a shear rate of 1000 s⁻¹. This corresponds to the sixth step of the invention procedure.

[0072] Finally, the product goes through the last curing step, by an electron beam, applied on the side of the sixth step, with a dose of 60 kGy and a voltage of 200 kV. This is all performed in an inert atmosphere with oxygen content below 200 ppm on the side of the sixth step, and physical inertization on the opposite side, to achieve complete in-depth curing by radiation in all the layers. The blocked isocyanate functionality on the sealing layer is thus preserved.

[0073] The product is thus finished and successively placed with the decorative side facing outward, on a pile of Kraft paper sheets impregnated with phenol-formaldehyde resin, and it is pressed to a temperature of 160°C and a pressure of 80 kg/cm², for 20 minutes. During the pressing process, the phenolic resin crosslinks with the blocked isocyanate available in the interface, so that a

covalent chemical bond is obtained, preventing the infiltration of water and atmospheric agents, and so ensuring chemical adhesion between the foil object of this patent and the underlying sheets, achieving a surface tensile strength value over 3 N/mm² (Z- Strength under DIN 52366).

Example 2

[0074] A 70 g/m² decorative paper is provided which is known in the state of the art, pigmented in mass, with decorative printing on the surface. Subsequently, it is sealed on the printed side by applying with a roller coater 7 g/m²-of dry content-of an urethane acrylate -based physical drying resin-i.e., first water-based resin-containing radiation-curable groups, which amounts to a non-limitative embodiment of the first two steps in the procedure.

[0075] The sealing mixture resin is made up of an aqueous dispersion of MIWON MIRAMER W8365NT, with a 43% solid content, to which bifunctional monomer hexanediol diacrylate (HDDA) is added, in a proportion of 8%, based on the resin dry content. The resulting paper foil is subjected to physical drying in a drying tunnel with hot air jets-i.e. first curing and/or drying.

[0076] The substrate or paper is impregnated-i.e. step four-on the other side with a roller coater, taking off the excess with a blade. For this purpose, 35 g/m² of a resin exclusively made up of a radiation-curable HDDA monomer are required. This resin-i.e. the resin applied in the fourth step of the invention procedure-presents a very low viscosity and penetrates very easily, completely saturating the part of the substrate comprised between the surface and the sealing membrane made up from the first resin.

[0077] Subsequently, the paper saturated in the previous steps with the first and second resins is exposed to an electron beam radiation, applying a 20 kGy, 135 kV dose on the impregnated side, with oxygen content of 500 ppm on the said side, and physical inertization on the sealing side. In this example, and after these steps, the semielaborated product is wound up for further processing in subsequent steps.

[0078] Subsequently, a resin-of the same type as the one described in the sixth step of example 1-is applied, but this time on the side where the first resin was applied. On the side impregnated with the second resin, 5 g/m² are applied of a third resin, which is equal to the sealing mixture-i.e. the first resin in example 1-, with the same drying process as in the drying and/or curing step from example 1.

[0079] Finally, the product goes through the last curing step, by an electron beam, applied on the side of the sixth step, with a dose of 60 kGy and a voltage of 225 kV. This is all performed in an inert atmosphere with oxygen content below 200 ppm on the side of the sixth step, and physical inertization on the opposite side, to achieve complete in-depth curing by radiation in all of the layers.

The blocked isocyanate functionality on the sealing layer is thus preserved.

[0080] The product is thus finished and successively placed with the decorative side facing outward, on a pile of Kraft paper sheets impregnated with phenol-formaldehyde resin, and it is pressed to a temperature of 160°C and a pressure of 80 kg/cm², for 20 minutes. During the pressing process, the phenolic resin crosslinks with the blocked isocyanate available in the interface, so that a covalent chemical bond is obtained, preventing the infiltration of water and atmospheric agents, and so ensuring chemical adhesion between the foil object of this patent and the underlying sheets, achieving a surface tensile strength value over 3 N/mm² (Z- Strength under DIN 52366).

