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(54) **Title:** A PROCESS FOR THE MANUFACTURING OF AN IMPROVED DECORATIVE LAMINATE AND A DECORATIVE LAMINATE OBTAINED BY THE PROCESS

(57) **Abstract:** A process for the manufacturing of floor elements, which floor elements comprises an upper decorative surface a lower surface, edges intended for joining and a core forming a carrying structure. A mixture of polyols, such as polyester or polyether, crude methylene diphenyl diisocyanate and possibly a small amount of blowing agent in a ratio forming a polymeric resin with a density in the range 600-1400kg/m³ is injected or casted into the mould, whereby a slightly porous or solid polyurethane core is formed. The polyurethane core is, possibly after surface treatment such as sanding, provided with an upper decorative surface and possibly a lower counter surface.

A process for the manufacturing of an improved decorative laminate and a decorative laminate obtained by the process.

The present invention relates to a process for manufacturing a decorative laminate and a decorative laminate obtained by the process.

Products clad with thermosetting laminates are quite common nowadays. They are most often used where the demand for abrasion resistance is great but also where resistance towards different chemical substances and moisture is required. Floors, floor skirtings, work tops, table tops, doors and wall panels can serve as an example of such products. The thermosetting laminate is most often made from a number of base sheets and a decorative sheet placed closest to the surface. The decorative sheet may be provided with the desired décor or pattern. Thicker laminates are often provided with a core of particle board or fibre board where both sides are covered with sheets of thermosetting laminate. The outermost sheet is, on at least one side, most often a decorative sheet.

One problem with such thicker laminates is that the core is much softer than the surface layer which is made from paper impregnated with thermosetting resin. This will cause a considerably reduced resistance towards thrusts and blows compared to a laminate with a corresponding thickness made of paper impregnated with thermosetting resin only.

Another problem with thicker laminates with a core of particle board or fibre board is that these normally will absorb a large amount of moisture, which will cause them to expand and soften whereby the laminate will warp. The surface layer might even, partly or completely come off in extreme cases since the core will expand more than the surface layer. This type of laminate can therefore not be used in humid areas, such as bath rooms or kitchens, without problem.

The problems can be partly solved by making the core of paper impregnated with thermosetting resin as well. Such a laminate is most often called compact laminate. These compact laminates are, however, very expensive and laborious to obtain as several tens of layers of paper have to be impregnated, dried and put in layers. The direction of the fibre in the paper does furthermore cause a moisture and

temperature difference relating expansion. This expansion is two to three times as high in the direction crossing the fibre than along the fibre. The longitudinal direction of the fibre is coinciding with the longitudinal direction of the paper. One will furthermore be restricted to use cellulose as a base in the manufacturing though other materials could prove suitable.

The above problems have through the present invention been solved whereby a flexible process for the manufacturing of a mainly isometric laminate has been achieved where floor elements with radically improved impact resistance, rigidity, moisture resistance is achieved. Accordingly the invention relates to a process for the manufacturing of floor elements, which floor elements comprises an upper decorative surface a lower surface, edges intended for joining and a core forming a carrying structure. The invention is characterised in that;

- i) A mixture of polyols, such as polyester or polyether, crude methylene diphenyl diisocyanate and possibly a small amount of blowing agent in a ratio forming a polymeric resin with a density in the range 600-1400kg/m³ is injected or casted into the mould. A slightly porous or solid polyurethane core to a floor element is hereby formed.
- ii) The polurethane core is, possibly after surface treatment such as sanding, provided with an upper decorative surface and possibly a lower counter surface.

The mixture forming the core is preferably containing a flame retardant comprising halogens such as tri-chlorophosphate.

The mould used for the moulding of the polyurethane core is preferably provided with ridges, cores, recesses, protrusions and the like along the edges which ridges, cores, recesses, protrusion and the like gives shape to joining members along the edges of the core. The joining members are possibly fine tuned by means of a milling operation after the moulding. This fine tuning may incorporate milling of geometries that are difficult to obtain in a moulding process. Among such geometries can be mentioned a single or double sided undercut in a groove. It may also show necessary to trim the edges in order to obtain a snug fit between the floor elements. It is also possible to provide the core with joining members by means of a milling operation after the moulding.

