



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 595 718 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
16.11.2005 Bulletin 2005/46

(51) Int Cl.7: **B44C 1/10**, B44C 5/04,
B32B 27/00, B32B 31/00,
C08G 12/32

(21) Application number: **04013999.0**

(22) Date of filing: **15.06.2004**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PL PT RO SE SI SK TR**
Designated Extension States:
AL HR LT LV MK

(72) Inventor: **Price, David Elwyn**
Williamstown, Victoria 3016 (AU)

(74) Representative: **Menges, Rolf**
Ackmann, Menges & Demski,
Tonhallenstrasse 16
47051 Duisburg (DE)

(30) Priority: **10.05.2004 EP 04011040**

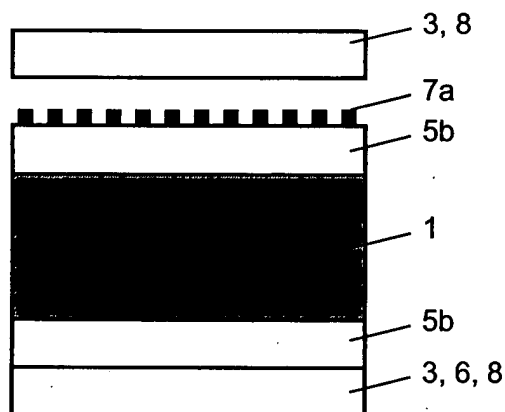
(71) Applicant: **Depco-Trh Pty Ltd**
Williamstown, Victoria 3016 (AU)

(54) **Method for manufacturing a laminate**

(57) The invention relates to a method for manufacturing a decorative laminate, in which a polymer (5a) is applied to the surface of a substrate (1) and subsequently stabilised with an overlying paper (4) or non-woven material, and to laminate products produced by the method according to the invention. A special feature of

the method is the curing of the polymer (5a) in different process steps, wherein in a first process step the applied polymer is partially cured to its b-stage. This b-stage polymer is subsequently fully cured after application of an overlying paper (4) or non-woven material. The use of papers as carrier materials for the base resins are minimised.

Fig. 4



Description

[0001] The invention relates to a method for manufacturing a decorative laminate, as well as decorative laminate products manufactured by the method according to the invention.

[0002] For the manufacture of decorative laminates, substrates for example particle-board or fibreboard, are laminated with one or more resin impregnated overlaying papers on one or both sides, in which these paper materials serve as a carrier for the pre-polymer a-stage resin starting material, pigments and print or any subset of those. These carrier materials also impart an internal stability to the final cured resin through their fibrous structure.

[0003] In the manufacture of low pressure melamine (LPM), also known as direct pressure melamine (DPL) and thermo-fused melamine (TFM), the overlaying paper or papers impregnated with resin starting material and partially cured are pressed onto the substrate in a hot press where the resin flows and bonds the carrier material to the substrate and is cured to its final state to form the laminate.

[0004] In the manufacture of high pressure laminates (HPL) several resin impregnated kraft papers are assembled to form the substrate or core material and a resin impregnated décor paper are placed above the kraft papers. In some cases, for instance when a printed décor paper is used, a resin impregnated clear overlay sheet is placed above the décor paper to provide wear protection of the print. Furthermore, in some cases the decorative paper is not impregnated and the clear overlay provides sufficient resin and the high pressure press sufficient pressure to form the uniformly impregnated HPL, this process being known as dry pressing. Hard particles such as fused alumina may be included in or on the clear overlay paper.

[0005] In another process known as continuous pressure laminate (CPL) the impregnated decorative paper and impregnated kraft paper or papers and optionally an impregnated clear overlay paper are fed from rolls into a double band hot press. The pressure and heating bonds the impregnated papers into a continuous laminate. Alternatively the impregnated papers can be applied directly and simultaneously onto a wood based panel substrate within the continuous press.

[0006] Various innovations have been proposed for visual and mechanical improvements of the laminate surface structure, such as to improve the abrasion resistance and the decorative appearance of the laminates thus manufactured. In addition to chemical and abrasion resistance, it is particularly important for the intended usage that the laminate, for example, as an imitation of a genuine wood flooring, looks as realistic as possible. For instance, a wooden substrate, which usually consists of composite board or chipboard of various types, is covered with a layered sequence of resin-impregnated materials, each material layer serving a

specific purpose. For example, a lowermost impregnated paper layer in the laminate layer structure provides the means to carry the pigments and decorative prints in the laminate. This carrying layer is usually referred to as the decor sheet. Some manufacturers also include an impregnated clear overlay paper layer to protect the decoration of the printed paper layer. This overlay paper can include hard particles in and or on the overlay paper to enhance the abrasion resistance of the laminate surface. Additionally, in the manufacture of a low pressure melamine laminate both sides of the substrate are covered. In flooring laminate an impregnated backer paper is applied to the non-decorative side of the laminate. The material layers arranged one above the other are usually impregnated with a liquid thermosetting resin and after impregnation the layers undergo treatment to dry and partially cure the thermosetting resin before their use in the laminate manufacture process. The partially cured stage of the resin is usually referred to as the b-stage. After impregnation the materials are laid onto the substrate and are bonded to the substrate in a hot press where the partially cured resin cures from its b-stage to its final state, called the c-stage.

[0007] Thus in the manufacturing process the resin is partially cured after impregnation of a fibrous material and then fully cured in the hot press. Final curing of the resin is conducted in a hot press as selected by the manufacturer in both methods where the impregnated papers or non-woven materials are bonded to the substrate surface.

[0008] Common to all processes in the prior art is that the dried and partially cured resin enters the manufacturing process absorbed into and coated onto the carrier papers. For low pressure melamine (LPM), also known as direct pressure laminate (DPL), or thermo fused melamine (TFM), the carrier paper is impregnated with melamine formaldehyde resin usually containing about 48% water, at a viscosity of approximately 30cps., and temperature of approximately 25C. Alternatively as a cost saving the core of the carrier paper is impregnated with urea formaldehyde resin usually containing about 48% water, partially dried and then coated on both sides with a water based melamine formaldehyde resin before further drying and curing to the desired properties and thereafter known as a b-stage laminate. This coating with a melamine formaldehyde resin on both sides is necessary to prevent the hygroscopic urea formaldehyde resin from taking up moisture from the atmosphere and to prevent the sheets of b-stage impregnated papers from sticking together. High pressure laminates (HPL) and continuous laminates (CPL) are usually a combination of kraft papers impregnated with phenol formaldehyde resin and a decorative paper impregnated with melamine formaldehyde resin. Clear overlay papers are usually only impregnated with melamine formaldehyde resin. These resins usually contain additives that impart particular properties, such as wetting agents, release agents, plasticisers and catalysts. They can al-

so be pigmented.

[0009] Laminates are also provided with a surface structure. These laminates do not only exhibit the decoration but also the surface structure of a genuine wood floor or other natural material surface. For these high quality laminates it is particularly important that the embossing, which is incorporated into the surface of the laminate, agrees structurally and topologically with the decor located thereunder. Especially in the case of high-contrast decors, it is important that the mutual alignment of the embossing and the decor layer agree precisely as otherwise the visual impression of a genuine natural product is impaired. The embossing is provided on the surface by use of a suitably embossed negative image on a press plate or continuous press belt.

[0010] In the conventional method for manufacturing laminates by the individual steps of laminate manufacture described above it is of importance that the papers to be used as the print base in the process are selected with high precision to have a particularly marked form or stability against distortion. It is a usual step in the manufacture of registered embossed type laminates according to the prior art that the carrier paper for any given print design is always taken from the same paper machine.

[0011] For the manufacture of embossed laminates in which the alignment of a surface texture should agree with the decor located thereunder, refined techniques need to be found to prevent any misalignment or distortion of the printed decor.