Example 3

[0081] On an 80 g/m² white base paper, one of the two sides is sealed, by applying with a roller coater 7 g/m²-of dry content-of a physical-drying urethane acrylate-based resin, containing radiation-curable groups, to which a blocked isocyanate water-based dispersion is added.

[0082] In a non-limitative practical embodiment, this first resin consists of Lamberti ESACOTE® LX 101 dispersion with solid content between 34% and 36%, where Covestro Bayhydur BL2867 is incorporated-a water-based dispersion of blocked isocyanates with 38% reagent content, so that the proportion of the second product is 5% in regard to the solid content of the resin. The bifunctional monomer hexanediol diacrylate (HDDA) has been incorporated to the mixture in a proportion of 10%, based on the resin dry content.

[0083] The resulting by-product is subject to physical drying (third step of the invention) in a drying tunnel with hot-air jets at a temperature of 100°C, so as not to induce a reaction from blocked isocyanate, which amounts to a non-limitative practical embodiment of the third step of the invention procedure.

[0084] Subsequently, the paper is impregnated with a waterless resin using a roller coater and taking off the excess with a blade. For this purpose, 40 g/m² of a resin made up of an HDDA monomer and 20% of white pigment KRONOS 2220 are required, further adding 1% of ultra-violet-absorber TINUVIN 400, as well as 1% of light stabilizer HALS TINUVIN 292. This resin presents a low viscosity and penetrates very easily, completely saturating the paper.

[0085] Subsequently, the paper saturated in the previous steps with the first and second resins is exposed to an electron beam radiation, applying a 20 kGy, 200 kV dose on the impregnated side, with oxygen content of 500 ppm on the said side, and physical inertization on the sealing side.

[0086] Next, printing is performed on the side impregnated with the second resin by means of a digital printer with light-reactive inks containing inorganic pigments, and the printed image is partially cured by ultraviolet ra-

diation exposure, so that when curing, the image is fixed upon the paper. However, at the same time, reactive groups remain active so that covalent bonds can be created with the next layer.

[0087] On the previously prepared material, on the side that was printed, another layer is applied-i.e. application of a third resin-with 80 g/m² of urethane acrylate resin Ebecryl 4680, adding 1% of Tinuvin 400 + 1% of light stabilizer HALS Tinuvin 292, and diluted with HDDA monomer to an application viscosity of 2000 mPa·s at 25°C, measured at a shear rate of 1000 s⁻¹.

[0088] Finally, the product goes through the last curing step, by an electron beam, applied on the side of the sixth step, with a dose of 60 kGy and a voltage of 200 kV. This is all performed in an inert atmosphere with oxygen content below 200 ppm on the side of the sixth step, and physical inertization on the opposite side, to achieve complete in-depth curing by radiation in all the layers. The blocked isocyanate functionality on the sealing layer is thus preserved.

[0089] The product is thus finished and successively placed with the decorative side facing outward, on a pile of Kraft paper sheets impregnated with phenol-formaldehyde resin, and it is pressed to a temperature of 160°C and a pressure of 80 kg/cm², for 20 minutes. During the pressing process, the phenolic resin is crosslinked with the blocked isocyanate available in the interface, so that a covalent chemical bond is obtained, preventing the infiltration of water and atmospheric agents, and so ensuring chemical adhesion between the foil object of this patent and the underlying sheets, achieving a surface tensile strength value over 3 N/mm² (Z- Strength under DIN 52366).

Example 4

[0090] An 80 g/m² white base paper known in the state of the art, pigmented in mass, is sealed on one side by applying with a roller coater 7 g/m²-of dry content-of an urethane acrylate -based physical drying resin-i.e., first water-based resin-containing radiation-curable groups, which amounts to a non-limitative embodiment of the first two steps in the procedure.

[0091] The sealing mixture resin is made up of an aqueous dispersion of MIWON MIRAMER W8365NT, with a 43% solid content, to which bifunctional monomer hexanediol diacrylate (HDDA) is added, in a proportion of 8%, based on the resin dry content. This resin layer helps accomplish a two-fold purpose-on the one hand, creating a membrane to prevent the impregnation from soaking through, and on the other hand, preparing the outer surface for the subsequent printing step. This thin layer, on account of its chemical composition, allows for a slight penetration of the ink within the surface, helping to get it better fixed. The resulting paper foil is subject to physical drying in a drying tunnel with hot air jets.

