The invention provides a process for producing a wallcovering comprising the steps of: providing a substrate; and providing on said substrate a polyester or polyurethane coating, thus obtaining a coated substrate; and - printing directly onto said coated substrate ink comprising a sublimable dye, thus obtaining a printed coated substrate; and - heating said printed coated substrate to a temperature sufficient to sublimate said water-based ink, thus obtaining a dye sublimated substrate, wherein said coating comprises one or more polymers selected from polyester, polyurethane and polyacrylate and optionally at least one fixing agent.
Title: Wallcovering and process for producing wallcoverings

The invention is directed to wallcoverings as well as to a process for producing wallcoverings.

Recently, the printing of a personal design on wallcoverings has become increasingly popular. Such wallcoverings are typically made of vinyl and may be printed directly with either a solvent ink or a UV-curable ink using inkjet printing.

Solvent inks work through mechanisms of penetration, reaction and/or dissolution in vinyl. A disadvantage of using solvent ink is that this ink is not suitable for printing on substrates different than vinyl, such as polyester. Solvent inks further contain large amounts of volatile organic compounds (VOCs), which may raise health and/or environmental concerns.

UV-curable inks have to be cured after printing by exposure to UV-light. An advantage of using UV-curable ink is that this ink can also be applied to other substrates than vinyl, such as polyester. A disadvantage using UV-curable ink is that UV-curable ink will stay on the surface of the substrate even after curing, providing the wallpaper with an often unwanted relief on the surface. Also there is a danger of damaging the print during application, because the printing is on top of the substrate.

Disadvantages of using vinyl for wallcoverings, in particular wallcoverings made from polyvinyl chloride (PVC), is that it comprises halogens and therefore poses threats to human and environmental health. Additionally, vinyl may be expensive to recycle.

An alternative printing method known in the art is dye-sublimation. In dye-sublimation, a sublimable dye is heated up until it turns into a gas, at which point it may be diffused onto a printing media where it solidifies. The dye sublimation inks are a pigment suspended in a liquid solvent, like water. A disadvantage of using these dyes is that they are not suitable for color printing onto paper substrates, because the ink can be smeared or scraped or rubbed off of such substrates.
An example of a dye-sublimation technique is sublimation dye thermal transfer recording. In this technique, an image is printed with a sublimable dye on a sublimation dye transfer paper as a reverse image of the final design, which is then transferred onto a substrate, usually polyester, by heating with a thermal head or a laser beam (see e.g. EP-A-O 709 230). Sublimation dye thermal transfer recording is currently widely used to print on polyester or other synthetic fabrics, such as t-shirts, flags, etc. Disadvantage of this technique is that it involves indirect printing, which increases the complexity of the printing process. Also thermal transfer printing gives less sharp images than direct printing. It adds an additional step in the process, which means lower production speeds and therefore higher costs.

WO-A- 9830397 describes a method for printing a wall covering material, wherein a decorative pattern is printed on a sublimation dye transfer paper, which transfer paper is then brought in overlapping contact with a paper-like, non-woven web material on a heated surface. Thus, the decorative pattern is transferred from the transfer paper to the web material. The transfer paper is then separated from the web material and may be disposed after use.

Thermal transfer image-receiving sheets are known from e.g. EP-A-O 709 230 and US-A-5 856 268. These sheets are used in thermal transfer recording, such as e.g. the method as described hereinabove, and form the final carrier of the image. A thermal transfer image-receiving sheet may comprise a substrate sheet provided with an intermediate layer and a receptive layer. The substrate sheet may be made from paper or polyester. The receiving layer serves to receive a dye which, upon heating, is transferred from a thermal transfer sheet and, at the same time, to hold thereon a formed image. Such a receiving layer is typically a resin coating, e.g. polyolefin resins, vinyl resins, polyester resins or cellulosic resins. The intermediate layer is typically a resin layer that varies in composition depending on the application of the thermal transfer image-receiving sheet.
Disadvantages of the methods and techniques described hereinabove is that the obtained printed color images often lack in sharpness and brightness.