[0012] If a paper decor sheet is immersed in an aqueous melamine resin layer for impregnation then this paper tends to expand inconsistently and or non-uniformly and thereby distorts any decor print which may be present on its surface. In order to achieve a sufficiently accurate alignment of the printed decor with an embossing and to maintain the visual impression of genuity, it is thus necessary to know and correlate the exact expansion characteristics of the paper and the press plate.

[0013] To account for the unwanted non-uniform expansion of the printed decor sheet by swelling and the heat-induced expansion of the structured press plates, complex technologies have been developed, which make use of a reverse distorted print that leads to a straightened decor by compensation of the non-uniform expansion of the paper through the corresponding reverse distorted print.

[0014] However, this technique of anticipating a non-uniform expansion at the decor print level requires a high precision in the uniformity of the paper for printing, impregnation and subsequent laminate manufacture. Moreover, once the paper expansion characteristics have been determined, it is not feasible to change paper qualities without re-determination of the relative expansion characteristics of the new paper.

[0015] Another disadvantage inherent to the method of manufacturing laminates according to the prior art is the re-introduction of water to the paper carrier as a

component of the impregnating resin. In order to produce a paper, an aqueous pulp mass of approximately 98% water is delivered to the wire section at the front of the paper machine, also called the wet end. It is then pressed and dried with considerable expenditure of energy. In a following process step of laminate manufacture according to the prior art, the dry paper thus obtained is then remoistened by placing the paper in an aqueous resin bath. The paper, which has initially contracted in the drying process of the paper manufacture, now has the opportunity to re-expand by swelling whilst absorbing humidity. Then the water incorporated in the decor sheet is removed again in a post impregnation step in a repeated step by energy-consumptive drying. Thus energy-consumptive drying is required twice in the process of manufacturing laminates from the raw material to the final laminate.

[0016] It is also well known that modern papermaking machinery cannot economically produce small lot sizes.

[0017] Thus a laminate manufacturing method which could be substantially carried out without using carrier materials for resin, pigments and without re-moisturising of any carrier for decor prints and only using reinforcing papers having very low grammage (weight per square metre) would result in many technical and economic advantages. Also, energy could be saved, unwanted non-uniform expansion could be minimized or circumvented, making the process easier to control and even some process steps could be left out, making the process less complex.

[0018] The object of the invention is thus to provide a method for manufacturing laminates in which the usage of carrier materials can be minimised and in which a sufficient build-up of resin layer thickness can be achieved.

[0019] It is another object of the invention to provide a method in which embossing of a texture in the laminate surface and alignment of the texture with a decor layer located thereunder is suitable and can be achieved by simple means and wherein a determination of carrier material expansion characteristics and calculation of a compensating decor distortion following therefrom can be avoided.

[0020] It is a further object of the invention to provide a method for manufacturing laminates by which repeated moistening and drying of any printed carrier material used can be minimized.

[0021] It is another object of the invention to provide a method for manufacturing laminates which, by saving material and energy, is more favourable than methods known from the prior art.

[0022] The objects according to the invention are solved by applying to the substrate surface a polymer in a first process step and subsequent partial curing of the polymer in a second process step, followed by a placement of an overlaying paper or non-woven material onto the polymer layer and finally curing the polymer under heat and pressure. Other advantageous embodiments of the invention are obtained from the dependent

claims.

[0023] In the method according to the invention a polymer layer is applied to the substrate to be laminated, wherein the polymer is cured in more than one process step and wherein the polymer is applied to the substrate without using a carrier material. After partial curing, an overlaying paper or non-woven material is incorporated into or onto the surface of the polymer so that the fibres of the fibrous material impart additional stabilisation to the polymer through their fibre network structure. After partial curing of the base resin on the substrate additional process steps can be conducted, for instance to print a decoration directly onto the partially cured polymer surface. The employed polymer is finally cured after the fibrous material has been incorporated into the surface of the partially cured polymer layer. In the final curing step the polymer layer forms an inner bond with the fibres of the overlaying paper or non-woven material.

[0024] According to the invention an overlaying paper or non-woven material may be applied to the polymer surface and the polymer subsequently partially and or fully cured.

[0025] By using the method according to the invention, an overlaying paper or non-woven material with a fibrous structure is used to stabilise the surface of and is applied to a polymer which is not completely set or cured and wherein the residual moisture content of the partially cured polymer is so low that it is impossible for the fibrous material or any carrier material for a decorative print to distort by absorbing humidity. Since swelling of carrier material is avoided, the tendency of a carrier material to expand is circumvented. Also, as a result of the initial partial curing further shrinking during the final curing of the resin is minimized. As a result, any decorative imprints applied directly to the partially cured polymer, or to an overlay paper or other carrier material remain undistorted. Undistorted in the context of the present document means that any distortion is negligibly small with respect to visual inspection by the human eye.

[0026] Another advantage obtained from the method according to the invention is the possibility to dispense with recurrent moistening and subsequent drying of carrier materials that are printed with a décor design designated for registered embossing. Therefore the method can be implemented using less energy than methods in the prior art. As a result, cost savings are obtained.

[0027] A further advantage of the method according to the invention is a possible dispensing of water as solvent or at least a serious reduction of the water content in the starting material before the application of the fibrous material, resulting in less heating and curing energy needed for the process. Though water as a solvent material is absent or reduced in the partially cured polymer, fibrous material layers introduced into the polymer surface can still be wetted and impregnated by using pressure and heat. By applying heat and pressure air is completely removed from the pores of the overlay paper

and as a result an increased deep gloss and clarity of the surface of the laminate is achieved.

[0028] Still a further advantage of the method according to the invention is the ability to make one or several individual decorative laminates without the need for a carrier material, which in the case of developing a new print or new colour, substantially reduces the cost of the development process. This is furthermore particularly advantageous when in the future only one or several sheets are required and the availability of such small quantities of a unicolour or printed paper in one or several widths is prohibitively expensive or otherwise just not available from the paper producer.

[0029] The build-up of layer thickness is advantageously facilitated by the method according to the invention without the need to use papers as a carrier material.

[0030] Another advantage of the method according to the invention is that there is no need for any carrier paper as a support for a fluid starting material for polymerisation. As a result less material is required to produce laminates than in the previously known methods and further results from this are cost savings.

[0031] Applicable resins / polymers for the method according to the invention are disclosed in the international patent application WO 01/44333 or in the European patent application EP 0 514 792. The two published documents are introduced as reference and are valid as part of the disclosure in this document.

[0032] It is also well known that in paper impregnation for decorative laminates it is commonly practised that urea formaldehyde is substituted for melamine formaldehyde to fill the core of the paper before applying a melamine formaldehyde coating to both the top and bottom of the paper. This is based on the economical advantage of using the less expensive urea formaldehyde resin.

[0033] Therefore, in an economically advantageous method according to the invention, urea or other amino derivatives or a combination of these can be used to substitute part or all of the triazine compound claimed in the disclosed patents WO 01/44333 and EP 0514792.

[0034] By using the method according to the invention, the liquid pre-polymer (a-stage) resin no longer needs be absorbed into or onto the paper or non-woven materials as a carrier but as a result of the possible higher viscosities, the polymer can be applied to one or both sides of the substrate in a layer thickness sufficient for laminate manufacture.

[0035] The viscous polymer employed wets the substrate surface and is partially cured in a first process step. If the polymer starting material contains residual water it is evaporated as the polymer progresses to b-stage, whereafter the fibrous material layer, like an overlaying paper or a non-woven material, is introduced to the laminate manufacturing process. Following the initial partial curing, the laminate can take up a décor sheet, and if necessary a protective overlay paper, be-

fore being placed in a hot press and put under pressure. According to the invention an additional layer or layers of resin may be applied above the printed design to enhance protection of the print. An additional resin layer placed above the printed design may include additives that provide specific properties, as an example, particles of fused alumina to improve abrasion resistance. The partial curing has the result that the unsupported or uncarried polymer resin no longer flows off the substrate in the final curing process and even supports the absorbed fibrous material layer, preventing its expansion under heat, pressure and residual moisture.