[0092] Subsequently, the paper is impregnated with the waterless resin using a roller coater and taking off

the excess with a blade. For this purpose, 40 g/m² of a resin made up of an HDDA monomer and 20% of white pigment KRONOS 2220 are required, further adding 1% of ultraviolet-absorber TINUVIN 400, as well as 1% of light stabilizer HALS TINUVIN 292. This resin presents a low viscosity and penetrates very easily, completely saturating the paper.

[0093] Subsequently, the paper saturated in the previous steps with the first and second resins is exposed to an electron beam radiation, applying a 20 kGy, 135 kV dose on the impregnated side, with oxygen content of 500 ppm on the said side, and physical inertization on the sealing side. After these steps, the semielaborated product is wound up for further processing in subsequent steps.

[0094] Next, printing is performed on the side impregnated with the first resin by means of a digital printer with light-reactive inks containing inorganic pigments, and the printed image is partially cured by ultraviolet radiation exposure, so that when curing, the image is fixed upon the paper. However, at the same time, reactive groups remain active so that covalent bonds can be created with the next layer.

[0095] On the previously prepared material, on the side that was printed, another layer is applied-i.e. application of a third resin-with 80 g/m² of urethane acrylate resin Ebecryl 4680, adding 1% of Tinuvin 400 + 1% of light stabilizer HALS Tinuvin 292, and diluted with HDDA monomer to an application viscosity of 2000 mPa·s at 25°C, measured at a shear rate of 1000 s⁻¹. On the side where the second resin was applied, 5 g/m² are applied of a third resin, which is equal to the sealing mixture-i.e. the first resin in example 1-, with the same drying process as in the drying and/or curing step from example 1.

[0096] Finally, the product goes through the last curing step, by an electron beam, applied on the side of the sixth step, with a dose of 60 kGy and a voltage of 225 kV. This is all performed in an inert atmosphere with oxygen content below 200 ppm on the side of the sixth step, and physical inertization on the opposite side, to achieve complete in-depth curing by radiation in all the layers. The blocked isocyanate functionality on the sealing layer is thus preserved.

[0097] The product is thus finished and successively placed with the decorative side facing outward, on a pile of Kraft paper sheets impregnated with phenol-formaldehyde resin, and it is pressed to a temperature of 160°C and a pressure of 80 kg/cm², for 20 minutes. During the pressing process, the phenolic resin is crosslinked with the blocked isocyanate available in the interface, so that a covalent chemical bond is obtained, preventing the infiltration of water and atmospheric agents, and so ensuring chemical adhesion between the foil object of this patent and the underlying sheets, achieving a surface tensile strength value over 3 N/mm² (Z- Strength under DIN 52366).

Example 5

[0098] An 80 g/m² decorative white paper known in the traditional technique, pigmented in mass, is sealed on one side applying with a roller coater 8 g/m² of a radiation-curable resin with 100% solids.

[0099] The resin mixture for the sealing in made up of tetrafunctional polyester acrylate MIWON Miramer P2291, diluted in bifunctional monomer HDDA to a viscosity of 1000 mPa·s at 25°C, measured at a shear rate of 1000 s⁻¹. 5% of blocked isocyanate is added to the mixture, with 100% solids Covestro Desmodur BL1100/1 and 3% of surface photoinitiator CIBA Darocure 1173 2-Hydroxy-2-methylpropiophenone (CAS no. 7473-98-5).

[0100] The resulting foil is subject to partial actinic drying on the surface by ultraviolet radiation exposure, taking particular care that temperatures during the said exposure do not induce the reaction of blocked isocyanate. The substrate is impregnated on the other side with a roller coater, taking off the excess with a blade. For this purpose, 40 g/m² of a resin exclusively made up of a radiation-curable HDDA monomer are required-i.e. impregnation of the second resin.