It is an object of the present invention to provide a method that overcomes at least in part the disadvantages in the prior art as described hereinabove.

In a first aspect, this object is met by providing a process for producing a wallcovering comprising the steps of

- providing a substrate;
- providing on said substrate a coating, thus obtaining a coated substrate;
- printing directly onto said coated substrate an ink comprising a sublimable dye, thus obtaining a printed coated substrate;
- heating said printed coated substrate to a temperature sufficient to sublimate said water-based ink, thus obtaining a dye sublimated substrate,

wherein said coating comprises one or more polymers selected from polyester, polyurethane and polyacrylates (or polyacrylics) and optionally at least one fixing agent.

During the heating step, the ink comprising the sublimable dye will transfer into the coating, where it is retained.

Preferred polyesters are sulfopolyester types, i.e. polyesters containing a sulfonomomer containing a -SO_3 group attached to an aromatic nucleus. Viscosity is in the low range, typically up to 500 mPa·s (measured using a Rotation Viscometer using plate and cone at 23 °C). The glass transition temperature of the polyester (Tg) can be between 20 and 125 °C.

When polyurethane is used, it is preferably water dispersed, typically with a viscosity from 10 - 100 mPa·s (Rotation Viscometer using plate and cone at 23 °C. Tg is typically from 20 to 45 °C.
When polyacrylate is used, it is preferably selected from the selfcrosslinking types, having a viscosity that is typically up to 500 mPa·s (Rotation Viscometer using plate and cone at 23 °C) and a $T_g$ that ranges typically from 22 to $>200$ °C.

Preferably the coating is hydrophilic. The coating can be made hydrophilic by adding hydrophilic additives like starch, carboxymethyl cellulose (CMC), polyvinyl alcohol (PVOH) or combinations thereof. The advantage of a hydrophilic coating and/or the addition of such compounds is that it improves the printability of the coating. In particular, it will improve the transfer and retention of the water-based ink in the coating.

The coating may further comprise one or more emulsifying agents. Suitable emulsifying agents are alginates and glycerol. These can be applied in amounts typically ranging from 0.5 to 2.0 wt.% (all weight percentages as used herein are based on the total weight of the coating, unless indicated otherwise).

The coating may further comprise one or more surfactants. Suitable surfactants are for instance fatty alcohol, fatty acid soaps or esters and can be applied in amounts typically ranging from 0.1 to 1.0 wt.% (based on the total weight of the coating).

The coating may further comprise one or more pH controlling agents. Suitable pH controlling agents are sodium hydroxide and sulfuric acid. They are typically applied in amounts up to 0.5 wt.% (based on the total weight of the coating).

The coating may comprise one or more fixing agents to improve fixation of the dye in the polymer coating. Preferred fixing agents are selected from cationic substances. More preferably the fixing agent is one or more compounds selected from cationic starch, polydiallyldimethylammonium chloride (polydadmac), poly aluminum chloride (PAC) or quaternary ammonium salts. The fixing agent can be applied in amounts ranging from 1 to 10 wt.% (based on the total weight of the coating).
The coating may further comprise one or more pigments. Suitable pigments are silica, CaC\textsubscript{3}, China Clay and talcum. These compound have an extra beneficial effect in the products of the present invention in that they also provide water absorption. They can be applied in amounts ranging from 0 to 15 wt.%, preferably from 1 to 10 wt.% (based on the total weight of the coating).

The coating may further comprise one or more binders. Suitable binders are starch, Latex Styrene-Butadiene-Rubbers (latex SBR), PVOH and CMC. They can be applied in amounts ranging from 0 to 10 wt.%, preferably from 0.5 to 8 wt.% (based on the total weight of the coating). A binder may form cross-links with the polymers in the coating. This may increase the capacity of the coating for holding and retaining ink, without the risk of smearing of the ink during the heating step (dye sublimation).

