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New Developments in Printed Electronics using Offset Lithography on Paper Substrates

Rakel Herrero[1]*, Maite Aresti[2]*, María Lasheras[2], Itziar Landa[2], Juncal Estella[2], Saioa Los Arcos[1]
[1]Materials Deposition Area, NAITEC, C/ Zaraputz 1, Estella-Lizarra (Spain); [2] Materials Area, NAITEC, Pol. Mocholí, Plaza Cein 4, 31110 Noain (Spain)
*corresponding authors

Abstract

In the graphic industry, a clear business opportunity has been identified using conventional printing technologies for the manufacture of high-performance, low-cost electronic products. However, despite having identified the business opportunity, often the developments can not be carried out because the right materials are not found.

Offset Lithography appears as the most suitable technique for paper substrates but it is not used in Printed Electronics due to the lack of conductive materials appropriated for this printing technology.

In this work the goal is to obtain a conductive offset ink that does not currently exist on the market. This achievement would mean a leap towards the manufacture of electronic products through offset on a more ecological substrate such as paper.

Introduction

Printing sensors and electronics over flexible substrates is an area of significant interest due to low-cost fabrication and the possibility of obtaining multifunctional electronics over large areas. Over the years, a number of printing technologies have been developed to pattern a wide range of electronic materials on diverse substrates.

Conventional printing techniques are applied to obtain products such as antennas [1], sensors for biomedical applications [2][3], passive devices, batteries [4] or displays. Although the definition is not as good as with microelectronic methods, the functional area can be greatly increased, being large-area printed electronics (OLAE) one of the fields with the greatest potential at the moment [5]. These techniques allow great flexibility, ease of integration, manufacture at a lower cost and scalability to large formats.

Using paper as a substrate for printed electronics [6] [7] has obvious advantages such as low cost, flexibility biodegradability, compostability and ease of disposal through fiber recycling or incineration. The existing paper-based industries can potentially benefit from added functionality beyond the printed graphic. This is the motivation for the new researches and developments of paper-based electronics. The future may well lie in mixed documents, containing both conventional printing and printed electronics [8].

The use of paper as an eco-friendly material shows a great potential to fulfill these demands, either exploring it as a substrate or as an active component. However, paper exhibits a porous structure and large surface roughness, which results in a series of shortcomings for hosting electronic devices on its surface, making it a challenging substrate compared to those that are smooth, but more expensive, such as non-biodegradable plastic foils, such as polyethylene terephthalate (PET) and polyimide (PI). To overcome this bottleneck, recyclable multilayer coated paper substrates with relatively high smoothness and good barrier properties can be used.

Several investigations explore the potential of paper as a substrate for thermochromic [9] and electrochromic displays [10], nonvolatile resistive memory devices [11], floating gate memory transistors , transistors [12], disposable radio frequency identification (RFID) tags [13], batteries [14], photovoltaic cells [15] [16]. Possible applications include sensing, diagnostic and pharmaceutical applications [17] [18].

Traditional approaches for printing electronics and sensors involve bringing pre-patterned parts of a module in contact with the flexible (or non-flexible) substrates and transferring the functional inks or solutions onto them. The development of a printing/coating system can be carried out by either contact or non-contact printing. Offset lithography is a contact printing technology which means that the ink is in physical contact with the substrate[5].

Offset lithography is a planar process where the printing chemistry is such that oil-based inks are attracted to the image area and water is attracted to the non-image area. This technique can achieve, high-resolution printing, minimum feature sizes of 10 µm are readily achieved.

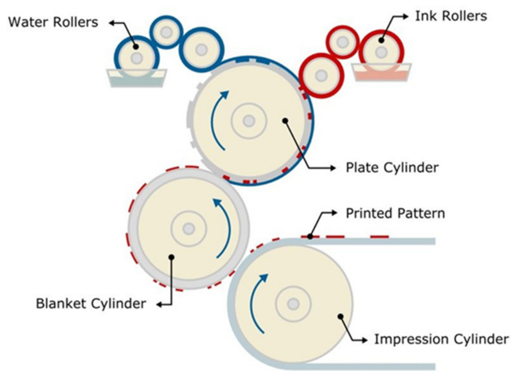

Figure 1. Offset Lithography printing process scheme.

