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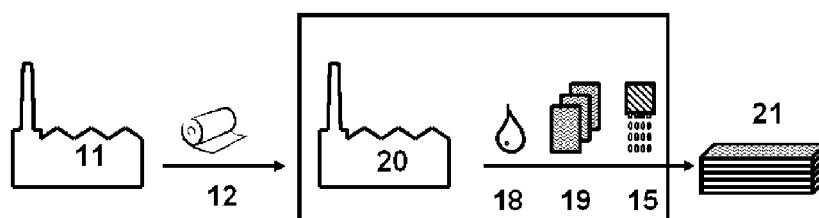


Fig. 2

(57) **Abstract:** A method for manufacturing decorative laminates including the steps of: a) impregnating a paper substrate with a thermosetting resin by submersion of the paper substrate in a bath of thermosetting resin; b) applying on the thermosetting resin impregnated paper substrate an ink acceptance layer containing an inorganic pigment P and a polymeric binder B having a weight ratio P/B of inorganic pigment to polymeric binder of larger than 1.5; c) jetting on the ink acceptance layer a colour pattern with one or more aqueous pigmented inkjet inks and/or organic solvent based pigmented inkjet inks containing a colour pigment C; and d) heat pressing the thermosetting paper into a decorative laminate, wherein the weight ratio P/C of the inorganic pigment of the ink acceptance layer to the jetted colour pigment in the colour pattern is larger than 4.0.

Description

Manufacturing of Decorative Laminates by Inkjet

Technical Field

[0001] The present invention relates to the manufacturing of decorative laminates using inkjet technology.

Background Art

[0002] Gravure, offset and flexography are being increasingly replaced for different applications by industrial inkjet printing systems, which have now proven their flexibility in use, such as variable data printing making short production runs and personalized products possible, and their enhanced reliability, allowing incorporation into production lines.

[0003] Inkjet technology has also caught the attention of manufacturers of decorative surfaces, such as laminate floor. In the current production process for manufacturing decorative panels as shown by Fig.1, a paper manufacturer (11) supplies a paper roll (12) to a decor printer (13) who uses gravure printing (14) in order to deliver a decor paper roll (16) to a warehouse (17) of a floor laminate manufacturer (20). Some decor printers (13) are now investigating inkjet printing (15) instead of gravure printing. Rotogravure printing on the porous decor paper generally uses ink having a viscosity at 25°C of 1 to 2 Pa.s, while the viscosity of inkjet inks is much lower, often about 1 to 15 mPa.s at 25°C. The floor laminate manufacturer (20) stores the decor paper rolls (16) having different decorative patterns in his warehouse (17). Depending on the market demand, the floor laminate manufacturer (20) then selects the decor rolls (16) with the desired decorative pattern in his warehouse (17). The selected decor rolls (16) are then impregnated (18) and cut to size (19) for manufacturing ready-to-use floor laminate (21). The warehouse (17) is necessary as a buffer for sudden large market demands of a specific floor laminate because there is a large time delay between ordering and delivering of new decorative paper rolls (16).

[0004] An approach to reduce the size of the warehouse and time delays is treated by EP 2431190 A (THEODOR HYMMEN) , which discloses in Fig.1 a method for producing a digitally printed sheet, web or plate-shaped

workpiece (20) with wear-resistant surface including the steps of: A) providing a digital data set to a digital printing device (1); B) providing a printable workpiece (20) to the printing apparatus (1); C) digital printing at least an acrylate printing ink (22) on the printable workpiece (20) using the printing apparatus (1) and thereafter supplying a resin mixture (5, 21) to the digitally printed workpiece; and D) curing the resin mixture (5, 21) by means of a heated press (7). The time delay can be avoided by the floor laminate manufacturer incorporating the manufacturing of decorative paper rolls into its own production process. Although acrylate based inks provide excellent image quality, on heat pressing into a decorative laminate adhesion problems are observed between the ink layer and the protective layer containing a thermosetting resin, such as melamine. The cause of these adhesion problems is that the water vapour produced during the polycondensation of the melamine cannot penetrate through the polymerized acrylate ink layer. Paragraph [0003] discloses that the adhesion problems are especially seen at high ink coverages of more than 10 g/m² (e.g. a dark wood laminate).

- [0005] EP 1857511 A (AGFA) discloses solvent based inkjet inks containing a polyalkyleneglycol dialkylether having a molecular weight of at least 250 that are suitable for manufacturing decorative laminates by single pass inkjet printing.
- [0006] Also aqueous inkjet inks have been used for manufacturing decorative laminates by single pass inkjet printing. For example, in the Palis roll-to-roll single pass printing systems (<http://www.palis-digital.com/en/portfolio/sp-drucker.html>) aqueous inkjet inks are printed on a paper substrate having a special ink acceptance layer.
- [0007] In order to obtain good image quality, the solvent based or aqueous inkjet inks are printed on non-impregnated paper which is able to absorb most of the water and organic solvents present in the inkjet inks. The decor paper printed by solvent based or aqueous inkjet inks is then impregnated by a thermosetting resin and cut into sheets ready to be heat pressed into a decorative laminate.

- [0008] In manufacturing decorative laminate having a wood decorative pattern, usually a wood grain is embossed into the decorative laminate during heat pressing. It has been observed that it is very difficult to align the wood grain with the wood decorative pattern due to the dimensional instability of the decor paper printed by solvent based or aqueous inkjet inks.
- [0009] Hence, there is still a need for improved manufacturing methods of decorative surfaces using inkjet technology and melamine resin as a wear coating.
- [0009a] Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.
- [0009b] It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

Summary of invention

- [0009c] According to a first aspect, the present invention provides a method for manufacturing decorative laminates including the steps of;
 - a) impregnating a paper substrate with a thermosetting resin by submersion of the paper substrate in a bath of thermosetting resin;
 - b) applying on the thermosetting resin impregnated paper substrate an ink acceptance layer containing an inorganic pigment P and a polymeric binder B having a weight ratio P/B of inorganic pigment to polymeric binder of larger than 1.5;
 - c) jetting on the ink acceptance layer a colour pattern with one or more aqueous pigmented inkjet inks and/or organic solvent based pigmented inkjet inks containing a colour pigment C; and
 - d) heat pressing the thermosetting paper into a decorative laminate, wherein the weight ratio P/C of the inorganic pigment of the ink acceptance layer to the jetted colour pigment in the colour pattern is larger than 4.0; wherein the dry weight of colour pigments jetted by the one or more aqueous pigmented inkjet inks and/or organic solvent based pigmented inkjet inks is at least 0.30 g/m²; and wherein the ink acceptance layer has a total dry weight between 2.0 g/m² and 10.0 g/m².

- [0009d] Unless the context clearly requires otherwise, throughout the description and the claims, the words “comprise”, “comprising”, and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.
- [0010] Preferred embodiments of the present invention have been realised with a method for manufacturing decorative surfaces as defined by claim 1.
- [0011] It was found that excellent image quality and adhesion was obtained by jetting an aqueous or solvent based pigmented inkjet ink on an ink acceptance layer containing an inorganic pigment P and a polymeric binder B in a specific ratio P/B and controlling the ratio P/C of the dry weight of inorganic pigment P of the ink acceptance layer over the dry weight of the colour pigment C jetted by the pigmented inks. The ink acceptance layer was present on a fully impregnated base paper. The advantage of first impregnating and then inkjet printing is the dimensional stability of the inkjet printed paper, allowing for a wood grain to be embossed in perfect alignment with the inkjet printed wood colour pattern.
- [0012] Another major advantageous effect of invention is the much simpler manufacturing process of decorative laminates, which is immediately visible by comparing Fig.1 and Fig.2 showing that our invention requires no longer an intermediate decor printer company (13) or a warehouse (17). Printing in-house at the floor laminate manufacturer (20) allows for maximum flexibility. Changes in design of a decorative colour pattern can be rapidly introduced in production, thereby also minimizing dependency on supply by the decor printer company (13). There are also no longer minimum purchase quantities to be negotiated with the decor printer company (13). In-house printing allows for fast adaptability to market

trends and an increase of product variety without substantial financial penalties.

- [0013] The replacement of gravure by inkjet also has many advantages. There is no longer a storage of gravure rolls necessary. Furthermore, inkjet allows easy colour reproduction compared to the time consuming colour matching issues in gravure which usually may take up to 5 hours of tuning. This immediately also illustrates that short print runs using inkjet is much more cost-efficient than gravure.
- [0014] Resin impregnation can cause major paper loss. Financial loss is minimized if the paper is first impregnated and then inkjet printed, because less digital print has to be thrown away.
- [0015] Further advantages and embodiments of the present invention will become apparent from the following description.

Brief description of drawings

- [0016] Fig. 1 shows the prior art production process for manufacturing decorative panels, wherein a paper manufacturer (11) supplies a paper roll (12) to a decor printer (13) using gravure printing (14) or inkjet printing (15) in order to deliver a decor paper roll (16) to a warehouse (17) of a floor laminate manufacturer (20). Depending on the market demand, the floor laminate manufacturer (20) selects one of the different decor rolls in his warehouse (17) to impregnate (18) and to cut to a size (19) for being heat pressed and finished into ready-to-use floor laminate (21).
- [0017] Fig. 2 shows a production process for manufacturing decorative panels, wherein a paper manufacturer (11) supplies a paper roll (12) directly to a floor laminate manufacturer (20) who impregnates (18) the paper roll (12), cuts to a size (19) for being inkjet printed (15) and then heat pressed and finished into ready-to-use floor laminate (21). The order of cutting to size (19) and inkjet printing (15) may also be reversed, i.e. printing on a impregnated paper roll before cutting to sheets.
- [0018] Fig. 3 shows a cross-section of a decorative panel (30) including a core layer (31) with a groove (32) and tongue (33) which is laminated on the top side by a decorative layer (34) and a protective layer (35) and on the back side by a balancing layer (36).

- [0019] Fig 4. shows a cross section of a decorative panel (30) having a tongue (33) and a groove (32) for a mechanical join requiring no glue.
- [0020] Fig.5 shows a photograph of a technical colour pattern of good image quality.
- [0021] Fig.6 shows a photograph of a technical colour pattern of bad image quality.
- [0022] Fig.7 shows a more detailed part of the photograph in Fig.5.
- [0023] Fig.8 shows a more detailed part of the photograph in Fig.6.

Detailed Description

Definitions

- [0024] The term “alkyl” means all variants possible for each number of carbon atoms in the alkyl group i.e. methyl, ethyl, for three carbon atoms: n-propyl and isopropyl; for four carbon atoms: n-butyl, isobutyl and tertiary-butyl; for five carbon atoms: n-pentyl, 1,1-dimethyl-propyl, 2,2-dimethylpropyl and 2-methyl-butyl, etc.
- [0025] Unless otherwise specified a substituted or unsubstituted alkyl group is preferably a C₁ to C₆-alkyl group.
- [0026] Unless otherwise specified a substituted or unsubstituted alkenyl group is preferably a C₁ to C₆-alkenyl group.
- [0027] Unless otherwise specified a substituted or unsubstituted alkynyl group is preferably a C₁ to C₆-alkynyl group.
- [0028] Unless otherwise specified a substituted or unsubstituted aralkyl group is preferably phenyl group or naphthyl group including one, two, three or more C₁ to C₆-alkyl groups.
- [0029] Unless otherwise specified a substituted or unsubstituted alkaryl group is preferably a C₁ to C₆-alkyl group including a phenyl group or naphthyl group.
- [0030] Unless otherwise specified a substituted or unsubstituted aryl group is preferably a phenyl group or naphthyl group
- [0031] Unless otherwise specified a substituted or unsubstituted heteroaryl group is preferably a five- or six-membered ring substituted by one, two or three oxygen atoms, nitrogen atoms, sulphur atoms, selenium atoms or combinations thereof.

[0032] The term “substituted”, in e.g. substituted alkyl group means that the alkyl group may be substituted by other atoms than the atoms normally present in such a group, i.e. carbon and hydrogen. For example, a substituted alkyl group may include a halogen atom or a thiol group. An unsubstituted alkyl group contains only carbon and hydrogen atoms

[0033] Unless otherwise specified a substituted alkyl group, a substituted alkenyl group, a substituted alkynyl group, a substituted aralkyl group, a substituted alkaryl group, a substituted aryl and a substituted heteroaryl group are preferably substituted by one or more substituents selected from the group consisting of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and tertiary-butyl, ester, amide, ether, thioether, ketone, aldehyde, sulfoxide, sulfone, sulfonate ester, sulphonamide, -Cl, -Br, -I, -OH, -SH, -CN and -NO₂.

Methods of Manufacturing Decorative Laminates

[0034] The method for manufacturing decorative laminates according to the present invention includes the steps of: a) impregnating a paper substrate with a thermosetting resin by submersion of the paper substrate in a bath of thermosetting resin; b) applying on the thermosetting resin impregnated paper substrate an ink acceptance layer containing an inorganic pigment P and a polymeric binder B having a weight ratio P/B of inorganic pigment to polymeric binder of larger than 1.5; c) jetting on the ink acceptance layer a colour pattern with one or more aqueous pigmented inkjet inks and/or organic solvent based pigmented inkjet inks containing a colour pigment C; and d) heat pressing the thermosetting paper into a decorative laminate, wherein the weight ratio P/C of the inorganic pigment P of the ink acceptance layer to the jetted colour pigment C in the colour pattern is larger than 4.0.