The mould is suitably also provided with surface embossing providing at least the upper decorative surface with a desired surface structure.

Suitable isocyanate-reactive compounds to be used in the process of the present invention include any of those known in the art for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams. Of particular importance for the preparation of rigid foams are polyols and polyol mixtures having average hydroxyl numbers of from 100 to 1000, especially from 100 to 700 mg KOH/g, and hydroxyl functionalities of from 2 to 8, especially from 3 to 8. Suitable polyols have been fully described in the prior art and include reaction products of alkylene oxides, for example ethylene oxide and/or propylene oxide, with initiators containing from 2 to 8 active hydrogen atoms per molecule. Suitable initiators include: polyols, for example glycerol, trimethylolpropane, triethanolamine, pentaerythritol, sorbitol and sucrose; polyamines, for example ethylene diamine, tolylene diamine (TDA), diaminodiphenylmethane (DADPM) and polymethylene polyphenylene polyamines; and aminoalcohols, for example ethanolamine and diethanolamine, and mixtures of such initiators. Other suitable polymeric polyols include polyesters obtained by the condensation of appropriate proportions of glycols and higher functionality polyols with dicarboxylic or polycarboxylic acids. Still further suitable polymeric polyols include hydroxyl terminated polythioethers, polyamides, polyesteramides, polycarbonates, polyacetals, polyolefins and polysiloxanes.

Suitable organic polyisocyanates for use in the process of the present invention include any of those known in the art for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams, and in particular the aromatic polyisocyanates such as diphenylmethane diisocyanate in the form of its 2,4', 2,2' and 4,4' isomers and mixtures thereof, the mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof known in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates) having an isocyanate functionality of greater than 2, toluene diisocyanate in the form of its 2,4 and 2,6 isomers and mixtures thereof, 1,5 naphthalene diisocyanate and 1,4 diisocyanatobenzene. Other organic polyisocyanates which may be mentioned include the aliphatic diisocyanates such as isophorone diisocyanate, 1,6 diisocyanatohexane and 4,4' diisocyanato- dicyclohexylmethane.

rigid polyurethane or urethane-modified polyisocyanurate foam to be produced and will be readily determined by those skilled in the art.

The water captured in the raw materials (especially the polyols) can be used as blowing agent, when properly monitored. Otherwise, the polyol stream needs to be desiccated before micro-dosing a blowing agent commonly used. Blowing agents proposed in the prior art include hydrochlorofluorocarbons, hydrofluorocarbons and especially hydrocarbons namely alkanes and cycloalkanes such as isobutane, n-pentane, isopentane, cyclopentane and mixtures thereof as well as water or any other carbon dioxide-evolving compounds.

In addition to the polyisocyanate and polyfunctional isocyanate-reactive compositions and the blowing agent mixture, the foam-forming reaction mixture will commonly contain one or more other auxiliaries or additives conventional to formulations for the production of rigid polyurethane and urethane-modified polyisocyanurate foams. Such optional additives include crosslinking agents, for example low molecular weight polyols such as triethanolamine, foam-stabilising agents or surfactants, for example siloxane-oxyalkylene copolymers, urethane catalysts, for example tin compounds such as stannous octoate or dibutyltin dilaurate or tertiary amines such as dimethylcyclohexylamine or triethylene diamine, isocyanurate catalysts, fire retardants, for example halogenated alkyl phosphates such as tris chloropropyl phosphate, colour pigmentation and fillers such as carbon black.

It is also possible to adapt the mechanical properties of the material by adding other materials such as particles or fibre. These type of additives can be used for a number of reasons. Additives may be used to alter adjust or improve acoustic properties, density, thermal coefficient of expansion, thermal conductivity, flexibility, rigidity and brittleness. A proper filler may also reduce the manufacturing costs. Typical particle fillers are minerals such as mica, glass beads and lime, while common fibre fillers are glass, carbon, steel, aramide and cellulose fibres.