Offset lithography is the most suitable for paper substrates and is the dominant industrial printing technique used for a wide range of products such as cards, stationery, leaflets, brochures, magazines, and books[19]. It can also be used for packaging such as boxes or cartons. The implementation of printed electronics in all these products opens a new broad field of new products and applications to be developed. However, nowadays it is not very used due to the lack of conductive materials appropriated for Printed Electronics.

In the early 2000's some work was done in the field of functional printing using offset lithography [20] [21] [22] [23] but it was discontinued.

The goal of this project is to obtain a conductive offset ink that does not currently exist on the market. In this way, achieving this development would mean a leap towards the manufacture of electronic products through offset on a more ecological substrate such as paper.

The focus is to formulate a conductive ink suitable for offset process on paper substrate. The ink has oxidative curing like graphic offset inks and need a post-treatment at 130ºC during 3 minutes in a belt furnace to obtain the conductive properties. Physical and functional properties after sintering were characterized to evaluate the ink.

Ink Formulation

Materials

For ink formulation the following materials were acquired from different suppliers (Lawter, Rokra, and Respol):

- Alkyl resins
- Rosin resins and derivatives

Also, additives and dispersants from BYK, Croda and Huber were used. Silver and silver/copper particles were also acquired from Metalor, C&S, Technic Inc, Hongw International and Dowa. Finally, solvents were supplied by Panreac.

Experimental Procedure

First, materials were identified to confer conductive properties to an offset ink, selecting silver and silver coated copper particles of different sizes and different coatings.

The offset technology is based on very viscous oily inks. The characteristic of this technology is that the ink must adhere to the geometries of the plate that are related to the oily part (hydrophobic area) while, in the rest of the plate, the ink repels due to its hydrophylity. Due to this characteristic, the selection of the dispersion medium is a very important factor since it establishes whether the ink is suitable for this type of technology.

The dispersion medium was selected considering that it must not oxidize the silver and silver copper coated particles. Various tests were done until the suitable medium was defined. Dispersion medium is formed by a resin, a solvent and additives to improve printability and to avoid oxidations during the use of the ink. The additives were dissolved in a mixture of the solvent and the resin. Afterwards, the particles were added. Each suspension was agitated using a mechanical mixer (Dispermat LC). The mixing speed was set at 3000 rpm.

To obtain a stable and homogeneous dispersion, a three-roll mill machine was used. The inks were milled during 20 min on a 127 mm x 65 mm triple roll mill (Torrey Hills T65) with roll surface speeds of 108-216-432 rpm and the nip gap was set at a constant 0.2 mm.

Rheological characterization of the inks was performed on an Anton Paar Phisica MC1 rotational rheometer. Measurements were taken at 23ºC±2 ºC. For measurements a concentric cylinder Z5 was used and the shear rate was measure between 0 and 5000 Pa.

Two commercial graphic inks were used as rheological models. Various dispersion mediums doped with silver and silver/copper particles were prepared to obtain a similar rheological curve (see Figure 2). Medium 3 presented the appropriate behavior for offset technology. This medium was selected to prepare the final ink (see Table 1).