[0035] In a preferred embodiment of the method for manufacturing decorative laminates, the step d) includes embossing a relief into the decorative laminate.

[0036] The paper of the decorative surface is first impregnated with a thermosetting resin before being inkjet printed upon. In one embodiment, the thermosetting resin impregnated paper is first inkjet printed and then

cut into a sheet. In a preferred embodiment, as also shown in Fig.2, the thermosetting resin impregnated paper is first cut into a sheet and then inkjet printed. In the latter, financial losses due to cutting errors is minimized.

- [0037] In a preferred embodiment of the method for manufacturing decorative laminates, the dry weight of colour pigments jetted by the one or more aqueous pigmented inkjet inks and/or organic solvent based pigmented inkjet inks is at least 0.30 g/m², more preferably at least 0.50 g/m², and most preferably at least 0.60 g/m². Such high colour pigment coverages allow to make dark images , e.g. for a dark wood laminate.
- [0038] In a preferred embodiment of the method for manufacturing decorative laminates, the ink acceptance layer has a total dry weight of no more than 10 g/m², preferably no more than 6 g/m² and most preferably between 2 and 5 g/m². At higher dry thicknesses of the ink acceptance layer, splitting in the ink acceptance layer tends to occur during the adhesion test.
- [0039] In a preferred embodiment of the method for manufacturing decorative laminates, the thermosetting resin is selected from the group consisting of melamine-formaldehyde based resins, ureum-formaldehyde based resins and phenol-formaldehyde based resins, most preferably the thermosetting resin is a melamine-formaldehyde based resin.
- [0040] The pigmented inkjet inks may be jetted by one or more print heads ejecting small droplets in a controlled manner through nozzles onto a substrate, which is moving relative to the print head(s).
- [0041] A preferred print head for the inkjet printing system is a piezoelectric head. Piezoelectric inkjet printing is based on the movement of a piezoelectric ceramic transducer when a voltage is applied thereto. The application of a voltage changes the shape of the piezoelectric ceramic transducer in the print head creating a void, which is then filled with ink. When the voltage is again removed, the ceramic expands to its original shape, ejecting a drop of ink from the print head. However the manufacturing method according to the present invention is not restricted to piezoelectric inkjet printing. Other inkjet print heads can be used and include various types, such as a continuous type.

- [0042] The inkjet print head normally scans back and forth in a transversal direction across the moving ink-receiver surface. Often the inkjet print head does not print on the way back. Bi-directional printing is preferred for obtaining a high area throughput.
- [0043] Another preferred printing method is by a “single pass printing process”, which can be performed by using page wide inkjet print heads or multiple staggered inkjet print heads which cover the entire width of the ink-receiver surface. In a single pass printing process the inkjet print heads usually remain stationary and the substrate surface is transported once under the inkjet print heads.
- [0044] In a preferred embodiment of the method for manufacturing decorative laminates, the jetting of the ink is performed in a single pass inkjet printing mode.

Decorative Layers

- [0045] The decorative layer includes a thermosetting resin impregnated paper and a colour pattern printed thereon by inkjet. A preferred decorative layer is an inkjet printed thermosetting resin impregnated paper including a colour pattern in an ink acceptance layer containing an inorganic pigment P and a polymeric binder B having a weight ratio of inorganic pigment to polymeric binder (P/B ratio) of larger than 1.5, wherein the weight ratio of the inorganic pigment P of the ink acceptance layer to the jetted colour pigment C in the colour pattern (P/C ratio) is larger than 4.0; and wherein the ink acceptance layer is substantially free of thermosetting resin.
- [0046] In a preferred embodiment, the ink acceptance layer containing an inorganic pigment and a polymeric binder has a weight ratio P/B of inorganic pigment to binder of larger than 3.0, preferably 3.5 or more.
- [0047] Before printing a colour pattern, or at least a portion thereof, the paper has been provided with resin. This measure improves the stability of the paper. In such cases at least a portion of the expansion or shrinkage due to the resin provision takes place before inkjet printing. The resin provided paper is dried before applying an ink acceptance layer and before inkjet printing, preferably to a residual humidity of 10% or less. In this case the most important portion of the expansion or shrinkage of the paper layer is

neutralized. The advantage of having this dimensional stability is especially observed in the cases where, like in EP 1290290 A (FLOORING IND), a correspondence between the relief and the printed decor is desired. Another advantage of drying the thermosetting resin provided paper before applying the ink acceptance layer is that no or substantially no thermosetting resin is present in the ink acceptance layer. The presence of thermosetting resin in the ink acceptance layer tends to deteriorate the ink bleeding of the inkjet printed image.

[0048] A decorative panel, like a floor panel, has on one side of the core layer a decorative layer and a balancing layer on the other side of the core layer. However, a decorative layer may be applied on both sides of the core layer. The latter is especially desirable in the case of laminate panels for furniture. In such a case, preferably also a protective layer is applied on both decorative layers present on both sides of the core layer.

Decorative Laminates

[0049] The decorative laminates are preferably rigid or flexible panels, but may also be rolls of a flexible substrate. In a preferred embodiment the decorative laminates are selected from the group consisting of kitchen panels, flooring panels, furniture panels, ceiling panels and wall panels.

[0050] A preferred decorative laminate contains the inkjet printed thermosetting resin impregnated paper as described above having an ink acceptance layer with a P/B ratio of larger than 1.5 and a colour pattern with a P/C ratio larger than 4.0 heat pressed with a core layer and a protective layer, wherein the decorative laminate is selected from the group consisting of flooring, kitchen, furniture and wall panels. In a more preferred embodiment, the decorative laminate includes a tongue and a groove capable of achieving a glue less mechanical join.

[0051] A decorative panel (30), illustrated by a flooring panel having also a tongue and groove join (33, 32) in Fig.3, includes preferably at least a core layer (31) and a decorative layer (34). In order to protect the colour pattern of the decorative layer (34) against wear, a protective layer (35) may be applied on top of the decorative layer (34). A balancing layer (36) may also be applied at the opposite side of the core layer (31) to restrict or prevent

possible bending of the decorative panel (30). The assembly into a decorative panel of the balancing layer, the core layer, the decorative layer, and preferably also a protective layer, is preferably performed in the same press treatment of preferably a DPL process (Direct Pressure Laminate).

- [0052] In a preferred embodiment of decorative panels, tongue and groove profiles (33 respectively 32 in Fig.3) are milled into the side of individual decorative panels which allow them to be slid into one another. The tongue and groove join ensures, in the case of flooring panels, a sturdy floor construction and protects the floor, preventing dampness from penetrating.
- [0053] In a more preferred embodiment, the decorative panels include a tongue and a groove of a special shape (e.g. 33 respectively 32 in Fig.4) which allow them to be clicked into one another. The advantage thereof is an easy assembly requiring no glue. The shape of the tongue and groove necessary for obtaining a good mechanical join is well-known in the art of laminate flooring, as also exemplified in EP 2280130 A (FLOORING IND) , WO 2004/053258 (FLOORING IND) , US 2008010937 (VALINGE) and US 6418683 (PERSTORP FLOORING) .
- [0054] The tongue and groove profiles are especially preferred for flooring panels and wall panels, but in the case of furniture panels, such tongue and groove profile is preferably absent for aesthetical reasons of the furniture doors and drawer fronts. However, a tongue and groove profile may be used to click together the other panels of the furniture, as illustrated by US 2013071172 (UNILIN) .
- [0055] The decorative laminates, especially decorative panels, may further include a sound-absorbing layer as disclosed by US 8196366 (UNILIN) .
- [0056] In a preferred embodiment, the decorative panel is an antistatic layered panel. Techniques to render decorative panels antistatic are well-known in the art of decorative laminates as exemplified by EP 1567334 A (FLOORING IND) .
- [0057] The top surface of the decorative laminate, i.e. at least the protective layer, is preferably provided with a relief matching the colour pattern, such as for example the wood grain, cracks and knots in a woodprint. Embossing

techniques to accomplish such relief are well-known and disclosed by, for example, EP 1290290 A (FLOORING IND) , US 2006144004 (UNILIN) , EP 1711353 A (FLOORING IND) and US 2010192793 (FLOORING IND) .

- [0058] Most preferably the relief is formed by pressing a digital embossing plate against the top layer of the decorative workpiece or nested decorative workpiece.
- [0059] A digital embossing plate is a plate which comprises elevations that can be used to form a relief on decorative workpiece by pressing the digital embossing plate against the top layer of the decorative workpiece or nested decorative workpiece. The elevations are cured inkjet droplets, jetted by an inkjet print device, and most preferably UV cured inkjet droplets. The elevations are preferably formed by printing and curing inkjet droplets on top of already cured or pin-cured inkjet droplets. The plate is preferably stiff by using metal or hard plastic.
- [0060] An alternative of a digital embossing plate may be a digital embossing cylinder which is a cylinder that comprises the elevations to form a relief on decorative workpieces by pressing and rotating the digital embossing cylinder against the top layer of the decorative workpiece or nested decorative workpiece. The elevations on the digital embossing cylinder are cured inkjet droplets, jetted by an inkjet print device, and most preferably UV cured inkjet droplets. The elevations are preferably formed by printing and curing inkjet droplets on top of already cured or pin-cured inkjet droplets.
- [0061] In a preferred embodiment, the decorative panels are made in the form of rectangular oblong strips. The dimensions thereof may vary greatly. Preferably the panels have a length exceeding 1 meter, and a width exceeding 0.1 meter, e.g. the panels can be about 1.3 meter long and about 0.15 meter wide. According to a special embodiment the length of the panels exceeds 2 meter, with the width being preferably about 0.2 meter or more. The print of such panels is preferably free from repetitions.

Core Layers

- [0062] The core layer is preferably made of wood-based materials, such as particle board, MDF or HDF (Medium Density Fibreboard or High Density

Fibreboard), Oriented Strand Board (OSB) or the like. Also, use can be made of boards of synthetic material or boards hardened by means of water, such as cement boards. In a particularly preferred embodiment, the core layer is a MDF or HDF board.

- [0063] The core layer may also be assembled at least from a plurality of paper sheets, or other carrier sheets, impregnated with a thermosetting resin as disclosed by **WO 2013/050910 (UNILIN)** . Preferred paper sheets include so-called Kraft paper obtained by a chemical pulping process also known as the Kraft process, e.g. as described in **US 4952277 (BET PAPERCHEM)** .
- [0064] In another preferred embodiment, the core layer is a board material composed substantially of wood fibres which are bonded by means of a polycondensation glue, wherein the polycondensation glue forms 5 to 20 percent by weight of the board material and the wood fibres are obtained for at least 40 percent by weight from recycled wood. Suitable examples are disclosed by **EP 2374588 A (UNILIN)** .
- [0065] Instead of a wood based core layer, also a synthetic core layer may be used ,such as those disclosed by **US 2013062006 (FLOORING IND)** . In a preferred embodiment, the core layer comprises a foamed synthetic material, such as foamed polyethylene or foamed polyvinyl chloride.
- [0066] Other preferred core layers and their manufacturing are disclosed by **US 2011311806 (UNILIN)** and **US 6773799 (DECORATIVE SURFACES)** .
- [0067] The thickness of the core layer is preferably between 2 and 12 mm, more preferably between 5 and 10 mm.

Paper Substrates

- [0068] The decorative layer and preferably, if present also the protective layer and/or balancing layer, include paper as substrate.
- [0069] The paper preferably has a weight of less than 150 g/m², because heavier paper sheets are hard to impregnate all through their thickness with a thermosetting resin. Preferably said paper layer has a paper weight, i.e. without taking into account the resin provided on it, of between 50 and 130 g/m² and preferably between 70 and 130 g/m². The weight of the paper cannot be too high, as then the amount of resin needed to sufficiently

impregnate the paper would be too high, and reliably further processing the printed paper in a pressing operation becomes badly feasible.

- [0070] Preferably, the paper sheets have a porosity according to Gurley's method (DIN 53120) of between 8 and 25 seconds. Such porosity allows even for a heavy sheet of more than 150 g/m² to be readily impregnated with a relatively high amount of resin.
- [0071] Suitable paper sheets having high porosity and their manufacturing are also disclosed by **US 6709764** (ARJO WIGGINS).
- [0072] The paper for the decorative layer is preferably a white paper and may include one or more whitening agents, such as titanium dioxide, calcium carbonate and the like. The presence of a whitening agent helps to mask differences in colour on the core layer which can cause undesired colour effects on the colour pattern.
- [0073] Alternatively, the paper for the decorative layer may be a bulk coloured paper including one or more colour dyes and/or colour pigments. Besides the masking of differences in colour on the core layer, the use of a coloured paper reduces the amount of inkjet ink required to print the colour pattern. For example, a light brown or grey paper may be used for printing a wood motif as colour pattern in order to reduce the amount of inkjet ink needed.
- [0074] In a preferred embodiment, unbleached Kraft paper is used for a brownish coloured paper in the decorative layer. Kraft paper has a low lignin content resulting in a high tensile strength. A preferred type of Kraft paper is absorbent Kraft paper of 40 to 135 g/m² having a high porosity and made from clean low kappa hardwood Kraft of good uniformity.
- [0075] If the protective layer includes a paper, then a paper is used which becomes transparent or translucent after resin impregnation so that for the colour pattern in the decorative layer can be viewed.
- [0076] The above papers may also be used in the balancing layer.
- [0077] For the sake of clarity, it should be clear that resin coated papers, so-called RC papers, are not the thermosetting resin impregnated papers of the decorative laminate manufacturing methods according to the invention. The RC papers used in home/office aqueous inkjet printing consist of a

porous paper core free of resin. The RC papers have only on their surface a resin coating, usually a polyethylene or polypropylene resin coating, with thereon one or more ink receiving layers. Such RC papers have a low permeability for the thermosetting resin leading to inhomogeneous resin absorption and higher risk for delamination after pressing.

