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Offset Printing of Conductive Features onto Paper Substrates

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Abstract

Offset litho printing offers a useful fabrication method for Printed Electronics. It is capable of high speed printing and there is a large installed base of presses on a variety of scales. Paper in various forms offers an interesting substrate for systems integration of Printed Electronics features. It is widely available at attractive prices, compatible with many existing industrial processes and has the potential to add interesting features to functional print.

Conductive features are a key element that enable the fabrication of Printed Electronics. The purpose of this paper is to explore some of the key issues arising from the printing of conductive features onto paper using a standard factory litho press. The whole ethos for this work was to use standard equipment and substrates commonly found in a litho print house and explore the issues that this implementation entails.

As a result the paper substrates chosen are those commonly in use for commercial litho printing, the press was an unmodified unit taken straight from commercial print runs and no specific drying protocols were instigated over and above the commercial print industry standard of stacking prints on the factory floor. As such it serves to illustrate the sort of features that could be produced in any commercial litho printing hall.

Impact printing for Printed Electronics

In recent years there has been a focus on the use of non-impact printing techniques such as inkjet for printed electronics. However, for high speed fabrication traditional impact printing techniques have a lot to offer. As an example, there are a number of groups working on gravure printing for printed electronics.[i] This work takes an alternative approach and illustrates the potential of offset litho printing as a fabrication method for printed electronics. The process is capable of very high speed printing with low set up and running costs and there is a large installed base of presses worldwide on a variety of scales.[ii] It should be noted at the outset that offset litho generates some quite thin printed layers, typically <1µ dry thickness. This makes for economical use of expensive inks but at the penalty of lower conductivity features.

It should be noted at the outset that the inherent nature of offset litho printing splits the ink film a number of times before impression and therefore generates very thin printed layers of typically <1µm dry thickness. This makes for economical use of expensive inks but the compromise is potentially lower conductivity features.

The offset litho process is therefore less forgiving than other print processes. However, depending on the specific resistance requirements of the final application, the proliferation of the offset litho process across the print industry may offer an especially cost effective mass production process for large area conductive features.

As the offset litho process may not be familiar to this community this section begins with an overview of the process.

The Offset Litho Printing Process

Lithography is a planographic process, meaning that both the image & non-image areas sit in the same plane on the printing plate. The image areas are oleophilic/hydrophobic; the non-image areas are hydrophilic.

The lithographic process is typically a rotary process. The printing plate is mounted around a cylinder, and the motion of the press is controlled by driving these cylinders.

Before each image is printed, in the printing process, the plate is first damped by rolling against a cylinder with a fount solution. The hydrophobic image areas repel the water of the damping system, whilst the hydrophilic non-image areas are wetted by the damping solution. When oil based lithographic ink is then transferred onto this damped plate by the inking roller, the ink transfers onto the dry surface of the image area, but does not transfer onto the wet non-image area of the printing plate.

The printing plate then rotates to transfer this inked image onto a transfer blanket, which is the offset step of the process, before the image is then transferred onto the substrate. This offset step protects the surface of the printing plate, by only ever allowing it to come into contact with the soft transfer blanket rather than the comparative roughness of the substrate.

Offset litho presses come in a variety of sizes and formats. This is one of the attractions of this deposition method – it is scalable. This work was done on a Heidelberg GTO, a small scale machine illustrated in Figure 1. Although (comparatively) small it is capable of rapid accurate A3 print production with 2 individual print units. This approach has also been used by previous groups to fabricate conductive features.[iii]

Figure 1 A Heidelberg GTO offset litho press

The Printing Plate

There are many different types of lithographic plate commercially available and the selection of the plate is usually regulated by the technical parameters of the specific press, cost and the length of print run. Typically offset litho plates are most commonly produced from aluminium, which has been processed to produce the image and non-image areas.

The Fount Solution

The primary function of the fount solution is to keep the non-image areas of the printing plate free from ink. However, the solution also maintains the hydrophilic nature of the non-image areas of the plate; it controls any emulsification of ink and water and lubricates both the plate and blanket.