[0101] Subsequently, the paper saturated in the previous steps with the first and second resins is exposed to an electron beam radiation, applying a 20 kGy, 200 kV dose on the impregnated side, with oxygen content of 500 ppm on the said side, and physical inertization on the sealing side. After these steps, the semielaborated product is wound up for further processing in subsequent steps.

[0102] On the previously prepared material, and on the opposite side to the one containing the sealing resin, a layer is applied with 50 g/m² of acrylate urethane resin EBECRYL 284, diluted with HDDA monomer and 8% oxide yellow pigment Lanxess Bayferrox 3910, to an application viscosity of 2200 mPa·s at 25°C, measured at a shear rate of 1000 s⁻¹.

[0103] On the side of a "release-foil" BOPET film with a microstructure, a layer is applied with 50 g/m² of urethane acrylate resin EBECRYL 284, with 25% of nanocryl nanoparticles, adding 1% of Tinuvin 400 + 1% of light stabilizer HALS Tinuvin 292, and diluted with HDDA monomer to an application viscosity of 2200 mPa·s at 25°C, measured at a shear rate of 1000 s⁻¹. The liquid surfaces on both foils are put in contact by means of a calender and are subsequently subject to curing by an electron beam.

[0104] Finally, the product goes through the last curing step, by an electron beam, applied on the side of the sixth step, with a dose of 60 kGy and a voltage of 225 kV. All of this is performed in conditions of physical inertization on both sides, to achieve complete in-depth curing by radiation in all the layers. The blocked isocyanate functionality on the sealing layer is thus preserved. When separating the PET, our foil is found to have adopted the said microstructure, which remains even if subsequently subject to high-temperature and high-pressure pressing.

[0105] The product is thus finished and successively placed with the decorative side facing outward, on a pile of Kraft paper sheets impregnated with phenol-formaldehyde resin, and it is pressed to a temperature of 160°C and a pressure of 80 kg/cm², for 20 minutes. During the pressing process, the phenolic resin is crosslinked with the blocked isocyanate available in the interface, so that a covalent chemical bond is obtained, preventing the infiltration of water and atmospheric agents, and so ensuring chemical adhesion between the foil object of this patent and the underlying sheets, achieving a surface tensile strength value over 3 N/mm² (Z- Strength under DIN 52366).

Example 6

[0106] An 80 g/m² decorative paper known in the traditional technique, pigmented in mass, with decorative printing on the surface, is sealed on the opposite side to the design, applying with a roller coater 7 g/m² of dry content of a physical-drying urethane acrylate-based resin, equipped with radiation-curable groups. The sealing resin consists of a Lamberti ESACOTE® LX 101 dispersion with solid content between 34% and 36%.

[0107] The bifunctional monomer hexanediol diacrylate (HDDA) has been incorporated to the mixture in a proportion of 6 %, based on the resin dry content, as well as 4%, based on the resin dry content, of a monofunctional hydroxylated monomer (-OH). The resulting paper foil is subject to physical drying in an evaporation furnace with hot air jets.

[0108] The substrate is impregnated on the other side using a roller coater and taking off the excess with a blade. For this purpose, 40 g/m² of a resin made up exclusively of a radiation-curable HDDA monomer are required, further adding 1% of ultraviolet-absorber Tinuvin 400, as well as 1% of light stabilizer HALS Tinuvin 292. This resin presents an exceptionally low viscosity and penetrates very easily, completely saturating the paper.

[0109] Subsequently, the paper saturated in the previous steps with the first and second resins is exposed to an electron beam radiation, applying a 20 kGy, 200 kV dose on the impregnated side, with oxygen content of 500 ppm on the said side, and physical inertization on the sealing side. After these steps, the semielaborated product is wound up for further processing in subsequent steps.

[0110] On the previously prepared material, on the side that was printed, another layer is applied-i.e. application of a third resin-with 80 g/m² of urethane acrylate resin Ebecryl 4680, adding 1% of Tinuvin 400 + 1% of light stabilizer HALS Tinuvin 292, and diluted with HDDA monomer to an application viscosity of 2000 mPa·s at 25°C, measured at a shear rate of 1000 s⁻¹.