Thermosetting resins

- [0078] The thermosetting resin is preferably selected from the group consisting of melamine-formaldehyde based resins, ureum-formaldehyde based resins and phenol-formaldehyde based resins. Other suitable resins for impregnating the paper are listed in [0028] of EP 2274485 A (HUELSTA).
- [0079] Most preferably the thermosetting resin is a melamine-formaldehyde based resin, often simply referred to in the art as a 'melamine (based) resin'.
- [0080] The melamine formaldehyde resin preferably has a formaldehyde to melamine ratio of 1.4 to 2. Such melamine based resin is a resin that polycondenses while exposed to heat in a pressing operation. The polycondensation reaction creates water as a by-product. It is particularly with these kinds of thermosetting resins, namely those creating water as a by-product, that the present invention is of interest. The created water, as well as any water residue in the thermosetting resin before the pressing, must leave the hardening resin layer to a large extent before being trapped and leading to a loss of transparency in the hardened layer. The available ink layer can hinder the diffusion of the vapour bubbles to the surface, however the present invention provides measures for limiting such hindrance.
- [0081] The paper is preferably provided with an amount of thermosetting resin equalling 40 to 250% dry weight of resin as compared to weight of the paper. Experiments have shown that this range of applied resin provides for a sufficient impregnation of the paper, that avoids splitting to a large extent, and that stabilizes the dimension of the paper to a high degree.
- [0082] The paper is preferably provided with such an amount of thermosetting resin, that at least the paper core is satisfied with the resin. Such satisfaction can be reached when an amount of resin is provided that

corresponds to at least 1.5 or at least 2 times the paper weight. Preferably the paper is firstly impregnated through or satisfied, and, afterwards, at least at the side thereof to be printed, resin is partially removed.

- [0083] Preferably the resin provided on said paper is in a B-stage while printing. Such B-stage exists when the thermosetting resin is not completely cross linked.
- [0084] Preferably the resin provided on said paper has a relative humidity lower than 15%, and still better of 10% by weight or lower while printing.
- [0085] Preferably the step of providing said paper with thermosetting resin involves applying a mixture of water and the resin on the paper. The application of the mixture might involve immersion of the paper in a bath of the mixture. Preferably the resin is provided in a dosed manner, for example by using one or more squeezing rollers and/or doctor blades to set the amount of resin added to the paper layer.
- [0086] Methods for impregnating a paper substrate with resin are well-known in the art as exemplified by **WO 2012/126816 (VITS)** and **EP 966641 A (VITS)** .
- [0087] The dry resin content of the mixture of water and resin for impregnation depends on the type of resin. An aqueous solution containing a phenol-formaldehyde resin preferably has a dry resin content of about 30% by weight, while an aqueous solution containing a melamine-formaldehyde resin preferably has a dry resin content of about 60% by weight. Methods of impregnation with such solutions are disclosed by e.g. **US 6773799 (DECORATIVE SURFACES)** .
- [0088] The paper is preferably impregnated with the mixtures known from **US 4109043 (FORMICA CORP)** and **US 4112169 (FORMICA CORP)** , and hence preferably comprise, next to melamine formaldehyde resin, also polyurethane resin and/or acrylic resin.
- [0089] The mixture including the thermosetting resin may further include additives, such as colorants, surface active ingredients, biocides, antistatic agents, hard particles for wear resistance, elastomers, UV absorbers, organic solvents, acids, bases, and the like.

[0090] The advantage of adding a colorant to the mixture containing the thermosetting resin is that a single type of white paper can be used for manufacturing the decorative layer, thereby reducing the stock of paper for the decorative laminate manufacturer. The use of a colored paper, as already described above, to reduce the amount of ink required for printing a wood motif, is here accomplished by the white paper being colored by impregnation by a brownish thermosetting resin. The latter allows a better control of the amount of brown colour required for certain wood motifs.

[0091] Antistatic agents may be used in thermosetting resin. However preferably antistatic agents, like NaCl and KCl, carbon particles and metal particles, are absent in the resin, because often they have undesired side effects such as a lower water resistance or a lower transparency. Other suitable antistatic agents are disclosed by EP 1567334 A (FLOORING IND) .

[0092] Hard particles for wear resistance are preferably included in a protective layer.

Ink Acceptance Layers

[0093] The ink acceptance layer contains an inorganic pigment and a polymeric binder having a weight ratio P/B of inorganic pigment P to polymeric binder B of larger than 1.5, preferably larger than 3.0. The inorganic pigment may be a single type of inorganic pigment or a plurality of different inorganic pigments. The polymeric binder may be a single type of polymeric binder or a plurality of different polymeric binders.

[0094] In a preferred embodiment, the ink acceptance layer has a total dry weight between 2.0 g/m² and 10.0 g/m², more preferably between 3.0 and 6.0 g/m² .

[0095] In a preferred embodiment, the ink acceptance layer includes a polymeric binder selected from the group consisting of hydroxyethyl cellulose; hydroxypropyl cellulose; hydroxyethylmethyl cellulose; hydroxypropyl methyl cellulose; hydroxybutylmethyl cellulose; methyl cellulose; sodium carboxymethyl cellulose; sodium carboxymethylhydroxethyl cellulose; water soluble ethylhydroxyethyl cellulose; cellulose sulfate; polyvinyl alcohol; vinylalcohol copolymers; polyvinyl acetate; polyvinyl acetal; polyvinyl pyrrolidone; polyacrylamide; acrylamide/acrylic acid copolymer;

polystyrene, styrene copolymers; acrylic or methacrylic polymers; styrene/acrylic copolymers; ethylene-vinylacetate copolymer; vinyl-methyl ether/maleic acid copolymer; poly(2-acrylamido-2-methyl propane sulfonic acid); poly(diethylene triamine-co-adipic acid); polyvinyl pyridine; polyvinyl imidazole; polyethylene imine epichlorohydrin modified; polyethylene imine ethoxylated; ether bond-containing polymers such as polyethylene oxide (PEO), polypropylene oxide (PPO), polyethylene glycol (PEG) and polyvinyl ether (PVE); polyurethane; melamine resins; gelatin; carrageenan; dextran; gum arabic; casein; pectin; albumin; chitins; chitosans; starch; collagen derivatives; collodion and agar-agar.

- [0096] In a particularly preferred embodiment, the ink acceptance layer includes a polymeric binder, preferably a water soluble polymeric binder (> 1 g/L water), which has a hydroxyl group as a hydrophilic structural unit, e.g. a polyvinyl alcohol.
- [0097] A preferred polymer for the ink acceptance layer is a polyvinylalcohol (PVA), a vinylalcohol copolymer or modified polyvinyl alcohol. The modified polyvinyl alcohol may be a cationic type polyvinyl alcohol, such as the cationic polyvinyl alcohol grades from Kuraray, such as POVAL C506, POVAL C118 from Nippon Goshei.
- [0098] The pigment in the ink acceptance layer is an inorganic pigment, which can be chosen from neutral, anionic and cationic pigment types. Useful pigments include e.g. silica, talc, clay, hydrotalcite, kaolin, diatomaceous earth, calcium carbonate, magnesium carbonate, basic magnesium carbonate, aluminosilicate, aluminum trihydroxide, aluminum oxide (alumina), titanium oxide, zinc oxide, barium sulfate, calcium sulfate, zinc sulfide, satin white, alumina hydrate such as boehmite, zirconium oxide or mixed oxides.
- [0099] The inorganic pigment is preferably selected from the group consisting of alumina hydrates, aluminum oxides, aluminum hydroxides, aluminum silicates, and silicas.
- [0100] Particularly preferred inorganic pigments are silica particles, colloidal silica, alumina particles and pseudo-boehmite, as they form better porous structures. When used herein, the particles may be primary particles

directly used as they are, or they may form secondary particles.

Preferably, the particles have an average primary particle diameter of 2 μm or less, and more preferably 200 nm or less.

- [0101] A preferred type of alumina hydrate is crystalline boehmite, or $\gamma\text{-AlO(OH)}$. Useful types of boehmite include DISPERAL HP14, DISPERAL 40, DISPAL 23N4-20, DISPAL 14N-25 and DISPERAL AL25 from Sasol; and MARTOXIN VPP2000-2 and GL-3 from Martinswerk GmbH
- [0102] Useful cationic aluminum oxide (alumina) types include $\alpha\text{-Al}_2\text{O}_3$ types, such as NORTON E700, available from Saint-Gobain Ceramics & Plastics, Inc, and $\gamma\text{-Al}_2\text{O}_3$ types, such as ALUMINUM OXID C from Degussa.
- [0103] Other useful inorganic pigments include aluminum trihydroxides such as Bayerite, or $\alpha\text{-Al(OH)}_3$, such as PLURAL BT, available from Sasol, and Gibbsite, or $\gamma\text{-Al(OH)}_3$, such as MARTINAL grades and MARTIFIN grades from Martinswerk GmbH, MICRAL grades from JM Huber company; HIGILITE grades from Showa Denka K.K..
- [0104] Another preferred type of inorganic pigment is silica which can be used as such, in its anionic form or after cationic modification. The silica can be chosen from different types, such as crystalline silica, amorphous silica, precipitated silica, fumed silica, silica gel, spherical and non-spherical silica. The silica may contain minor amounts of metal oxides from the group Al, Zr, Ti. Useful types include AEROSIL OX50 (BET surface area $50 \pm 15 \text{ m}^2/\text{g}$, average primary particle size 40 nm, SiO_2 content > 99.8%, Al_2O_3 content < 0.08%), AEROSIL MOX170 (BET surface area 170 g/m², average primary particle size 15 nm, SiO_2 content > 98.3%, Al_2O_3 content 0.3-1.3%), AEROSIL MOX80 (BET surface area $80 \pm 20 \text{ g/m}^2$, average primary particle size 30 nm, SiO_2 content > 98.3%, Al_2O_3 content 0.3-1.3%), or other hydrophilic AEROSIL grades available from Degussa-Hüls AG, which may give aqueous dispersions with a small average particle size (<500 nm).
- [0105] Generally depending on their production method, silica particles are grouped into two types, wet-process particles and dry-process (vapour phase-process or fumed) particles.

- [0106] In the wet process, active silica is formed through acidolysis of silicates, and this is polymerized to a suitable degree and flocculated to obtain hydrous silica.
- [0107] A vapour-phase process includes two types; one includes high-temperature vapour-phase hydrolysis of silicon halide to obtain anhydrous silica (flame hydrolysis), and the other includes thermal reduction vaporization of silica sand and coke in an electric furnace followed by oxidizing it in air to also obtain anhydrous silica (arc process). The "fumed silica" means to indicate anhydrous silica particles obtained in the vapour-phase process.
- [0108] For the silica particles used in the invention, especially preferred are the fumed silica particles. The fumed silica differs from hydrous silica in point of the density of the surface silanol group and of the presence or absence of pores therein, and the two different types of silica have different properties. The fumed silica is suitable for forming a three-dimensional structure of high porosity. Since the fumed silica has a particularly large specific surface area, its ink absorption and retention are high. Preferably, the vapour-phase silica has an average primary particle diameter of 30 nm or less, more preferably 20 nm or less, even more preferably 10 nm or less, and most preferably from 3 to 10 nm. The fumed silica particles readily aggregate through hydrogen bonding at the silanol groups therein. Therefore, when their mean primary particle size is not larger than 30 nm, the silica particles may form a structure of high porosity.
- [0109] In a further preferred embodiment, said ink receiving layer can be further crosslinked. Any suitable crosslinker known in the prior art can be used. Boric acid is particularly preferred as crosslinker for the ink receiving layer according to the present invention.
- [0110] The ink acceptance layer may include other additives, such as colorants, surfactants, biocides, antistatic agents, hard particles for wear resistance, elastomers, UV absorbers, organic solvents, plasticizers, light-stabilizers, pH adjusters, antistatic agents, whitening agents, matting agents and the like.

- [0111] The ink acceptance layer may consist of a single layer or of two, three or more layers even having a different composition.
- [00112] The ink acceptance layer(s) can be coated onto the support by any conventional coating technique, such as dip coating, knife coating, extrusion coating, spin coating, slide hopper coating and curtain coating.
- [0113] Alternatively the ink acceptance layer(s) can also be applied by a printing techniques, such as flexographic printing, screen printing and inkjet printing. The inkjet printer preferably employs valvejet printing heads.

