Method and apparatus for printing photocurable ink

The present invention relates to a method of printing photocurable conductive inks onto board materials having an ink receivable layer which result in improved conductivity. A method of forming a conductive pattern on a board material characterised providing a board having an ink receivable layer; applying a photocurable ink composition to the ink receivable layer; maintaining the photocurable ink composition in a non-cured state to allow the composition to penetrate the ink receivable layer. There is also provided a printing apparatus characterised by a plurality of printing stations arranged sequentially and at least one curing station; wherein a first printing station upstream of the curing station is configured to print a photocurable composition; and at least one of the plurality of printing stations other than the first printing station is located between the curing station and the first printing station.
Figure 5
Method

The present invention relates to methods of printing conductive inks which contain carbon, silver, copper or other conductive metals as the conductive particles. In particular, the present invention relates to methods of printing such inks directly onto packaging materials which result in improved conductivity.

Board materials used for packaging such as cardboard typically comprise a fibre layer and an ink receivable layer which allows various inks to be printed on the board material. Typically, such ink receivable layers comprise *inter alia* calcium carbonate and a clay such as kaolin, in combination with suitable binder polymers such as latexes. Such materials are well known in the art and find common use as packaging materials for consumable goods, as well as many other applications. The combination of the board material and ink receivable layer provides a cheap material having both strength and stiffness, but which can be decorated with high levels of ink so as to take on almost any appearance. The use of an ink receivable layer in general is desirable, since the fibre layer of the board material is typically highly absorbent. Consequently, printing ink formulations directly onto the fibre layer usually results in low resolution patterns, and/or undesirable mixing of printed patterns.

Conductive inks represent a special class of inks which, after printing and development, result in a conductive pattern on the substrate. In the formation of printed circuit boards and the like, typically such conductive inks contain silver particles and a glass frit, together with various organic components to provide suitable rheological properties for printing. The silver particles will typically be present at high levels, most often around 80% or more by weight. After printing, the inks are typically fired to remove the organics, sinter the frit and provide a conductive silver pattern on the printed surface. Clearly, these processing steps incur significant cost and are often incompatible with fibre layer-containing board materials used for packaging.

An alternative class of conductive ink uses carbon or silver powder as the conductive material. Such inks typically contain a photocurable polymer, photoinitiator, and carbon or silver powder together with other additives provide a suitable rheological properties. After printing, such inks may be cured under UV to provide a conductive pattern. Although such technologies are well established,
ird materials used in packaging is not known. One drawback with
photocurable conductive inks containing carbon powder is that higher levels of
carbon powder cannot be incorporated without the viscosity of the ink becoming too
high. Moreover, inks containing higher levels of carbon powder typically do not
form dispersions which are stable enough to be used in commercial offset printing
processes. Clearly, higher levels of carbon powder are desirable to provide printed
patterns having low resistivity.

There is a growing need to apply conductive inks to packaging materials, so
as to allow electronic information to be stored on the package product in the form of
a scannable microchip such as an RF tag or the like. Typically, such electronic tags
are formed on a separate substrate which is then transferred onto the package
material in the form of a sticker.

In view of the foregoing, there is a need for low cost methods of forming
highly conductive patterns on a board material.

Summary of Invention

The present invention provides a method of forming a conductive pattern on
a board material comprising:

(a) providing a board material comprising an ink receivable layer;
(b) applying a photocurable ink composition to the ink receivable layer, said
composition comprising a curable binder polymer, a photoinitiator and conductive
particles;
(c) maintaining the photocurable ink composition in a non-cured state to
allow the composition to penetrate the ink receivable layer; and
(d) curing the photocurable ink composition.

Preferably, step (b) comprises applying the photocurable ink composition to
the ink receivable layer to an optical density of at least 1.5, more preferably to an
optical density of at least 1.8, or at least 2.0.

Preferably, step (c) comprises maintaining the photocurable ink composition
in a non-cured state for at least 3 seconds. More preferably, step (c) comprises
maintaining the photocurable ink composition in a non-cured state for at least 5, or
at least 8, or at least 10, or at least 15, or at least 20, or at least 30, or at least 60
seconds.
ly, the board material has a substrate absorbency of at least 10%, more preferably at least 20%, and more preferably at least 30%.