The coating may further comprise one or more viscosity controlling agents. Suitable viscosity controlling agents are carboxy methyl cellulose (CMC), polyvinylalcohol (PVOH) or starch. They can be applied in amounts ranging from 0 to 3 wt.%, preferably from 0.5 to 2 wt.% (based on the total weight of the coating).

One of the main advantages of using the process of the present invention is that a superior color gamut can be printed in comparison with the direct printing methods of the prior art that use solvent ink or UV-curable ink. Thus, the process of the present invention yields sharper images and allows for brighter and stronger colors.

The printed images of the dye sublimated substrate according to the present invention lie in the polymer coating. This provides the printed wallcovering with a good durability, as well as nice and smooth looks. It also allows for wallcoverings having a smooth surface.

Furthermore, by applying a coating to the substrate according to the present invention, it becomes possible to print on any surface, including paper substrates. Paper substrates are preferred over vinyl substrates for environmental and health reasons.
A further advantage of the invention is that it allows for the use of water-based ink, which is environmentally friendly. Preferably the ink is therefore a water-based ink.

The process according to the present invention makes it furthermore possible to print directly onto large substrates, such as wallcoverings.

An additional advantage of the coating applied in the process of the present invention is that such a coating makes the wallcovering water-resistant.

The ink used in the method of the invention may be any ink that may suitably contain a sublimable dye. Suitable inks that may be used in the method of the invention are solvent-based inks (i.e. dye-sublimation inks) and water-based inks. Oil-based inks may also be used in the present invention. Preferably, water-based inks are used, because these inks are environmentally friendly.

Preferably, the ink is digitally printed onto the coated substrate. Thus, an image created on a computer can directly be printed onto a coated substrate. The ink is preferably applied using an ink-jet printer. However, any other means with which an image can be digitally printed on a substrate may also be used.

The dye sublimated substrate obtained by the process of the present invention typically has a smooth surface. If desirable, the dye sublimated substrate may be provided with texture. In this case, the process of the present invention further comprises the step of applying texture to the printed dye sublimated substrate. Preferably, this is done by using a texture roller.

Applying structure is preferably conducted after printing of the substrate, because this generally gives a better image. However, sometimes it may be suitable to apply structure, e.g. by using a texture roller, before printing.

The substrate may be any kind of substrate suitable as a substrate for a wallcovering. Preferably, the substrate is made of cellulose or polyester fibers.
The coating applied in the second step of the process of the present invention is preferably made of polyester or polyurethane.

The coating is typically applied in amounts of 5 to 30 g/m² (absolute dry weight), preferably in amounts of 7 to 25 g/m² (absolute dry weight).

The coating may comprise one or more layers. If multiple layers are present, preferably all layers are hydrophilic. The coating may comprise a first layer, which first layer is closest to the substrate, and an outer layer, which layer is furthest away from the substrate. The ink is printed on the outer layer, which is therefore also called the receiving layer.

The outer layer is typically made of polyester or polyurethane and is preferably of the same composition as the first layer. Alternatively, the outer layer has the same polymer composition as the first layer, but comprises a different additive composition.

The first layer is the layer to which the ink is transferred through dye sublimation and which layer eventually holds the ink. The first layer comprises one or more polymers selected from polyester, polyurethane and polyacrylate and optionally at least one fixing agent.

Intermediate layers may be present between the first and outer layer. Such layers may add additional desirable properties to the coating, for example by including certain additives therein. The intermediate layers are preferably made of polyester or polyurethane.

Alternatively, the coating may comprise one layer, which functions both as receiving layer and as the layer that holds the ink after dye sublimation.

Additives may be added to any of the layers present in the coating. For example, flame retardants and UV-catchers may be added. Such additives are preferably added in an amount of 5-10% (flame retardants or more depending on the type) and 1-6% (UV-catchers).

The layers in the coating are preferably transparent or white of color, in particular when water-based inks are used. The reason for this is that
it there is no water-based ink comprising a sublimable dye that gives the color white.