Colour Patterns

- [0114] The colour pattern is obtained by jetting the pigmented inkjet inks on the ink acceptance layer present on the surface of a thermosetting resin impregnated paper substrate.
- [0115] There is no real restriction on the content of the colour pattern. The colour pattern may also contain information such as text, arrows, logo's and the like. The advantage of inkjet printing is that such information can be printed at low volume without extra cost, contrary to gravure printing.
- [0116] In a preferred embodiment, the colour pattern is a wood reproduction or a stone reproduction, but it may also be a fantasy or creative pattern, such as an ancient world map or a geometrical pattern, or even a single colour for making, for example, a floor consisting of black and red tiles or a single colour furniture door.
- [0117] An advantage of printing a wood colour pattern is that a floor can be manufactured imitating besides oak, pine and beech, also very expensive wood like black walnut which would normally not be available for house decoration.
- [0118] An advantage of printing a stone colour pattern is that a floor can be manufactured which is an exact imitation of a stone floor, but without the cold feeling when walking barefooted on it and that it is easy replaceable over time according to fashion.

Protective Layers

- [0119] Preferably a protective layer is applied above the colour pattern after inkjet printing, e.g. by way of an overlay, i.e. a resin provided carrier, or a liquid

coating, preferably while the decor layer is laying on the substrate, either loosely or already connected or adhered thereto.

- [0120] In a preferred embodiment, the carrier of the overlay is a paper impregnated by a thermosetting resin that becomes transparent or translucent after heat pressing in a DPL process.
- [0121] A preferred method for manufacturing such an overlay is described in **US 2009208646 (DEKOR KUNSTSTOFFE)** .
- [0122] The liquid coating includes preferably a thermosetting resin, but may also be another type of liquid such as a UV- or an EB-curable varnish.
- [0123] In a particularly preferred embodiment, the liquid coating includes a melamine resin and hard particles, like corundum.
- [0124] The protective layer is preferably the outermost layer, but in another embodiment a thermoplastic or elastomeric surface layer may be coated on the protective layer, preferably of pure thermoplastic or elastomeric material. In the latter case, preferably a thermoplastic or elastomeric material based layer is also applied on the other side of the core layer.
- [0125] Liquid melamine coatings are exemplified in **DE 19725829 C (LS INDUSTRIELACKE)** and **US 3173804 (RENKL PAIDIWERK)** .
- [0126] The liquid coating may contain hard particles, preferably transparent hard particles. Suitable liquid coatings for wear protection containing hard particles and methods for manufacturing such a protective layer are disclosed by **US 2011300372 (CT FOR ABRASIVES AND REFRACTORIES)** and **US 8410209 (CT FOR ABRASIVES AND REFRACTORIES)** .
- [0127] The transparency and also the colour of the protective layer can be controlled by the hard particles, when they comprise one or a plurality of oxides, oxide nitrides or mixed oxides from the group of elements Li, Na, K, Ca, Mg, Ba, Sr, Zn, Al, Si, Ti, Nb, La, Y, Ce or B.
- [0128] The total quantity of hard particles and transparent solid material particles is typically between 5% by volume and 70% by volume, based on the total volume of the liquid coating. The total quantity of hard particles is between 1 g/m² and 100 g/m², preferably 2 g/m² to 50 g/m².

- [0129] If the protective layer includes a paper as carrier sheet for the thermosetting resin, then the hard particles, such as aluminium oxide particles, are preferably incorporated in or on the paper. Preferred hard particles are ceramic or mineral particles chosen from the group of aluminium oxide, silicon carbide, silicon oxide, silicon nitride, tungsten carbide, boron carbide, and titanium dioxide, or from any other metal oxide, metal carbide, metal nitride or metal carbonitride. The most preferred hard particles are corundum and so-called Sialon ceramics. In principle, a variety of particles may be used. Of course, also any mixture of the above-mentioned hard particles may be applied.
- [0130] In an alternative embodiment of a protective layer including a paper as carrier sheet for the thermosetting resin, the inkjet printing is performed on the thermosetting resin impregnated paper of the protective layer. The other paper substrate including a whitening agent, such as titanium dioxide, may then merely be used to mask surface defects of the core layer.
- [0131] The amount of hard particles in the protective layer may be determined in function of the desired wear resistance, preferably by a so-called Taber test as defined in EN 13329 and also disclosed in WO 2013/050910 A (UNILIN) and US 8410209 (CT FOR ABRASIVES AND REFRCTOR) .
- [0132] Hard particles having an average particle size of between 1 and 200 μm are preferred. Preferably an amount of such particles of between 1 and 40 g/m^2 is applied above the printed pattern. An amount lower than 20 g/m^2 can suffice for the lower qualities.
- [0133] If the protective layer includes a paper, then it preferably has a paper weight of between 10 and 50 g/m^2 . Such a paper is often also referred to as a so-called overlay commonly used in laminate panels. Preferred methods for manufacturing such an overlay are disclosed by WO 2007/144718 (FLOORING IND) .
- [0134] Preferably the step of providing the protective layer of thermosetting resin above the printed pattern involves a press treatment. Preferably a temperature above 150°C is applied in the press treatment, more

preferably between 180° and 220°C, and a pressure of more than 20 bar, more preferably between 35 and 40 bar.

[0135] In another preferred embodiment, the decorative laminate is manufactured using two press treatments, because this results in an extremely high abrasion resistance. Indeed, during the first press treatment, preferably the layers immediately underlying the wear resistant protective layer are substantially or wholly cured. The hard particles comprised in the wear resistant protective layer are thereby prevented from being pushed down out of the top area of the floor panel into the colour pattern or below the colour pattern and stay in the zone where they are most effective, namely essentially above the colour pattern. This makes it possible to reach an initial wear point according to the Taber test as defined in EN 13329 of over 10000 rounds, where in one press treatment of layers with the same composition only just over 4000 rounds were reached. It is clear that the use of two press treatments as defined above, leads to a more effective use of available hard particles. An alternative advantage of using at least two press treatments lies in the fact that a similar wearing rate, as in the case where a single press treatment is used, can be obtained with less hard particles if the product is pressed twice. Lowering the amount of hard particles is interesting, since hard particles tend to lower the transparency of the wear resistant protective layer, which is undesirable. It becomes also possible to work with hard particles of smaller diameter, e.g. particles having an average particle diameter of 15 µm or less, or even of 5 µm or less.

Balancing Layers

[0136] The main purpose of the balancing layer(s) is to compensate tensile forces by layers on the opposite side of the core layer, so that an essentially flat decorative panel is obtained. Such a balancing layer is preferably a thermosetting resin layer, that can comprise one or more carrier layers, such as paper sheets.

[0137] As already explained above for a furniture panel, the balancing layer(s) may be a decorative layer, optionally complemented by a protective layer.

[0138] Instead of one or more transparent balancing layers, also an opaque balancing layer may be used which gives the decorative panel a more appealing look by masking surface irregularities. Additionally, it may contain text or graphical information such as a company logo or text information.

Pigmented Inkjet Inks

[0139] The colour pattern is printed using one or more aqueous pigmented inkjet inks and/or organic solvent based pigmented inkjet inks containing a colour pigment.

[0140] The liquid phase of the aqueous pigmented inkjet inks can be pure water, but preferably some organic solvents are present, such as a humectant.

[0141] The organic solvent based pigmented inkjet inks do not contain intentionally added water, but may contain a very small amount of water, generally less than 5 wt% of water based on the total weight of the ink. . This water was not intentionally added but came into the formulation via other components as a contamination, such as for example polar organic solvents. Higher amounts of water than 5 wt% of water based on the total weight of the ink tend to make the inkjet inks unstable, preferably the water content is less than 1 wt% based on the total weight of the ink and most preferably no water at all is present.

[0142] The pigmented aqueous inkjet ink preferably include at least one or more colour pigments and water, preferably completed with one or more dispersants if the colour pigment is not a self-dispersible colour pigment. The organic solvent based pigmented inkjet inks preferably include at least one or more colour pigments, one or more dispersants and one or more organic solvents.

[0143] The inkjet inks are composed into a inkjet ink set having differently coloured inkjet inks. The inkjet ink set may be a standard CMYK ink set, but is preferably a CRYK ink set wherein the magenta (M) ink is replaced by red (R) inkjet ink. The use of a red inkjet ink enhances the colour gamut for wood based colour patterns, which represent the majority of decorative laminates in flooring laminates.

[0144] The inkjet ink set may be extended with extra inks such as white, brown, red, green, blue, and/or orange to further enlarge the colour gamut of the image. The inkjet ink set may also be extended by the combination of the full density inkjet inks with light density inkjet inks. The combination of dark and light colour inks and/or black and grey inks improves the image quality by a lowered graininess. However preferably the inkjet ink set consists of no more than 3 or 4 inkjet inks, allowing the design of multi-pass inkjet printers of high throughput at acceptable cost.

[0145]

Colour Pigments

[0146] The colorant of the inkjet inks preferably consists of one or more colour pigments. Colour pigments have much higher light stability than dyes. The pigmented inkjet ink preferably contains a dispersant, more preferably a polymeric dispersant, for dispersing the pigment. In addition to the polymeric dispersant, the pigmented inkjet ink may contain a dispersion synergist to further improve the dispersion quality and stability of the ink.

[0147] In a pigmented aqueous inkjet ink, the aqueous inkjet ink may contain a so-called “self dispersible” colour pigment. A self-dispersible colour pigment requires no dispersant, because the pigment surface has ionic groups which realize electrostatic stabilization of the pigment dispersion. In case of self-dispersible colour pigments, the steric stabilization obtained by using a polymeric dispersant becomes optional. The preparation of self-dispersible colour pigments is well-known in the art and can be exemplified by EP 904327 A (CABOT) ;

[0148] The colour pigments may be black, white, cyan, magenta, yellow, red, orange, violet, blue, green, brown, mixtures thereof, and the like. A colour pigment may be chosen from those disclosed by HERBST, Willy, et al. Industrial Organic Pigments, Production, Properties, Applications. 3rd edition. Wiley - VCH , 2004. ISBN 3527305769.

[0149] A particularly preferred pigment for a cyan aqueous inkjet ink is a copper phthalocyanine pigment, more preferably C.I. Pigment Blue 15:3 or C.I. Pigment Blue 15:4.

- [0150] Particularly preferred pigments for a red aqueous inkjet ink are C.I. Pigment Red 254, C.I. Pigment Red 176 and C.I. Pigment Red 122, and mixed crystals thereof.
- [0151] Particularly preferred pigments for yellow aqueous inkjet ink are C.I. Pigment Yellow 151, C.I. Pigment Yellow 180 and C.I. Pigment Yellow 74, and mixed crystals thereof.
- [0152] For the black ink, suitable pigment materials include carbon blacks such as Regal™ 400R, Mogul™ L, Elftex™ 320 from Cabot Co., or Carbon Black FW18, Special Black™ 250, Special Black™ 350, Special Black™ 550, Printex™ 25, Printex™ 35, Printex™ 55, Printex™ 90, Printex™ 150T from DEGUSSA Co., MA8 from MITSUBISHI CHEMICAL Co., and C.I. Pigment Black 7 and C.I. Pigment Black 11.
- [0153] Also mixed crystals may be used. Mixed crystals are also referred to as solid solutions. For example, under certain conditions different quinacridones mix with each other to form solid solutions, which are quite different from both physical mixtures of the compounds and from the compounds themselves. In a solid solution, the molecules of the components enter into the same crystal lattice, usually, but not always, that of one of the components. The x-ray diffraction pattern of the resulting crystalline solid is characteristic of that solid and can be clearly differentiated from the pattern of a physical mixture of the same components in the same proportion. In such physical mixtures, the x-ray pattern of each of the components can be distinguished, and the disappearance of many of these lines is one of the criteria of the formation of solid solutions. A commercially available example is Cinquasia™ Magenta RT-355-D from Ciba Specialty Chemicals.
- [0154] Also mixtures of pigments may be used. For example, a black inkjet ink may include a carbon black pigment and at least one pigment selected from the group consisting of a blue pigment, a cyan pigment, a magenta pigment and a red pigment. It was found that such a black inkjet ink allowed easier and better colour management for wood colours.
- [0155] In a particularly preferred embodiment, the jetted pigmented inks include at least three aqueous pigmented inkjet inks and/or organic solvent based

pigmented inkjet inks include a pigment selected from the group consisting of carbon black, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Yellow 151, C.I. Pigment Yellow 180, C.I. Pigment Yellow 74, C.I. Pigment Red 254, C.I. Pigment Red 176, C.I. Pigment Red 122, and mixed crystals thereof. It was found that in such a case, very lightstable colour patterns could be obtained.

- [0156] The pigment particles in the pigmented inkjet ink should be sufficiently small to permit free flow of the ink through the inkjet printing device, especially at the ejecting nozzles. It is also desirable to use small particles for maximum colour strength and to slow down sedimentation.
- [0157] The average particle size of the pigment in the pigmented inkjet ink should be between 0.005 µm and 15 µm. Preferably, the average pigment particle size is between 0.005 and 5 µm, more preferably between 0.005 and 1 µm, particularly preferably between 0.005 and 0.3 µm and most preferably between 0.040 and 0.150 µm.
- [0158] The pigment is used in the pigmented inkjet ink in an amount of 0.1 to 20 wt%, preferably 1 to 10 wt%, and most preferably 2 to 5 wt% based on the total weight of the pigmented inkjet ink. A pigment concentration of at least 2 wt% is preferred to reduce the amount of inkjet ink needed to produce the colour pattern, while a pigment concentration higher than 5 wt% reduces the colour gamut for printing the colour pattern with print heads having a nozzle diameter of 20 to 50 µm..