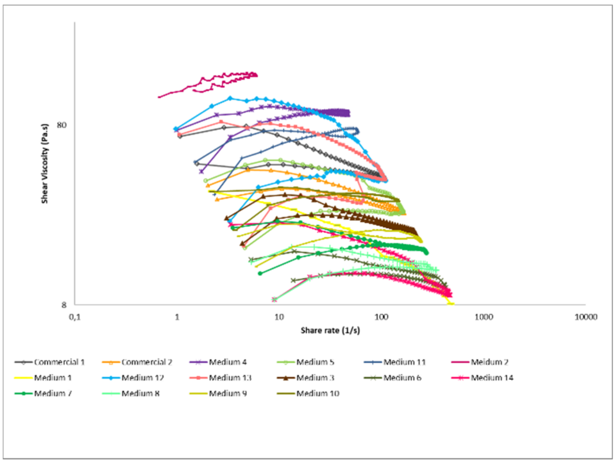

Figure 2. Rheological behavior of tested vehicles.

Table 1. Ink formulation

Ink formulation	% wt
Oily resin	9-22
Solvent	1-5
Additives	1-10
Solid content	63-89

The ink was tested in an offset lab machine (IGT C1 Offset Printability Tester) with positive results.

Figure 3. IGT C1 Offset Printability Tester

For the pre-scale of the ink a Miravalles three roll mill was used. Milling time was optimized and was set at 7 minutes for each batch. Production rate was 1kg/hour and 6 kilograms were produced for an industrial printing test (see Figure 8a).

Printing Procedure

After the first laboratory tests were passed, pre-industrial tests were done using a standard sheet-fed lithographic printing press (Heidelberg GTO 46) (see Figure 4). The printing speed was set at 5000 sheets/hour. Water balance was 47% and powder was used in the printing to avoid offsetting problems. A printing plate was designed using Illustrator design software (Adobe Corp LOCATION), containing rectangular and conductive tracks. Initially, several papers were tested and, after analysing the printing results, a 350 gr gloss paper was chosen (Ensocoat 350gr).

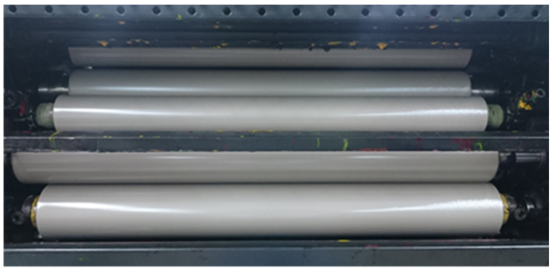

Figure 4. Ink distribution in the plate cylinders.

The developed ink has an oxidative curing as in graphic offset inks. However, a post-treatment at 130ºC during 3 minutes in a belt furnace is needed to obtain the sintering of the silver and conductive properties.

After setting the appropriated printing conditions and substrate, several CTPs (ComputerToPlate) were designed with distinctive features and several printing tests were done.

Several printing layers (from 1 to 4) were prepared for the validation of the functionality of the conductive layer.

Finally, an industrial test was done at Estella Print Company in a six-bodies KBA offset printing machine to validate the ink. Two of the six bodies were used for this test. For this purpose, 6 kg of conductive ink were formulated and used to print different prototypes using the 350g gloss coated paper. Printing speed was set at 8000 sheets/hour, water balance 47%. The designs consisted on a musical device “piano”, sliders, interdigitated electrodes and non-faradaic biosensors (see Figure 8). Also control features such as different thickness lines and control squares were added to the final design.

Physical and functional properties after sintering were characterized to evaluate the ink

Validation of Results

A multimeter Amprobe 5XP was used for resistance measurements and a Nikon Microscope 3D Model AZ100 was used for track width measurements (see Figure 7). Density measurements were done with a X-Rite 530 Spectrophotometer.

Measurements of the resistance were done in samples with up to 4 printed layers. Best results were obtained with 4 layers, but conductivity was achieved also with one printed layer (see Figure 6).

Figure 5. Validation of printing features.

Density measurements were used trying to correlate printing density values with conductivity values. It was found that density values higher than 1,05 give good conductivity and the best values were obtained when wet density values were 1,3.