[0036] After partial curing, the polymer resin forms a layer on the substrate. This layer is sufficiently viscous and stable to prevent it from flowing off the substrate. Still, an overlaying paper or any other non-woven or fibrous material layer placed thereon can be impregnated with the partially cured polymer by embedding it in the surface of the partially cured polymer resin layer.

[0037] In an alternative embodiment of the method according to the invention an unprinted and clear overlaying paper or non-woven material is pre-coated and or impregnated with a synthetic resin, preferably with a melamine rich synthetic resin, most preferably a synthetic melamine based thermosetting resin. Impregnated overlaying papers known as prepregs are easy to handle and adhere very well to the surface of the partially cured polymer on the substrate. The overlaying papers or non-woven materials can be produced in a parallel process step or can be obtained from third sources.

[0038] In a particular embodiment, the overlaying paper or non-woven material is preferably coated or impregnated with a melamine layer by vapour phase deposition in order to provide a melamine rich surface, especially advantageous if the overlaying paper or non-woven material with the melamine rich surface will be situated at the outermost position of the laminate. The melamine layer will also stabilize the overlaying paper or non-woven prior to printing. It is a well known fact that melamine powder will sublime under appropriate conditions. For the method according to the invention the European patent application EP1325968 is introduced as reference and is valid as part of the disclosure in this document.

[0039] In order to apply a decorative effect to the laminate, a print can be applied directly onto the partially cured polymer surface, just before adding an overlay paper or a prepreg. By printing onto the partially cured polymer, the b-stage resin, it is possible to dispense with using any carrier material as support for the decorative print. This leads to cost savings as a result of the lower material consumption.

[0040] It can be advantageous to pre-treat the surface of the partially cured polymer. Possible treatments among others are electric charging or coating with a very thin layer of an ionic material. Also a printing primer can be deposited on the partially cured polymer surface. For this purpose, the layer to be printed on is advantageously

ly pre-treated to enhance printability. If the polymer surface is pre-treated by electrically charging the surface in any of the ways mentioned above, the electric surface charges attract counter-charged printing colours, such as dyes, pigments or toners. The attraction of the printing colour to the pre-treated surface prevents bleeding of the printing colour resulting in a more stable and more precise printing.

[0041] In an alternative embodiment of the method according to the invention, a decorative print is advantageously applied to the overlaying paper or non-woven material in a parallel process step. It is possible to use an overlaying material which is colourless and transparent or which is coloured with pigments or dyes. By using the method according to the invention it is thus possible to apply a decorative print to a light weight overlaying material instead of to a heavier and more absorbent decor sheet. In this case, the viscous polymer resin layer can serve as a support for dissolved dyes and/or dispersed pigments for covering the substrate surface. By printing onto the overlaying material and inserting dyes and/or pigments into the polymer layer, the usual grammage of a paper layer which usually carries the printed decor can be reduced. In this case, the overlaying material has to serve two different purposes, firstly to strengthen the surface structure of the cured resin through its fibre structure and secondly to serve as a support for a décor print.

[0042] In an especially advantageous fashion the clear overlaying paper is printed with a mirror-inverted image wherein this case the overlaying material is placed on the surface of the polymer resin so that the imprint points downwards onto the polymer layer. Of course it is obvious to someone skilled in the art that the print can be applied in the usual manner to the clear overlaying paper and the print protected by a further appropriate protective layer.

[0043] If the decorative print is printed using more than one colour, the colour sequence is preferably reversed. In a usual print, for instance a standard four colour print, a first printing colour is printed on a substrate, followed by the next printing colour covering or altering the first colour in some areas of the first printing colour layer. This process is repeated for all printing colours until the desired print is obtained. If the print is meant to be visible through a clear overlaying paper layer, the succession of printing colours is advantageously reversed to obtain the same printing result.

[0044] The unimpregnated overlaying material has a grammage between 10 g/m² and 120 g/m². If dyes, pigments or mixtures thereof are added to the viscous polymer, these assist the optical coverage of the substrate in order to prevent any undesirable surface structures or colour of the substrate from becoming evident.

[0045] It is well known in the art that tannin is used in the manufacture of bonding resins and imparts a reddish brown colour to the resin. Tannin is also a known scavenger of formaldehyde. Therefore according to method

of the invention for manufacturing a decorative laminate, tannin can be incorporated into the resin to provide pigmentation and to act as a scavenger for free formaldehyde.

[0046] In a preferred embodiment of the method according to the invention for manufacturing a laminate, the surface is provided with a structure during hot pressing, for example, by using an embossed pressplate, or an embossed continuous press belt, in the final step of hot pressing.

[0047] The structure produced by embossing the laminate surface is preferably aligned with a decor print located under the surface. If the decor is printed onto the overlaying material then this is achieved by aligning the overlaying material with the embossing tool. As a result, the apparent genuineness of the laminate thus produced is more convincing than laminates produced by methods according to the prior art with imprinted carrying materials having expanded non-uniformly. The alignment can be achieved by various methods such as applying centering crosses in the corners of the overlaying material by which this layer can be aligned shortly before pressing.

[0048] Partial curing of the polymer can be conducted by heat, or radiation, or by electron bombardment. UV light is preferably used for partial curing of the polymer. As a result, the polymer can be partially cured by application of less energy in comparison with thermal polymerisation. The choice of method for introducing energy into the polymer at the start of polymerisation can be selected freely and can be adapted to the preferred polymeric material.

[0049] In an especially preferred method dissolved dyes or dispersed pigments are used in the polymer to cover the surface of the substrate. By employing dyes or pigments in the polymer a background colour for the printed decor is achieved and the realistic appearance of the laminate thus produced is further increased.

[0050] To improve adhesion, a primer can be applied under the polymer layer onto the substrate surface. This can be selected according to the porosity, absorptivity and surface structure according to the choice for a painting primer, wherein the primer is compatible with the polymer. Compatibility in the current context means that no reactions of the possibly different polymers of the primer and polymer located thereabove result in structural changes to the surface. It is also possible to heat the surface of the substrate to improve adhesion of the polymer.

[0051] In the method for manufacturing a laminate the partial polymerisation of the resin prior to the application to the substrate surface is to a degree that it has a viscosity in excess of 40 mPa.s, and up to and including the manufacture of a powder resin. The ideal polymer viscosity for application to the substrate depends on the application method. The polymer can be applied to the substrate as a fine powder or granulate.

[0052] It is possible to apply a polymer provided with

dispersed pigments and/or dissolved dyes to the substrate with sufficiently large layer thickness. The layer thickness depends on the preferred degree of optical coverage of the substrate colour.

[0053] The polymer layer is advantageously applied to the substrate surface by any of a plurality of well known methods, not limited to spraying, dipping, brushing, roller or curtain coating or printing. Another method is powder coating. However, the ideal method can be chosen with respect to the properties of the selected polymer and substrate.

[0054] According to the invention the preferred method of polymer application can be chosen freely, with independence of carrier materials.

[0055] The polymer used in the method for manufacturing a laminate according to the invention preferably has the property of at least partially curing under UV light or any other appropriate radiation. It is hereby achieved that the initially merely viscous but still flowable polymer layer which has been applied to the upper side of the substrate, is cured to such an extent that an unimpregnated paper may be applied to the surface. For the polymerisation of resins, many techniques are known in the prior art to provide these with additives which form chemical radicals under UV light which for their part result in polymerisation of the monomer units in the resins. For this purpose the polymer should be suitable for radical polymerisation. Ionic polymerisation reactions and condensation polymerisation reactions are also feasible. However, radical polymerisation can be very well controlled by exposure time to UV light. The alternative polymerisation reactions on the other hand are generally less well controllable. If the additives do not exhibit broad-band absorption in UV light, additive and corresponding light source should be matched to one another.