According an embodiment of the invention the first surface webs, constituting a decorative upper surface, is manufactured by laminating at least one uppermost so-called overlay web of melamine-formaldehyde resin impregnated α -cellulose paper with at least one decorative web of decorated melamine-formaldehyde resin impregnated α -cellulose paper and possibly a group of support webs under heat and

According to an embodiment of the invention a the decorative upper surface, is manufactured by laminating at least one uppermost so-called overlay web of melamine-formaldehyde resin impregnated α -cellulose paper with at least one decorative web of decorated melamine-formaldehyde resin impregnated α -cellulose paper and possibly a group of support webs under heat and pressure so that the resin cures at least partially and the webs are bonded to one another, possibly while being pressed towards polyurethane core. It is also possible to glue the decorative upper surface towards the core. In this case it might show necessary to perform a milling operation of the edges after having applied the decorative upper surface. Support layer webs are suitably forming a part of the decorative upper surface. The group of support layer webs comprises one or more monochromatic webs of α -cellulose impregnated with melamine-formaldehyde resin and/or one or more Kraft-paper webs impregnated with phenol-formaldehyde resin, urea-formaldehyde resin, melamine-formaldehyde resin or combinations thereof. In order to improve the abrasion resistance the overlay webs and optionally the decorative paper webs preferably includes 2 - 100 g/m² per layer of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 150 μ m. The scratch resistance is preferably improved by sprinkling 2 - 100 g/m² of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 30 μ m on the upper surface of the uppermost overlay web. The decorative upper surface is laminated and at least partially cured prior to the part of the process where the core is achieved and bonded to the decorative upper surface.

According to another embodiment of the invention the decorative upper surface comprises by a printed foil. The printed foil is suitably made of α -cellulose impregnated with a polymeric lacquer or resin such as melamine-formaldehyde, urea-formaldehyde acrylic, maleamid, polyurethane or the like. The printed foil may also be made of a polymer such as polyvinyl-chloride, polyester, polypropylene, polyethylene, polyurethane, acrylic or the like. The upper surface is preferably coated with one or more wear-resistant layers of acrylic or maleamid lacquer on top of the printed foil. The lacquer is suitably of an UV- or electron-beam curing type.

The lacquer is suitably applied in two or more layers with intermediate stages of partial or complete curing. In order to further increase the abrasion resistance the lacquer preferably includes 2 - 100 g/m² per layer of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 150 μ m. In order to improve the scratch resistance, 2 - 100 g/m² of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 30 μ m is sprinkled on the upper surface of the uppermost layer of lacquer.

According to yet another embodiment of the invention the decorative upper surface comprises a translucent or semi-translucent layer and that particles with sizes in the range 0.5 - 10mm are applied together with the polymeric resin. The particles are preferably deviating in colour from the polymeric resin. It is also possible to include pigmentation in the polymeric resin. The semi-translucent layer is preferably constituted of a sheet which is provided with a printed décor. The printed décor is possibly semi-translucent but can also be opaque, covering only parts of the surface of the sheet. This will give depth to the décor. The semi-translucent foil or web is preferably constituted of α -cellulose impregnated with a polymeric resin or lacquer such as melamine-formaldehyde, urea-formaldehyde, polyurethane, acrylic or maleamide. The semi-translucent sheet may also be constituted of a polymer such as polyvinyl-chloride, acrylic, polyester, polypropylene, polyethylene, polyurethane or the like. The wear resistance is preferably improved by applying a wear layer or a number of wear layers on top of the décor layer. The wear layers are preferably constituted of α -cellulose impregnated with a polymeric resin or lacquer such as melamine-formaldehyde, urea-formaldehyde, polyurethane, acrylic or maleamid. The wear layers may also be constituted of a lacquer such as acrylic or maleamide, possibly of a UV or electron-beam curing type. Such a lacquer is then preferably applied in two or more layers with intermediate stages of partial or complete curing. In order to further improve the abrasion resistance the wear layers includes 2 - 100 g/m² per layer of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 150 μ m. In order to improve the scratch resistance the upper surface of the uppermost of the wear layers

contains 2 - 100 g/m² of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 30 μ m.

