GRAVURE-OFFSET PRINTING IN THE MANUFACTURE OF ULTRA-FINE-LINE THICK-FILMS FOR ELECTRONICS

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Abstract
In gravure offset printing, ink is transferred with the help of an offset material from a patterned gravure plate to a substrate. This thesis is concerned with the study and further development of this printing process for electronics; on alumina, glass and polymers.

The work has been divided into five parts. In the first section, the printing process is described. The second section describes the composition of the inks for gravure offset printing and the resulting ink properties. It also presents the ink transfer mechanism; the model that explains how the ink is transferred between an offset material and a substrate. The third chapter details the printing process explained by a solvent absorption mechanism. The forth chapter describes the firing/curing of printed samples and their properties. The last chapter describes applications of the method.

The inks used to produce conductors on ceramics (ceramic inks) and conductors on polymers (polymer inks) contain silver particles, and were under development for gravure offset printing. The major achieved properties were the high ink pickup to the offset blanket and high transfer percentage to the substrate. 100% ink transfer from blanket to substrate for ceramic inks and almost 100% ink transfer for polymer inks was obtained. The printing of ceramic inks was able to produce 8 μm of relatively thick, 300 μm wide lines with <10 mΩ/sq. resistance. The minimum line width for conducting lines was 35 μm, with one printing. Multi printing was applied producing as many as 10 times wet-on-wet multiprinted lines with 100 % ink transfer from blanket to substrate resulting in a square resistance of 1 mΩ/sq. Polymer inks were able produce a square resistance of 20 mΩ/sq. for 300 μm wide lines after curing at 140 °C for about 15 min, and the minimum width was down to 70 μm.

In the optimised manufacturing process, the delay time on the blanket was reduced to 3 s. In addition to ultra-fine-line manufacturing of conductors, the method enables the manufacture of special structures e.g. laser-solder contact pads with 28/28 μm lines/spaces resolution. With industrial printing equipment it is possible to produce 100 m²/h with the demonstrated printing properties.

Keywords: ceramic materials, conductive inks, gravure-offset, intaglio, printing, thick-film
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Finally my deepest gratitude to my wife Regina from all the support.

Oulu, March, 2004

Marko Pudas
List of original papers

This thesis consists of the compendium and the following original papers, which are referred to throughout the text by their Roman numbers.


III Pudas M, Hagberg J and Leppävuori S. Printing parameters and ink components affecting ultra-fine-line gravure-offset printing for electronics applications. Accepted to: Journal of the European Ceramic Society.


V Pudas M, Hagberg J and Leppävuori S. The self-cleaning gravure (SCG), a solution for gravure groove blocking and a novel printing method. Accepted to: Journal of Imaging science and Technology.


VII Pudas M, Hagberg J and Leppävuori S. Roller type gravure offset printing of conductive inks for high resolution printing on ceramic substrates. Accepted to: Active and passive components.

The object of Paper I was to introduce a gravure offset printing method for electronics. The paper describes gravure plate manufacture, the printing process and gives indications of the narrowest lines that can be printed.

Paper II deals with an approach used in the selection of ink components for gravure offset printing. It deals with multivariate analysis using multiple linear regression (MLR) and partial least squares (PLS) multivariate methods with the aid of Modde 4.0 software.

Paper III studies the physical parameters affecting the gravure offset printing process and the significance of the ink solid content.
Paper IV describes the ink transfer theories observed for gravure offset printing. Absorption ink transfer theory is considered in more detail because the inks resulting in the highest printed mass and line quality have their behaviour best described by this theory.

Paper V proposes a novel solution for gravure groove cleaning and a novel printing method derived from the same. Blocking of gravure grooves by ink was found to be a major issue in the studied printing method.

Paper VI describes the background and properties of the polymer inks containing silver particles, that have been used to print conductors.

Finally, paper VII is a summary of gravure offset printing properties. It presents inductor, capacitor and laser soldering substrates as potential applications. Limitations of the gravure offset technique are listed.

All practical printing work described in papers was the contribution of the author with the assistance of technical staff. All measurements in papers were carried out by the author. The author has had a major role in the preparation of the manuscripts for papers II-VII and has contributed to manuscripts for papers I and VII. The experiments were carried out in The Microelectronics Laboratory, Department of Electrical and Information Engineering, University of Oulu, Finland. Printing equipment was from the laboratory and the research was done in the HiReCiPri EU-research project.
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1 Introduction

1.1 Printing processes in electronics manufacture

Trends in microelectronics have been towards smaller features, lower prices, increased operational frequencies and more reliable products [1]. In order to create these products, a decrease in circuitry (board) size is required. One of the major factors limiting the size of the product is the density of conductor lines on the substrate and the board. There is also a demand for higher manufacturing speeds and a reduced number of process steps.

Printing of conductor inks (paste) selectively onto the substrate is a direct and additive process that offers a potential solution for future demands. Thus printing offers a more environmentally friendly manufacturing method with improved properties, compared to those of conventional copper printed circuitry board (PCB) manufacture. The latter is a subtractive process and it involves many steps and more waste products than an additive printing process.

