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SCREEN-PRINTED ELECTRICALLY CONDUCTIVE FUNCTIONALITIES IN PAPER SUBSTRATES

ELEKTROPREVODNE OBLIKE, PRIPRAVLJENE S SITOTISKOM NA PAPIRNIH PODLAGAH

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The topological and electrical properties of screen-printed conductive lines, applying silver-based conductive ink are analyzed. The influence of the substrate, curing time and wet-to-wet overprinting is analyzed. The mechanical profilometer, optical microscope and SEM images did not give the same information about the topography of the prints. Areas without functional particles on the line boundaries could be seen on the SEM micrographs, whereas the profilometer and optical microscope could not support such information, and thus provide wider lines. Careful analysis confirms that the printing parameters influence the electrical resistivity of the printed products. Overprinting does not influence a great deal on the shape of lines; however, these lines have a smaller resistivity. The larger resistivity of the prints was obtained on a rough and porous substrate and was smaller on the smooth one. The influence of curing time was also shown.

Keywords: printed electronics, screen printing, conductive ink, electrical resistivity

Analizirali smo topološke in električne lastnosti linij, ki so bile natisnjene s sitotiskom prevodne tiskarske barve s srebrovimi delci. Ugotavljali smo vpliv tiskovne podlage, časa termičnega sušenja in večkratnega tiska mokro-na-mokro. Mehanski profilometer, optični in elektronski mikroskop ne dajejo nujno enakih podatkov o topografiji potiskanih oblik. Območja brez funkcionalnih delcev opazimo le na posnetkih elektronskega mikroskopa, optični mikroskop in profilometer pa taka območja ne ločita od funkcionalnih delov linij. Analiza je pokazala, da parametri tiska vplivajo na električne lastnosti izdelkov. Tisk mokro-na-mokro ima zanemarljiv vpliv na tiskane oblike, pač pa imajo taki odtisi manjšo električno upornost. Na hrapavi in porozni podlagi dobimo večje upornosti kot na gladki. Na upornost potiskanih linij vpliva tudi čas segrevanja pri sušenju odtisov.

Ključne besede: tiskana elektronika, sitotisk, prevodna tiskarska barva, električna prevodnost

1 INTRODUCTION

Printed electronics, i.e., fabricating an entire electronic device by printing, is expected to provide low-cost electronic systems on common surfaces such as paper, plastic and textiles. The simplified structures of electronic devices, printed by a minimal number of different printing inks, should provide the lowest possible target price, which was estimated to be below 0.2 € per piece [1].

All printed electronic devices require some printed conductor to replace the metal layers used in conventional electronics. Polymer inks containing electrically conductive particles are the most common choice for this purpose in the field of printed electronics. They consist of a suitable polymer resin with metal particles, which in most cases are silver, gold, copper, nickel, platinum or carbon [2–6]. These conductive inks have various resistivities; the lowest was obtained with silver particles. Specific physical properties, such as viscosity, suitable rheology characteristics and appropriate curing, are demanded for each printing technology to obtain feasible prints of acceptable quality [7–9].

Conductive inks are available on the market for conventional technologies, i.e., screen printing, offset, and pad-printing. In most cases the producers provide resistivity data for a layer with a specified thickness prepared by a recommended application (printing) method and drying conditions. However, the resistivity of a shape, printed by a particle-based conductive printing ink, depends on the internal microstructure of the printed lines. This structure could be influenced by several parameters that may affect the functional properties of the final application [5–7,9].

The objective of our research was to analyze the influence of the printing parameters on the resistivity of screen-printed lines using a silver-based conductive ink. Two flexible substrates were used, the gloss-coated paper and the clear matt film. The topology of screen-printed lines was examined with several techniques. The resistivity of the test structures was measured and the influence of printing parameters was analyzed thoroughly.

2 EXPERIMENTAL

Electrodag PM-470 conductive screen-printable ink (Acheson Colloiden B.V., Netherlands) was used. It contains finely distributed silver particles in a thermoplastic resin. Its density is about 2140 kg/m^3 and the solid content 58–62 %. The manufacturer specifies the Broofield viscosity of the ink to be 11 000–140 000 mPa s (30 °C, 20 r/min) and the sheet resistance of a 25-µm-thick layer at a sheet resistance of 0.008–0.015 Ω/□. This corresponds to a specific resistivity of $2.0–3.75 \cdot 10^{-5}$ Ω cm.