According to yet another embodiment of the invention a décor is applied on the upper side of the core. The décor is printed directly on the surface or applied on the surface via transfer printing. In order to protect the décor a wear layer or a number of wear layers are preferably applied on top of the décor. These wear layers are suitably constituted of α -cellulose impregnated with a polymeric resin or lacquer such as melamine-formaldehyde, urea-formaldehyde, polyurethane, acrylic or maleamid. The wear layers are alternatively constituted of a lacquer such as acrylic or maleamide, possibly of a UV or electron-beam curing type. A lacquer is preferably applied in two or more layers with intermediate stages of partial or complete curing. In order to improve the abrasion resistance the wear layers preferably includes 2 - 100 g/m² per layer of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 150 μ m. In order to improve the scratch resistance, 2 - 100 g/m² of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 30 μ m is sprinkled on the upper surface of the uppermost layer of lacquer.

CLAIMS

1. A process for the manufacturing of floor elements, which floor elements comprises an upper decorative surface a lower surface, edges intended for joining and a core forming a carrying structure,
c h a r a c t e r i s e d in that;
 - i) a mixture of polyols, such as polyester or polyether, crude methylene diphenyl diisocyanate and possibly a small amount of blowing agent in a ratio forming a polymeric resin with a density in the range 600-1400kg/m³ is injected or casted into the mould, whereby a slightly porous or solid polyurethane core is formed, whereby,
 - ii) the polurethane core, possibly after surface treatment such as sanding, is provided with an upper decorative surface and possibly a lower counter surface.
2. A process according to claim 1, c h a r a c t e r i s e d in that a flame retardant comprising halogens such as tri-chlorophosphate is included in the mixture forming the core.
3. A process according to claim 1 or 2, c h a r a c t e r i s e d in that the mould is provided with ridges, cores, recesses, protrution and the like along the edges which ridges, cores, recesses, protrution and the like gives shape to joining members along the edges of the core.
4. A process according to claim 3, c h a r a c t e r i s e d in that the joining members are fine tuned by means of a milling operation after the moulding.
5. A process according to claim 1 or 2, c h a r a c t e r i s e d in that the mould is provided with surface embossing providing at least the upper decorative surface with a desired surface structure.
6. A process according to claim 1 or 2, c h a r a c t e r i s e d in that the core is provided with joining members by means of a milling operation after the moulding.

7. A process according to claim 1 - 6, characterised in that the decorative upper surface, is manufactured by laminating at least one uppermost so-called overlay web of melamine-formaldehyde resin impregnated α -cellulose paper with at least one decorative web of decorated melamine-formaldehyde resin impregnated α -cellulose paper and possibly a group of support webs under heat and pressure so that the resin cures at least partially and the webs are bonded to one another, possibly while being pressed towards polyurethane core.
8. A process according to claim 7, characterised in that support layer webs are forming a part of the decorative upper surface which group of support layer webs comprises one or more monochromatic webs of α -cellulose impregnated with melamine-formaldehyde resin and/or one or more Kraft-paper webs impregnated with phenol-formaldehyde resin, urea-formaldehyde resin, melamine-formaldehyde resin or combinations thereof.
9. A process according to claim 7 or 8, characterised in that the overlay webs and optionally the decorative paper webs includes 2 - 100 g/m² per layer of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 150 μ m.
10. A process according to claim 9, characterised in that the upper surface of the uppermost overlay web contains 2 - 100 g/m² of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 30 μ m.
11. A process according to any of the claims 7 - 10, characterised in that the decorative upper surface is laminated and at least partially cured prior to the part of the process where the core is achieved and bonded to the decorative upper surface.
12. A process according to claim 1 - 6, characterised in that the decorative upper surface comprises a printed foil.

13. A process according to claim 12, characterised in that the printed foil is made of α -cellulose impregnated with a polymeric lacquer or resin such as melamine-formaldehyde, urea-formaldehyde acrylic, maleamid, polyurethane or the like.
14. A process according to claim 12, characterised in that the printed foil is made of a polymer such as polyvinyl-chloride, polyester, polypropylene, polyethylene, polyurethane, acrylic or the like.
15. A process according to any of the claims 12 - 14, characterised in that the upper surface is coated with one or more wear-resistant layers of acrylic or maleamid lacquer on top of the printed foil.
16. A process according to claim 15, characterised in that the lacquer is of an UV- or electron-beam curing type.
17. A process according to claims 15 or 16, characterised in that the lacquer is applied in two or more layers with intermediate stages of partial or complete curing.
18. A process according to any of the claims 15 - 17, characterised in that the lacquer includes 2 - 100 g/m² per layer of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 150 μ m.
19. A process according to claim 18, characterised in that the upper surface of the uppermost layer of lacquer contains 2 - 100 g/m² of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 30 μ m.
20. A process according to claim 1 - 6, characterised in that the upper decorative surface comprises a translucent or semi-translucent layer and that particles with sizes in the range 0.5 - 10mm are applied together with the polymeric resin.