Preferably, the ink receivable layer has a surface roughness 5 μm or less, preferably 2 μm or less, as measured by ISO 8791-3:2005.

In a further aspect, the present invention relates to a printing apparatus comprising:

- a plurality of printing stations arranged sequentially; and
- at least one curing station, wherein
- at least one of the printing stations upstream of the curing station is configured to print a photocurable ink composition comprising a curable binder polymer, a photoinitiator and conductive particles, and
- at least one of the plurality of printing stations other than the printing station configured to print a photocurable ink composition is located between the curing station and the at least one printing station configured to print a photocurable ink composition.

The printing apparatus may be an offset printing apparatus or any other suitable printing apparatus.

By "curing station" is meant zone or section of the printing apparatus which applies UV light or other suitable radiation to cure any photocurable compositions on the printed substrate.

The skilled person would readily recognise that printing apparatus such as offset printing apparatus typically contain rollers which move the substrate, some of which may simultaneously apply ink to the substrate. As such, a typical offset printing apparatus moves the substrate in a given direction during the printing process. In this context, "upstream" means that the printing station configured to apply the photocurable ink composition is located earlier in the apparatus than the curing station, such that the photocurable ink is applied before the substrate passes into the curing station.

Preferably, the offset printing apparatus of the invention has at least two, preferably at least three, more preferably at least four of the plurality of printing stations other than the printing station configured to print a photocurable ink composition located between the curing station and the at least one printing station configured to print a photocurable ink composition.

Preferably, the printing apparatus of the invention has the curing station located downstream of all of the plurality of printing stations.
nstream" is meant that the curing station is located later on in the offset printing apparatus. In other words, the printing apparatus of the invention preferably has the curing station located after all of the plurality of printing stations which apply ink, such that no further ink would be applied to the substrate after it has passed through the curing station.

Preferably, the printing apparatus of the invention has the printing station configured to print a photocurable ink composition as the first printing station in the apparatus.

Description of the Invention

For most applications, conductive ink films should have a resistance from zero to upper limit in the range of 10,000 $\Omega/cm$. Devising a suitable photocurable conductive ink formulation requires balancing several factors, including the rheology of the un-cured ink, the durability of the cured ink, conductivity of the cured ink, as well as other properties of the cured ink such as hardness and the like. During the course of investigating suitable photocurable ink compositions for printing onto board materials, it was surprisingly found that several unexpected factors contributed towards the conductivity of the cured ink composition. More specifically, it was observed that there was a correlation between the time lag between printing and curing and the conductivity of the resultant cured composition. In other words, allowing the printed ink to reside on the board material prior to curing actually resulted in an increase in the conductivity of the cured composition. Moreover, the conductivity of a given composition was also found to correlate with the absorbency of the ink receivable layer on the board material.

By "lag time" is meant the time between printing and curing the photocurable ink composition.

Without wishing to be bound by theory, it is believed that maintaining the uncured ink on the ink receivable layer in accordance with the present invention allows some of the components in the ink to be absorbed into the ink receivable layer, leaving behind an abundance of conductive particles at the surface of the layer. Consequently, using a board material having an ink receivable layer with a higher absorbency, and/or increasing the lag time between printing and curing in accordance with the present invention, allows the formation of highly pigmented ink compositions at the surface of the printed substrate prior to curing, which once
ighly conductive cured inks. Using the method of the present invention overcomes the inherent difficulties in forming highly conductive photocurable ink compositions containing conductive particles which arise due to the limitations on the amount of conductive particles that can be included in these inks.

The various components used in the method of invention will now be described in more detail.

Photocurable Ink Composition

The photocurable ink composition used in the method of the present invention comprises curable binder polymer, photoinitiator and conductive particles. Typical curable binder polymers include acrylates such as polyester acrylates, epoxy acrylates, urethane acrylates and the like. Typically, a combination of such polymers will be used to provide ink compositions having a viscosity and rheology which is suitable for printing. Suitable commercially available curable binder polymers include acrylate resins such as Ebecryl 657, Ebecryl 859, Ebecryl 870, and Ebecryl 1290 from Cytec Surface Specialties. Typically, the amount of binder polymer present in the photocurable ink composition is from 40-85 wt%, preferably 50-80 wt%, more preferably 60-75 wt%.