The print form contained suitable structures for resistivity measurements and several horizontal and vertical lines (in series of four equally separated strips) with a width from 5 mm to 0.5 mm. The shape of narrowest lines (500 µm width on print form) was evaluated in detail.

The ink was screen printed by applying the SEFAR® high-modulus monofilament polyester plain weave mesh 43/80Y and a squeegee with a hardness of 75 °Sh. Two substrates were used, i.e., clear matt film (thermally and antistatically treated for transfer printing) and gloss-coated paper. Single and double layer prints (wet-on-wet) were made. The off-prints were cured at 120 °C for 4, 9 and 13 min. In all cases, dry prints were obtained.

The thickness and profile of the lines were measured with a Talysurf profilometer (Rank Taylor Hobson Series 2). The microtexture and profile of the narrow lines were monitored with a scanning electron microscope SEM – 6060 LV (JEOL, Japan). The shape of the edges, the degree of wicking and the width of narrowest line were also evaluated using a Nanometrics optical microscope (Olympus).

The electrical resistivity of the samples was measured by applying a four-terminal measurement method [5,6]. A constant DC-current source was used to force a current of ~1 µA through the outer contacts of the structure. The voltage drop was measured with an electronic voltmeter (FLUKE 289) on the inner contacts. In this way the contact resistance was completely eliminated and the results represent the pure resistance of the layer between the inner contacts. The specific electrical resistivity ρ of the printed layer with a thickness d was calculated using the measured voltage drop V_x and known current I according to the equation:

$$\rho = \frac{V_x}{I} \cdot \frac{W}{L} \cdot d \qquad (1)$$

where W and L denote the width and the length of the measured strip between the inner contacts.

The adhesion of printed layers on both substrates was evaluated using the standard cross-cut test, applying the Byko-cut universal inspection guage (Byk-Gardner Instruments, Germany). This method evaluates the coating resistance to separation from the substrate when a right-angle lattice pattern is cut up to the substrate. The micrographs of the prepared samples are then rated into classes with values 0–5, according to ISO 2409:1997.

3 RESULTS AND DISCUSSION

3.1 Print quality

The surfaces of all the printed lines clearly show silver flakes, which are not completely covered by the binder (**Figure 1**). This is the consequence of the very high solids content in the wet paint.

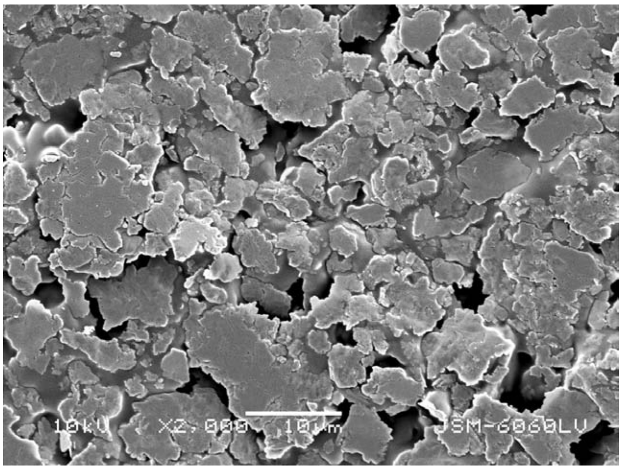

Figure 1: SEM micrograph of a typical front surface of printed conductive line. The silver flakes are not fully covered by the binder
Slika 1: SEM-posnetek površine tiskane prevodne linije. Srebrne luske niso popolnoma zakrite z vezivom

The dried, printed conductive lines were analyzed using line-profile measurements and an SEM image analysis. They are well separated. Surface-profile measurements show the different surface roughnesses of the two applied paper substrates and the similar roughnesses of the lines printed on them (**Figure 2**). Such results were obtained on all the prepared samples. These profiles were applied to determine the average thickness of the dry printed layers. In general, thinner layers were measured on the gloss-coated paper and thicker on the clear matt film. The wet-to-wet over-