[0056] It is also advantageous if the polymer does not only cure in UV light but also under the application of heat.

[0057] It is also particularly advantageous if the selected polymer has an optimum polymerisation rate at a temperature of 150°C to 220°C. On the one hand, the polymer should not polymerise too quickly to avoid mechanical stress in the structure which can result in surfaces fractures. On the other hand the speed also should not be too slow to ensure a minimum throughput of the presses and to avoid the energy consumption of the pressure plates being too high or at least unnecessarily high. The afore-mentioned temperature interval corresponds to the temperature of conventional laminate presses so that existing presses can advantageously be used when using the method according to the invention.

[0058] The polymer for use in the method according to the invention is preferably produced by condensation of a triazine together with an aldehyde and an olefin component with the assistance of a catalyst.

[0059] The triazine component can be a melamine

formaldehyde resin, a hydroxyl alkyl melamine or a mixture of two or more of these components. It is also well known to those skilled in the art that urea or other amino derivative or a combination of these, can be used as a substitute for melamine.

[0060] The aldehyde component is preferably used as formaldehyde in the form of formalin solution, or urea stabilized formalin solution, or urea formaldehyde resin or a paraformaldehyde.

[0061] The olefin for use in the method according to the invention is preferably selected from acrylates, crotonates, acrylamides, crotyl amides, enones, acrylonitriles or a mixture of two or more of these components, and preferably containing an hydroxy carbon chain.

[0062] Preferably used as catalyst in the polymer for use in the method according to the invention is: 1,4-diazabicyclo[2.2.2]octane, chinuclidine, 3-chinuclidinone, azacyclo[2.2.1]heptane or a mixture of two or more of these substances. In another embodiment of the method according to the invention, chemical radical formers such as azoisobutyronitrile are used which break down not only under the action of ionising radiation but also under the action of heat and thus form chemical radicals. These chemical radicals initiate the remainder of the curing wherein the cross-linking of the polymer chains formed is constructed especially.

[0063] In this document the term overlaying material has been used as a synonym for overlaying paper and non-woven material. The term resin and polymer have been used as synonyms for each other.

[0064] The above and other objects and advantages of the present invention will be apparent upon consideration of the following detailed description, taken in conjunction with the accompanying drawings, in which like reference characters refer to like parts throughout, and in which

- Fig. 1 depicts a simplified layer diagram of a laminate according to the prior art
- Fig. 2 is a schematic diagram of the process steps according to the invention
- Fig. 3 is a schematic layer diagram of a simple laminate according to the invention
- Fig. 4 is a schematic layer diagram of an intermediate product of a laminate with a print on the decorative layer
- Fig. 5 is a schematic layer diagram of an intermediate product of a laminate with a mirror inverted and/or reverse order printed decorative design on a clear overlay paper
- Fig. 6 is a schematic layer diagram of an intermediate product of a laminate with a decorative print on a low basis weight decor paper

Fig. 7 is a schematic layer diagram of an intermediate product of a laminate with a decorative layer and a layer containing an additive

5 Fig. 8 is a schematic layer diagram of an intermediate product of a laminate with a printing primer and a polymer layer with or without pigments and/or dyes

10 Fig. 9 shows a laminate layer structure seen from above with centering crosses for alignment of an embossing press plate with a printed structure in the laminate layer structure

15 Fig. 10 schematically shows a parallel process step in that an overlaying paper or a non-woven material is coated by vapour phase deposition

20 Fig. 11 schematically depicts the optional use of a primer below the polymer layer

Fig. 12 depicts a schematic of the process steps according to the invention

25 Fig. 13 depicts schematically depicts the application of a stabilising layer prior to printing

[0065] In order to convey the difference between the manufacturing process of a laminate according to the prior art and the manufacturing process of a laminate according to the invention a laminate layer diagram of a laminate product according to the prior art is shown in figure 1, in which on a first side of a substrate 1 a resin impregnated decor paper 2 is laminated onto the surface of substrate 1. This decor paper 2 can also be covered by a resin impregnated overlay paper 3 in order to impart additional stability to the final cured laminate layer structure exposed to mechanical and abrasive stress. So called low pressure laminates also comprise a resin impregnated paper which is laid onto the opposite surface of substrate 1, in the case of laminate flooring as a balancing paper usually directed towards the non-decorative laminate side. This backer paper 4 prevents, as a consequence of unequal resin contraction or moisture or thermally induced change of the structure of substrate 1, the laminate from warping or bowing. By introduction of resin impregnated backer paper 4 to the laminate manufacturing process both sides of substrate 1 are kept in a similar state resulting in cancellation of possible internal mechanical forces resulting in a warped or bowed surface of the final laminate product.

[0066] Figure 2 depicts a schematic diagram of the process steps according to the invention in which a a-stage resin 5a is applied to substrate 1 shown in subfigure 2a in a first process step depicted in subfigure 2b, in which the a-stage resin 5a may be applied to both or just one side of substrate 1. The applied a-stage resin

5a is then partially cured in a following process step shown in subfigure 2c by the use of electromagnetic radiation, preferably UV-Light, from radiation sources 14. After partial curing a-stage resin 5a becomes partially cured b-stage resin 5b. In a subsequent process step shown in subfigure 2d an overlaying paper or a non-woven material, 6, or a melamine coated stabilising paper 8 is placed onto the partially cured b-stage resin 5b obtained from a-stage resin 5a in subfigure 2b in conjunction with radiation treatment in subfigure 2c. As with the application of the resin in subfigure 2b the materials 6 and 8 may be placed on both or on one side of substrate 1 depending on which side of substrate 1 a-stage resin 5a is applied. Alternatively the intermediate product obtained from process step according to subfigure 2c or 2d can undergo additional process steps, for instance to receive a decorative print or additional material layers and re-enter the process in process step according to figure 2e. In a final process step depicted in subfigure 2e the laminate structure is placed between members 16 of a hot press, where an embossed or smooth pressplate or press belt 15 is used to add a structure and gloss level to the surface of the final laminate product. The b-stage resin 5b from subfigure 2d then cures to its final state, called c-stage resin 5c.

[0067] Figure 3 shows a schematic layer diagram of a simple laminate product according to the invention having substrate 1, fully cured c-stage resin 5c and a layer of an overlaying paper or a non-woven material 6 or stabilising paper 8, whereby the materials 6 are impregnated with c-stage resin 5c in the process shown in Figure 2. Not shown in this figure is a laminate with only one coated or laminated side according to the invention, with the alternative side coated or laminated according to the prior art.

[0068] Figure 4 is a schematic layer diagram of an intermediate product of a laminate being manufactured by an alternative embodiment of the method according to the invention, which is between process step as depicted in subfigure 2c and subfigure 2d and which carries a decorative print layer 7a printed directly onto the partially cured b-stage resin layer 5b. The resin impregnated overlay paper 3 or the melamine coated stabilising paper 8, instead, is placed onto the printed and partially cured b-stage resin layer 5b in the process step according to subfigure 2d.

[0069] Figure 5 is a schematic layer diagram of an intermediate product of a laminate being manufactured by another alternative embodiment of the method according to the invention, which is between process step as depicted in subfigure 2c and subfigure 2d and which carries a mirror inverted and reversed print 7b on a clear overlay paper 10, which is printed onto the underside of the clear overlay paper 10. The clear overlay paper 10 is then covered with a resin impregnated overlay paper 3 and re-enters the process according to figure 2 in the process step according to subfigure 2e.