Screen-printing, also known as silk-screen printing, is widely used in the graphic printing industry. It has long been used in the manufacture of electronic hybrid circuits and PCBs. Although it is possible to print a variety of inks with screen printing, its limitation is the resolution. When the screen is replaced by metal (or polymer) with holes patterned in it, the method is called stencil printing. Stencil printing is used for solder paste printing [2] and simple patterns [3].

When a groove-patterned surface is doctored with ink and the gravure plate is pressed directly onto the substrate, the method is called gravure printing. Gravure printing methods have been used for many years in the graphic printing industry. 'Offset', as a later part of the 'gravure offset printing' name, refers to an elastic part of the printer which picks up the ink from the gravure plate grooves and transfers it on to the target surface. The offset step enables printing of ink on to surfaces that cannot be directly pressed against the hard gravure plate. Printing of patterns onto non-planar surfaces is made with pad-printing, a form of gravure offset printing. In this method the ink is picked up from gravure plate grooves and then transferred onto a substrate by a soft offset pad. Requirements of the electronics manufacturing industry do, however, differ considerably from those of the graphic printing industry. The major differences between these
applications are the required printed ink thickness (thick layers for electronics compared to the graphic industry) and quality requirements.

Development of the method for electronics relates back to 1984-1985, when pad- and gravure printing, was described [4,5]. Early works with low temperature co-fired ceramics (LTCC) materials printed with gold, used roller type gravure offset printing [6]. The application of colour filters on glass for liquid crystal display (LCD) displays was demonstrated in 1991 [7]. Two Japanese conference papers published in 1991 describe the use of roller type gravure offset printing to manufacture large scale electronics [8,9]. The reproducible line width was down to 20 µm, with one micrometer printed line thickness. In the same year the use of a pad-type gravure offset method was published for the manufacture of 25/25 µm line/space resolution for 'LTCC' [10]. The use of pad-printing for 50 µm wide lines with PZT (Pb(Zr, Ti)O3) and 100 µm diameter vias manufacture by diffusion patterning and gold ink were presented from Microelectronics laboratory of University of Oulu at 1994 [11,12].

Gravure offset printing is not widely used in the electronics industry and, because of its many potential benefits, further research is needed [13].

1.2 Objective and outline of this thesis

In this thesis conductors are printed using ceramic conductor ink (ceramic inks) and polymer inks which are metal-particle filled. During the work, inks were under development for the gravure offset process by industrial partners in the related EU-project.

The overall objectives of this thesis are to study gravure offset printing process, and relevant mechanisms behind the ink transfer. The principle factors affecting printing will be determined. Furthermore, the printing time parameters should be set to be the minimum for high manufacturing speed. The final goal of this thesis is to gain basic knowledge for development of gravure offset printing to an industrially applicable level. A high ink transfer percentage onto printed substrates at high speed is required and issues affecting the print quality should also be studied.

In this thesis, a manually operated roller-type gravure offset printer was used, with horizontally fixed gravure plate and substrate tables and a moving roller. This work has been divided to chapters:

Chapter 2 explains the use of gravure offset in electronics manufacture. Chapter 3 analyses the ink properties for the gravure offset process.

Chapter 4 analyses the printing process, ink transfer mechanisms and printing parameters. Chapter 5 explains the firing/curing process.

Chapter 6 presents applications for roller-type gravure offset printing. It contains conclusions on the results obtained and on the use of gravure offset printing in the production of ultra-fine line thick film circuitry.
2 Printing methods

Printing is by definition the transfer of ink to a substrate in a desired pattern. The ink (or paste) is generally fluid material and in most cases printing is selective. Printed inks have been formulated to carry their functional components, e.g. silver for conductors. There is a variety of printing methods in use for manufacturing electronics (referred to in the text), each with its own benefits and limitations and listed in Appendix I. Knowledge of these methods is required of understanding the phenomena in the process.

2.1 The gravure offset printing method

In the gravure offset printing method, the ink is first doctored with a doctor blade into the grooves of a gravure plate (Fig. 1). For this the ink must have suitable rheology, generated by ink components as described in Paper II. In the optimum case, the grooves are filled completely and all of the ink is removed from non-image areas. Large image-areas can cause the doctor knife to bend to the bottom of a gravure plate groove.
Fig. 1. Flow of roller-type gravure offset printing. Parameters are given in the Table 1.

The gravure plates are made by etching, laser engraving and photopolymer methods. The resolution of these gravure plates is limited to about 50 to 100 µm wide grooves, depending on the technology used. Also, a groove’s depth is dependent on its width.

The ink is picked up from the gravure plate grooves ($pg$ in Table 1, Fig. 1) with an offset material. For roller type gravure offset printing, a roller rotates over the gravure plate. Either a uniform roller with an elastic coating or alternatively a blanket wrapped around a metallic roller core are used (Fig. 2). In pad-printing, an offset surface called a pad is used. This can be shaped according to the printed (non-planar) surface.