[0111] Finally, the product goes through the last curing step, by an electron beam, applied on the side of the sixth step, with a dose of 60 kGy and a voltage of 200 kV. This is all performed in an inert atmosphere with oxygen con-

tent below 200 ppm on the side of the sixth step, and physical inertization on the opposite side, to achieve complete in-depth curing by radiation in all of the layers.

[0112] The product developed in this example is adhered using a thermofusible polyurethane moisture-reactive adhesive (PUR) on an aluminium honeycomb panel, and in this example, a matching square aluminium section is also wrapped. A covalent chemical bond is obtained between the polyurethane reactive adhesive and -OH functional groups, which ensure an excellent level of adhesion, preventing water infiltration and providing strong resistance to atmospheric agents, ensuring mechanical cohesion between the laminated product object of this patent and the supports to which it is adhered.

[0113] Finally, although the previous examples illustrate the principles of this invention in one or more particular applications, it will be obvious to any expert in the field that numerous modifications can be made to the form, use, and implementation details without any exercise of inventive activity, and without drifting away from the principles and notions of the invention as described in the following claims.

Claims

1. A manufacturing procedure for a decorative foil, comprising the execution of:

- a first step of providing a substrate;
- a second step of sealing one of the sides of the substrate with a first resin;
- a third step of drying and/or curing the sealed side with the first resin;
- a fourth step of impregnating the substrate with a waterless resin containing radiation-curable functional groups on the side of the substrate opposite to the side sealed with the first resin;
- a fifth step of curing the by-product resulting from the previous steps;
- a sixth step of applying one or several layers of a resin or resins to one of the two sides of the by-product resulting from the previous steps, with at least one resin containing radiation-curable functional groups; and
- a seventh step of drying and/or curing the foil resulting from all the above steps.

2. The procedure according to claim 1, wherein the substrate consists of:

- a cellulose-based paper with a weight comprised between 25 g/m² and 200 g/m², preferably between 50 g/m² and 140 g/m², and more preferably between 60 g/m² and 120 g/m²; or
- a non-woven textile with a weight comprised between 5 g/m² and 100 g/m², preferably between 10 g/m² and 60 g/m², and more preferably be-

tween 15 g/m² and 50 g/m².

3. The procedure according to either claim 1 or 2, wherein:

the first resin is of a type selected between: physical drying, radiation-curable, thermal initiator-induced polymerization, crosslinking between hydroxylated groups and free and/or blocked isocyanates, or a combination of any of the above;

and where the said first resin, moreover:

in case of being configured to promote adhesion, has a weight comprised between 1 g/m² and 30 g/m², preferably between 2 g/m² and 25 g/m², and more preferably between 5 g/m² and 20 g/m²; or

in case of being configured to act as an adhesive, has a weight comprised between 1 g/m² and 80 g/m², preferably comprised between 20 g/m² and 60 g/m², more preferably between 25 g/m² and 55 g/m²; with an amount of resin penetrating the substrate between 1 and 30 g/m², preferably between 1 and 25 g/m², and more preferably between 1 and 15 g/m².

4. The procedure, according to any one or more claims 1 to 3, wherein during the third step a drying and/or curing process is carried out, by means of at least one process selected among: ultraviolet radiation curing, radiation by electron beam, physical drying.

5. The procedure, according to any one or more claims 1 to 4, wherein during the fourth step, radiation-curing functional groups go together with thermal initiators, and/or hydroxylated groups and free and/or blocked isocyanates.

6. The procedure according to any one or more claims 1 to 4 wherein the resin from the fourth step contains at least 50% of monomers with unsaturated acrylate and/or methacrylate groups, preferably over 75%, and more preferably over 85%.

7. The procedure according to any one or more claims 1 to 6, wherein in the fifth step curing is performed by an electron beam, with a dose between 1 and 90 kGy, preferably between 10 and 80 kGy, more preferably between 20 and 60 kGy, with a voltage comprised between 80 and 300 kV, preferably between 100 and 300 kV, more preferably between 120 and 250 kV, with oxygen content that can range from minimum values, obtained through the physical inertization technique, to concentrations like oxygen natural content in the air.

