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On the Enhanced Wax Patterning Offset Printing for the manufacturing of Printed Electronics

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Abstract

In order to manufacture various kinds of printed electronics, the offset lithography printing method on wax patterned papers was introduced by using a conductive ink. This mechanism is that a non-printed area patterned by the hydrophobic wax does not transfer the ink on the paper while it can well penetrate the ink onto the hydrophilic printed area. Also, we demonstrated a new hydrophilic conductive ink, which is suitable for trench patterned fine lines and for sufficient penetration by offset printing pressure. In this research, we obtained the results of printed samples of 100 ㎛ width trench pattern with 3.1Ω resistance. This printing method was found to be superior in terms of penetration depth, formation and conductivity of the ink compared to the conventional simple capillary coating method because we were able to eliminate the obstacles caused by uneven formation of papers and irregular penetration depth of the ink. Accordingly, we propose this wax patterning offset printing method as an environment-friendly manufacturing method for fine line printed electronics.

Keywords: conductive ink, wax patterning, offset printing, printed electronics

INTRODUCTION

The offset lithography printing method uses a roll-to-plate or roll-to-roll method and can be done as an online process. There have been consistent attempts to apply this method to the manufacture of printed electronics due to fast printing speed.[1] Offset lithography printing is a printing method that is divided into the lipophilic non-printed area which transfers dampening water and the hydrophobic printed area which transfers ink. This printing method uses the principle in which only the printed area is stained with ink because of repulsive force between the two areas. However, since this method delivers ink from the plate cylinder to the printed object through a blanket, film thickness of transferred ink is only several micrometers and dot gain phenomenon occurs.[2~4] Therefore, the screen printing method is primarily used to manufacture printed electronics such as PCB(printed circuit boards), and the ink jet or gravure printing methods are applied to the manufacturing of some printed electronics.[5~7] However, the most common screen printing method has problems like difficulty of roll-to-roll continuous work, slow printing speed, and damaging of substrate or pattern from irregular printing pressure. There are studies attempting to apply the ink jet printing method to the electronics production process despite many technical limitations, the ink jet printing technology is difficult to form high quality and high fidelity patterns and still faces limitations such as clogging of nozzles and lack of adhesive strength.[8] Accordingly, this study aimed to apply the offset lithography printing method to the manufacturing of printed electronics in order to overcome problems of the screen and ink jet printing methods. The traditional offset lithography printing method has somewhat inadequate resolution compared to other printing methods, however this study added a partition-making process that performs patterning on the paper using wax with extreme hydrophobicity.[9-11] Unlike other printing methods introduced above, the wax patterning offset printing (WPOP hereafter) method proposed in this study is a method of spreading hydrophobic paraffin on the surface of the non-printed area and increasing the amount of ink in the printed area to reinforce penetrating power and allowing conductive ink to sufficiently penetrate into the printed area. In addition, this method minimizes loss from pressure by using a blanket with high elasticity. In other words, the purpose of this study is to propose a new printing technology that accommodates for characteristics of diversifying printed electronics, reviewing the potential of the WPOP method and finding the optimal condition based on significant experimental results.

EXPERIMENT

Materials

A conductive paste was used as a conductive ink for the experiment. This ink was turned into paste by dispersing and recombining a water-soluble resin, which plays the role of a binder, using a water-based solvent. The conductive powder used in this study was a conductive silver paste made by dispersing silver Nano particles (Ag, silver paste). The reason for using the silver paste is because it is relatively inexpensive and silver powder does not oxidize easily because of low reactivity.

Small powders with size of 1 ㎛ or below can be dispersed stably, allowing for post-processes like flaking. Physical properties of the silver paste used in this experiment are presented in Table 1 below.

Table 1. Physical Properties of Silver Paste.

Physics	Average values
Viscosity (cps)	600
Conductor size (㎚)	100
Sintered temperature (℃)	150
Sintered time (s)	1,800

The ratio of the water-soluble resin for binder, varnishing solvent and silver powder was preliminary experimented for limit values. The ratio was adjusted within the range obtained from the preliminary experiment, and 10 varnishes for the silver paste were manufactured by tenderizing them using a small ink tenderizer. The ranges for major chemical components of the varnishes used are as shown in Table 2.

Table 2. Major Chemical Components of Varnish.