When a roller is rotated over the gravure plate, there must be a sufficient pressure to push the elastic material into contact with the ink in the grooves. Usually printers have the gearing system installed on the sides of the roller core, which force the roller to rotate at an exact speed (Fig. 2). This set up is called forced rotation. In this case, the gravure plate and the substrate pressures must be the same. An alternative technique is to allow the roller to rotate freely over the gravure plate. Then the pressure is adjusted by lifting the gravure plate and substrate tables separately.
Fig. 2. The roller gravure offset printer showing the blanket and the gearing system.

When the ink is picked up on the blanket, the roller rotates forward and the ink onto the substrate (ink lay down). The position is defined accurately by the gearing system, thus enabling multiprinting (i.e. printing the same pattern more than once on the same substrate). For a freely rotating roller, the printing location is affected by the pressures, and it makes multiprinting difficult.

After printing, the roller rises to its upper position and is then pushed back to the starting position. In the case of incomplete printing (some ink is left on blanket), the residual ink must be removed before the next print operation.

It is a characteristic of gravure offset printing that wide lines are printed thicker than narrow lines (Paper I). With an increased solvent content, the ink cohesion decreases and thus the thickness of wide lines decreases too. The limiting physical ink properties can be significant, e.g. metal particle size.

2.1.1 Roller type printing equipment used in this thesis

Roller-type gravure offset printing was done with a manually operated, Grauel gravure offset printer (modified, FID/60-160-PZ-TPO). In the initial phases of the work, doctoring was performed with hand held doctoring knives. Later, a pneumatic doctoring unit was installed with up and down moving steel doctoring blades (from Miller Graphics Scandinavia Ab) at a fixed 60° angle (Fig. 3). The printer allowed the use of uniform rubber rollers or blankets attached over a metallic roller core. Both free and forced rotations were used during the printing tests. With free rotation, smooth metallic wheels instead of rack and pinion gearing were used in order to counter the problem of accurate
placement. In this case the gravure plate and substrate tables are not in constant contact with the roller and the placement accuracy of printing is decreased.

Fig. 3. The doctoring device set up used with movable doctor blades in 60° angle.

In order to overcome the disadvantages of conventional gravure plates, a new electroplating method for the manufacture of high quality gravure plates was used. In the method a thin (<1 mm) metal (nickel) gravure plate is created upside-down, on the electrolysis substrate. First the electrolysis substrate is coated with a photoresist. After patterning it creates topographical patterns on its surface, which will correspond to grooves of the gravure, and therefore the photoresist thickness defines the gravure groove depths. Secondly, patterned photoresist is coated with a conductive seed layer, with sputtering (copper) or chemical methods as in mirror making. Thirdly, metal is electrolytically grown over an electrolysis substrate and photoresist patterns. The completed gravure is peeled off from the electrolysis substrate, and photoresist (and the possible seed layer) is removed from the grooves. The resulted gravure can be further coated with electroless nickel to form a much harder surface. Firing in an inert atmosphere at 400 °C is required for optimum hardness. Added metal on the gravure surface will reduce gravure groove widths (Paper I) [14].

The produced gravure plates have an outer surface as smooth as the electrolysis substrate and gravure grooves as smooth as the surface of the used photoresist (and coating metal). Manufactured smooth surfaces are beneficial for ink doctoring and ink pickup. The gravure groove cross section is close to rectangular and the depth is uniform for wide lines (lines up to 34 µm deep were produced). Line widths down to 9 µm wide were manufactured, but these already show narrowing at the bottom due to material and process limitations as shown in Fig. 4 (Paper I).
Fig. 4. Cross section of electroformed gravure grooves, 9-35 μm wide.

With forced rotation the roller had a compressed radius of 30.00 mm and the uncompressed radius with the blanket was 30.40 mm (0.40 mm compression thickness). The compression thickness was changed by adding intermediate papers underneath the blanket. The set up enabled a placement accuracy of about ± 5 μm.

The home-made blanket was made from silicone polymers moulded to form the surface of a thin (1 mm) non-elastic back fabric. The silicone polymer thickness was about 0.6 - 0.7 mm and the back fabric was 1 mm. The blankets were tightened over circular rollers and the hardness of the blankets was ~65 - 75 Shore A (Paper VI). The pressure used with the blankets is expressed as compression thickness with the ratio as given in Paper IV.

The printing process is significantly affected by the choice of printing parameters described in Paper III. Adjustable parameters during the printing experiments with the roller type gravure offset printer (Fig. 1) are listed in Table 1.