The fount solution itself is a controlled formulation generally consisting of –

- Water to damp the plate.
- A desensitiser, typically gum arabic or carboxymethyl cellulose, which replenishes the printing plate's fragile non-image area, maintaining the ability to repel ink.
- A pH modifier, usually an acid, which keeps the plate image area sensitive to ink as well as keeping the background areas sensitive to water. High pH will create emulsification problems between the ink & water and too low a pH may cause drying issues, poor print definition or in extreme cases damage to the plate.
- Wetting agents or surfactants to lower the surface tension of the water. This maintains the primary wetting characteristics of the non-image areas of the plate. The wetting agents also reduce the amount of water necessary to keep the plate clean and therefor reduce the amount of ink required for printing.
- Additives, which include anti corrosives to minimise the effect of the acid on the aluminium printing plate. Most solutions also contain antifoam and anti-fungal agents. The fount solution will often also contain buffering compounds to keep the solution acidic, as well as other additives to balance specific plate/ink/blanket/substrate characteristics.

The fount solution is usually supplied as a concentrate to be let down with water before use. During a print run it is important to monitor and maintain both the pH and conductivity of the fount solution as contaminants from the substrate change the properties of the fount solution. These contaminants can interfere with fountain solution performance and can manifest themselves as press problems such as scumming in the non-image areas etc.

The acid in the fount solution helps the desensitiser to combine with the aluminium oxide on the non-image areas of the plate, maintaining the hydrophilic properties, which would otherwise degrade rapidly. The pH must be monitored and kept stable, as contaminates such as calcium carbonate from paper substrates will change the solution pH.

The conductivity of the fount solution is raised by an increase in the number of ions present from minerals in the water. Conductivity is a good indication of the concentration of contaminates entering the fountain solution. As contaminates enter, the conductivity will rise.

The pH and conductivity should be monitored on press during any print run. A single measurement will give no indications of any potential problems. Tracking pH and conductivity will begin to show when adjustments or top ups to the fount solution are required.

When using a fount concentrate, another factor in managing consistent press chemistry is the hardness of the water supply, which will in turn depend on the local water supply. Hard water will contain calcium and magnesium minerals, which will act together with the contaminants in the paper and can create build up on blankets. Water hardness can be monitored by the conductivity measurements. Many modern press configurations will be fitted with a Reverse Osmosis unit to purify the water supply.

The Offset Blanket

The functions of the offset blanket are to squeeze away any excess water, which would otherwise saturate the substrate in any non-image areas, and to collect the ink image and transfer it to the substrate with a consistent, uniform pressure, accommodating any substrate surface texture. Traditionally made from a rubber type material there are many different types of blanket commercially available.

On-Press Control

During the print run there are a number of variables coming into play to achieve a reproducible, consistent result. It is important to monitor and control a number of parameters.

Dot gain is used in the same fashion as with inkjet printing. In this context it describes the increase in dot size between the image on the original design/plate and the final dot size achieved on the finished print. Dot gain is an inevitability when considering the transfer of a fluid ink through pressure from the printing plate to the blanket and the blanket to the substrate.

When printing with conductive features it is unlikely that the image will contain dots, more likely tracks & solid areas. However, when printing fine lines and gaps the plate image should be adjusted in press to allow for the anticipated gain, which could otherwise result in unwanted short circuits.

Optical Density of the printed inks should be measured and monitored during a run by using a densitometer. The density of the printed ink will indicate the final weight of ink being transferred to the substrate. A greater density will indicate greater ink transfer and therefore a lower final sheet resistance of the printed conductive ink. A corresponding lower density will indicate reduced ink transfer and therefore a greater sheet resistance of the printed conductive ink.

In isolation the optical density is of little use except perhaps as an aesthetic measurement. However, as a continuous check, during the print run, the measurements can serve as a very useful comparison of sheet to sheet and as an early indication of where adjustment to the amount of ink being applied can prevent inconsistency issues in the final sheet resistance of the printed conductive ink.