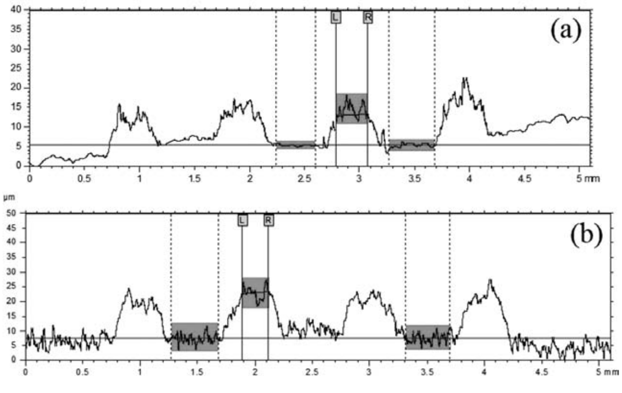

Figure 2: Surface profile of four parallel lines printed on gloss-coated paper (a) and clear matt film (b) as obtained by the profilometer. The lines are single-layer prints that were cured for 9 min. The average thickness is 9.1 µm and 15.5 µm, respectively. It was determined as the distance between the average lines of the substrate and top of the printed lines, determined on the marked regions.
Slika 2: Površinski profil štirih vzporednih črt, ki so bile natisnjene na sijajnem premazanem papirju (a) in na hrapavi foliji (b). Meritve so bile narejene na profilometeru. Črte so bile natisnjene z enkratnim prehodom in sušene 9 min. Povprečna debelina prikazanih linij je 9.1 µm (a) in 15.5 µm (b). Določena je kot razdalja med podlago in vrhom tiskanih linij; položaj vsake od teh je določen kot povprečna lega obarvanih področjih.

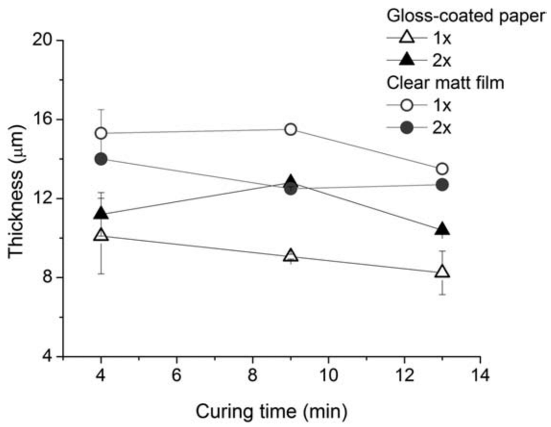

Figure 3: The thickness of strips single- (open signs) and double (solid signs) wet-to-wet overprinted on gloss coated paper (triangles) and clear matt film (circles) as a function of the curing time

Slika 3: Debelina črt natisnjenih z enkratnim (prazni znaki) in dvakratnim prehodom raklja (polni znaki) na sijajnem premazanem papirju (trikotniki) in na hrapavi foliji (krogi) v odvisnosti od časa sušenja

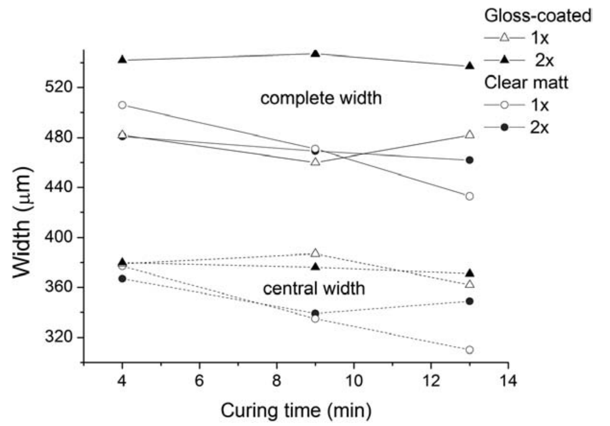

Figure 5: The fully functional width (central part of strips, broken lines) and the corresponding complete width (wicking area taking into account, full line) of strips printed by single- (open signs) and double (solid signs) wet-to-wet overprinting on gloss coated paper (triangles) and clear matt film (circles) as a function of the curing time.

Slika 5: Širina električno funkcionalnega dela črt (osrednji del, črtkane črte) in celotna širina (z upoštevanjem nagubanih robov, polne črte) v odvisnosti od časa sušenja. Črte so bile natisnjene z enkratnim (prazni znaki) in dvakratnim prehodom raklja (polni znaki) na sijajnem premazanem papirju (trikotniki) in hrapavi foliji (krogi).

printed layers are slightly thicker than the single-printed, but their thickness is much less than doubled. All the layers become thinner when longer curing was applied. The influence of curing time and overprinting is small (**Figure 3**).