Chemical components	Usual name	Content (%)
Resin	Nitro cellulose	10~20
Additive	Polyethylene wax compound	0.1~1
Solvent	Ethyl acetate methyl ethyl ketone	20~30 40~50

This study conducted a 3-dimensional printing experiment using penetrative characteristic of the conductive ink caused by the capillary phenomenon. Therefore, three paper samples (called samples 1, 2 and 3) with different physical properties were used in the experiment. As in Table 3, sample 1 had weight of 47.7g/㎡, thickness of 68 ㎛ and roughness 3.5~3.7 ㎛. Sample 2 had weight and thickness of 80g/㎡ and 93 ㎛, and its roughness was 1.8~3.5 ㎛. Sample 3 had weight of 150g/㎡, thickness of 146 ㎛ and roughness of 1.4~2.7 ㎛. Porosity of paper samples 1, 2 and 3 was measured using a Densometer (Gurley model 58-03, TMI, U.S). Porosity of each sample was 400~500ml/min, 100ml/min and 5ml/min, respectively.

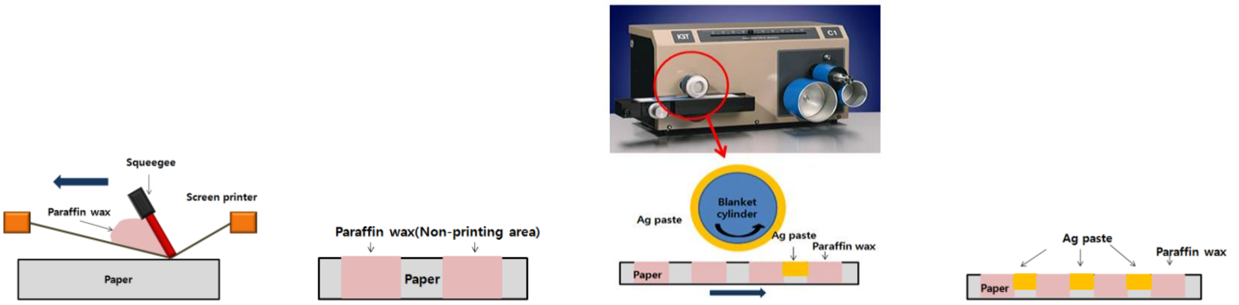
Methods

The WPOP experiment can also use a commercial common wax paper printed with partition printed by wax trench patterns, but the thickness of wax is not enough for this experiments, So this experiment was started by printing wax partition in the non-printed area of the papers using trench patterns. Since printing interval of patterns determines resolution, a wax printer may be used to form high resolution patterns, but the screen printing method was used in this experiment to create a thick wax layer with extreme hydrophobicity.[12] Here, it is important to prevent blocking of the plate by maintaining wax temperature at around 80℃. First, when the wax is printed on the printed object using a screen printer as shown in Figure 1 (a), the wax is printed in the non-printed area in the form of Figure 1 (b). If temperature of the paper is increased to 120℃ or above after printing, appropriate amount of wax penetrates into the paper and remaining wax settles down on the surface. Commercial paraffin wax was used for the wax, and viscosity of the paraffin wax was adjusted by mixing gelatin.[13] In the next step, the hydrophilic conductive ink was printed on the printed object formed with the wax partition using an offset printability tester model (IGT-C1, Holland), as shown in Figure 1 (c). The offset printability experiment was carried out in 5 steps by setting the range of printing pressure to 100~500N and printing rate to 0.3m/s. Due to the difference in repulsive force from the extremely hydrophobic wax, the ink is transferred to the printed area excluding the partition. A portion of the transferred ink remains on the surface and the remaining ink penetrates into the paper, forming a 3-dimensional conductive ink layer in the printed area.[14] Experimental temperature was maintained at room temperature of 20±3℃ and humidity of 17±5%. Ultimately, the object 3-dimensionally printed with the conductive ink was obtained as shown in Figure 1 (d) by printing the conductive ink in the printed area using the desired pattern.

Printing pressure, temperature and paste sintering time of the final objects printed with trench patterns and electrical resistance according to changing experimental conditions were measured to review whether the method can be applied to the manufacturing process of new printed electronics, and the experiment was carried out to find the optimal conditions.

Table 3. Physical Properties of Paper Samples.