Table 1. Recorded and adjustable parameters during the printing process in chronological order.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect</th>
<th>Place</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pg$</td>
<td>Pressure / compression thickness at gravure plate when ink is picked up</td>
<td></td>
</tr>
<tr>
<td>$ps$</td>
<td>Pressure / compression thickness at substrate at lay down</td>
<td></td>
</tr>
<tr>
<td>$v1$</td>
<td>Speed the doctoring speed</td>
<td></td>
</tr>
<tr>
<td>$t1$</td>
<td>Time the time from doctoring to pickup</td>
<td></td>
</tr>
<tr>
<td>$v2$</td>
<td>Speed the pickup speed</td>
<td></td>
</tr>
<tr>
<td>$t2$</td>
<td>Time the time from pickup to lay down</td>
<td></td>
</tr>
<tr>
<td>$v3$</td>
<td>Speed the lay down speed</td>
<td></td>
</tr>
</tbody>
</table>

2.1.2 Pad-printing equipment used in this thesis

In order to print non-planar surfaces, offset material is needed that is elastic and reforming. In pad-printing the ink is first doctored to the gravure plate and the elastic pad is pressed against it to pick up the ink. The pad is then moved over the substrate and pressed against it to transfer the pattern. This pressure causes the pad to reform over the substrate and the ink to transfer. The use of gravure plate enables high-resolution printing, but this is limited to 25-50 μm due to the elastic nature of the pad. The “jiggling” of the
pad after its movement reduces the placement accuracy and resolution [15]. Compared to roller-type gravure offset printing, pad-printing is a slower process with a significantly smaller potential printing area.

In this thesis, pad-printing has been used for the printing of polymer inks (Paper VI). A computer controlled XYZ-printing machine with 10 µm placing accuracy (from Tryckteknik Ab) was used to pad-print polymer inks on alumina [16].

### 2.2 Self-Cleaning Gravure (SCG)

Ink pickup from gravure plate grooves is made with a roller (blanket) rotating with high pressure over the substrate. When the blanket starts to separate from the gravure and ink, there is a momentarily negative pressure, at which time the ink is torn out from the gravure plate grooves (Fig. 5) [17]. It is this action that is responsible for the ribbing effect (section 4.4).

![Fig. 5. Schematic presentation of ink being picked up by the blanket from a gravure groove.](image)

With ceramic inks, the residue ink in the gravure plate grooves tends to dry (depending on the printer set up) before being covered by added ink. This, together with pressure during pickup, will lead with too low solvent content at the bottom of gravure grooves. For high metal content inks, gravure groove blocking can not be solved with high levels of ink solvent as has been done in the graphical printing industry.

The Self-Cleaning Gravure (SCG) method was proposed to solve gravure plate groove blocking. The aim of this technique is to bring solvent or gas to the bottom of the grooves of the gravure plate (from inside it), under the doctored ink (Fig. 6). This is done by connecting a gas or liquid flow to a porous (such as porous polymer) gravure interior material. This increases the solvent percentage of the ink at the bottom of the groove, thus locally decreasing the viscosity of the ink. As a result, better and more repeatable ink removal from the gravure plate grooves can be achieved. An essential benefit for solid-particle containing ink is the ability to pick up more ink from the narrowest grooves of a
gravure plate. Also, in the SCG plate, the ink tearing out at pickup is counter balanced by pressure from inside the gravure, thus reducing the ribbing.

If liquid ink is brought through the gravure, the method is a novel printing method (resembling lithographic printing), as ink doctoring is not needed. Such printing can be done with low printing pressures, very long printing series, SCG surfaces of any shape and low printing costs over all.

Fig. 6. Schematic diagram of SCG structures as a gravure plate and lithographic printing plate, before and after inking.
3 Inks

Graphic printing inks contain large amount of solvent(s) (>50%), binder and pigment particles. In order to transfer ink onto the substrate, the solvent of the ink must be absorbed into it as in the case of graphical offset lithography printing [18,19]. Respectively, when printing on non-absorbing surfaces such as plastic, surface energy (wetting of the printed surface) plays an important role [20,21]. Inks containing a high percentage of solvent(s) have good flowing properties. Furthermore, a high solvent content allows the wetting of partially dried ink in the gravure plate and this prevents gravure plate groove blocking (drying in) in most graphical printing industry applications [22]. In order to produce an electrically conductive printed trace on ceramics, pigment particles are replaced with higher concentrations of metallic particles while the concentration of solvent is decreased.

The process of ceramic ink manufacture is described in Fig. 7. The process begins at the first stage with the binder component and solvent, and at the second stage with powder mixing. These are described in sections 3.2 (Paper II) and 3.5 for ceramic and polymer inks respectively. The ink is then mixed in a triple roll mill (3RM) which incorporates three rollers rotating near to each other but turning at different speeds. After passing the final roller, the ink is scalped off with a scraper plate. The 3RM is an efficient process after preliminary ink mixing, because it forces all the individual ink components to mix with each other [23].
3.1 Rheology