Dispersants

- [0159] The pigmented inkjet ink may contain a dispersant, preferably a polymeric dispersant, for dispersing the pigment.
- [0160] Suitable polymeric dispersants are copolymers of two monomers but they may contain three, four, five or even more monomers. The properties of polymeric dispersants depend on both the nature of the monomers and their distribution in the polymer. Copolymeric dispersants preferably have the following polymer compositions:
 - statistically polymerized monomers (e.g. monomers A and B polymerized into ABBAABAB);

- alternating polymerized monomers (e.g. monomers A and B polymerized into ABABABAB);
- gradient (tapered) polymerized monomers (e.g. monomers A and B polymerized into AAABAABBABBB);
- block copolymers (e.g. monomers A and B polymerized into AAAAABBBBBB) wherein the block length of each of the blocks (2, 3, 4, 5 or even more) is important for the dispersion capability of the polymeric dispersant;
- graft copolymers (graft copolymers consist of a polymeric backbone with polymeric side chains attached to the backbone); and
- mixed forms of these polymers, e.g. blocky gradient copolymers.

[0161] Suitable dispersants are DISPERBYK™ dispersants available from BYK CHEMIE, JONCRYL™ dispersants available from JOHNSON POLYMERS and SOLSPERSE™ dispersants available from ZENECA. A detailed list of non-polymeric as well as some polymeric dispersants is disclosed by MC CUTCHEON. Functional Materials, North American Edition. Glen Rock, N.J.: Manufacturing Confectioner Publishing Co., 1990. p.110-129.

[0162] The polymeric dispersant has preferably a number average molecular weight Mn between 500 and 30000, more preferably between 1500 and 10000.

[0163] The polymeric dispersant has preferably a weight average molecular weight Mw smaller than 100,000, more preferably smaller than 50,000 and most preferably smaller than 30,000.

[0164] The polymeric dispersant has preferably a polymeric dispersity PD smaller than 2, more preferably smaller than 1.75 and most preferably smaller than 1.5.

[0165] Commercial examples of polymeric dispersants are the following:

- DISPERBYK™ dispersants available from BYK CHEMIE GMBH;
- SOLSPERSE™ dispersants available from NOVEON;
- TEGO™ DISPERST™ dispersants from DEGUSSA;
- EDAPLAN™ dispersants from MÜNZING CHEMIE;
- ETHACRYL™ dispersants from LYONDELL;
- GANEX™ dispersants from ISP;

- DISPEX™ and EFKATM dispersants from CIBA SPECIALTY CHEMICALS INC;
- DISPONERTM dispersants from DEUCHEM; and
- JONCRYL™ dispersants from JOHNSON POLYMER.

[0166] Particularly preferred for non-aqueous ink jet inks include Solsperse™ dispersants from NOVEON, Efka™ dispersants from CIBA SPECIALTY CHEMICALS INC and Disperbyk™ dispersants from BYK CHEMIE GMBH.

[0167] Particularly preferred dispersants for solvent based pigment dispersions are Solsperse™ 32000 and 39000 from NOVEON.

[0168] The polymeric dispersant is preferably used in the pigment dispersion in an amount of 2 to 600 wt%, more preferably 5 to 200 wt% based on the weight of the pigment.

[0169] In a particularly preferred embodiment, the polymeric dispersant used in an aqueous pigmented inkjet ink is a copolymer comprising between 3 and 11 mol% of a long aliphatic chain (meth)acrylate wherein the long aliphatic chain contains at least 10 carbon atoms.

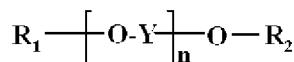
[0170] The long aliphatic chain (meth)acrylate contains preferably 10 to 18 carbon atoms. The long aliphatic chain (meth)acrylate is preferably decyl (meth)acrylate. The polymeric dispersant can be prepared with a simple controlled polymerization of a mixture of monomers and/or oligomers including between 3 and 11 mol% of a long aliphatic chain (meth)acrylate wherein the long aliphatic chain contains at least 10 carbon atoms.

[0171] A commercially available polymeric dispersant being a copolymer comprising between 3 and 11 mol% of a long aliphatic chain (meth)acrylate is Edaplan™ 482, a polymeric dispersant from MUNZING.

Organic Solvents

[0172] The one or more organic solvent based pigmented inkjet inks include preferably at least one polyalkyleneglycol dialkylether having a molecular weight of at least 250.

[0173] The polyalkyleneglycol dialkylether is preferably represented by Formula (I):



Formula (I)

wherein, R_1 and R_2 are each independently selected from an alkyl group having 1 to 4 carbon atoms; Y represents an ethylene group or a propylene group; and n is an integer selected from 5 to 20. The alkylgroups R_1 and R_2 of the polyalkyleneglycol dialkylethers according to Formula (I) preferably represent methyl and/or ethyl. Most preferably, the alkylgroups R_1 and R_2 are both methyl groups. In a preferred embodiment the polyalkyleneglycol dialkylethers according to Formula (I) are polyethyleneglycol dialkylethers.

- [0174] The one or more organic solvent based pigmented inkjet inks preferably include a second polyalkyleneglycol dialkylether according to Formula (I) having the integer n selected from 4 to 20, more preferably the integer n is selected from 6 to 17.
- [0175] In a preferred embodiment, the organic solvent based pigmented inkjet inks include a mixture of at least two polyalkyleneglycol dialkylethers having four or more alkylene glycol groups but wherein the number of alkylene glycol groups is not the same in the two polyalkyleneglycol dialkylethers.
- [0176] Suitable mixtures of polyalkyleneglycol dialkylethers for the pigment dispersions according to the present invention include mixtures of polyethylene glycol dimethyl ethers having a molecular weight of at least 200, such as Polyglycol DME 200TM, Polyglycol DME 250TM and Polyglycol DME 500TM from CLARIANT. The polyalkyleneglycol dialkylethers used in the non-aqueous inkjet ink have preferably an average molecular weight between 200 and 800, and more preferably no polyalkyleneglycol dialkylethers with a molecular weight of more than 800 are present. The mixture of polyalkyleneglycol dialkylethers is preferably a homogeneous liquid mixture at room temperature.
- [0177] The organic solvent based pigmented inkjet ink may include a polyalkyleneglycol derivative selected from the group consisting of polyalkyleneglycol monoalkyl ether acetates, and polyalkyleneglycol

monoalkyl ethers. In a preferred embodiment the polyalkyleneglycol derivative is selected from the group consisting of dipropyleneglycol monomethyl ether acetate, diethyleneglycol monobutyl ether acetate, triethyleneglycol monobutyl ether and tripropyleneglycol monomethylether.

- [0178] In a very preferred embodiment the polyalkyleneglycol monoalkyl ether acetate is selected from the group consisting of dipropyleneglycol monomethyl ether acetate and diethyleneglycol monobutyl ether acetate.
- [0179] In another very preferred embodiment the polyalkyleneglycol monoalkyl ether is selected from the group consisting of triethyleneglycol monobutyl ether and tripropyleneglycol monomethylether.
- [0180] In another very preferred embodiment, the organic solvent based pigmented inkjet ink has a liquid phase consisting of one or more polyalkyleneglycol derivatives and a mixture of polyalkyleneglycol dialkylethers.
- [0181] The organic solvent based pigmented inkjet ink may include a small amount of an organic solvent selected from the group consisting of alcohols, ketones, esters, ethers, glycols and polyglycols and derivatives thereof, lactones, N-containing solvents such as amides.
- [0182] Examples of suitable alkylene glycol mono alkyl ethers include ethylene glycol mono methyl ether, ethylene glycol mono ethyl ether, ethylene glycol mono propyl ether, ethylene glycol mono butyl ether, ethylene glycol mono hexyl ether, ethylene glycol mono 2-ethyl-hexyl ether, ethylene glycol mono phenyl ether, propylene glycol mono methyl ether, propylene glycol mono ethyl ether, propylene glycol mono n-propyl ether, propylene glycol mono n-butyl ether, propylene glycol mono iso-butyl ether,

propylene glycol mono t-butyl ether and propylene glycol mono phenyl ether.

- [0183] Examples of suitable alkylene glycol dialkyl ethers include ethylene glycol dimethyl ether, ethylene glycol diethyl ether, ethylene glycol methyl ethyl ether, ethylene glycol dibutyl ether, propylene glycol dimethyl ether, propylene glycol diethyl ether and propylene glycol dibutyl ether.
- [0184] Examples of suitable polyalkylene glycol mono alkyl ethers include diethylene glycol mono methyl ether, diethylene glycol mono ethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono n-butyl ether, diethylene glycol mono hexyl ether, triethylene glycol mono methyl ether, triethylene mono ethyl ether, triethylene glycol mono butyl ether, dipropylene mono methyl ether, dipropylene glycol mono ethyl ether, dipropylene glycol n-propyl ether, dipropylene glycol mono n-butyl ether, dipropylene mono t-butyl ether, tripropylene glycol mono methyl ether, tripropylene glycol mono ethyl ether, tripropylene glycol mono n-propyl ether and tripropylene glycol mono n-butyl ether.
- [0185] Examples of suitable polyalkylene glycol dialkyl ethers include diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, diethylene glycol diethyl ether, triethylene glycol diethyl ether, diethylene glycol methyl ethyl ether, triethylene glycol methyl ethyl ether, dipropylene glycol dimethyl ether, dipropylene glycol diethyl ether, dipropylene di n-propyl ether, dipropylene di t-butyl ether, tripropylene glycol dimethyl ether and tripropylene glycol diethyl ether.
- [0186] Examples of suitable glycol esters include ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, ethylene glycol monopropyl ether acetate, ethylene glycol monobutyl ether acetate, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether acetate and propylene glycol monomethyl ether propionate.
- [0187] Suitable commercial glycol ether solvents include CellosolveTM solvents and CarbitolTM solvents from UNION CARBIDE, EktasolveTM solvents from EASTMAN, DowanolTM solvents from DOW, OxitollTM solvents, DioxitollTM

solvents, Proxitoll™ solvents and Diproxitoll™ solvents from SHELL CHEMICAL and Arcosolv™ solvents from LYONDELL.

- [0188] Lactones are compounds having a ring structure formed by ester bonds and can be of the γ -lactone (5-membered ring structure), δ -lactone (6-membered ring structure) or ϵ -lactone (7-membered ring structure) types. Suitable examples of lactones include γ -butyrolactone, γ -valerolactone, γ -hexalactone, γ -heptalactone, γ -octalactone, γ -nonalactone, γ -decalactone, γ -undecalactone, δ -valerolactone, δ -hexalactone, δ -heptalactone, δ -octalactone, δ -nonalactone, δ -decalactone, δ -undecalactone and ϵ -caprolactone.
- [0189] Suitable examples of N-containing organic solvents include 2-pyrrolidone, N-methylpyrrolidone, N,N-dimethylacetamid, N,N-dimethylformamid, acetonitril and N,N-dimethyldodecanamide.

Polymer Latex Binders

- [0190] The aqueous pigmented inkjet inks may contain a polymeric latex binder.
- [0191] The polymer latex is not particularly limited as long as it has stable dispersibility in the ink composition. There is no limitation on the main chain skeleton of the water-insoluble polymer. Examples of the polymer include a vinyl polymer and a condensed polymer (e.g., an epoxy resin, polyester, polyurethane, polyamide, cellulose, polyether, polyurea, polyimide, and polycarbonate). Among the above, a vinyl polymer is particularly preferable because of easily controlled synthesis.
- [0192] In a particularly preferred embodiment the polymer latex is a polyurethane latex, more preferably a self-dispersible polyurethane latex. The polymer latex binder in the one or more aqueous inkjet inks is preferably a polyurethane based latex binder for reasons of compatibility with the thermosetting resin.
- [0193] The polymer latex in the invention is preferably a self-dispersing polymer latex, and more preferably a self-dispersing polymer latex having a carboxyl group, from the viewpoint of ejecting stability and stability of the liquid (particularly, dispersion stability) when using a colour pigment. The self-dispersing polymer latex means a latex of a water-insoluble polymer that does not contain a free emulsifier and that can get into a dispersed

state in an aqueous medium even in the absence of other surfactants due to a functional group (particularly, an acidic group or a salt thereof) that the polymer itself has.

- [0194] In preparing a self-dispersing polymer latex, preferably a monomer is used selected from the group consisting of an unsaturated carboxylic acid monomer, an unsaturated sulfonic acid monomer, and an unsaturated phosphoric acid monomer.
- [0195] Specific examples of the unsaturated carboxylic acid monomer include acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, citraconic acid, and 2-methacryloyloxy methylsuccinic acid. Specific examples of the unsaturated sulfonic acid monomer include styrene sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, 3-sulfopropyl (meth)acrylate, and bis-(3-sulfopropyl)-itaconate. Specific examples of the unsaturated phosphoric acid monomer include vinyl phosphoric acid, vinyl phosphate, bis(methacryloyxyethyl)phosphate, diphenyl-2-acryloyloxyethyl phosphate, diphenyl-2-methacryloyloxyethyl phosphate, and dibutyl-2-acryloyloxyethyl phosphate.
- [0196] The latex binder polymer particles preferably have a glass transition temperature (Tg) of 30°C or more.
- [0197] The minimum film-forming temperature (MFT) of the polymer latex is preferably -25 to 150°C, and more preferably 35 to 130 °C.