The next important property is the width of the printed lines, which was evaluated with SEM and optical micrographs. The edges of the lines are not perfectly straight. A considerable amount of wicking was detected on the optical micrographs (**Figure 4a**). SEM micrographs show that such edges could lack conductive particles; some regions could also remain without any electrical functionality (**Figure 4b**). Therefore, the contribution of this region to the electrical conductivity is not the same as it is in the bulk of the printed shape.

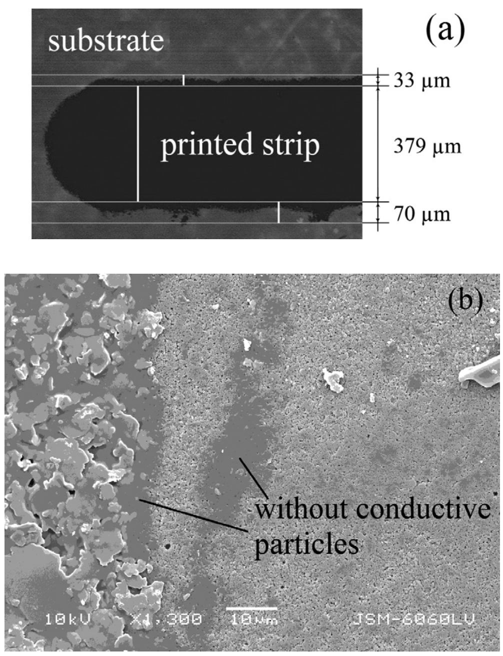

Figure 4: The edges of a printed line as observed by optical (a) and SEM micrographs (b). The width of the lines was evaluated from optical micrographs, taking into account the inner tangents. The printing squeegee was moved perpendicularly to the printed strip.

Slika 4: Robovi tiskanih črt, posneti z optičnim (a) in elektronskim mikroskopom (b). Širino črt smo določili med premicama, ki označujeta notranjost robov. Pri tisku se rakelj giblje v smeri od zgoraj navzdol.

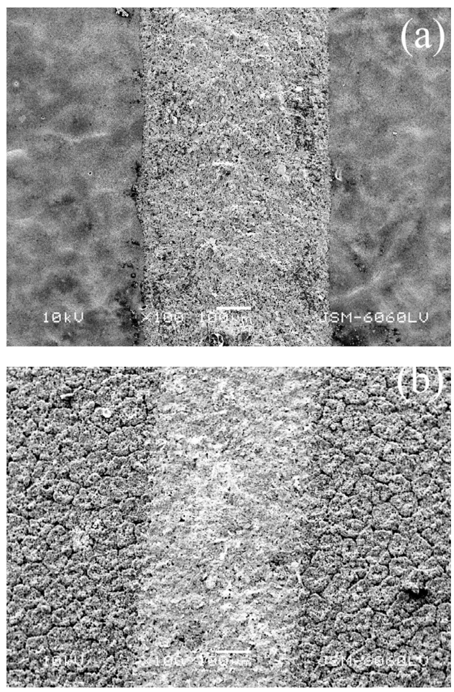

Figure 6: SEM micrograph of analyzed strip printed on gloss-coated paper (a) and clear matt film (b)

Slika 6: SEM-posnetek analizirane črte, natisnjene na sijajnem premazanem papirju (a) in hrapavi foliji (b)

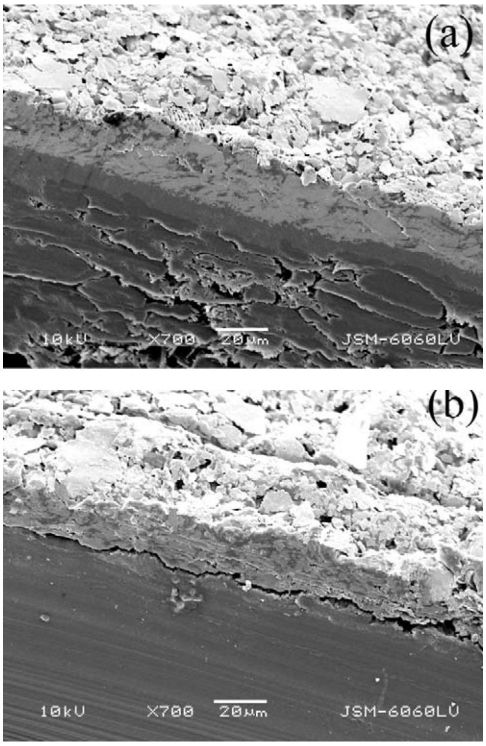

Figure 7: SEM micrographs of cross-sections of samples printed on gloss-coated paper (a) and clear matt film (b)