It should be noted here that the optical density measurement of metallic inks can contain significant challenges.

Key characteristics of offset litho inks

For this work the offset inks were based on typical oil based oxidative drying ink systems. They are thick pastes, typically between 100-400 poise when standing. However the inks are thixotropic, meaning that when standing they are high viscosity, however when under constant shear their apparent viscosity decreases. This non-Newtonian nature of offset inks is advantageous within the process in that it allows the ink to transfer uniformly onto the substrate whilst under shear and quickly regain viscosity and structure immediately following the print impression to hold the clarity & accuracy of the features printed.

These offset inks dry by a combination of physical penetration into the substrate and air oxidation. As ink is printed onto the substrate, liquid components within the formulation penetrate into the substrate before oxidation of the printed ink takes place; where the varnishes within the vehicle system harden through a chemical process that occurs on contact with oxygen in the air.

For this work two ink systems were formulated based on different conductive pigments. The first was a high cost, but lower resistance silver particle and the second a significantly more cost effective, but more resistive carbon.

These inks have been formulated to be slightly over-pigmented when compared to normal graphic inks. This allows greater contact between conductive particles in the dried ink film, maximizing the achievable conductivity.

Paper substrates for printed electronics

This work also considers the potential of paper substrates for printed electronics. Paper has a number of attributes that make it an attractive substrate for printed electronics.[iv] The aim of this section is to lay out some of the key issues in the selection process.

The issue of surface topography

One of the key features in the selection of paper for printed electronics is the surface topography.[v,vi] In particular it has been shown that there is a correlation between conductivity and coated paper surface roughness.[vii] There are a number of ways in which this issue can be addressed for the fabrication of paper based electronics.

One method is to use another printing process to planarise the surface, reducing the surface roughness to a more desirable level. This can also have the advantage of reducing the absorbance of the paper surface.[viii] Whilst this method introduces an additional printing step it does facilitate the use of much cheaper paper substrates.

An alternative to this is to use a coated paper substrate to bring the surface closer to an optimum surface.[ix] There are a number of options on this that are covered in the references in this work. However, this study focussed on the use of standard offset paper.

Offset printing paper

Offset printing paper offers some useful options for printed electronics production. First and foremost, it is readily available at reasonable pricing for commercial print work and is widely found in factories producing offset litho work. Second, it is coated to reduce absorbency and produce a smooth surface with sharper line detail. It has been noted that the porosity of offset paper is not optimal for technologies such as inkjet.[x] However, it does produce good conductive feature from offset litho printing and some element of post processing of the inks.

The need to post process conductive inks

One common thread in the literature on conductive inks is the need for thorough drying/curing of the print to render the inks conductive either through additional heat or through extended drying times. Residual fluids, such as volatile organics impede the contact between individual conductive particles in the printed ink film. This is particularly the case for non-porous materials such as PET or polyimide where there is no other route than evaporation to remove these residual "contaminants".**Error! Bookmark not defined.** Even coated papers exhibiting high porosity have been shown to need post-print treatment such as heating / sintering to render inkjet printed silver conductive.[xi]

However, isolated instances do occur when this has been shown not to be necessary. For example, it has been shown that aqueous based silver inkjet inks can become conductive without post processing when deposited onto coated proofing paper.[vi] A similar situation has been presented at this conference on a coated product with very fine pore sizes.[xii]

This was seen as being a particularly interesting area to explore, particularly for methods such as offset litho. That is because they are capable of particularly high speed print production resulting in the need for supplementary large high speed driers that could compromise the value potential of the process. In addition, these units do not currently exist in commercial litho printing halls, hindering the uptake of this production method.