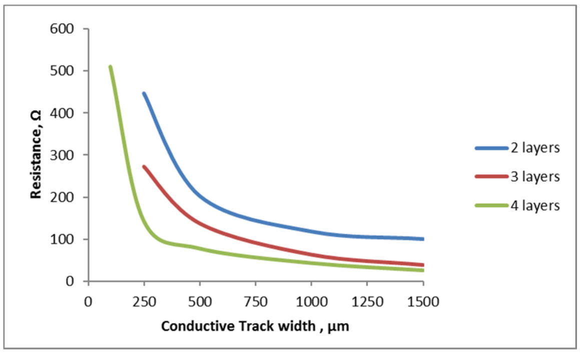

Figure 6. Resistance measurements. Comparison between resistance values and layer number.

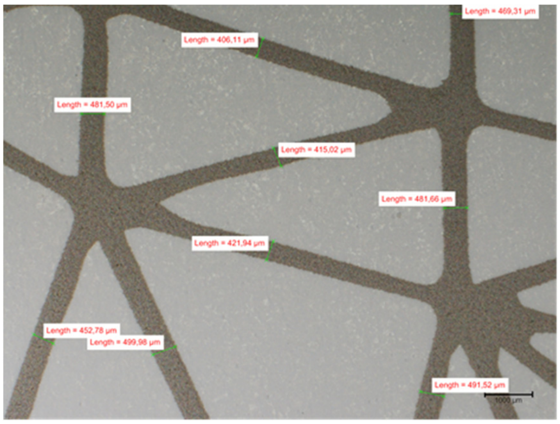

Figure 7. Track width.

For the final validation of the ink, a musical device was printed and integrated with commercial software. It consisted on a capacitive sensor integrated using a cypress board, making a paper piano.

The fabricated device was based on "button-type" capacitive sensors, i.e. capable of detecting an action or pulsation by the user. These types of sensors are common in the Interfaces Man-machine (HMI) interactions. The function of a capacitive detector is to indicate a change of state, based on the variation of the stimulation of an electric field. Capacitive sensors detect metallic or non-metallic objects, measuring the change in capacitance, which depends on the dielectric constant of the material to be detected, its mass, size, and distance to the sensitive surface of the detector.

Usually, capacitive-type sensors require very specific circuitry, so it is common to find integrated circuits specifically designed to interact with them in the market.

The sensing mechanism is based on the CapSense ® technology of the Cypress House. This mechanism is based on a capacitor switching circuit, which converts the measured capacitance into an equivalent series resistance connected to an internal reference voltage