Biocides

- [0198] Suitable biocides for the aqueous inkjet inks include sodium dehydroacetate, 2-phenoxyethanol, sodium benzoate, sodium pyridinethion-1-oxide, ethyl p-hydroxybenzoate and 1,2-benzisothiazolin-3-one and salts thereof.
- [0199] Preferred biocides are Proxel™ GXL and Proxel™ Ultra 5 available from ARCH UK BIOCIDES and Bronidox™ available from COGNIS.
- [0200] A biocide is preferably added in an amount of 0.001 to 3.0 wt.%, more preferably 0.01 to 1.0 wt. %, each based on the total weight of the pigmented inkjet ink.

Surfactants

[0201] The one or more pigmented inkjet inks may contain at least one surfactant. The surfactant(s) can be anionic, cationic, non-ionic, or zwitter-ionic and are usually added in a total quantity less than 5 wt% based on the total weight of the inkjet ink and particularly in a total less than 2 wt% based on the total weight of the inkjet ink.

[0202] The one or more pigmented inkjet inks preferably have a surface tension between 18.0 and 45.0 mN/m at 25°C, more preferably between a surface tension between 21.0 and 39.0 mN/m at 25°C.

[0203] Suitable surfactants for the pigmented inkjet inks include fatty acid salts, ester salts of a higher alcohol, alkylbenzene sulphonate salts, sulphosuccinate ester salts and phosphate ester salts of a higher alcohol (for example, sodium dodecylbenzenesulphonate and sodium dioctylsulphosuccinate), ethylene oxide adducts of a higher alcohol, ethylene oxide adducts of an alkylphenol, ethylene oxide adducts of a polyhydric alcohol fatty acid ester, and acetylene glycol and ethylene oxide adducts thereof (for example, polyoxyethylene nonylphenyl ether, and SURFYNOL™ 104, 104H, 440, 465 and TG available from AIR PRODUCTS & CHEMICALS INC.).

[0204] Preferred surfactants are selected from fluoro surfactants (such as fluorinated hydrocarbons) and/or silicone surfactants.

[0205] The silicone surfactants are preferably siloxanes and can be alkoxylated, polyester modified, polyether modified, polyether modified hydroxy functional, amine modified, epoxy modified and other modifications or combinations thereof. Preferred siloxanes are polymeric, for example polydimethylsiloxanes. Preferred commercial silicone surfactants include BYK™ 333 and BYK™ UV3510 from BYK Chemie.

[0206] A particularly preferred commercial fluorosurfactant is Capstone™ FS3100 from DU PONT.

Humectants

[0207] Suitable humectants include triacetin, N-methyl-2-pyrrolidone, 2-pyrrolidone, glycerol, urea, thiourea, ethylene urea, alkyl urea, alkyl thiourea, dialkyl urea and dialkyl thiourea, diols, including ethanediols, propanediols, propanetriols, butanediols, pentanediols, and hexanediols;

glycols, including propylene glycol, polypropylene glycol, ethylene glycol, polyethylene glycol, diethylene glycol, tetraethylene glycol, and mixtures and derivatives thereof. Preferred humectants are 2-pyrrolidone, glycerol and 1,2-hexanediol, since the latter were found to be the most effective for improving inkjet printing reliability in an industrial environment.

[0208] The humectant is preferably added to the inkjet ink formulation in an amount of 0.1 to 35 wt% of the formulation, more preferably 1 to 30 wt% of the formulation, and most preferably 3 to 25 wt% of the formulation.

pH adjusters

[0209] The aqueous inkjet inks may contain at least one pH adjuster. Suitable pH adjusters include NaOH, KOH, NEt₃, NH₃, HCl, HNO₃, H₂SO₄ and (poly)alkanolamines such as triethanolamine and 2-amino-2-methyl-1-propaniol. Preferred pH adjusters are triethanol amine, NaOH and H₂SO₄.

Preparation of Inkjet Inks

[0210] The one or more pigmented inkjet inks may be prepared by precipitating or milling the colour pigment in the dispersion medium in the presence of the polymeric dispersant, or simply by mixing a self-dispersible colour pigment in the ink.

[0211] Mixing apparatuses may include a pressure kneader, an open kneader, a planetary mixer, a dissolver, and a Dalton Universal Mixer. Suitable milling and dispersion apparatuses are a ball mill, a pearl mill, a colloid mill, a high-speed disperser, double rollers, a bead mill, a paint conditioner, and triple rollers. The dispersions may also be prepared using ultrasonic energy.

[0212] If the inkjet ink contains more than one pigment, the colour ink may be prepared using separate dispersions for each pigment, or alternatively several pigments may be mixed and co-milled in preparing the dispersion.

[0213] The dispersion process can be carried out in a continuous, batch or semi-batch mode.

[0214] The preferred amounts and ratios of the ingredients of the mill grind will vary widely depending upon the specific materials and the intended applications. The contents of the milling mixture comprise the mill grind and the milling media. The mill grind comprises pigment, dispersant and a

liquid carrier such as water. The pigment is usually present in the mill grind at 1 to 50 wt%, excluding the milling media. The weight ratio of pigment over dispersant is 20:1 to 1:2.

- [0215] The milling time can vary widely and depends upon the pigment, mechanical means and residence conditions selected, the initial and desired final particle size, etc. In the present invention pigment dispersions with an average particle size of less than 100 nm may be prepared.
- [0216] After milling is completed, the milling media is separated from the milled particulate product (in either a dry or liquid dispersion form) using conventional separation techniques, such as by filtration, sieving through a mesh screen, and the like. Often the sieve is built into the mill, e.g. for a bead mill. The milled pigment concentrate is preferably separated from the milling media by filtration.
- [0217] In general it is desirable to make the colour ink in the form of a concentrated mill grind, which is subsequently diluted to the appropriate concentration for use in the ink-jet printing system. This technique permits preparation of a greater quantity of pigmented ink from the equipment. If the mill grind was made in a solvent, it is diluted with water and optionally other solvents to the appropriate concentration. If it was made in water, it is diluted with either additional water or water miscible solvents to make a mill grind of the desired concentration. By dilution, the ink is adjusted to the desired viscosity, colour, hue, saturation density, and print area coverage for the particular application.

EXAMPLES

Materials

- [0218] All materials used in the following examples were readily available from standard sources such as Aldrich Chemical Co. (Belgium) and Acros (Belgium) unless otherwise specified. The water used was demineralized water.
- [0219] PR254 is the abbreviation for C.I. Pigment Red 254 for which IrgazinTM DPP Red BTR from Ciba Specialty Chemicals was used.
- [0220] Edaplan is an abbreviation used for EdaplanTM 482, a polymeric dispersant from MUNZING.

- [0221] Proxel is an abbreviation used for the biocide Proxel™ Ultra 5 from AVECIA.
- [0222] PEG 200 is a polyethylene glycol having an average molecular mass of 200 from CLARIANT.
- [0223] TEA is triethanol amine.
- [0224] Syloid™ 72 is a synthetic, amorphous silica appearing as a white free flowing powder available from GRACE.
- [0225] PVA-sol is a 7.5 wt% solution of a polyvinylalcohol polymer Erkol™ W48/20 available from ERKOL.

Measurement Methods

1. Surface Tension

- [0226] The static surface tension of the aqueous inkjet inks was measured with a KRÜSS tensiometer K9 from KRÜSS GmbH, Germany at 25°C after 60 seconds.

2. Viscosity

- [0227] The viscosity of an inkjet ink was measured, using a Brookfield DV-II+ viscometer at 32°C at a shear rate of 1,000 s⁻¹.

3. Average Particle Size

- [0228] An ink sample is diluted with ethyl acetate to a pigment concentration of 0.002 wt%. The average particle size of pigment particles is determined with a Nicomp™ 30 Submicron Particle Analyzer based upon the principle of dynamic light scattering.
- [0229] For good ink jet characteristics (jetting and print quality) the average particle size of the dispersed particles is preferably below 250 nm.

4. Sharpness (S)

- [0230] The sharpness of a printed image after the DPL process was evaluated in accordance with a criterion on a scale of 0 to 6 as described in Table 1.

- [0231]

Table 1

Criterion	Observation
0	Unacceptable, completely distorted image
1	Very bad, very rough unsharp edges
2	Bad, rough edges

3	Acceptable sharpness
4	Good sharpness
5	Very good sharpness
6	Excellent sharpness

5. Ink Bleeding (IB)

[0232] The colour bleeding of inks occurs due to the water vapour produced during the DPL process, which deplaces colour pigments. An evaluation was made in accordance with a criterion on a scale of 0 to 6 as described in Table 2.

[0233]

Table 2

Criterion	Observation
0	Unacceptable, completely distorted image
1	Very bad, very large amount of bleeding visible by the naked eye
2	Bad, large amount of bleeding visible by the naked eye
3	Acceptable, some bleeding visible by the naked eye
4	Good, almost no bleeding visible by the naked eye
5	Very good, some bleeding visible by microscope
6	Excellent, no bleeding visible by microscope

6. Homogeneity (H)

[0234] The homogeneity was evaluated on a binary scale (OK / Not OK) in rectangles of 9 cm x 2.5 cm present in a technical colour pattern.

7. Adhesion (A)

[0235] Adhesion is evaluated by a cross-cut test according to ISO2409:1992(E). Paints . *International standard*. 1992-08-15. using a Braille No.1536 Cross Cut Tester from BRAIVE INSTRUMENTS with spacing of a 1 mm between cuts and using a weight of 600 g, in combination with a Tesatape™ 4104 PVC tape. The evaluation was made in accordance with a criterion described by Table 3.

Table 3

Criterion	Observation
0	The edges of the cuts are completely smooth: none of the squares of the lattice is detached (=perfect adhesion).

1	Detachment of small flakes at the intersections of the cuts. A cross-cut area not greater than 5% is affected.
2	Flaked along the edges and/or at the intersections of the cuts. A cross-cut area greater than 5%, but not significantly greater than 15%, is affected.
3	Flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area significantly greater than 15%, but not significantly greater than 35%, is affected.
4	Flaked along the edges of the cuts in large ribbons, and/or some of the squares has detached partly or wholly. A cross-cut area significantly greater than 35%, but not significantly greater than 65%, is affected.
5	Any degree of flaking that cannot even be classified by classification 4

[0236]

Example 1

[0237]

Preparation of Aqueous Pigmented Inkjet Ink

[0238] A concentrated aqueous pigment dispersion was made by mixing a composition according to Table 4 for 30 minutes using a Disperlux™ Yellow mixer.

Table 4

Component	Concentration (wt%)
PR254	15.00
Edaplan	15.00
Proxel	0.02
Water	to complete 100.00 wt%

[0239] The concentrated aqueous pigment dispersion was then milled using a Dymomill™ KDL with 0.04 mm yttrium stabilized zirconium beads YTZ™ Grinding Media (available from TOSOH Corp.). The mill was filled to half its volume with the grinding beads and the dispersion was milled for 3 hours at flow rate of 200 mL/min and a rotation speed of 15 m/s. After milling, the dispersion is separated from the beads. The concentrated

aqueous pigment dispersion served as the basis for the preparation of the inkjet ink.

[0240] A red pigmented inkjet ink “Ink R” was prepared by diluting the concentrated pigment dispersion with the other ink components according to Table 7, wherein the weight % is based on the total weight of the ink. The component TEA was used to set the pH to 8.2. Water was added to complete the ink to the desired pigment concentration.

[0241]

Table 5

Component (in wt%)	Ink R
PR254	2.70
Edaplan	2.70
1,2-Hexanediol	3.00
Glycerine	20.00
PEG 200	18.00
Proxel	0.01
TEA	0.50
Water	to complete 100.00wt%
Viscosity at 32°C	5.3 mPa.s
Surface Tension	35.6 mN/m
Average particle size	150 nm

Preparation of Coating Solutions for Ink Acceptance Layers

[0242] The coating solutions DIS-1 to DIS-4 were all prepared in the same manner using the amounts listed in Table 6. The inorganic pigment Syloid™ 72 was dispersed for 30 minutes using a Disperlux™ mixer in PVA-sol. Ammonia was added to the dispersion to raise the pH above 8.0. The pH of each coating solution was measured at 25°C.

[0243]

Table 6

g of Component	DIS-1	DIS-2	DIS-3	DIS-4
PVA-sol	88.89	66.67	44.44	26.67
Syloid™ 72	3.33	5.00	6.67	8.00

Ammonia	0.24	0.30	0.29	0.29
Water	7.54	28.03	48.60	65.04
<hr/>				
pH	8.9	8.4	8.2	8.4

[0244] The coating solution DIS-5 was prepared by diluting 83 g of PVA-sol with 968 g of water. No inorganic pigment was included in DIS-5.

Preparation of Ink Acceptance Layers

[0245] An 80 g/m² porous paper used for decor printing was impregnated with an aqueous solution containing 60 wt% of melamine-formaldehyde based resin having a formaldehyde to melamine ratio of 1.7, and dried to a residual humidity of about 8 g/m².