Oxidative drying, exposed to ambient air has been reported for litho printed conductive inks.[iii] The inks formulated for this work however were designed to be printed onto absorbent papers and dry by oxidation – they require no other post processing method over and above the commercial print industry standard of stacking prints on the factory floor. Whilst it is acknowledged that the post processing methods described in the literature could have sped up the process they would not have increased the final conductivity of the printed conductors. For this work the applications considered did not make additional drying processes necessary or, from a production standpoint, desirable. The only method that was considered was Joule heating as a method of post processing in the final device as an automated way to trim the final characteristics.[xiii]

Experimental examples

A Heidelberg GTO press of the type illustrated in Figure 1 was used to produce the prints illustrated here. A number of test patterns were printed as part of this work and these are described in the relevant sections below.

Materials

The silver and carbon based offset litho inks as described above were printed onto 2 papers, both in sheet sizes of 0.45 x 0.32m (SRA3).

- 150gsm Arjowiggins Cocoon Silk paper. A 100% recycled paper with a silk finish coating for offset presses.
- 120gsm Digicolor smooth uncoated paper. More a general purpose paper than specifically offset quality.

The resultant prints were stacked straight from the press and left to cure. Immediately following printing the features were non-conductive but over a period of 1-2 days the conductivity rose to the measured values.

Conductivity results

Even at a most basic level, conductivity results reveal a substantial difference between these 2 paper for this application. A series of 180 x 3mm lines were printed to test for conductivity. The results achieved are illustrated in Table 1.

	Carbon ink	Silver ink
Cocoon Silk paper	43MΩ	8.5kΩ
Digicolor paper	Non conductive	Non conductive
Digicolor paper – printed twice	12MΩ	Non conductive

Table 1 Resistance figures for the printed lines

It will be noted immediately that these resistance figures are rather high. This is partly due to the thin layers produced by offset litho printing but a set of photomicrographs were used to investigate this further.

All photomicrographs are of the same scale with a 1.1mm horizontal size.

Ink on ink test pattern

The primary test pattern used to produce the photomicrographs in this publication is shown in Figure 2.

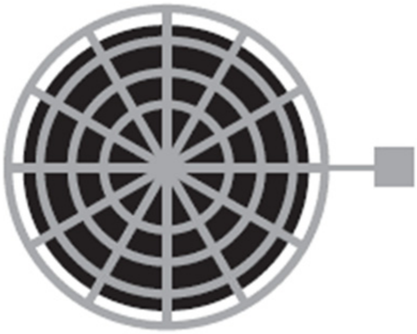
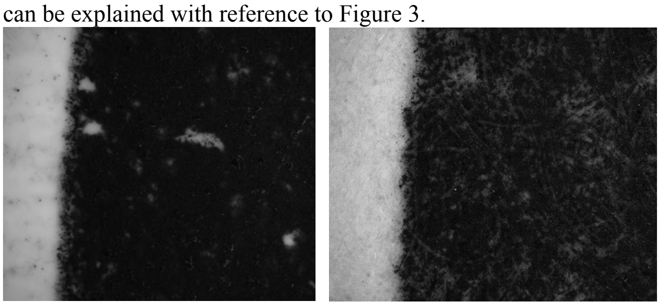


Figure 2 Test pattern for in work. The diameter of the outer circle was 25mm.

The test pattern was printed in 2 steps. First, the carbon ink, illustrated in black in Figure 2 was printed and the prints were left to cure for >2 days before the silver ink, illustrated in grey in Figure 2 was printed. The aim of this rather cumbersome regime was to investigate the use of 2 inks without any wet-on-wet interactions.

Carbon ink on paper

It can be seen from Table 1 that there are significant conductivity differences between the 2 paper substrates. This can be explained with reference to Figure 3.