[0070] Alternatively a decorative print 7c can be print-

ed onto an unimpregnated low basis weight decor paper 12 as depicted in the schematic layer diagram of an intermediate product of a laminate according to the invention in figure 6 and the obtained intermediate product can re-enter the process according to figure 2 in the process step depicted in subfigure 2e.

[0071] As drafted in figure 7 a decorative print layer 7a, 7b or 7c can be protected by a resin layer 13 containing additives such as abrasive resistant particles. This resin layer 13 is then covered with an overlaying material 6 or a melamine coated stabilising paper 8 and the intermediate product according to figure 7 re-enters the process according to figure 2 in the process step according to subfigure 2e.

[0072] Figure 8 is a schematic layer diagram of an intermediate product of a laminate with a printing primer 17 arranged on top of the partially cured b-stage resin 5b to enhance printability of the partially cured b-stage resin 5b. Alternatively the b-stage resin layer 5b may contain pigments and/or dyes 19 to cover the appearance of substrate 1 in the final laminate product. The intermediate product according to figure 8 can re-enter the process according to figure 2 in the process step according to subfigure 2d.

[0073] In figure 9 a laminate layer structure of an intermediate product of a laminate is shown seen from above with centering crosses 18 for alignment of an embossing press plate 15 or embossing press belt 16 with a decorative print 7a, 7b or 7c within the laminate layer structure.

[0074] Figure 10 schematically depicts vapour phase deposition onto overlaying materials 6 in a vacuum chamber (not drawn) in that vapour 21 of a material capable of sublimation 20 deposits on an overlaying material cooled by a cold finger 23.

[0075] Figure 11 schematically depicts the optional use of a primer below the a-stage resin layer 5a that improves adhesion of the a-stage resin 5a to the substrate 1.

[0076] Figure 12 depicts a schematic of the process steps according to the invention in which an a-stage resin 5a is applied to a previously impregnated overlay paper 3 as depicted in subfigure 12b. The applied a-stage resin 5a is then partially cured in a following process step shown in subfigure 12c by the use of electromagnetic radiation, preferably UV light, from radiation sources 14. After partial curing a-stage resin layer 5a becomes partially cured b-stage resin layer 5b. In a subsequent process step shown in subfigure 12d the overlay paper 3 and partially cured b-stage polymer 5b is inverted and placed onto a lay-up of one or more kraft papers, which are impregnated with phenol formaldehyde resin 9, also in a b-stage or partially cured. This layer sequence is then placed onto one or both sides of a substrate 1. In a final process step depicted in subfigure 12e the laminate structure is placed between members 16 of a hot press where an embossed or smooth pressplate or press belt 15 is used to add a structure

and gloss level to the surface of the final laminate product. The lay-up, as depicted in subfigure 12d, then cures to its final state, so-called c-stage high pressure laminate, or cures to its final state, so-called c-stage low pressure laminate.

[0077] Fig. 13 depicts schematically a non impregnated overlaying paper 6 or low basis weight décor paper 12 stabilized prior to printing with a layer of melamine 24 applied by vapour deposition in three different alternatives, 13a, 13b or 13c, where the melamine layer 24 is applied before printing as in subfigure 13a, after printing as in subfigure 13c or where the layer of melamine is applied to a two sided printing as in subfigure 13b.

REFERENCE LIST

[0078]

1	substrate	
2	decor paper	20
3	overlay paper	
4	backer paper	
5a	a-stage resin	
5b	b-stage resin	
5c	c-stage resin	25
6	overlaying paper / non-woven material	
7a	print	
7b	reverse print	
7c	print	
8	vapour coated stabilising paper	30
9	phenol formaldehyde impregnated kraft papers	
10	printed overlay paper	
12	low basis weight decor paper	
13	resin with additive	
14	radiation source	35
15	pressplate / continuous belt	
16	hot press	
17	print primer	
18	centering crosses	
19	pigments / dyes	40
20	material for sublimation	
21	vapour	
22	primer	
23	cold finger	
24	melamine layer	45

Claims

1. A method for manufacturing a decorative laminate, **characterized by** applying to a substrate (1) surface a polymer (5a) in a first process step and subsequent partial curing of the polymer (5a) in a second process step, followed by a placement of an overlaying paper or non-woven material (3,6,8) onto the polymer layer (5b) and finally fully curing the polymer (5b) under

heat and pressure.

2. The method for manufacturing a decorative laminate according to Claim 1,

characterized by

coating and/or impregnation of the overlaying paper or non-woven material (6) in a parallel process step or by using an overlay paper or non-woven material (3) pre-coated and/or pre-impregnated with a synthetic resin, preferably with a melamine rich synthetic resin.

3. The method for manufacturing a decorative laminate according to Claim 2,

characterized by

coating the overlaying paper or non-woven material (6) by vapour deposition.

4. The method for manufacturing a decorative laminate according to any one of the preceding claims,

characterized by

printing a decorative design (7a) onto the partially cured polymer (5b) surface.

5. The method for manufacturing a decorative laminate according to Claim 4

characterized by

pre-treating the partially cured polymer (5b) by charging or applying a print primer (17) the surface to enhance printability.

6. The method for manufacturing a decorative laminate according to any one of the preceding claims,

characterized by

printing of the overlaying paper or non-woven material(6,8) in a parallel process step, wherein the overlaying material (6,8) is transparent or pigmented.

7. The method for manufacturing a decorative laminate according to any one of the preceding claims,

characterized by

the application of a stabilizing melamine layer by means of vapour deposition prior to printing

8. The method for manufacturing a decorative laminate according to Claim 7,

characterized by

the use of a mirror-inverted image (7b) and/or reverse order printed image (7b) onto a clear overlay paper (10) or non-woven material (10) wherein the overlay paper (10) or overlaying material (10) is placed with the printed side on the polymer (5b) layer.

9. The method for manufacturing a decorative laminate according to any one of the preceding claims,

characterized by

embossing a surface structure during the final curing of the polymer.

10. The method for manufacturing a decorative laminate according to Claim 9,
characterized by
alignment of the embossing tool with the decor print on the partially cured polymer or the overlaying paper or non-woven material.

5

11. The method for manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
the use of heat, radiation or electron bombardment for partial curing of the polymer.

10

15

12. The method for manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
the use of a hot press (16) for final curing of the polymer.

20

13. The method for manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
the use of a textured press plate or continuous belt (15) for surface embossing.

25

14. The method for manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
colouring the polymer (5a) using suitable dyes or pigments dispersed and/or dissolved in the polymer.

30

15. The method of manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
colouring the polymer (5a) using a tannin powder or dispersion.

35

40

16. The method for manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
the application of a primer (22) to the substrate surface before coating with the polymer.

45

17. The method for manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
the use of a polymer having a viscosity in excess of 40 mPa.s up to a solid powder resin.

50

18. The method for manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
applying the polymer (5a) to the substrate (1,3) by any appropriate method, but not limited to spraying,

55

dipping, brushing, roller coating, curtain coating, printing or powder coating.

19. The method for manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
the use of a polymer (5a) which partially cures under the action of electromagnetic radiation.

20. The method for manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
the use of a polymer (5a) which cures under heat, preferably a polymer which cures at 130°C to 220°C.

21. The method for manufacturing a decorative laminate according to any one of the preceding claims,
characterized by
the use of a polymer (5a) which is produced under condensation of a triazine with an aldehyde and an olefin component with the assistance of a catalyst.

22. The method for manufacturing a decorative laminate according to any one of claims 1 to 20,
characterized by
the use of a polymer (5a) which is produced under condensation of urea or other amino derivatives or a triazine, or any combination thereof, with an aldehyde and an olefin component with the assistance of a catalyst.

23. The method for manufacturing a decorative laminate according to claims 21 and 22,
characterized by
the use of a melamine, melamine formaldehyde resin, hydroxyl alkyl melamines or a mixture of two or more of these substances as a triazine component.