The conductive particles are preferably selected from conductive carbon, silver, copper and the like. Conductive carbon particles are particularly preferred. The conductive carbon particles typically have a primary particle size of about 10 to about 40 nm, suitably about 20 nm. Typically, the conductive carbon particles will have a BET surface area of about 150 to about 250 m²/g. Commercially available conductive carbon particles suitable for use in the photocurable conductive ink composition include Conductex SC Ultra from Columbian Chemicals Company; and Printex L, Printex L6, and Printex XE-2 from Evonik. Typically, the conductive particles are present in the ink composition at levels of from 10-30 wt% for conductive carbon particles, preferably from 15-25 wt%. Conductive metal particles tend to be more conductive than carbon particles, and so may be included in the ink compositions at lower amounts relative to conductive carbon particles. However, as conductive metal particles are significantly denser than conductive carbon, particularly so in the case of silver particles, the actual weight percent of conductive
ncluded in the ink compositions may be higher, for example 30-60 wt%.

The photoinitiator activates the curing of the curable binder polymer. Suitable photoinitiators include benzophenone, benzildimethylketal, isopropylthioxanthone, and Irgacure 369, Irgacure 379 and Darocure 1173 of Ciba. Typically, the photoinitiators are present in an amount from 1-20 wt% of the ink composition, preferably 5-15 wt%.

Optional additional ingredients include pigment, filler to reduce misting, viscosity adjusting agents, scratch resistance agents such as wax, and the like.

Typically, when formulating the photocurable ink composition, the composition is milled to ensure that any agglomerated conductive particles are broken down and the particles are well dispersed in the ink. Typically, a triple roll mill is used due to the high viscosity of the compositions. If necessary, the composition may be milled through two or three times to ensure the conductive particles are fully dispersed.

When used in lithographic (offset) printing, a typical viscosity for the photocurable ink composition at a shear rate of 0.2s\(^{-1}\) is from 1000 to 7000 Pa.s, preferably from 2000 to 5000 Pa.s. However, for other types of printing such as gravure printing, a broader range of viscosity may be suitable.

**Board Material**

The board material used in the method of the present invention comprises an ink receivable layer. By "ink receivable layer" is meant a smooth layer which acts as a receiving surface for the ink composition during the printing process. The ink receivable layer is not liquid impermeable, and has a degree of porosity that allows some of the components in the ink composition to be absorbed. Preferably, the ink receivable layer has a substrate absorbency of at least 10%, preferably at least 20%, preferably at least 25%.

The "substrate absorbency" may be measured using a SCAN test method SCAN-P70:09. In this test, Noir Porometrique Ink - 3809 from Sun Chemicals is applied in excess to the substrate to be tested using a spatula or the like. The ink is allowed to reside on the board material for a total of 60 seconds before the excess ink is removed. The substrate absorbency is expressed as the loss in reflectance of the board between the ink and the non-inked areas, measured in percent.
receivable layer in the board material typically comprises minerals such as clay. Preferred types of clay include kaolin, smectite, illite and chlorite type clays, such as kaolinite, dickite, halloysite, nacrite, montmorillonite, nontronite, saponite, laponite, sepiolite and attapulgite. Preferred clays present in the ink receivable layer include kaolin, montmorillonite and laponite. Other preferred components in the ink receivable layer include filler and a binder polymer. Typical fillers include calcium carbonate, titanium dioxide, talc, silica and the like. Preferably, the filler is calcium carbonate.

Preferably, the ink receivable layer comprises calcium carbonate, kaolin and latex. However, there is no particular restriction on the components present in this layer providing that it has the necessary absorbency in order to provide the advantages of the method of invention.

Preferably, the board material comprises an ink receivable layer and a fibre layer. There is no particular restriction on the nature of the fibre layer in the method of the invention. The purpose of the fibre layer is to provide structural integrity to the board material such that it is suitable for packaging or any other desired purpose. Suitable fibre materials include cardboard, compacted paper and the like.

Typically, the board material used in the method of the invention will have a basis weight of at least 150 grams/m², preferably at least 200 grams/m².