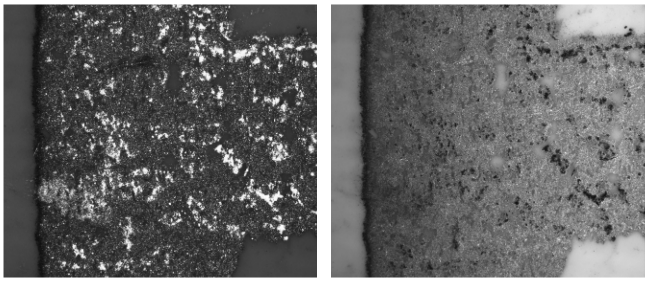
Cocoon silk Digicolor

Figure 3 Photomicrographs of the carbon ink on paper

Close examination of Figure 3 reveals that for the Digicolor paper the integrity of the conductive carbon print is disrupted by the fibrous structure of this uncoated paper surface, whereas the smoother layer of the Cocoon Silk paper produced a more continuous surface. It was found that a second print pass with the carbon ink produced a conductive feature but this did not prove to be a route that worked for the silver ink. This was also found to occur on a previous study with another non-coated paper. It may be possible to improve the lay of the ink on the Digicolor paper by adjustment of the ink formulations to reduce the tack and/or viscosity of the ink.

Silver ink on Cocoon Silk paper

It can be seen from Table 1 that the silver ink on Cocoon Silk paper produced significant conductivity. This morphology of this printed silver is illustrated in Figure 4, taken from a region on the centre left hand edge of Figure 2.



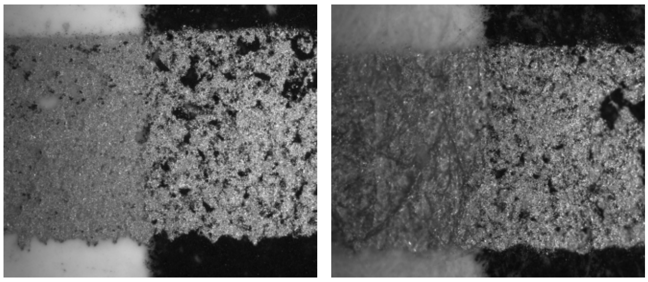
Bright field illumination Dark field illumination

Figure 4 Photomicrographs of the silver ink on cocoon silk paper

While these printed lines (approximately 0.5mm width) are conductive, careful study of these features reveals significant voids in the lines. This not only limits average conductivity but also puts a practical limit on narrow line widths. It may be possible to improve this with amendment to the process conditions, such as ink reformulation to reduce emulsification of the fount/ink to improve ink transfer or by exploring different blanket options and /or tuning of the press chemistry.

Silver ink on carbon ink

Figure 2 shows that this work also investigated the effect of printing silver on top of the carbon ink too. This produced some interesting effects, as illustrated in Figure 5.



Cocoon silk 2nd uncoated paper

Figure 5 Photomicrographs of silver printed on top of carbon ink

In the case of the Cocoon Silk paper it can be seen that voids in the silver ink are much more evident when printed on top of carbon ink. This is not just an optical contrast phenomenon; the silver was found to me much less conductive when printed on top of the carbon ink. This is likely to be caused by the carbon ink effectively sealing the surface of this paper substrate and therefore not allowing penetration of slower drying volatiles within the silver ink formulation which would create the voids when they do eventually evaporate from the surface of the printed silver ink. The dried carbon ink may also be presenting a lower surface energy which could create slight reticulation issues which would mar the formation of a continuous ink film.

This test was also conducted on a comparatively porous, uncoated paper as part of another body of work. In this case the carbon ink tuned the silver from nonconductive to conductive. Although this was not investigated in detail it would appear from reference to Figure 5 that the carbon ink effectively covers the fibrous nature of this uncoated paper, thus allowing the silver ink to produce a continuous film.

Discussion

The aim of this work was to identify application areas for offset litho onto paper based products for Printed Electronics applications. Here are some of the findings that we feel come from this work.