21. A process according to claim 20, characterised in that the particles are deviating in colour from the polymeric resin.
22. A process according to claim 20 or 21, characterised in that the polymeric resin also comprises pigmentation.
23. A process according to any of the claims 20 - 22, characterised in that the semi-translucent layer is constituted of a sheet which is provided with a printed décor.
24. A process according to claim 23, characterised in that the printed décor is semi-translucent.
25. A process according to claim 23, characterised in that the printed décor is opaque, covering only parts of the surface of the sheet.
26. A process according to any of the claims 20 - 25, characterised in that the semi-translucent layer is constituted of α -cellulose impregnated with a polymeric resin or lacquer such as melamine-formaldehyde, urea-formaldehyde, polyurethane, acrylic or maleamide.
27. A process according to any of the claims 20 - 25, characterised in that the semi-translucent layer is constituted of a polymer such as polyvinyl-chloride acrylic, polyester, polypropylene, polyethylene, polyurethane or the like.
28. A process according to any of the claims 20 - 27, characterised in that a wear layer or a number of wear layers are applied on top of the sheet.
29. A process according to any of the claims 28, characterised in that the wear layers are constituted of α -cellulose impregnated with a polymeric resin or lacquer such as melamine-formaldehyde, urea-formaldehyde, polyurethane, acrylic or maleamid.
30. A process according to any of the claims 28, characterised in that the wear layers are constituted of a lacquer such as acrylic or maleamide, possibly of a UV or electron-beam curing type.

31. A process according to claims 29 or 30, characterised in that the lacquer is applied in two or more layers with intermediate stages of partial or complete curing.
32. A process according to any of the claims 28 - 31, characterised in that the wear layer includes 2 - 100 g/m² per layer of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 150 μ m.
33. A process according to claim 32, characterised in that the upper surface of the uppermost layer contains 2 - 100 g/m² of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 30 μ m.
34. A process according to claim 1 - 6, characterised in that a décor is applied on the upper side of the core and that the décor is printed directly on the surface or applied on the surface via transfer printing.
35. A process according to any of the claims 34, characterised in that a wear layer or a number of wear layers are applied on top of the décor.
36. A process according to any of the claims 35, characterised in that the wear layers are constituted of α -cellulose impregnated with a polymeric resin or lacquer such as melamine-formaldehyde, urea-formaldehyde, polyurethane, acrylic or maleamid.
37. A process according to any of the claims 35, characterised in that the wear layers are constituted of a lacquer such as acrylic or maleamide, possibly of a UV or electron-beam curing type.
38. A process according to claims 36 or 37, characterised in that the lacquer is applied in two or more layers with intermediate stages of partial or complete curing.

39. A process according to any of the claims 35 - 38, characterised in that the lacquer includes 2 - 100 g/m² per layer of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 150 μ m.
40. A process according to claim 35 - 39, characterised in that the upper surface of the uppermost layer of lacquer contains 2 - 100 g/m² of hard particles of α -aluminium oxide, silicon carbide or silicon oxide having an average particle size in the range 50nm - 30 μ m.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC7: B32B 27/40, B44C 5/04

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)

IPC7: B32B, B44C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5904886 A (STECKER), 18 May 1999 (18.05.99), column 4, line 6 - line 15, claims 1-2, abstract --	1-40
X	WO 9703847 A1 (SURFACE TECHNOLOGIES, INC), 6 February 1997 (06.02.97), page 2; page 5; page 10, claims 1-2,5 --	1-40
A	File WPI, Derwent accession no. 2000-468670 LG Chem Ltd: "Decorative polyvinyl chloride floor covering has a melamine resin impregnated layer on a PVC resin substrate, with a balance layer of sheet, woven, or non woven material between the layers or under the substrate layer, JP,A,2000170361,20000620, DW200041 --	1-40

 Further documents are listed in the continuation of Box C.
 See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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