Sample no. / Property	# 1	# 2	# 3
Thickness (㎛)	68	93	146
Weight (g/㎡)	47.7	80	150
Porosity (ml/min)	400~500	100	5
Roughness (㎛)	3.5~3.7	1.8~3.5	1.4~2.7
Bulk (g/cc)	1.5	2.0	3.0



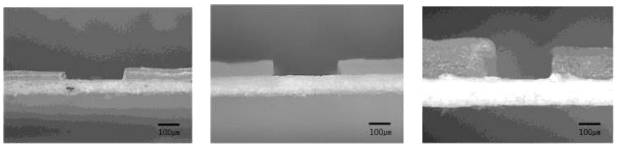
(a) wax patterning **(b) wax patterned paper** **(c) offset lithography** **(d) printed electronics**

Figure 1. Schematic diagram of WPOP (wax patterning offset printing) process for the manufacturing a printed electronics.

RESULTS AND DISCUSSIONS

Wax Patterning

Thickness and penetration depth of the wax transferred to the paper surface changes according to porosity, surface temperature of the paper, viscosity of ink and heating time etc. of the wax.[15] Variables that showed biggest effects were temperature and heating time of the wax. In other words, penetration depth of the wax was adjusted by concentration and temperature of the gelatin used. Penetration depth increases at high temperature as viscosity of the paraffin wax is decreased by the gelatin. On the contrary, low liquidity of the gelatin caused by low temperature leads to relatively high viscosity of the paraffin wax, causing the wax to penetrate thinly from the paper surface. Maximum penetration depth was adjusted based on this. Figure 2 shows the cross sectional view of the wax printed papers, and the wax is mostly transferred to the surface.



(a) **(b)** **(c)**

Figure 2. Cross sectional view of wax printed papers by screen printing. (a), (b) and (c) are samples of 1, 2 and 3 respectively.

The wax penetrates in the depth direction of the paper when temperature is increased to adjust penetration depth of the wax, but this can also cause a phenomenon in which it spreads out and smudges in the lateral direction. Especially irregular smudging can result from non-uniform formation of the paper. Therefore, it is necessary to choose papers that have uniform formation and distribution of pulp component. That is, a chromatography paper with uniform composition would be appropriate as the printing paper for the WPOP method. As described above, Figure 3 shows the measurement results after printing the wax and increasing temperature before penetration. In other words, Figure 3 shows values comparing the front and back sides of paper sample 1 after heating the printed wax to 120℃ for 10 ~ 60 minutes. Figure 3 implies that there is no smudging in the lateral direction of the wax when it approaches the 45° line. Although penetration in the depth direction of the wax is essential in creating a 3-dimensional partition, spreading in the lateral direction is undesirable. In particular, large difference between the front and back sides of the paper is probably caused by irregular gaps caused by paper formation and problems in surface chemistry. Width (w) of the wax partition used in this experiment did not differ until 400 ㎛, but a slight difference was shown between the front and back sides with thin partitions. However, a complete partition that can block electrical flow both on the front and back sides was formed up to 100 ㎛.

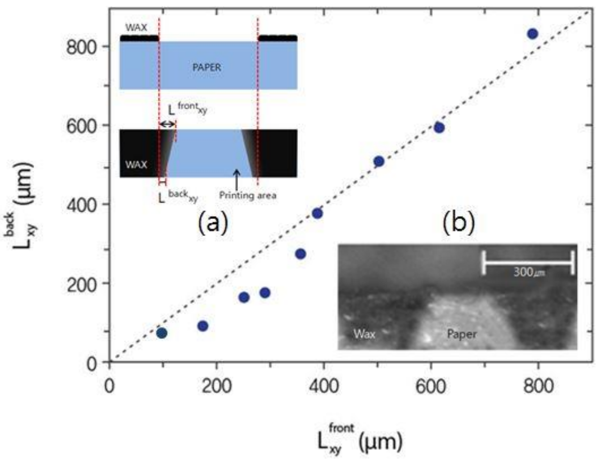


Figure 3. Cross sectional view of paper sample which was patterned by wax. Schematic (a) is a wax patterned model and photography (b) is a wax patterned paper sample 1.

In other words, it is important to adjust penetration rate of the wax in order to precisely form the wax partition. Figure 4 is the result of measuring penetration depth according to time while heating the wax transferred to the three papers to 120℃ for 90 minutes.