1. Reference to Table 1 will show that the printed features cannot be classed as highly conductive. However, there are application areas where resistance could be a positive benefit. Printed heaters and resistive strain sensors[iii] could be examples.
2. There are some challenges with printing offset litho conductive inks. One key challenge is the thin ink film, of around 1 micron, actually printed onto the substrate.
3. Reference to the photomicrographs will show that the thin printed layers of conductive inks onto these substrates are broken up in many places. Whilst further work to tune the process and adjust the ink formulations, the press chemistry, substrate and different plates/blankets may improve this This may put a practical limit on the print resolutions that could be achievable in practice. However, there are many wide area electronics applications where fine line widths are not required. It also suggests that if fine line widths are required commensurately smoother media would have to be used.
4. Many offset litho presses feature multiple in line printing units. Multiple passes of the same printed ink have been shown to help this break up of printed layers and offset printers with multiple units could achieve this in practice.
5. Industrial scale offset litho presses often consist of a serial arrangement of a number of printing units, each of which can be loaded with an individual ink. These can be used to print multiple layers of the same material in one print pass to increase conductivity. Alternatively they can be used to produce multilayer features. An example of this is shown in Figure 5 but the use of industry standard UV cured varnishes can also add insulation layers to printed areas.
6. Offset litho printed conductors need not be used in isolation. As an example separate work from this has demonstrated that these features will make an electrical connection to screen printed conductors.
7. A standard litho production route with an unmodified press in a standard dusty press hall using normal press chemistry and industry standard coated offset paper can produce some useable Printed Electronics features without the use of additional post processing. This could be a low cost entry into the mass production of large area conductive features.

Potential applications

This work points the way to some potential applications for offset litho printed features in Printed Electronics.

This is a useful production route to large area conductors, perhaps 1cm in width where small voids are not an issue. Indeed, in some cases this could be turned into a feature. For example, these features make very acceptable wide area heaters, opening the way to large area heated sensors. This could be a particularly powerful attribute when considering the properties of a paper substrate.

The benefit of paper substrates

The benefits of paper as a Printed Electronics substrate have been described previously.[iv] However, paper has more potential than simply being the substrate for conductive features. It also offers the possibility of being the sensing element, converting a conductive feature into a fully functioning sensor. A good example of this is the propensity of paper to change characteristics with humidity, the basis of metal-paper coil hygrometer.

Polyimide and coated photographic papers have already been shown to work in this manner, using planar interdigitated electrodes produced by inkjet.[xiv] Similar work using screen printed interdigitated electrodes on recycled paper and cardboard also produced functional sensors.[xv] Although not investigated as a part of this work there is a high level of expectation that litho printed planar interdigitated electrodes should also function as a humidity sensor without other added elements.

Although again not studied here, it is likely that a smoother substrate surface would enable production of finer features. This is currently being investigated by other groups.

Biographies

Alan Hodgson has 30 years experience in printed hard copy and a background in photography and image science. After consultancy work in Printed Electronics and Security Printing he has also spent 7 years at 3M, specialising in print solutions for high security documents and the integration of Printed Electronics into 3M manufacturing. He has recently returned to his consultancy business, working on printing consultancy projects that include functional print.

Alan is active in Printed Electronics, both as a practitioner and Chair of IEC TC119 (Printed Electronics). He has a BSc in colorant chemistry and a PhD in instrumentation, both from the Department of Chemistry at the University of Manchester. He is a Visiting Academic with the University of Manchester Centre for Digital Fabrication and immediate past President of the IS&T.

Chris Jones has been involved with conductive print since working on conductive ink formulations for RF applications in 2000. He joined Novalia in 2010 as the ink and print expert. He has over 25 years practical print & packaging industry experience, having previously held senior positions within leading ink manufacturers & print and packaging organisations in the UK, Europe & South America.

Within Novalia he is responsible for identifying and leading conductive & functional ink formulation, print production and process developments, working closely with global materials and production suppliers to develop consistent, repeatable manufacture processes. He works directly with senior internal and external scientists from Industry and Academia.

Chris is an External Researcher at the University of Cambridge Graphene Centre and he serves as the Vice Chairman on the UK Plastic Electronics Leadership Group, and he is a member of IEC/TC119.

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