[0246] An ink acceptance layer was coated on the impregnated paper in accordance with Table 7 by means of a bar coater, providing a wet layer thickness of 20 µm or 40 µm micron. The coated samples were dried in an oven for 1 minute at 125°C.

[0247]

Table 7

Sample	Coating Solution	Ink Acceptance Layer	
		Wet coating thickness (µm)	Dry Weight (g/m ²)
COMP-1	DIS-1	40	4.0
COMP-2	DIS-2	40	4.0
INV-1	DIS-3	40	4.0
INV-2	DIS-4	40	4.0
INV-3	DIS-3	20	2.0
INV-4	DIS-4	20	2.0
COMP-3	DIS-5	40	3.2
COMP-4	DIS-5	20	1.6
COMP-5	DIS-1	40	4.0
COMP-6	DIS-2	40	4.0
INV-5	DIS-3	40	4.0
INV-6	DIS-4	40	4.0

COMP-7	DIS-5	40	3.2
COMP-8	DIS-1	40	4.0
COMP-9	DIS-2	40	4.0
INV-7	DIS-3	40	4.0
INV-8	DIS-4	40	4.0
COMP-10	DIS-5	40	3.2
COMP-11	DIS-1	40	4.0
COMP-12	DIS-3	40	4.0
INV-9	DIS-4	40	4.0
COMP-13	DIS-5	40	3.2

Results and Evaluation

[0248] Decorative layers were obtained according to Table 8 by printing a technical colour pattern (see Figure 5 and Figure 6) on the melamine-formaldehyde based resin impregnated paper using the Ink R of Table 5 and a KJ4B Kyocera print head at a head temperature of 32°C at 600 dpi. The printed samples were dried for 30 minutes at 50°C. The amount of jetted colour pigment C (=PR254) is listed in Table 8 as g C/m². The P/B ratio is the weight ratio of the inorganic pigment P (=Syloid™ 72) over the polymeric binder. The P/C ratio is the weight ratio of the inorganic pigment P (=Syloid™ 72) over the jetted colour pigment C (=PR254).

[0249] An assembly was made as shown in Figure 3, wherein the prepared decorative layer was interposed between a HDF core and a protective layer of unprinted melamine-formaldehyde resin impregnated paper containing aluminium oxide for durability. The assembly was then heat pressed for 20 seconds at 195°C into a laminate by a DPL process using 138 bar and 50 kg/cm² as settings.

[0250] The resulting floor laminates were examined for sharpness (S), ink bleeding (IB), homogeneity (H) and adhesion (A). The results are shown in Table 8.

[0251]

Table 8

Sample	P/B ratio	Ink g C/m ²	P/C ratio	Evaluation			
				(S)	(IB)	(H)	(A)

COMP-1	0.5	0.18	7.4	1	1	Not OK	5
COMP-2	1.0	0.18	11.1	2	2	OK	5
INV-1	2.0	0.18	14.8	4	4	OK	5
INV-2	4.0	0.18	17.8	6	5	OK	5
INV-3	2.0	0.18	7.4	3	4	OK	5
INV-4	4.0	0.18	8.9	4	5	OK	5
COMP-3	0.0	0.18	0.0	6	2	Not OK	5
COMP-4	0.0	0.18	0.0	6	4	Not OK	5
COMP-5	0.5	0.36	3.7	0	0	Not OK	5
COMP-6	1.0	0.36	5.6	1	1	Not OK	5
INV-5	2.0	0.36	7.5	3	4	OK	5
INV-6	4.0	0.36	8.9	5	4	OK	5
COMP-7	0.0	0.36	0.0	5	5	Not OK	5
COMP-8	0.5	0.54	2.5	0	0	Not OK	5
COMP-9	1.0	0.54	3.7	1	0	Not OK	5
INV-7	2.0	0.54	5.0	3	4	OK	5
INV-8	4.0	0.54	6.0	4	4	OK	5
COMP-10	0.0	0.54	0.0	5	3	Not OK	5
COMP-11	0.5	0.72	1.9	0	0	Not OK	5
COMP-12	2.0	0.72	3.7	3	3	OK	5
INV-9	4.0	0.72	4.5	4	4	OK	5
COMP-13	0.0	0.72	0.0	4	4	Not OK	5

[0252] From Table 8, it should be clear that good results for sharpness, ink bleeding, homogeneity and adhesion if the P/B ratio is higher than 1.5 and the P/C ratio is higher than 4.0

Reference Signs List

[0253]

Table 9

- 11 Paper manufacturer
- 12 Paper roll
- 13 Decor printer
- 14 Gravure printing

- 15 Inkjet printing
- 16 Decor Paper roll
- 17 Warehouse
- 18 Impregnation
- 19 Cutting to size
- 20 Floor laminate manufacturer
- 21 Floor laminate
- 30 Decorative panel
- 31 Core layer
- 32 Groove
- 33 Tongue
- 34 Decorative layer
- 35 Protective layer
- 36 Balancing layer

[0254]

Claims

1. A method for manufacturing decorative laminates including the steps of:
 - a) impregnating a paper substrate with a thermosetting resin by submersion of the paper substrate in a bath of thermosetting resin;
 - b) applying on the thermosetting resin impregnated paper substrate an ink acceptance layer containing an inorganic pigment P and a polymeric binder B having a weight ratio P/B of inorganic pigment to polymeric binder of larger than 1.5;
 - c) jetting on the ink acceptance layer a colour pattern with one or more aqueous pigmented inkjet inks and/or organic solvent based pigmented inkjet inks containing a colour pigment C; and
 - d) heat pressing the thermosetting paper into a decorative laminate, wherein the weight ratio P/C of the inorganic pigment of the ink acceptance layer to the jetted colour pigment in the colour pattern is larger than 4.0; wherein the dry weight of colour pigments jetted by the one or more aqueous pigmented inkjet inks and/or organic solvent based pigmented inkjet inks is at least 0.30 g/m²; and wherein the ink acceptance layer has a total dry weight of between 2.0 g/m² and 10.0 g/m².
2. The method according to claim 1, wherein step d) includes embossing a relief into the decorative laminate.
3. The method according to claim 1 or claim 2 wherein the thermosetting resin is selected from the group consisting of melamine-formaldehyde based resins, ureum-formaldehyde based resins and phenol-formaldehyde based resins.
4. The method according to any one of claims 1 to 3, wherein the inorganic pigment is selected from the group consisting of alumina hydrates, aluminum oxides, aluminum hydroxides, aluminum silicates, and silicas.
5. The method according to any one of claims 1 to 4, wherein the polymeric binder is a water soluble polymeric binder including a hydroxyl group as a hydrophilic structural unit and having a water solubility of more than 1 g/L water.
6. The method according to any one of claims 1 to 5, wherein the jetting of the ink is performed in a single pass inkjet printing mode.
7. The method according to any one of claims 1 to 6, wherein one or more

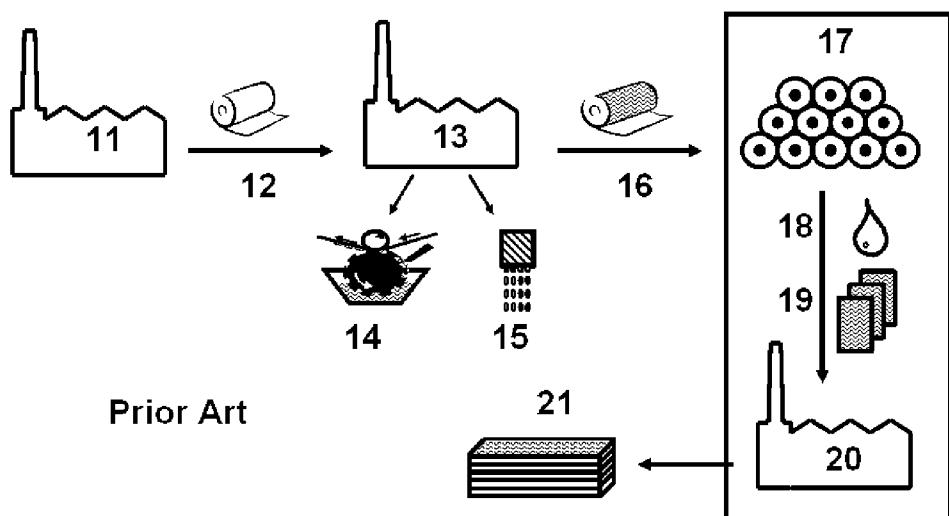
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organic solvent based pigmented inkjet inks include at least one polyalkyleneglycol dialkylether having a molecular weight of at least 250.

8. The method according to any one of claims 1 to 7, wherein the paper substrate is a bulk coloured paper.
9. The method according to any one of claims 1 to 8, wherein the aqueous pigmented inkjet ink includes at least one polymeric latex.
10. The method according to any one of claims 1 to 9, wherein at least three aqueous pigmented inkjet inks and/or organic solvent based pigmented inkjet inks include a pigment selected from the group consisting of carbon black, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:4, C.I. Pigment Yellow 151, C.I. Pigment Yellow 180, C.I. Pigment Yellow 74, C.I. Pigment Red 254, C.I. Pigment Red 176, C.I. Pigment Red 122, and mixed crystals thereof.