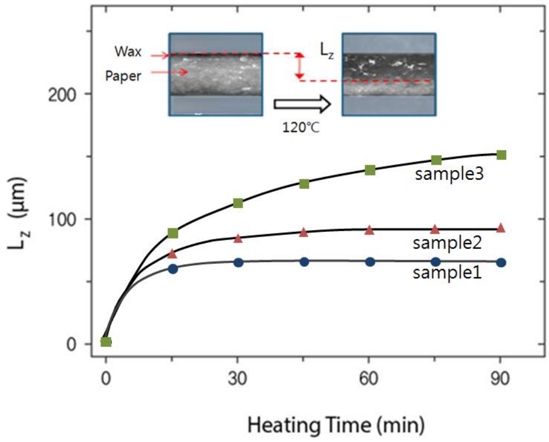


Figure 4. Microscopic measurements of depth of penetration of wax pattern onto papers. (a),(b) and (c) are the sample of 1, 2, and 3 respectively.

Patterning by WPOP

In the conventional offset lithography printing, the dampening water is used in the non-printed area to make it hydrophilic, and the ink is made to be lipophilic. The printed area and non-printed area are distinguished by repulsive force between water and oil. However, the WPOP method of this study performs offset printing on a paper where a partition is already formed by the extremely hydrophobic wax. Inversely to the conventional printing method, a hydrophilic ink can be printed in the printed area. Figure 5 shows the printing result. The printing result shows that the ink pattern is formed properly according to the wax partition. Based on the results of this experiment, the transfer amount of the ink was found to be affected by composition of the ink, surface characteristics of the paper as the printed object, and printing conditions like printing pressure and speed. Whereas sample 1 with high porosity has large transfer amount on the surface and greater penetration depth at high pressure and low speed, sample 3 with low porosity has large transfer amount on the surface but low penetration depth at low pressure, as shown in Figure 5. Sharpness of the printing results is related to surface roughness of the paper, and soft paper was found to have desirable sharpness of the surface.

(a) **(b)** **(c)**

Figure 5. Printed patterns of conductive ink on papers printed by WPOP method. (a), (b) and (c) are sample of 1, 2 and 3 respectively. The width of a line of each pattern is 100 ㎛.

The hydrophilic ink can be used by mixing and dispersing the silver paste with a commercial hydrophilic varnish and the ink, but offset printing requires tack of the ink to adjust the transfer amount of the ink.[16] We maintained the tack value to be constant, lowering the value by adding the varnish when the ink is dry or has high viscosity. When the value was too low, it was necessary to adjust the value because roller-to-roller or roller-to-paper transfer became poor.

Electric Conductivity of Pattern

Electric resistance was measured to predict electric conductivity after the silver paste pattern printing. Since the resistance value is affected by initial penetration depth from printing pressure, sintering temperature and sintering time among printability properties, the experiment intended to find the optimal value as presented in Figures 6~7. In other words, printing was done on the printed object while varying printing pressure to 5 steps within the range of 100~500N. The resistance value was measured while changing sintering temperature from 80 to 200℃ and sintering time from 10 to 90 minutes at every 30 minutes. It is a known fact that printing pressure is directly proportional to penetration depth of the ink[1], and this experiment also discovered that the resistance value decreases with increasing penetration depth of the ink. The effect on printing pressure increased with increasing porosity of the paper and increasing roughness of the surface.

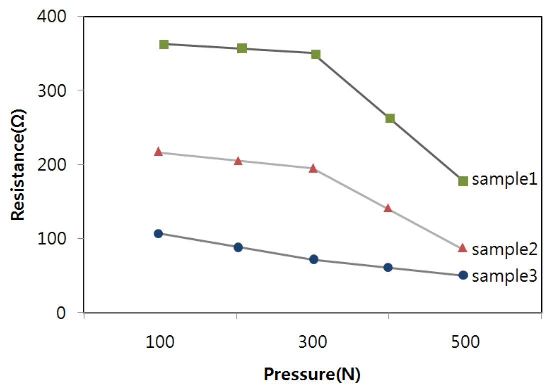


Figure 6. Electric resistances differences on the depth of conductive silver paste inks at temperature 80℃.