As outlined above, it is believed that the improvement in conductivity obtained when using the method of invention arises due to some of the ink being absorbed into the ink receivable layer. Clearly, a more absorbent substrate does not require a very long lag time between printing and curing in order to achieve a noticeable improvement in conductivity. In principle, there is no limit on the absorbency of the ink receivable layer present on the board material. However, it is important to ensure that an ink receivable layer is used. In particular, it has been found that applying a photocurable ink composition containing conductive particles directly onto a board material consisting of a fibre layer with no ink receivable layer results in very poor conductivity. The low conductivity can be understood by the high absorbency and high surface roughness of the fibre layer. In other words, it is possible that the conductive particles themselves may be absorbed into board material if the absorbency is too high. Moreover, if the surface roughness is too high, the ink composition either directly after printing or after being absorbed into the board material will not form a continuous film over the board material due to the
ness in the board material surface. The discontinuities in the printed pattern will result in the cured ink composition having high resistivity.

In view of the foregoing, it is important for the surface of the ink receivable layer to have a low surface roughness. A suitable surface roughness for the ink receivable layer is an $R_d$ of 5 $\mu$m or less, preferably 4 $\mu$m or less, more preferably 3 $\mu$m or less, and even more preferably 2 $\mu$m or less, and most preferably 1 $\mu$m or less, as measured according to ISO 8791-3:2005.

Examples of commercially available board materials that may be used in the method of the invention include Incada Exel available from Iggesund. An SEM image of Incada Exel is shown in Figure 1, in which the ink receivable layer is clearly visible as a smooth surface over the rough fibre-containing-layer.

**Method of Forming the Cured Composition**

The high viscosity of the photocurable ink composition means it is most suitably applied by an offset printing method. Such methods are known in the art and would be familiar to the skilled person. Suitable printing pressures are from 300 to 700 N, typically about 400-500 N. Other preferred printing methods include flexo and gravure printing.

As noted above, it has been found that increasing the lag time between printing and curing photocurable ink compositions in accordance to the method of the present invention results in a higher conductivity of the cured composition. In principle, the longer the lag time, the higher the conductivity of the cured composition.

In a commercial process, a long lag time is undesirable since it may lead to lower production rates. Nevertheless, the method of the invention can easily be applied in a commercial scale printing process such as an offset printing process by simply ensuring that the lag time prior to curing is maximised. One possible way of increasing a lag time in a commercial printing process using a typical multi-ink printing machine is to ensure that the photocurable conductive ink composition is the first or at least an early composition that is applied to the substrate. More specifically, typical commercial printing apparatus involve a number of printing stations arranged sequentially prior to the final curing zone, as shown in Figure 2. Applying the photocurable ink at printing station 1 as opposed to printing station 6 maximises the time between the printing and curing, which occurs once the
essed through all the printing stations. However, the photcurable ink printing station need not be the first in the apparatus.

Preferably, the photcurable ink composition is applied to an optical density of at least 1.5, more preferably to an optical density of at least 1.8, or at least 2.0, relative to the unprinted board material.

By "optical density" is meant the absorbance, as defined by:

\[ \text{Optical density} = -\log_{10}(I / I_0) \]

where \( I \) is the intensity of light that has passed through the sample, and \( I_0 \) is the intensity of the incident light.

The cure time of the ink will vary depending on a number of factors, including the amount of ink applied to the board material, and the type of photcurable binders and photoinitiator in the photcurable ink composition. In commercial scale printing operations, the cure time will typically be about 1 second or less, preferably about 0.3 seconds.

The present invention will be described in more detail with reference to the following examples.

**Procedures**

**Measuring Sample Resistance**

To assess the surface electrical conductance of ink films produced, the ohm meter function on a multi-meter was used. A multi-meter is a multifunctional tool that can be used to measure resistance, voltage and current among other things.