The most commonly quoted rheological factor of the ink is the viscosity as a function of shear rate. Ceramic inks printed with pad-printing have a viscosity of about 10-100 Pas and with screen-printing of 6-10 Pas at 10 l/s [16,24]. For inks studied in this thesis (Paper II) containing 70 wt.% and 85 wt.% of silver, there is a one to two orders of magnitude difference in viscosity (Fig. 8). Despite this difference, wide lines with both inks were printed successfully. However, with low viscosity inks most narrow line printing in the pattern B (Appendix II) was possible.
The rheological behaviour of the ink originated from all of the ink’s components. The ink binder is the basis of the observed behaviour, while the solvent changes it most significantly. Addition of solvent decreases the viscosity at 10 l/s in approximately the same proportion as with 100 l/s (6 wt.% decrease in viscosity with addition of 1 wt.% of oil, Paper VI). Yield stress defines the force required for enabling the ink flow from rest. There has been criticism about the wide range of yield stress measurement methods [25], so the yield stress definition used for ink was only an approximation to give the relevant range of values [26]. With large particle size distribution, yield stress decreases, thus also affecting the viscosity [27]. An increase in line height has been observed with increasing yield stress for high viscosity inks. Finally, other ink components, often called 'additives', can have a significant effect on rheology.

Other observed rheological properties are elasticity and thixotropy. Elasticity was measured with an oscillation test shown in Paper II. The thixotropy requirement for screen printing inks is justified by the need to level the ink after it has come through the screen. In gravure offset printing there is no similar justification, although the addition of the thixotropic ink additive has had an effect on the printed mass of the test pattern A in the statistical model of inks. The studied inks have low thixotropy.

Surface tension is commonly used for liquid material characterisation and to describe ink transfer. To study the surface tension like properties, a pull-off method has been used. The pull-off test, described in Paper II, is similar to the tack-test used to study inks in the graphic printing industry [28]. In the test a probe is lowered to the ink’s surface and the pull-off force is then measured, as shown in the Paper II. A round button-shaped piece of blanket is made to contact with the ink and is then pulled away at a constant rate, while a
scale measures the effecting force. For low viscosity samples, it has been shown that the edge area of the probe is critical [29]. For high viscosity materials the surface area also has an effect, thus complicating the surface tension measurement. The data was used in optimisation of the inks.

3.2 Conductor inks on ceramics

Ceramic conductor ink contains solvent, organic binder, glass-frit and functional metal particles. After printing, they are dried and fired at high temperatures (above 600 °C), in order to remove all organic material and to sinter the metal particles to create the conducting pattern.

A vehicle is mixture of organic binder, solvent and other components, e.g. organic rheological additives. It has the function of enabling proper ink flow with the correct rheological properties and maintaining the ink’s internal cohesion. The binder must be compatible with other ink components. Screen printable ceramic conductor inks based on silver have traditionally been made with ethylcellulose binder and terpineol solvent. For gravure offset printing use (pad-printing), these commercial inks have been modified by adding solvent in order to make them compatible with the process [16,30]. However, this kind of ink did not exhibit the same printing behaviour as hydrocarbon resin based inks.

The gravure offset process sets many requirements for the inks. When the ink is put on the gravure plate, it must not separate (like sand in water), create ink blocking, chemically react with the printer surfaces, and it must not dry too rapidly. The ink must also contain only particles that are sufficiently small to go smoothly into the gravure plate grooves. For stencil printing, the maximum particle size should be smaller than one half to one third (1/2-1/3) of the stencil hole diameter [31]. The studied inks have silver powder particle size that ranges from 0.5 to 20 µm (Table 2, Fig. 9), suggesting a minimum line width of 17 to 60 µm.

Fig. 9. 24 µm wide SEM pictures of inks listed in Table 3 a) G1 (type 1, Table 2), b) G3 (type 2), and c) G14 (type 3) [Paper II].
Table 2. The ink particle distribution. D90 means for type 1 inks, that 90% of particles have sizes smaller than 5.7 μm [Paper II].

<table>
<thead>
<tr>
<th>Grade</th>
<th>Type 1 / μm</th>
<th>Type 2 / μm</th>
<th>Type 3 / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>D90</td>
<td>5.7</td>
<td>20</td>
<td>9</td>
</tr>
<tr>
<td>D50</td>
<td>2.3</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>D10</td>
<td>0.5</td>
<td>2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

For normal atmospheric firing, silver offers the best solution because it creates on its surface only a very thin, easily breakable oxide layer. Generally, smaller particles have a lower sintering temperature [32], but they tend to agglomerate in the ink manufacture process. While the melting point of solid silver is 962 °C, for inks containing micrometer scale particles, ~850 °C has generally been used.

Increasing the metal content (70 - 85 wt.%) of the ink causes an increase in the printed mass of the test pattern and thus a decrease in the square resistance (Fig. 10, hydrocarbon resin based inks, Paper III). However, the practical limitation in the use of high metal content ink is gravure plate groove blocking during long printing series and decreased ink flow to narrow lines. The inorganic binder in ceramic ink is usually 2.5 wt.% of glass-frit. During sintering, this component creates a high adhesion to glass, used in alumina substrates.