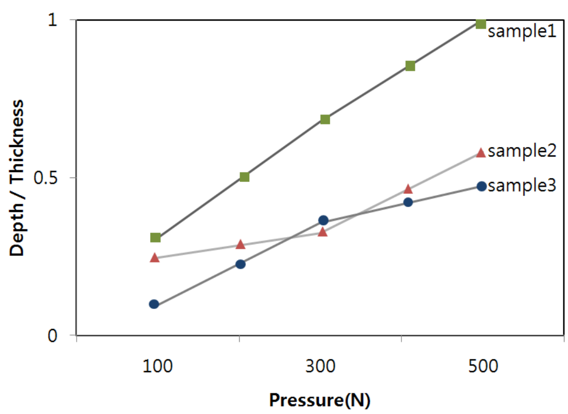
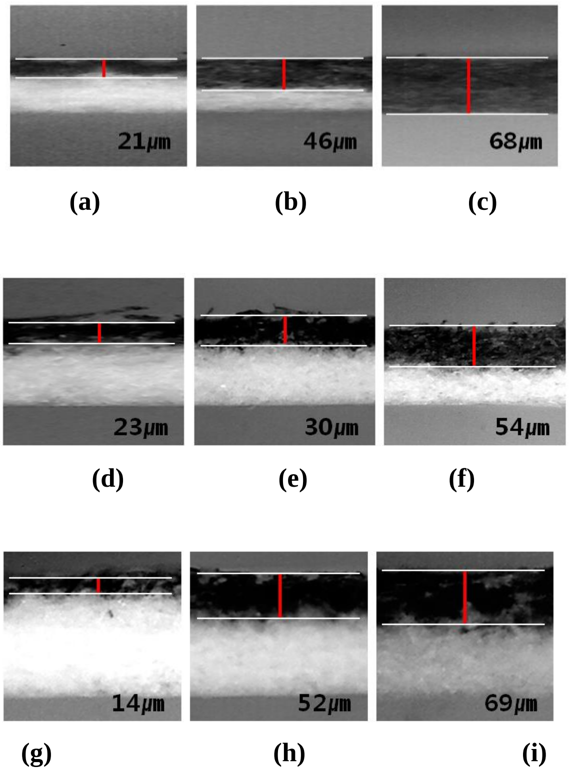


Figure 7. Electric resistances differences on the constant printing pressure of WPOP.

The resistance value decreases when sintering temperature increases. However, excessively high sintering temperature can affect the paper and wax partition. Based on the results of this experiment, the value of electric resistance becomes almost constant at temperature of 160℃ or above, optimal electric conductivity was obtained by setting temperature at or below 160℃ within the range of not causing deformation of the wax and paper and after about 60 minutes past printing. There can be differences among paper samples, but sample 3 showed the resistance value drop to 3.1Ω when a wax partition of 100 ㎛ width was made on the printed object, printing was done at printing pressure of 500N, and sintering was done for 60 minutes at 160℃. This resistance value indicates that the WPOP method is adequate for the manufacturing of printed electronics. Penetration depth of the ink is greatly affected by composition and formation of the paper, and Photograph 1 shows depth of penetration of the ink after printing. In Photograph 1, (a)~(c) are showing the depth of penetration and shapes of the printings when printing pressure is varied to 100, 300 and 500N, respectively. Similarly, (d)~(f) are photographs for sample 2 and (g)~(i) are photographs for sample 3.



Photograph 1. Cross sectional views and depth of penetration of inks onto paper samples. ((a)~(c) are sample of 1, (d)~(f) are sample of 2, and (g)~(i) are sample of 3.) (a),(d) and (g) were printed under 100N, and (b),(e) and (h) were printed under 300N, and (c),(f) and (i) were printed under 500N printing pressure by WPOP method respectively..

CONCLUSIONS

This study printed a conductive ink using the WPOP method, an offset lithography printing method, on three types of papers with wax partition to manufacture various printed electronics, trying to find the possibility and optimal condition of the process. The following conclusions were drawn.

1. When the silver paste ink was printed by patterning printing of 100 ㎛ width using this WPOP method, electric resistance was lowered to 3.1Ω. This result is adequate enough to be applied to the manufacturing process of printed electronics.
2. Although this study had limitations in resolution and penetration depth because commercial papers were used, the WPOP method can maximize penetration effect of porous papers by applying appropriate printing pressure. However, it was discovered that resolution and quality can be greatly improved by using papers with uniform composition.
3. The WPOP method that prints on papers can be used to manufacture flexible printed electronics. It can exhibit outstanding conductivity and stability through 3-dimensional penetration of the ink compared to the conventional printing method that simply prints on the surface.

Accordingly, the WPOP method proposed in this study can be used as one of methods for the manufacture of printed electronics in the era of flexible printed electronics and wearable devices. Also, we hope this WPOP study can help the development of fast and stable printed electronics process technologies.

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