Slika7: SEM-posnetek prereza vzorcev, natisnjenih na sijajnem premazanem papirju (a) in hrapavi foliji (b)

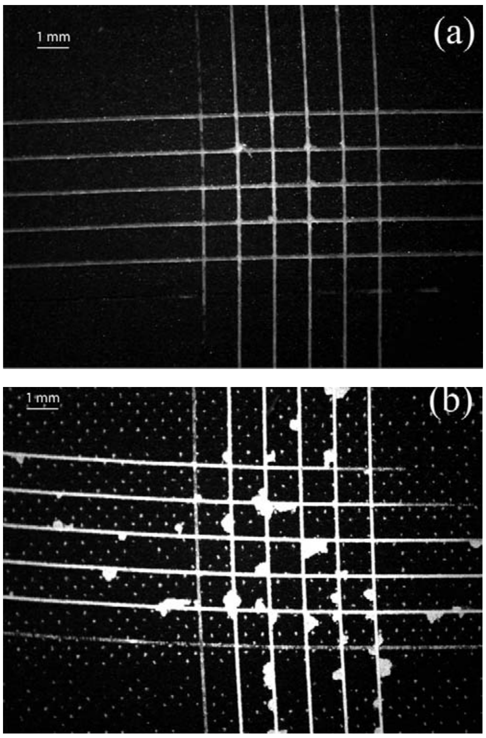

Figure 8: The cross-cut test of single-layer printed on gloss-coated paper (a, adhesion ISO class 1) and clear matt film (b, adhesion ISO class 3)

Slika 8: Metoda križnega reza enoslojne plasti, tiskane na sijajnem premazanem papirju (a, ISO adhezija razreda 1) in hrapavi foliji (b, ISO adhezija razreda 3)

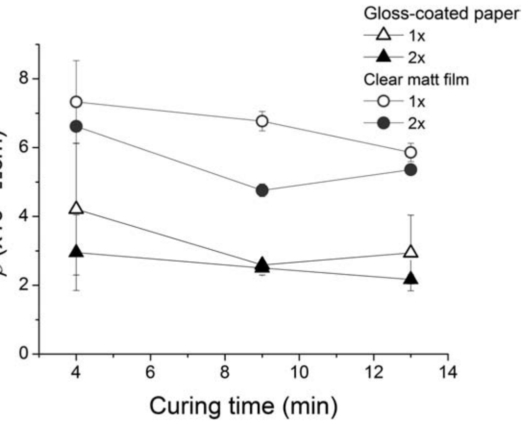

Figure 9: Specific resistivity of single- (open signs) and double-printed layers (solid signs) printed on clear matt film (circles) and gloss-coated paper (triangles)

Slika 9: Specifična upornost eno- (prazni znaki) in dvoplastnih linij (polni znaki), tiskanih na hrapavi foliji (krogi) in na sijajnem premazanem papirju (trikotniki)

The width of the wicking area was evaluated using two straight lines, limiting it on both sides of printed strip on the optical micrograph. Electrically, the fully functional width of the strips was determined between the inner tangents, whereas the rest was considered as the amount of wicking (**Figure 4a**). An about 10 % narrower wicking area was obtained on the top of the horizontally printed strips than on the opposite side. This is the consequence of the moving direction of the squeegee during the printing. The width of the central line (i.e., the fully functional shape) is larger on the gloss-coated paper and smaller on the clear matt film. It tends to diminish with curing time; however, the effect is observable on single-printed samples having a gloss-coated paper substrate, but could be neglected elsewhere (**Figure 5**). The complete width of the strips is the sum of the fully functional central part and the wicking area on both sides. It is about the corresponding width on the print form (i.e., 500 µm), being about 10 % broader when the shape was double printed on gloss-coated paper and could be up to about 10 % narrower elsewhere. In general, narrower lines were obtained on the gloss-coated paper and wider on the clear matt film (**Figure 5**).