Drawings



Prior Art

Fig. 1

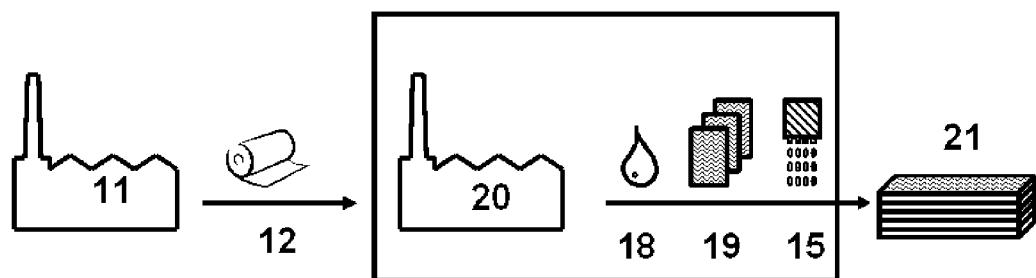


Fig. 2

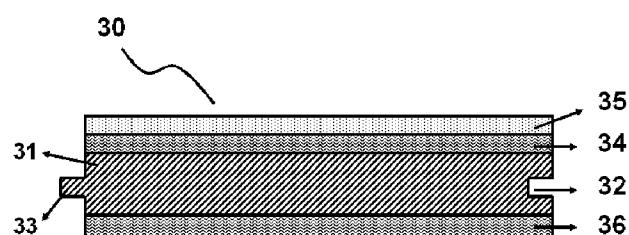


Fig. 3

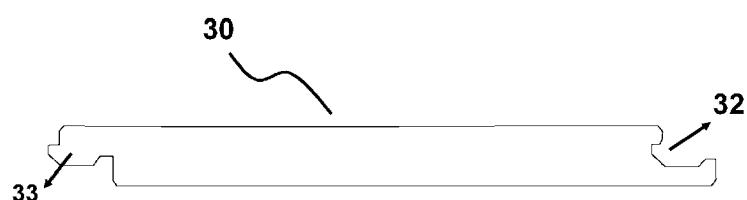


Fig. 4

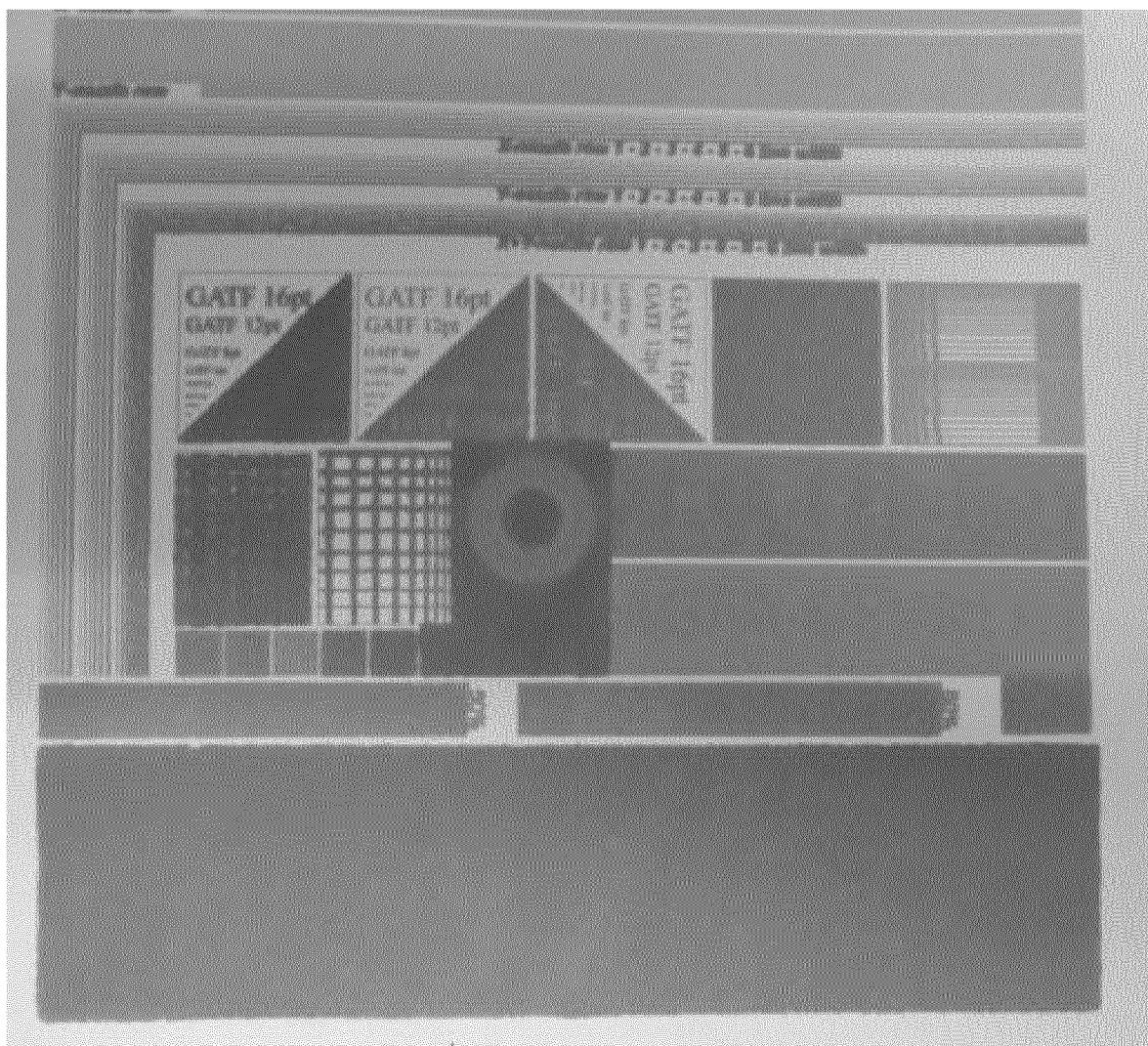


Fig.5

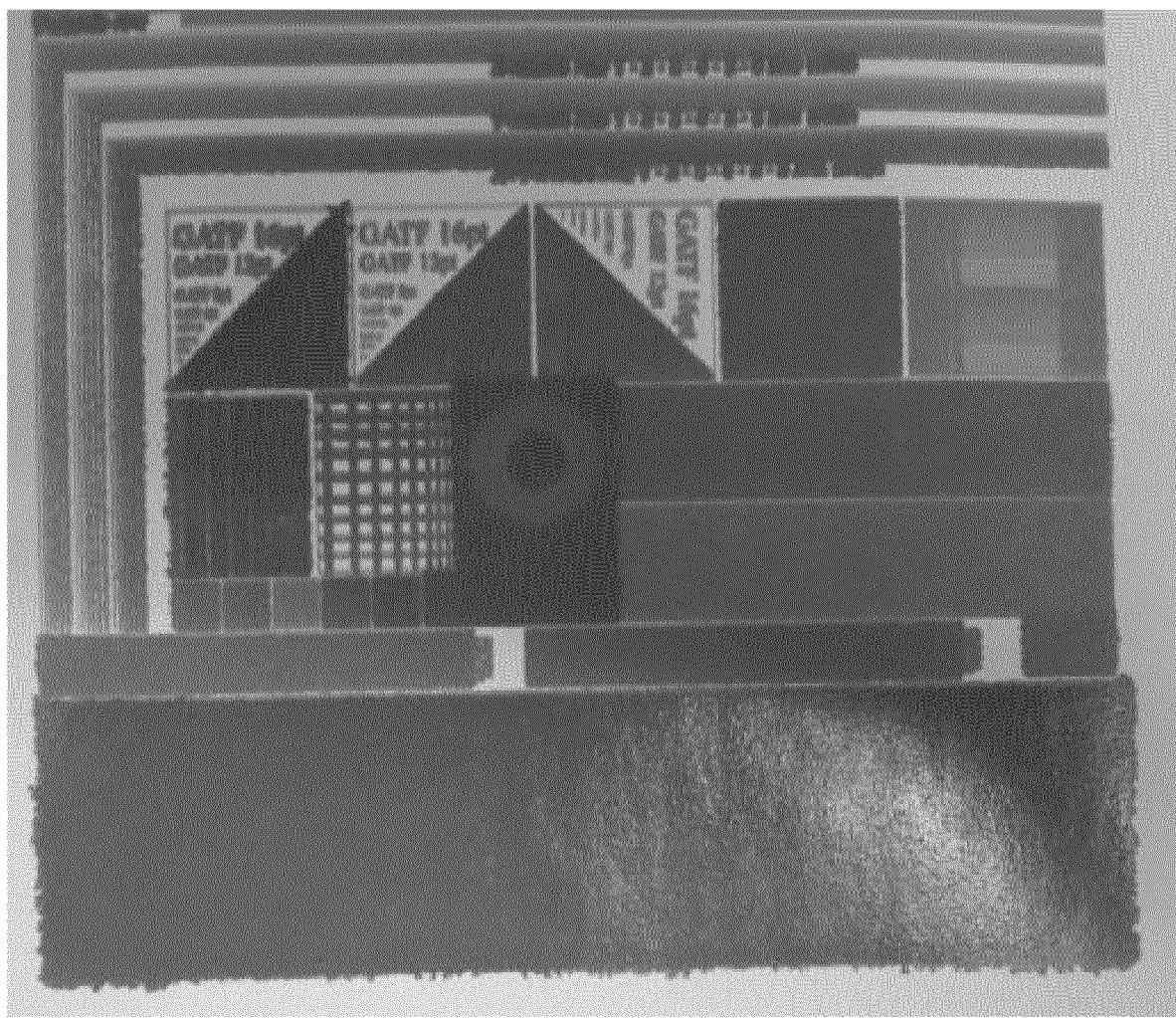


Fig.6

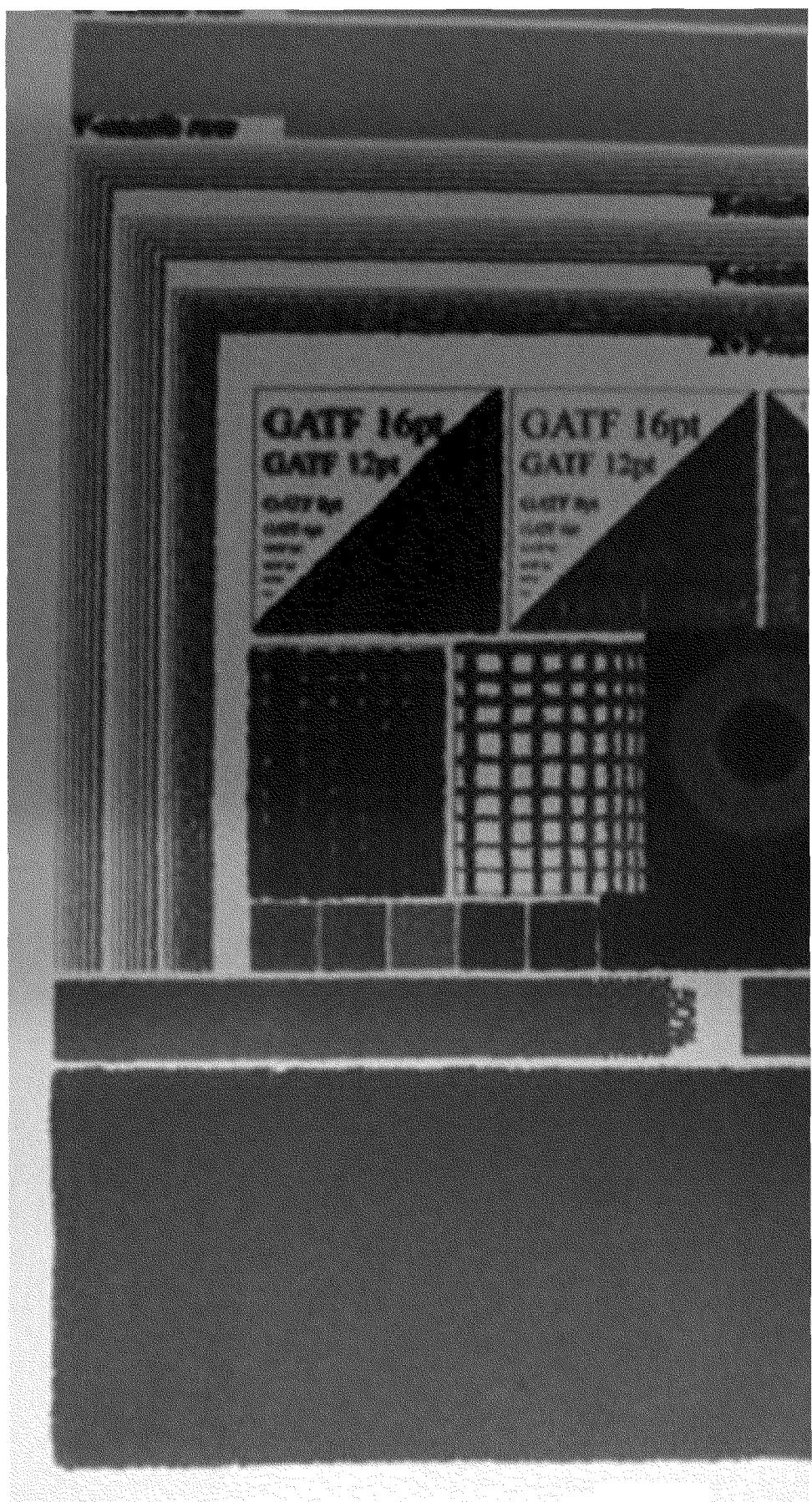


Fig.7

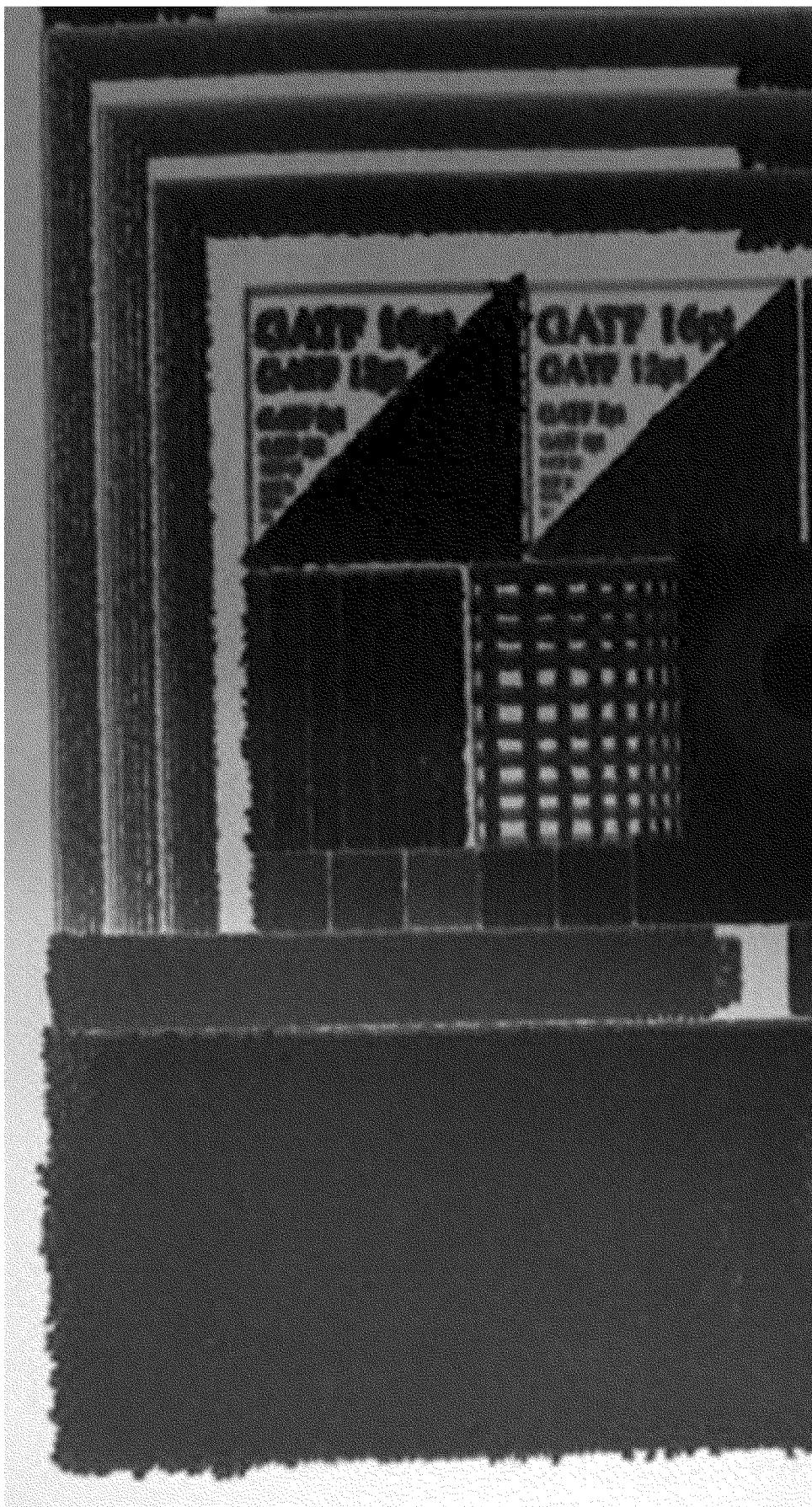


Fig.8