The water-based ink, which is preferably used in the process of the present invention comprises a sublimable dye and an aqueous liquid. The sublimable dyes used in the present invention are disperse dyes, viz. dyes suspended in the aqueous liquid. The disperse dyes can interact with the coating of the present invention. Generally disperse dyes are small, non-ionic molecules, with attached polar functional groups like -NO2 and -CN. The dye molecules are believed to fit between the polymer chains. The polar groups improve the water solubility and the dipolar bonding between dye and polymer. Also the polar groups affect the color of the dye. The dye is generally applied under pressure, at temperatures of 150-200 °C. At this temperature, thermal agitation causes the polymer's structure to become looser and less crystalline, opening gaps for the dye molecules to enter.

Preferred dyes are azo-dyes, in particular aminoazobenzene dyes, heterocyclic aminoazobenzene dyes, dyes based on heterocyclic coupling components and diazo dyes.

In a second aspect, the invention is directed to a wallcovering obtained by the process of the present invention.

In a third aspect, the invention is directed to a coated wallcovering comprising a substrate comprising one or more polymers selected from polyester, polyurethane and polyacrylate and optionally at least one fixing agent.

The coating allows the use of any substrate in the process according to the present invention.

The wallcoverings of the present invention typically have a size of 0.5-3.20 m width and a length of 1 or 2 up to 20 m or more.

The printing of the coated substrate in accordance with the present invention is carried out using (industrial scale) inkjet printers.
Figure 1 shows a schematic representation of one embodiment of the process of the present invention. A paper substrate of typically 1 by 3 meters is provided to coater (1) where a polyester coating is provided on the paper substrate. A pattern created on a computer is digitally printed on the coating with an ink comprising a sublimable dye using ink-jet printer (2). Subsequently, the printed coated substrate is heated to 180 °C using heater (3), causing the dye to sublimate. The thus obtained substrate is then led through a structure roller (4), which applies a relief to the substrate. Thus, a digitally printed wallcovering is obtained.

Example 1. Digital dyesub wall paper

A base paper of (90 g/m² cellulose kraft paper) was coated with the following composition.

A coating mixture was prepared by adding 5 g of Skogin MV (supplier: Acatris) to 500 ml water. This mixture was dispersed during 15 minutes. 100 g of this solution was mixed with 100 g of Hydro-Rez 830 (supplier: Hexion).

This coating composition was brought onto the paper with a K-coater using rod number 5 at speed 10. This resulted in an absolute dry coatweight of 11.9 g/m².

In a separate run a similar piece of paper was coated with rod number 6, giving a coat weight of 13.7 g/m².

The coated papers were printed with an Epson inkjet printer using water based disperse inkjet dyes from Sensient. After printing the paper is was heated for 30 seconds at 180 °C.

After heating the paper was finished and could be used for wallcovering.
Example 2. Digital dyesub wall paper

The same base paper as in Example 1 was coated with a composition that was obtained by mixing 1000 ml water and 150 g of Amylofax PW (supplier: Avebe). This mixture was stirred and heated for 10 minutes at 95 °C to obtain a dispersion. 100 g of this solution was mixed with 100 g of Emuldur 360 (supplier: BASF).

This coating composition was applied to the paper with a K-coater using rod number 7 at speed 10. This resulted in an absolute dry coating weight of 25.4 g/m².

The coated paper was printed with a Roland inkjet printer using solvent based disperse inkjet dyes from Hilord. After printing the paper was heated for 40 seconds at 160 °C.

After heating the paper was finished and could be used for wallcovering.
Claims

1. Process for producing a wallcovering comprising the steps of
   - providing a substrate;
   - providing on said substrate a coating, thus obtaining a coated substrate;
   - printing directly on said coated substrate an ink comprising a sublimable dye, thus obtaining a printed coated substrate;
   - heating said printed coated substrate to a temperature sufficient to sublimate said dye, thus obtaining a dye sublimated substrate,
wherein said coating comprises one or more polymers selected from polyester, polyurethane and polyacrylate.