24. The method for manufacturing a decorative laminate according to claims 21 to 22,
characterized by
the use of formaldehyde in the form of formalin or urea stabilized formalin, or urea formaldehyde resin or paraformaldehyde.

25. The method for manufacturing a decorative laminate according to any one of claims 21 to 22,
characterized by
the use of acrylates, crotonates, acrylamides, crotyl amides, enones, acrylnitriles with an hydroxy carbon chain, or a mixture of two or more of these substances as the olefin.

25. The method for manufacturing a decorative laminate according to any one of claims 21 to 22,
characterized by
the use of 1,4-diazabicyclo[2.2.2]octane, chinuclid-

ine, chinuclidinone, azacyclo[2.2.1]heptane, azoisobutyro-nitrile or a mixture of two or more of these substances as a catalyst for polymerisation, especially partial curing of the polymer.

5

26. A decorative laminate product manufactured by the method according to any one of the preceding claims.

10

15

20

25

30

35

40

45

50

55

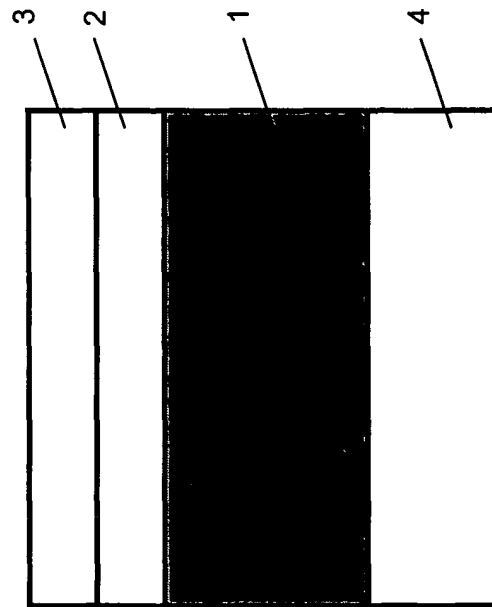


Fig. 1

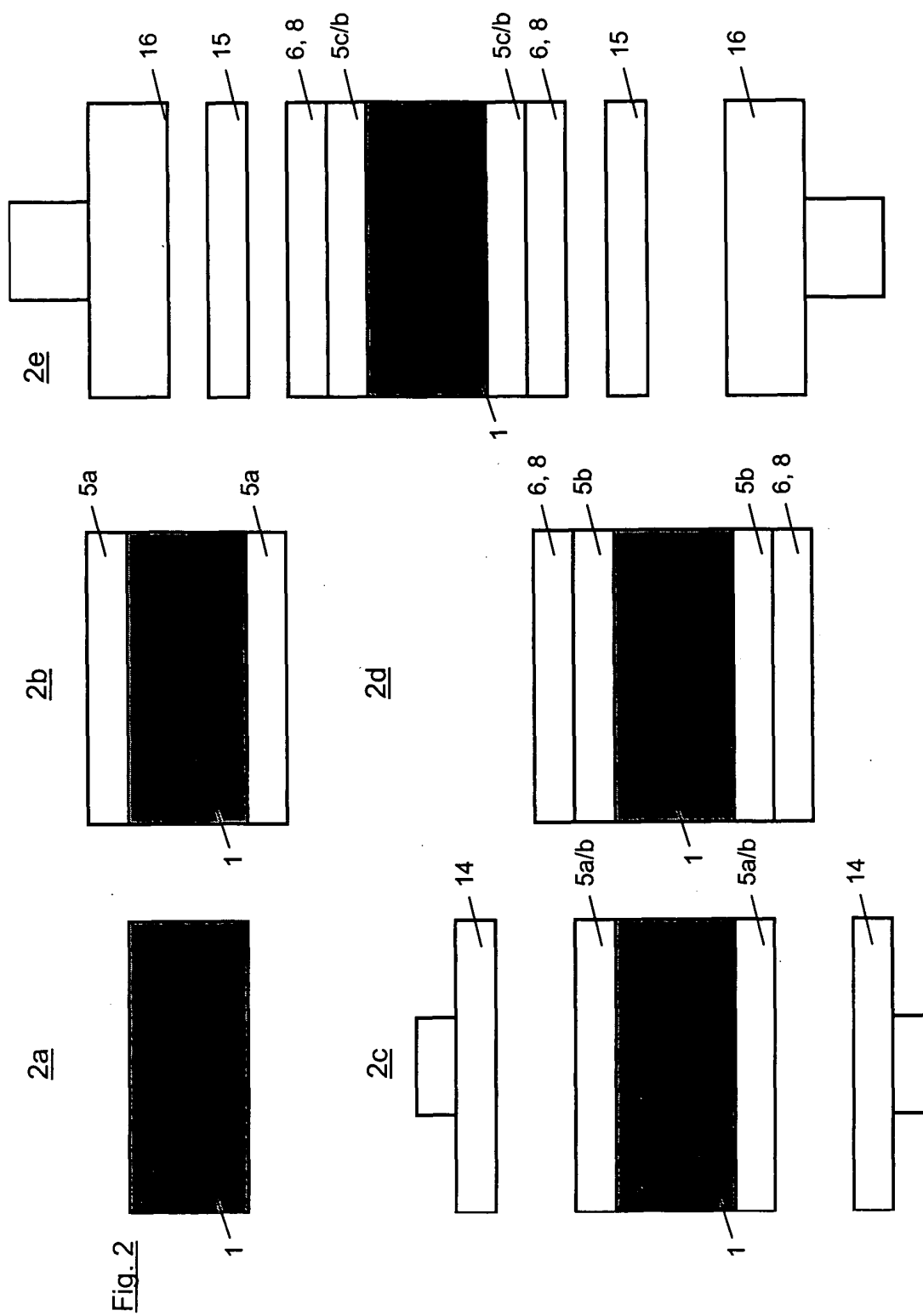


Fig. 3

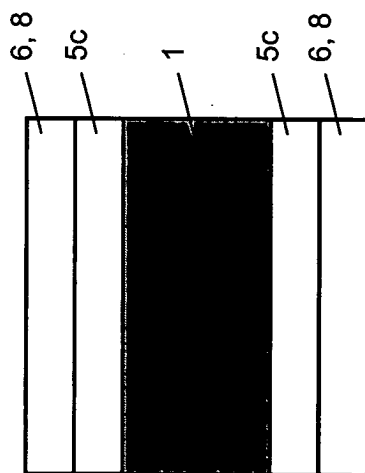


Fig. 5

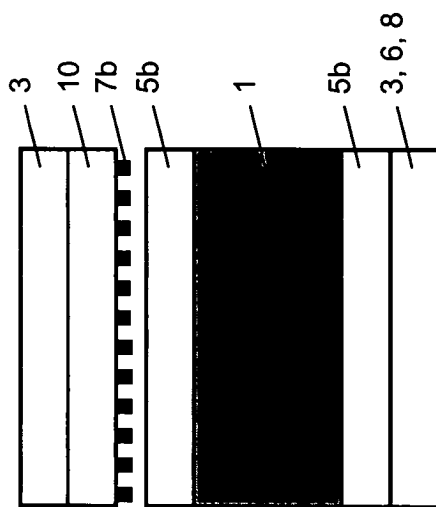


Fig. 4

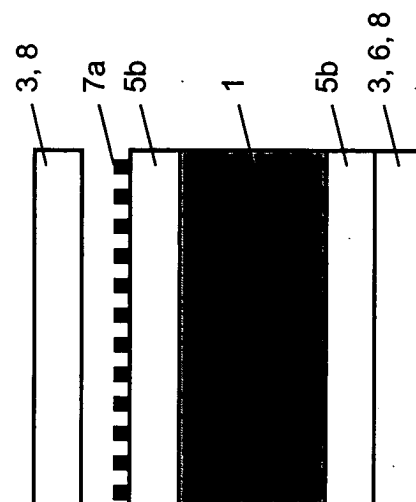
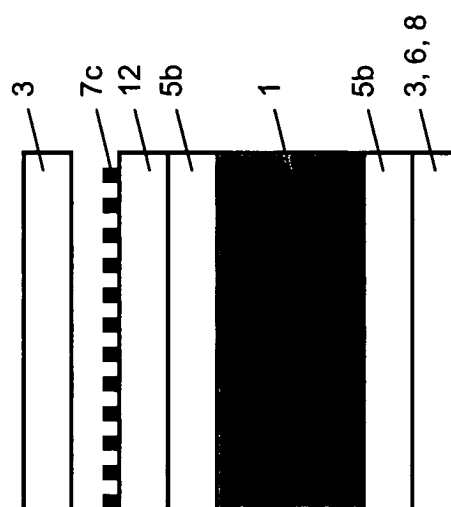