A similar analysis was also performed on vertically printed strips; narrower lines were obtained in this case. The wicking area strongly depends on the direction of the printed shape with respect to the moving of the squeegee. This effect is known within the graphics industry [8]. The width of all the printed shapes is systematically broader when directed perpendicularly to the moving direction of the squeegee.

The dependence of the printed strips on the applied substrate can be attributed to the different roughness, porosity and the ability of the ink to diffuse into the substrate. The clear matt film has a very porous and rough surface, whereas the gloss-coated paper has much smaller pores and a rather smooth surface (**Figure 6**). The smooth surface of the gloss-coated paper enables good orientation of the flakes, which gives thinner layers than the rough, clear matt film. The porosity of the substrates, together with the wettability (which was not evaluated here), influences the width of the printed strips. They are narrower on the gloss-coated paper and wider on the surface of the clear matt film. The additional difference between the prints on both substrates could be seen on the cross-sections. The layers printed on clear matt film do not adhere properly to the substrate (**Figure 7b**), while no such effect was observed on gloss-coated paper (**Figure 7a**). Most likely, this crack-like feature was created due to the large diffusion of liquid constituents of the ink through the pores of the substrate. Because the flakes are rather large, the polymer binder could not permeate sufficiently from the above positions, and therefore the layer and the substrate are not entirely merged. No such effects were observed on the gloss-coated paper (**Figure 7**). The existence of a partial separation between the printed layer and the substrate gives rise to poor adhesion. The effect was evaluated by cross-cut tests (**Figure 8**). The gloss-coated paper has a ISO class 1 (good adhesion, cross-cut area not significantly greater than 5 % is affected), while the clear matt film ISO class 3 (poorer adhesion, cross-cut area between 15 % and 35 % is affected).

3.2 Electrical resistivity

The specific resistivity of all the prepared prints is shown in **Figure 9**. Higher values were obtained for the conductive lines on the clear matt film and smaller on the gloss-coated paper. In general, single-printed layers have a higher resistivity and the double-printed, a lower. The specific resistivity also depends on the curing time: up to 9 min of curing, the resistivity diminishes and then this effect becomes smaller.

The electrical conductivity of composites having conductive particles in a dielectric medium (as with our silver-based printing ink) depends, among other parameters, on the concentration of particles and their orientation within the film [10]. It is well known that flaky particles orient preferably parallel to the substrate [11]. The distribution of silver flakes is influenced by the printing, overprinting and drying, giving rise to arrange, rearrange or distribute themselves evenly across the layer. The flakes are well oriented on the gloss-coated paper and more random on the clear matt film, according to their different surface roughness. This effect could explain the larger resistivity of the strips printed on clear matt film. During the curing process the volume of liquid components diminishes due to the evaporation of the solvents, due to the spreading of the strips and the penetration into the substrate; because of that the concentration of the flakes increases, which diminishes the specific resistivity. The last two processes are intensified on double-printed layers, which may explain the different specific resistivity of single- and double-printed strips on the same substrate: double-printed layers have a higher concentration of flakes.

4 CONCLUSIONS

A detailed analysis of screen-printed, silver-based, conductive lines with a target width of 500 µm for applications in printed electronics is shown here. The influence of the substrate, curing time and wet-to-wet overprinting were considered. While profilometer, optical microscope and SEM images do not give the same information about the topography of prints, the specific resistivity of printed layers has to be determined very carefully.

Two flexible substrates were applied, one with a smooth surface and the other with a rough and highly porous surface. The smooth substrate provides a well-merged interface between the layer and the substrate, whereas the porous substrate is not in full contact with the layer, giving rise to poor adhesion. Thinner and wider lines were obtained on the smooth surface, but thicker and narrower lines were seen on the rough one. All the lines have some wicking area where the content of the functional particles is, in general, much smaller than in its central part. Many of such features cannot contribute to the functional width of the printed line. The second wet-to-wet overprinted layer does not double the layer thickness but increases the width of the lines, especially the area with no proper functionality. These effects are stronger on the rough and porous substrate. Longer curing gives somewhat thinner and narrower strips.

The resistivity of the layers on smooth paper is smaller than that printed on the rough and porous surface. Wet-to-wet overprinting gives a smaller resistivity. It diminishes with a curing time up to 9 min. The specific resistivity depends on the concentration of flakes and the microstructure of printed line; it is influenced by the drying process, the surface roughness of the substrate and its porosity.

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