2. Process according to claim 1, wherein said coated substrate is printed using an ink-jet printer.

3. Process according to any of the previous claims, wherein the ink is a water-based ink or solvent-based ink, preferably a water-based ink.

4. Process according any of the previous claims, wherein the coating further comprises at least one fixing agent selected from from the group consisting of cationic starch, polydiallyldimethylammonium chloride, poly aluminum chloride (PAC) and quaternary ammonium salts.

5. Process according to claim 3 or 4, wherein the amount of fixing agent ranges from 1 to 10 wt.% based on the total weight of the coating.

6. Process according to any of the previous claims, wherein the coating is a hydrophilic coating.

7. Process according to any of the previous claims, wherein the coating further comprises a binder selected from the group consisting of starch, carboxymethyl cellulose (CMC), polyvinyl alcohol (PVOH), Latex Styrene-Butadiene-Rubbers and combinations thereof.
8. Process according to claim 7, wherein the amount of binder ranges from 1 to 10 wt.% based on the total weight of the coating.

9. Process according to any of the previous claims, further comprising the step of applying texture to the printed dye sublimated substrate, preferably by using a texture roller.

10. Process according to any of the previous claims, wherein said coating comprises a first layer closest to the substrate and a second outer layer, wherein the two layers have the same polymer composition, but a different additive composition.

11. Process according to claim 10, wherein the coating comprises one or more intermediate layers, positioned in between the first and second layer.

12. Process according to any of the previous claims, wherein said substrate is made of cellulose or polyester fibers.

13. Process according to any of the previous claims, wherein said ink is a water-based or solvent based ink, which comprises a sublimable disperse dye.

14. Wallcovering obtainable by a process according to any of the previous claims.

15. Wallcovering according to the previous claim, wherein said coating comprises one or more sulfopolyesters.
Fig. 1
**A. CLASSIFICATION OF SUBJECT MATTER**

INV. B41M3/18  
B41M7/00  
E04F13/18  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC.

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

B41M  
E04F

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

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

EPO-Internal, CHEM ABS Data, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
</tr>
</thead>
</table>
| A        | JP 10 309764 A (KIMOTO K.K.)  
paragraphs [0001], [0007], [0016], [0017], [0021] - [0026], [0034] - [0038]  
----- | 1-15 |
| A        | EP 1 586 459 A (AGFA-GEVAERT)  
19 October 2005 (2005-10-19)  
paragraphs [0001], [0015] - [0017], [0053], [0063] - [0070], [0091] - [0095], [0106]; claims 1-16  
----- | 1-15 |
| A        | US 5 631 071 A (A. FUKUNISHI ET AL.)  
20 May 1997 (1997-05-20)  
column 1, line 5 - line 14  
column 1, line 47 - column 2, line 24  
column 5, line 6 - line 11  
claims 1-11; examples 1-5  
----- | 1-15 |

Further documents are listed in the continuation of Box C

See patent family annex

Special categories of cited documents

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

*E* earlier document but published on or after the international filing date

*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

*D* document referring to an oral disclosure, use, exhibition or other means

*P* document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"A" document member of the same patent family

Date of the actual completion of the international search  
28 July 2010

Date of mailing of the international search report  
11/08/2010

Name and mailing address of the ISA/  
European Patent Office, P B 5818 Patentlaan 2  
NL - 2280 HV RIjsijk  
Tel (+31-70) 340-2040,  
Fax (+31-70) 340-3016

Authorized officer  
Bacon, Alan
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>JP 10309764 A</td>
<td>24-11-1998</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td>EP 1586459 A</td>
<td>19-10-2005</td>
<td>CN 1657288 A</td>
<td>24-08-2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 602004008424 T2</td>
<td>28-08-2008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2005231371 A</td>
<td>02-09-2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 7331582 A</td>
<td>19-12-1995</td>
</tr>
</tbody>
</table>