Fig. 10. Square resistance of 300 and 150 μm wide printed lines of hydrocarbon resin containing inks, plotted against silver concentration [Paper III].
3.3 Ink transfer mechanisms in gravure offset

An ink transfer mechanism (also known as ‘ink transfer theory’ in the literature) explains the ink transfer during the printing process. Different printing methods and types of inks have different mechanisms. In order to transfer ink onto the substrate, the solvent of the ink must be absorbed into it, or the solvent must wet the printed surface. In graphic flexo-printing, the surface energy of the substrate can be modified by corona treatments [33]. For offset surfaces in the case of micro contact printing, the offset surface itself has been modified to fit within the limits of acceptable surface energy [34]. However, in letterpress printing it has been concluded that the surface energy is not as important as the printing pressure, especially on rough surfaces [35].

The ink transfer mechanism describes ink transfer in the complete gravure offset printing process: how ink is picked up from the grooves of the gravure plate to an offset material and further transferred to a substrate. Different types of inks can also have different ink transfer mechanisms. The commonly described and observed ink transfer mechanisms for the gravure offset printing are presented below.

Ink evaporation transfer mechanism (The traditional ink transfer mechanism)

The evaporation ink transfer mechanism is most commonly referred to in the literature for ceramic conductor [36] and graphic inks. For the pad-printing type of gravure offset printing, these inks have been diluted with solvents from screen printing inks [16]. One commonly used offset material has been a natural rubber. Inks transferred with pad-printing have a specific solvent evaporation rate. Evaporation creates a sticky outer surface, which makes the ink stick to the next surface. As this mechanism does not concern the surface between the ink and the offset material, there is always a rupture of the ink layer (Fig. 5), which results in less than 100 % ink transfer [4].

Absorption ink transfer mechanism

The hydrocarbon resin based inks used in this thesis, have non-polar binders and solvents which absorb into the offset material. Such behaviour for gravure offset printing had been indicated earlier in reference [9]. Non-polar offset material with a smooth, uniform surface gives the best results for these inks. However, the industrial use of absorbed solvents requires removal of the solvent from the offset material in order to prevent offset material swelling out of its defined dimensions. For the inks described here, a high solvent content is not required, thus enabling higher viscosity and internal cohesion (thick inks). Therefore, the high pressures encountered during the printing process do not cause significant line widening problems. In general, these factors result in thicker printed layers and less line widening compared to traditional ethyl cellulose based inks.

The absorption ink transfer mechanism suggested is based on ink solvent absorption to the blanket which, due to the used pressures, can be called forced diffusion. When the ink is on the blanket and some proportion of the solvent has been absorbed from the ink into the blanket, their surfaces and thus their interfacial forces change. There is then a decrease in ink adhesion to the blanket. Furthermore, when the blanket material is compressed over the substrate at lay down, this interfacial effect is at its peak and 100 % ink transfer is possible (Paper IV).
Absorption is based on the property of an offset material to absorb solvent from ink. A porous structure (or structure that is able to swell) absorbs solvent more effectively than a non-porous absorbing material. Generally, an increased absorption time causes more absorption. If the offset material already contains filler material (oil), a critical interfacial state can be reached more rapidly. Similarly, the critical interfacial state is reached more rapidly with smaller molecules, due to their faster diffusion rate. Thus solvents with lower boiling points have a shorter time requirement for 100 % ink transfer. When the ink on the blanket is pressed against the substrate, the increased pressure in the blanket forces out part of the solvent, thus making the adhesion to the blanket decrease even further. Increased pressure enables better ink release from the blanket to the substrate.

**Thermoplastic ink transfer mechanism**

Thermoplastic inks have temperature dependent shear thinning and temperature dependent adhesive forces. These inks are printed with a printer incorporating thermal management to control the temperature. This allows the control of the ink’s temperature and its rheology in each required phase of the printing; essential for this ink transfer mechanism. These inks generally also have a high wax content, which reduces the solid matter percentage of the ink and also the obtainable line resolution.

**UV ink transfer mechanism**

UV-curing inks are usually used when inks are needed to be cured quickly after printing. This gives the benefit of reducing volatile organic compound (VOC) emissions and increasing energy savings, because the solvents are not dried. Another alternative is the use of UV-curing to increase viscosity during the printing process in the gravure plate grooves after doctoring, and the blanket after pickup and the substrate after lay down (for multi-printing) [37]. Similar effects occur, for example, with two reactive component inks after mixing.

### 3.4 Ink component optimisation

For the related HiReCiPri-project, the best-suited ceramic ink components had been selected and their ratios optimised in co-operation with the ink manufacturer (Gwent Electronic Materials Ltd.) (Paper II). All studied inks and their studied properties are listed in the Table 3. In the ink component optimisation, printed mass of the test pattern was selected to be the observed parameter. 'Printed mass' has a high correlation with inverse square resistance, as shown in Fig. 11 for single and multiprints of a hydrocarbon resin based ink.
Fig. 11. The inverse square resistance of 300 μm wide lines vs. printed mass of the test pattern of ceramic silver ink G32 (Table 3), using single and multi-prints on alumina [Paper VII].