Fig. 6



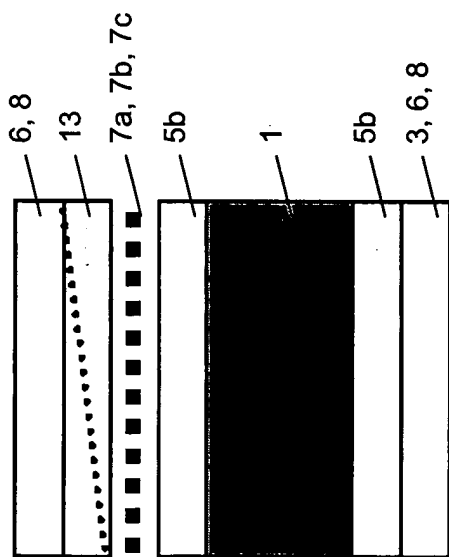


Fig. 7

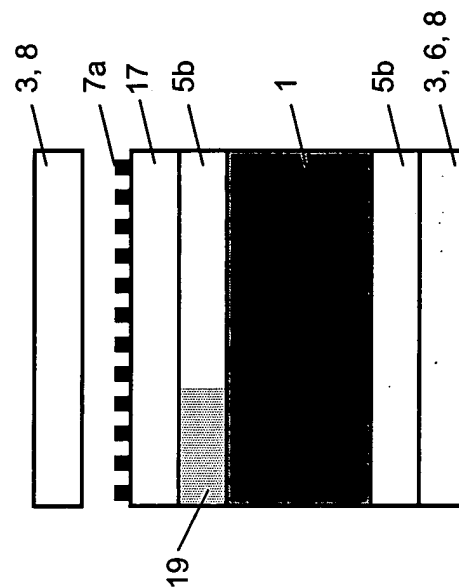


Fig. 8

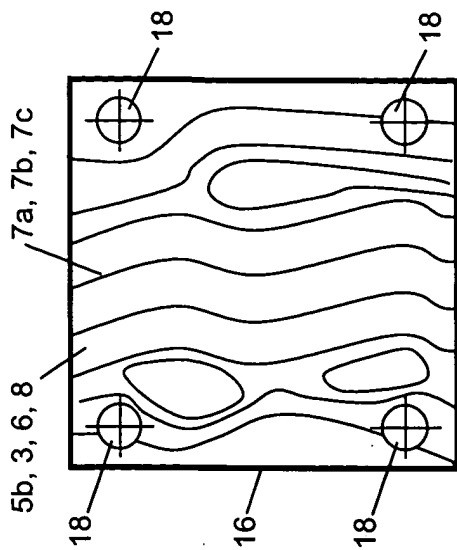


Fig. 9

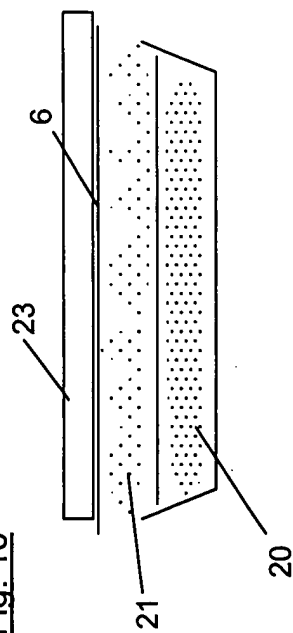


Fig. 10

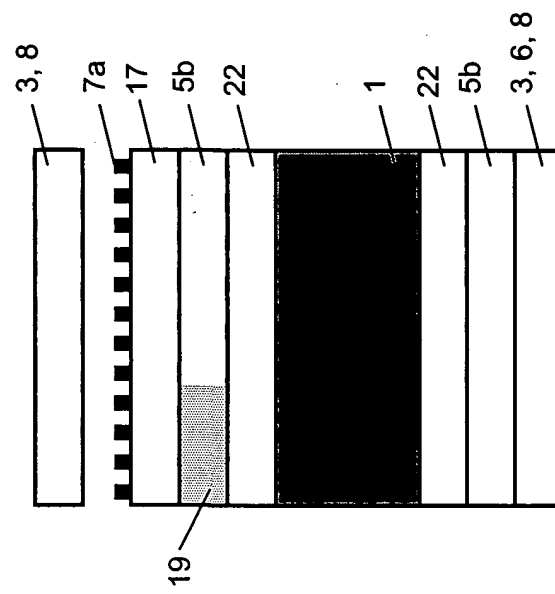


Fig. 11

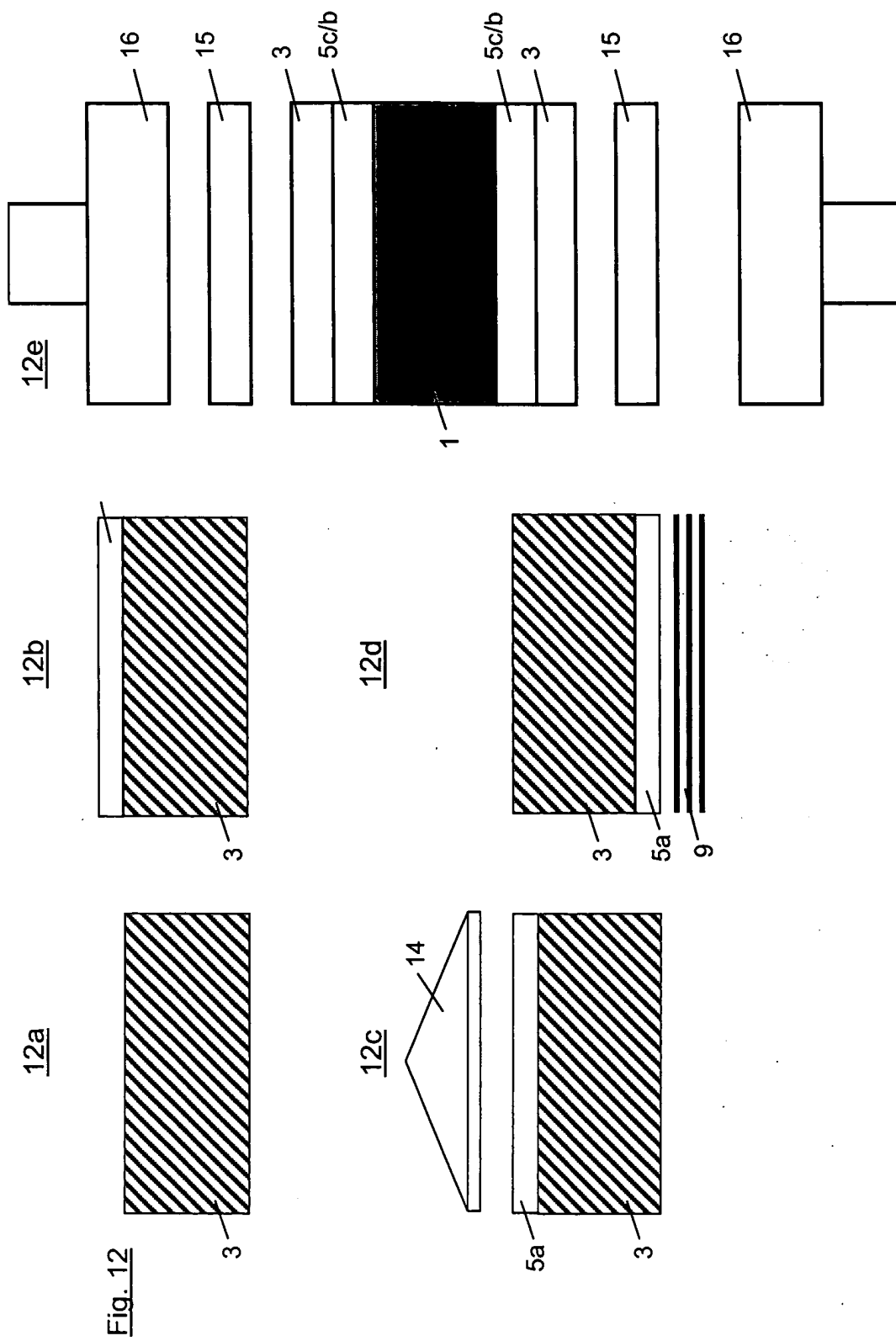
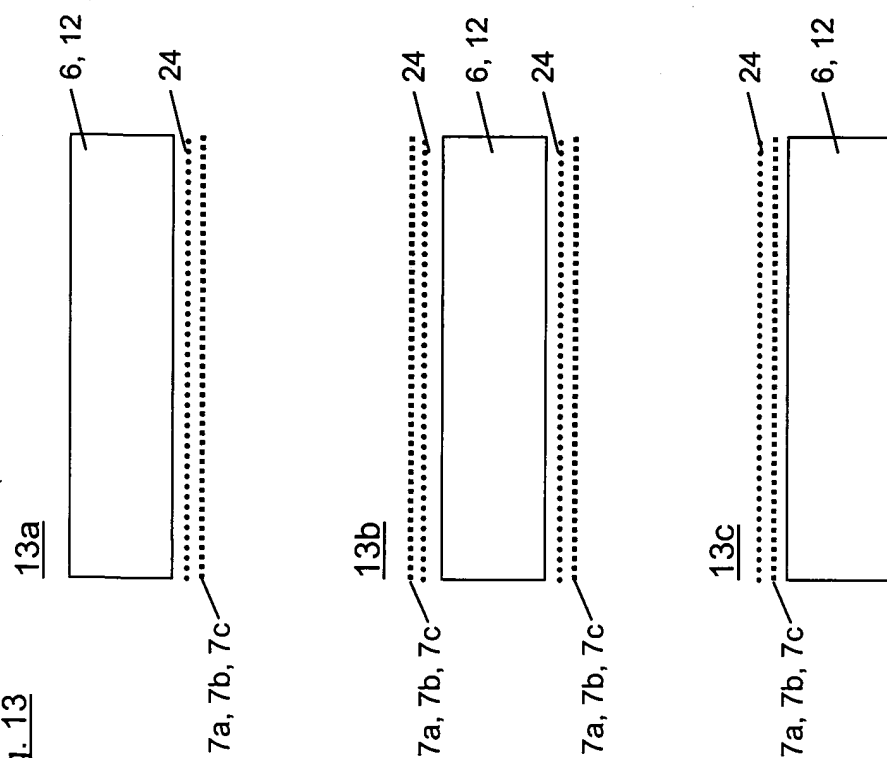


Fig. 13





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 01 3999

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)
A	WO 00/43132 A (AKZO NOBEL N.V; AKZO NOBEL INC) 27 July 2000 (2000-07-27) * page 4, line 30 - page 5, line 15 *	1-26	B44C1/10 B44C5/04 B32B27/00 B32B31/00 C08G12/32
A	EP 0 764 550 A (DAI NIPPON PRINTING CO., LTD) 26 March 1997 (1997-03-26) * examples 1,2 *	1-26	
A	US 5 405 705 A (FUJIMOTO ET AL) 11 April 1995 (1995-04-11) * column 3, line 49 - column 4, line 20 *	1-26	
A	WO 95/06568 A (NEVAMAR CORPORATION) 9 March 1995 (1995-03-09) * page 6, line 28 - page 7, line 23; figure 1 *	1-26	
A	EP 0 371 743 A (MITSUI PETROCHEMICAL INDUSTRIES, LTD) 6 June 1990 (1990-06-06) * page 2, line 52 - page 3, line 35 *	1-26	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			B44C B32B C08G
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 7 June 2005	Examiner Sartor, M
<p>CATEGORY OF CITED DOCUMENTS</p> <p>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</p> <p>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</p>			

1
EPO FORM 1503 03.82 (P04C01)

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

EP 04 01 3999

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
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-06-2005

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0043132	A	27-07-2000	AU 2858900 A	07-08-2000
			BR 0007620 A	15-01-2002
			CA 2358668 A1	27-07-2000
			CN 1336851 A	20-02-2002
			EP 1169139 A1	09-01-2002