The device uses two probes to connect to the object to be measured, these probes have sharp points that may potentially damage or destroy the thin ink film so care had to be taken when making measurements. The contact resistance effect on results is proportional to the contact area, with a larger contact area lessening the effect. To achieve a larger contact area, a standard measurement device as shown in Figure 3 was used, consisting of copper tape (2) on a piece of circuit board (1) was used, which connects to the multi-meter device via wire connectors (3). The multi-meter often took several seconds to reach a steady reading, falling several ohms before it settled.
An ink composition was formulated having the following components:

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Ebecryl 870</td>
<td>(PE Acrylate resin)</td>
<td>15 wt%</td>
</tr>
<tr>
<td></td>
<td>Ebecryl 859</td>
<td>(PE Acrylate resin)</td>
<td>12 wt%</td>
</tr>
<tr>
<td></td>
<td>Ebecryl 1290</td>
<td>(Urethane acrylate resin)</td>
<td>38 wt%</td>
</tr>
<tr>
<td></td>
<td>Additol 5120</td>
<td>(Stabiliser)</td>
<td>1 wt%</td>
</tr>
<tr>
<td></td>
<td>Printex L</td>
<td>(Conductive carbon)</td>
<td>15 wt%</td>
</tr>
<tr>
<td>10</td>
<td>Photoinitiators</td>
<td></td>
<td>14 wt%</td>
</tr>
<tr>
<td></td>
<td>OTA 40 Monomer</td>
<td>(Viscosity adjuster)</td>
<td>4 wt%</td>
</tr>
<tr>
<td></td>
<td>Rad-Wax</td>
<td></td>
<td>1 wt%</td>
</tr>
</tbody>
</table>

wherein the photoinitiators are a mixture of commercially available photoinitiators including Irgacure 369, BDK, BP, ITX and EDB. The various components other than conductive carbon were mixed together to form a consistent formulation, to which the carbon particles were then added. The formulation was then milled in a triple roll mill until a consistent formulation was obtained.

The ink composition was printed on various board materials to an optical density of around 2.5 and cured under an ultraviolet lamp. For each board material, one sample was cured immediately after printing, while a second sample was cured after 10 minutes. The resistance of 6 mm of the cured ink was measured. The results are summarised in Table 1.

<table>
<thead>
<tr>
<th>Example</th>
<th>Substrate on which the ink was printed</th>
<th>Resistance when cured immediately (kΩ)</th>
<th>Resistance when cured after ten minutes delay (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-a</td>
<td>Incada Exel</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>1-b</td>
<td>Greenplex</td>
<td>45</td>
<td>18</td>
</tr>
<tr>
<td>1-c</td>
<td>Maule GC2</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>1-d</td>
<td>Cascades Imprint</td>
<td>420</td>
<td>736</td>
</tr>
</tbody>
</table>

Table 1
1-b and 1-c show that a delay between ink application and ink cure gave a cured ink having higher conductivity. The boards used in Examples 1-a, 1-b, and 1-c have an ink receivable layer on the top surface, which is made from calcium carbonate, kaolin and latex. It is believed that the ink receivable layer helps the ink vehicle to soak into the substrate, giving a top surface enriched with more pigment which leads to a more conductive cured composition.

The board used in Example 1-d has no clay-containing ink receivable layer on its surface. Moreover, the board used in Example 1-d is very rough and the continuity of the ink layer was adversely affected. Consequently, the resistivity of the cured composition on this board was significantly higher.

Example 2

A photocurable ink composition was prepared with the following ingredients:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Description</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ebecryl 870</td>
<td>(PE Acrylate resin)</td>
<td>13 wt%</td>
</tr>
<tr>
<td>Ebecryl 859</td>
<td>(PE Acrylate resin)</td>
<td>13 wt%</td>
</tr>
<tr>
<td>Ebecryl 1290</td>
<td>(Urethane acrylate resin)</td>
<td>38 wt%</td>
</tr>
<tr>
<td>Additol 5120</td>
<td>(Stabiliser)</td>
<td>1 wt%</td>
</tr>
<tr>
<td>Printex L</td>
<td>(Conductive carbon)</td>
<td>15 wt%</td>
</tr>
<tr>
<td>Photoinitiators</td>
<td></td>
<td>14 wt%</td>
</tr>
<tr>
<td>OTA 40 Monomer</td>
<td>(Viscosity adjuster)</td>
<td>5 wt%</td>
</tr>
<tr>
<td>Rad-Wax</td>
<td></td>
<td>1 wt%</td>
</tr>
</tbody>
</table>

wherein the photoinitiators are a mixture of commercially available photoinitiators including Irgacure 379, Darocure 1173, BDK, BP and ITX.