8. The procedure according to claim 7, wherein curing is performed in a partially oxygen-enriched inert atmosphere or it can even be done without inerting, with oxygen partially or totally inhibiting surface curing on at least one of the two sides of the foil.

9. The procedure according to any one or more claims 1 to 8, comprising an optional step, involving printing decorative designs on either side, executable after the fifth step of curing and before the sixth step of applying one or several layers of a radiation-curable resin or resins.

10. The procedure according to claim 9, wherein a digital printer is used, and ink is partially cured, by means of ultraviolet radiation and/or electron beam; and where, when partially curing, the image is fixed upon the decorative foil, but at the same time, keeping active at least a part of surface reactive groups configured so that they can establish covalent bonds with the subsequent layer in the sixth step.

11. The procedure according to any one or more claims 1 to 10, comprising an optional step, involving applying one or several layers of adhesion-promoting and/or adhesive resin or resins, before or after the sixth step; and where such layer or layers of adhesion-promoting and/or adhesive resin or resins are applied on the opposite side to the side where the sixth step was or will be executed; subsequently, if necessary, a drying and/or curing step may be applied.

12. The procedure according to claim 11, wherein:

the adhesion-promoting and/or adhesive layer or layers are of a type selected between physical drying, radiation-curing, thermal initiator-induced polymerization, crosslinking between hydroxylated groups and free blocked isocyanates, or a combination of any of the types above;

wherein, if such resin or resins are configured so as to promote adhesion, they have a weight comprised between 1 g/m² and 30 g/m², preferably between 2 g/m² and 25 g/m², and more preferably between 2 g/m² and 10 g/m²; or wherein, if such resin or resins are configured so as to act as an adhesive, they have a weight comprised between 10 g/m² and 80 g/m², preferably between 20 g/m² and 60 g/m², and more preferably between 25 g/m² and 55 g/m².

13. The procedure according to any claim 1 to 12, wherein in the seventh step curing is performed by an electron beam, with a dose between 1 and 90 kGy, preferably comprised between 10 kGy and 80 kGy, and more preferably between 20 and 60 kGy, at a voltage

between 80 kV and 300 kV, preferably comprised between 100 kV and 300 kV, and more preferably between 150 kV and 250 kV. This is done in conditions of physical inertization, or else an inert atmosphere with oxygen content below 1000 ppm, preferably below 500 ppm, and more preferably below 200 ppm.

14. The procedure according to any claim 1 to 13, wherein radiation-curable components have been selected from the unsaturated acrylate and methacrylate group.
15. The procedure according to any claim 1 to 14, wherein radiation-curable components in the sixth step are formed by an epoxy acrylate oligomer, preferably an polyester acrylate oligomer, and particularly an urethane acrylate oligomer or the corresponding methacrylate oligomers, such as polymers capable of radiation polymerization, and if appropriate, diluted with mono- and/or polyfunctional acrylate monomers and/or their corresponding methacrylates.
16. The procedure according to any or more of the previous claims, wherein the prepolymer in the sixth step is an aliphatic urethane acrylate oligomer, that has been duly diluted with a diacrylate or triacrylate monomer.
17. Use of the decorative foil resulting from the procedure in any of the claims 1 to 16 on a panel selected among: HPL panel, CPL panel or 2D flat or curved element lined with Finish-Foil.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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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

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)

EP0-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	WO 2010/104380 A1 (TRESA INT BV [NL]; VONCKEN HENDRIKUS HUBERTUS GERARDUS [NL]) 16 September 2010 (2010-09-16) claims 1-19	1-17
X	US 2002/081393 A1 (KJELLQVIST ANN KERSTIN BIRGITT [SE] ET AL) 27 June 2002 (2002-06-27) paragraph [0018] claims 1-8	1-17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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19 January 2021

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/ES2020/070445

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REFERENCES CITED IN THE DESCRIPTION

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- EP 2574476 B1 [0007]

Non-patent literature cited in the description

- CHEMICAL ABSTRACTS, 7473-98-5 [0099]