			WO 0043132 A1	27-07-2000

EP 0764550	A	26-03-1997	JP 9262934 A	07-10-1997
			AU 709126 B2	19-08-1999
			AU 6570796 A	27-03-1997
			CA 2186080 A1	21-03-1997
			DE 69625016 D1	09-01-2003
			DE 69625016 T2	21-08-2003
			EP 0764550 A2	26-03-1997
			TW 387844 B	21-04-2000
			US 5827788 A	27-10-1998

US 5405705	A	11-04-1995	JP 3043532 B2	22-05-2000
			JP 6039808 A	15-02-1994
			CA 2085193 A1	14-06-1993
			KR 9607008 B1	27-05-1996

WO 9506568	A	09-03-1995	US 5466511 A	14-11-1995
			AT 173437 T	15-12-1998
			AU 679565 B2	03-07-1997
			AU 7720194 A	22-03-1995
			BR 9407383 A	29-10-1996
			CA 2170905 A1	09-03-1995
			DE 9422233 U1	17-06-1999
			DE 69414713 D1	24-12-1998
			DE 69414713 T2	29-04-1999
			DK 716635 T3	02-08-1999
			EP 0716635 A1	19-06-1996
			ES 2124429 T3	01-02-1999
			JP 2935897 B2	16-08-1999
			JP 8512255 T	24-12-1996
			KR 175713 B1	01-04-1999
			NZ 273775 A	24-10-1997
			RU 2128263 C1	27-03-1999
			WO 9506568 A1	09-03-1995
			US 5866207 A	02-02-1999
			US 5866208 A	02-02-1999
			US 5866209 A	02-02-1999
			US 5807608 A	15-09-1998

EP 0371743	A	06-06-1990	JP 2214650 A	27-08-1990

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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

EP 04 01 3999

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
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-06-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0371743 A		JP 2694991 B2	24-12-1997
		JP 2234986 A	18-09-1990
		JP 2145331 A	04-06-1990
		JP 2577464 B2	29-01-1997
		AT 122286 T	15-05-1995
		AU 610767 B2	23-05-1991
		AU 4574089 A	14-06-1990
		CA 2004041 A1	28-05-1990
		DE 68922587 D1	14-06-1995
		DE 68922587 T2	28-09-1995
		EP 0371743 A2	06-06-1990
		KR 9109521 B1	21-11-1991
		NZ 231565 A	26-05-1992
		US 4997707 A	05-03-1991
		CN 1043467 A ,C	04-07-1990
		CN 1059684 A ,C	25-03-1992