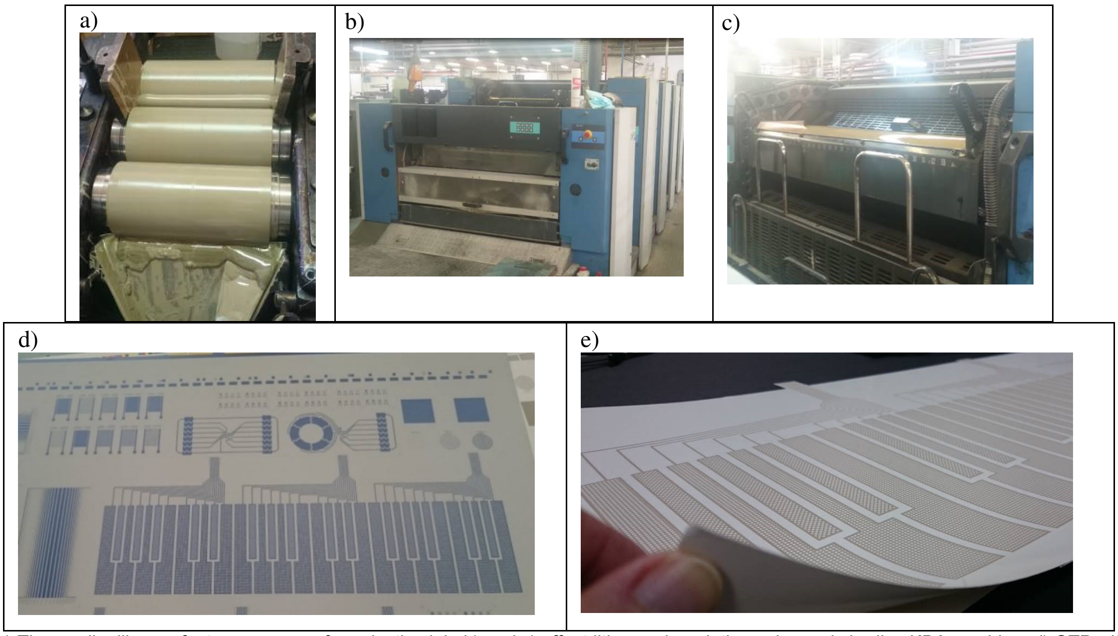

Figure 8: a) Three roll mill manufacture process of conductive ink; b) and c) offset lithography printing using a six bodies KBA machine; d) CTP with various printing designs; e) musical device printed on paper substrate

A Sigma-Delta modulator converts the current through this resistance to a digital value. When the target approaches the sensor, the capacitance increases, resulting in a decrease in the value of the equivalent series resistance and, therefore, an increase in the current flowing through it. The Sigma-Delta modulator compensates for this increase, resulting in an increase in the quantified digital value. In order to decide when white is detected, some algorithms are applied to the digital value provided by the Sigma-Delta modulator.

Although the measurement technique of each electrode is similar to the one described (CapSense ® of Cypress), in this case there is an added complexity since it is not only to evaluate the response of a single sensor, but it is necessary to measure the way in which each sensor affects the sensor next to the one pressed.

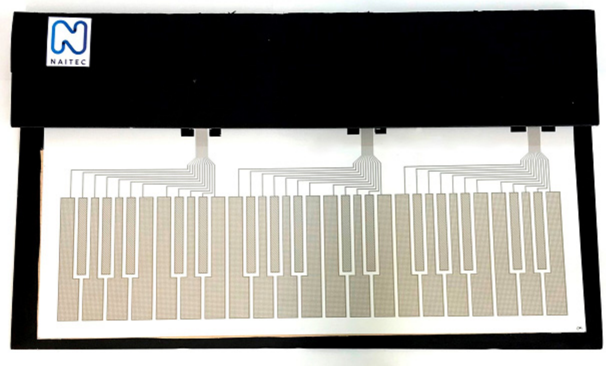

Figure 9. Paper printed piano device.

Therefore, this type of device requires an adjustment mechanism in which a detection threshold is established which takes into account the interference with the rest, the noise and the robustness. For these sensors, the sensitivity is regulated so that distance detection is not carried out, but it is necessary to touch with the finger on the paper to obtain a response.

A complex filtering algorithm decides which sensor is the one being touched, and the software on the evaluation board uses that information to emit a pulse of a default frequency using a buzzer. Each sensor is software-associated with a frequency corresponding to the music notes on the same scale, thus creating a piano.

Figure 9 shows the integration of the printed piano with the plate that controls the sensor. This device is ready to be used, so when playing on one of the keys it emits a musical note.

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Author Biography

Dr. Rakel Herrero is Project Manager at NAITEC. M.Sc. in Polymer Chemistry (1999) and PhD (2002) at The Manchester Metropolitan University.

She joined CEMITEC in 2003 working in polymer materials and biodiesel R&D projects in the Materials Area. She has being working in functional printing since 2006, first in functional inkjet printing and since 2011 in the Materials Deposition Area of NAITEC using the following printing techniques: R2R flexo printing, gravure coating, rotary and flat screen printing and sheet to sheet offset printing. Her job is mainly focused on printed electronics. Lately she has been working on bio-active materials printing, e-textile development and on the start-up of a new functional inks company MATEPRINCS, which commercialized the inks developed at NAITEC.