The various components other than conductive carbon were mixed together to form a consistent formulation, to which the carbon particles were then added. The formulation was then milled in a triple roll mill until a consistent formulation was obtained.

The ink composition was printed on Incada Exel and a non-porous plastic (PET) sheet using the same print settings. Figures 4 (Incada Exel, magnification 6,000) and 5 (plastic sheet magnification 10,000) show electron microscope images
s. As can be seen from Figures 4 and 5, the coating on the plastic is over twice as thick as the coating on the board (2.2μm to 0.9μm). This can be explained by the different substrates having different affinities for the ink off the printing roller which results in different amounts of ink being printed, and also some of the ink being absorbed into the board before the ink is cured lowering the top film weight on the board. The effect of this physical difference is that the film on the board is much more conductive than on the plastic, despite the larger film layer on the plastic. These results demonstrate the importance of having an ink receivable layer on the board material.

Example 3

A photocurable ink composition was prepared with the following ingredients:

- Ebecryl 870  (PE Acrylate resin)  24 wt%
- Ebecryl 859  (PE Acrylate resin)  20 wt%
- Ebecryl 1290 (Urethane acrylate resin) 25 wt%
- Additol 5120  (Stabiliser)  1 wt%
- Printex XE2  (Conductive carbon)  10 wt%
- Photoinitiators  14 wt%
- OTA 40 Monomer (Viscosity adjuster)  5 wt%
- Rad-Wax  1 wt%

wherein the photoinitiators are a mixture of commercially available photoinitiators including Irgacure 369, BDK, BP, ITX and EDB. The various components other than conductive carbon were mixed together to form a consistent formulation, to which the carbon particles were then added. The formulation was then milled in a triple roll mill until a consistent formulation was obtained.

Samples were printed then cured at lag times of 0 minutes, 2 minutes, 5 minutes, 10 minutes and 15 minutes. The results of the various samples are recorded in Table 2.
Table 2

<table>
<thead>
<tr>
<th>Lag time (minutes)</th>
<th>Resistance (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
<td>3</td>
</tr>
</tbody>
</table>

Though the lag time seemed to have no effect on cure rate, it appeared to affect resistance. The most likely cause of this effect would be absorption of ink vehicle into the board material.

In a further experiment, samples were printed then left uncured over the weekend to give a very long lag time. One sample was left in the light, and was measured to have a resistance of 2.5kΩ after curing, compared to the sample in Table 2 left for 15 minutes which had a resistance of 3kΩ. The other sample was left in the dark so no curing could take place at all over the weekend. This sample was measured to have a resistance of 1.9kΩ after curing. These results demonstrate that the longer the ink composition is maintained on the ink receivable layer in an uncured state, the greater the improvement in conductivity.

Example 4

In this example, Incada Exel (Iggesund) was used as the board material in a Komori Lithrone 40 printing press (a 6 colour commercial scale printing apparatus, similar to that shown in Figure 2). The printing apparatus had nine printing stations, with a curing zone immediately following the final printing station. The ink composition used in Example 1 was printed to an optical density of 2.0, which meant higher resistances but more realistic curing speed through the press. In two separate runs, the ink was applied on the first printing station, when it has the chance to travel the full length of the nine-colour machine, and on the final printing station immediately before the curing zone. The transit time from first printing station to the curing zone is around 10 seconds. The results are shown in Table 3 below.
Table 3

<table>
<thead>
<tr>
<th>Resistance when cured immediately (applied on the final printing station) (kΩ)</th>
<th>Resistance when cured after ten seconds delay (applied on the first printing station) (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;2000</td>
<td>1200</td>
</tr>
</tbody>
</table>

This demonstrated that the delay effect is still evident when the delay is much shorter.

Example 5

Using the same commercial scale apparatus as described in Example 4, the ink composition was applied to several substrates using the first printing station (i.e. the printing station furthest from the curing zone). The ink was applied at the same levels on each substrate. The only difference between the runs is therefore due to the absorbency of the substrates themselves. The absorbency of each board was quantified by the “substrate absorbency” test described above (SCAN test method SCAN-P 70:09)

The results are shown in Table 4 below.