Ink transfer has been studied by weighing the mass of wet ink that has been picked up, printed or not printed. The calculated ink transfer % gives the ratio of ink transfer from the blanket to the substrate. The measurement inaccuracy was smaller than 1 % of the 'printed mass'. Variation in the mass of clean substrates was within an accuracy range of ± 0.1 mg. The ink picked up from the gravure plate or left on the roller after printing can be measured by the use of anti-statically treated adhesive films that can remove all of the ink from the blanket. With a blank-test performed on a clean blanket, the standard deviation was 0.8 mg. The 'printed mass' of the gravure pattern B in Appendix II (used for all experiments, unless otherwise stated) can be compared to the graphical industry standard term of printed mass per square metre with 100 % coverage by an approximate coefficient of 0.8 (g/m²).

Two gravure patterns (Appendix II) resulting in different printed masses were used because one pattern was not available for all the measurements. All inks listed in Table 3 are used in figures of this thesis and in the multivariate analysis of section 3.4. Listed ink properties are measured and relevant for ink printing properties (Pull-off measurement and rheological properties in Paper II). Ink numbering is in the order of ink development, i.e. G33 (same as G32 with 5.3 wt.% of its specific solvent added to it) is the final ink of the work.
Table 3. Properties and resulted printed mass of studied ceramic inks (G1-G33), cumulatively developed during the work. Gravure patterns are shown in Appendix II.