Table 4

<table>
<thead>
<tr>
<th>Example</th>
<th>Substrate</th>
<th>Resistance when cured (kΩ)</th>
<th>Substrate absorbency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-a</td>
<td>PET polyester</td>
<td>1300</td>
<td>2</td>
</tr>
<tr>
<td>3-b</td>
<td>Incada Exel</td>
<td>1200</td>
<td>35</td>
</tr>
<tr>
<td>3-c</td>
<td>Venofreeze</td>
<td>480</td>
<td>60</td>
</tr>
</tbody>
</table>

The data in Table 4 show that the conductivity of a conductive ink was promoted by the use of a substrate having an absorbent ink receivable layer.
Claims

1. A method of forming a conductive pattern on a board material comprising:
   (a) providing a board material comprising an ink receivable layer;
   (b) applying a photocurable ink composition to the ink receivable layer, said composition comprising a curable binder polymer, a photoinitiator and conductive particles;
   (c) maintaining the photocurable ink composition in a non-cured state to allow the composition to penetrate the ink receivable layer; and
   (d) curing the photocurable ink composition.

2. The method of claim 1, wherein the ink receivable layer has a surface roughness $R_s$ of 5 $\mu$m or less, as measured according to ISO 8791-3:2005.

3. The method of claim 1, wherein the ink receivable layer has a surface roughness $R_s$ of 2 $\mu$m or less, as measured according to ISO 8791-3:2005.

4. The method of any preceding claim, wherein step (c) comprises maintaining the photocurable ink composition in a non-cured state for at least 5 seconds.

5. The method of any preceding claim, wherein step (c) comprises maintaining the photocurable ink composition in a non-cured state for at least 8 seconds.

6. The method of any preceding claim, wherein the board material has a substrate absorbency of at least 10%.

7. The method of any preceding claim, wherein the board material has a substrate absorbency of at least 20%.

8. The method of any preceding claim, wherein step (b) comprises applying the photocurable ink composition to the ink receivable layer to an optical density of at least 1.5.
9. The method of any preceding claim, wherein in step (b), the photocurable ink composition is applied using an offset, flexo or gravure printing process.

10. The method of any preceding claim, wherein the ink receivable layer contains clay.

11. The method of claim 10, wherein the ink receivable layer comprises clay, filler and a binder polymer.

12. The method of claim 11, wherein the ink receivable layer comprises kaolin, calcium carbonate and latex.

13. The method of any preceding claim, wherein the board material additionally comprises a fibre layer.

14. The method of any preceding claim, wherein the conductive particles are selected from conductive carbon, silver and copper particles.

15. The method of claim 14, wherein the conductive particles are conductive carbon particles.

16. A printing apparatus comprising:
   a plurality of printing stations arranged sequentially; and
   at least one curing station, wherein
   at least one of the printing stations upstream of the curing station is configured to print a photocurable ink composition comprising a curable binder polymer, a photoinitiator and conductive particles, and
   at least one of the plurality of printing stations other than the printing station configured to print a photocurable ink composition is located between the curing station and the at least one printing station configured to print a photocurable ink composition.
17. The offset printing apparatus of claim 16, wherein at least two, preferably at least three, more preferably at least four of the plurality of printing stations other than the printing station configured to print a photocurable ink composition are located between the curing station and the at least one printing station configured to print a photocurable ink composition.

18. The offset printing apparatus of claim 16 or claim 17, wherein the curing station is the located downstream of all of the plurality of printing stations.

19. The offset printing apparatus of any one of claims 16 to 18, wherein the printing station configured to print a photocurable ink composition is the first printing station in said apparatus.
### PATENTS ACT 1977: SEARCH REPORT UNDER SECTION 17

#### Documents considered to be relevant:

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Search of GB, EP, WO & US patent documents classified in the following areas of the UKC:

- Worldwide search of patent documents classified in the following areas of the IPC
  - B41F; B41J; B41M

The following online and other databases have been used in the preparation of this search report:

- EPODOC, WPI
### International Classification:

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