<table>
<thead>
<tr>
<th>Ink</th>
<th>Silver % -type</th>
<th>Printed / mg</th>
<th>Pickup / mg</th>
<th>Transfer / %</th>
<th>Maximum distance / mm</th>
<th>Pull-off / mg</th>
<th>F-max / mg</th>
<th>Yield / Pas</th>
<th>Viscosity at 60 1/s /Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravure pattern A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>72.5-1</td>
<td>6.2</td>
<td>8.8</td>
<td>71</td>
<td>0.72</td>
<td>2500</td>
<td>290</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>G2</td>
<td>72.5-2</td>
<td>9.5</td>
<td>15.7</td>
<td>61</td>
<td>0.64</td>
<td>300</td>
<td>42</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>G3</td>
<td>72.5-2</td>
<td>8.5</td>
<td>14.2</td>
<td>60</td>
<td>0.57</td>
<td>440</td>
<td>550</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>G4</td>
<td>72.5-2</td>
<td>9.2</td>
<td>15.0</td>
<td>61</td>
<td>0.91</td>
<td>210</td>
<td>45</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>G5</td>
<td>72.5-2</td>
<td>8.9</td>
<td>16.7</td>
<td>53</td>
<td>1.06</td>
<td>170</td>
<td>6</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>G6</td>
<td>72.5-3</td>
<td>9.0</td>
<td>19.0</td>
<td>47</td>
<td>1.07</td>
<td>180</td>
<td>2</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>G7</td>
<td>72.5-2</td>
<td>5.3</td>
<td>19.8</td>
<td>27</td>
<td>0.87</td>
<td>220</td>
<td>110</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>G8</td>
<td>72.5-2</td>
<td>1.4</td>
<td>1.4</td>
<td>100</td>
<td>0.57</td>
<td>450</td>
<td>29</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>G9</td>
<td>72.5-2</td>
<td>10.6</td>
<td>16.6</td>
<td>64</td>
<td>1.09</td>
<td>250</td>
<td>68</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>G10</td>
<td>72.5-2</td>
<td>10.3</td>
<td>18.2</td>
<td>56</td>
<td>1.23</td>
<td>180</td>
<td>11</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>G11</td>
<td>72.5-2</td>
<td>8.2</td>
<td>16.0</td>
<td>51</td>
<td>0.98</td>
<td>180</td>
<td>29</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>G12</td>
<td>72.5-2</td>
<td>12.2</td>
<td>17.4</td>
<td>70</td>
<td>0.41</td>
<td>780</td>
<td>69</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>G13</td>
<td>72.5-3</td>
<td>12.5</td>
<td>16.0</td>
<td>78</td>
<td>0.45</td>
<td>790</td>
<td>127</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>G14</td>
<td>72.5-3</td>
<td>25.1</td>
<td>25.1</td>
<td>100</td>
<td>0.82</td>
<td>310</td>
<td>35</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>G15</td>
<td>72.5-3</td>
<td>19.0</td>
<td>25.0</td>
<td>42</td>
<td>0.72</td>
<td>940</td>
<td>114</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>G16</td>
<td>72.5-3</td>
<td>9.6</td>
<td>15.5</td>
<td>62</td>
<td>0.56</td>
<td>600</td>
<td>560</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>G17</td>
<td>72.5-3</td>
<td>7.9</td>
<td>15.8</td>
<td>50</td>
<td>0.46</td>
<td>1040</td>
<td>600</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>G18</td>
<td>72.5-3</td>
<td>20.0</td>
<td>26.7</td>
<td>75</td>
<td>0.55</td>
<td>390</td>
<td>27</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>G19</td>
<td>72.5-3</td>
<td>14.7</td>
<td>25.4</td>
<td>58</td>
<td>0.36</td>
<td>440</td>
<td>39</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>G20</td>
<td>82.5-3</td>
<td>11.5</td>
<td>27.3</td>
<td>42</td>
<td>0.68</td>
<td>850</td>
<td>63</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>G21</td>
<td>67.7-3</td>
<td>18.6</td>
<td>18.6</td>
<td>100</td>
<td>0.68</td>
<td>350</td>
<td>94</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>G22</td>
<td>70.3-3</td>
<td>20.1</td>
<td>20.1</td>
<td>100</td>
<td>0.84</td>
<td>380</td>
<td>68</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>G23</td>
<td>69.4-3</td>
<td>18.9</td>
<td>18.9</td>
<td>100</td>
<td>0.47</td>
<td>360</td>
<td>66</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>G24</td>
<td>69.3-3</td>
<td>18.9</td>
<td>18.9</td>
<td>100</td>
<td>0.47</td>
<td>290</td>
<td>59</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Gravure pattern B, 100 % transfer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G14</td>
<td>72.5</td>
<td>40.4</td>
<td>40.4</td>
<td>-35</td>
<td>0.82</td>
<td>310</td>
<td>35</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>G21</td>
<td>67.7</td>
<td>33.8</td>
<td>33.8</td>
<td>-35</td>
<td>0.68</td>
<td>350</td>
<td>94</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>G22</td>
<td>70.3</td>
<td>34.6</td>
<td>34.6</td>
<td>-35</td>
<td>0.84</td>
<td>380</td>
<td>68</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>G23</td>
<td>69.4</td>
<td>35.2</td>
<td>35.2</td>
<td>-35</td>
<td>0.47</td>
<td>360</td>
<td>66</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>G24</td>
<td>69.3</td>
<td>36.1</td>
<td>36.1</td>
<td>-35</td>
<td>0.47</td>
<td>290</td>
<td>59</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>G25</td>
<td>72.5</td>
<td>39.4</td>
<td>39.4</td>
<td>-35</td>
<td>0.73</td>
<td>710</td>
<td>125</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>G26</td>
<td>72.5</td>
<td>39.3</td>
<td>39.3</td>
<td>-35</td>
<td>1.23</td>
<td>950</td>
<td>190</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>G27</td>
<td>72.5</td>
<td>37.8</td>
<td>37.8</td>
<td>-35</td>
<td>0.64</td>
<td>470</td>
<td>400</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>G28</td>
<td>84.3</td>
<td>50.6</td>
<td>50.6</td>
<td>-35</td>
<td>0.63</td>
<td>2900</td>
<td>850</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>G30</td>
<td>83.8</td>
<td>33.5</td>
<td>33.5</td>
<td>-35</td>
<td>0.91</td>
<td>4400</td>
<td>790</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>G31</td>
<td>73.4</td>
<td>39.3</td>
<td>39.3</td>
<td>13.0</td>
<td>0.35</td>
<td>900</td>
<td>180</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>G32</td>
<td>73.8</td>
<td>39.3</td>
<td>39.3</td>
<td>10.5</td>
<td>0.82</td>
<td>1250</td>
<td>118</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>G33</td>
<td>73.6</td>
<td>37.9</td>
<td>37.9</td>
<td>6.5</td>
<td>-0.40</td>
<td>650</td>
<td>430</td>
<td>26</td>
<td></td>
</tr>
</tbody>
</table>
The study was carried out firstly as a function of ink components and secondly as a function of rheological properties of the ink. The obtained results were analysed with the Modde 4.0 program, which allows the use of multiple linear regression (MLR) and partial least squares (PLS) algorithms to find the best-fit mathematical equation. This program was designed for such purposes as multiple parameter optimisation for simultaneous chemical analysis of elements [38]. Using the program, it possible to study unknown systems with a low number of samples (experiments). Other methods which have been used in the case of optimisation of stencil printing of solder, are Taguchi [39], Fuzzy-logic [40], analysis of variance (Anova) [41], principal component analysis (PCA) [42] and a custom made closed loop quality control program [43].

Models are based on seeking the best-fit mathematical model of behaviour linking variables (factors) to a response value(s). The “response” was, in both studied cases, the 'printed mass'. "Factors” in the first model were the ink components shown in Table 4.

In the second model, pull-off and rheological values were used as factors: maximum distance in pull-off, maximum force in pull-off, mass at the end of pull-off, yield stress and phase angle (for e.g. elasticity information). Maximum force in the pull-off test had a high correlation with 'printed mass'.

Table 4. Minimum and maximum content (theoretical wt.%) of hydrocarbon resin based ink (Table 3) components and corresponding masses printed with them. Values are based on the ratios of components [Paper II].

<table>
<thead>
<tr>
<th>Solids</th>
<th>Resin %</th>
<th>Solvent %</th>
<th>Thixotropic %</th>
<th>Additive %</th>
<th>Printed mass mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>72.5</td>
<td>2.7</td>
<td>2.5</td>
<td>0</td>
<td>0</td>
<td>15.4</td>
</tr>
<tr>
<td>87.5</td>
<td>20.0</td>
<td>12.8</td>
<td>5.8</td>
<td>0.5</td>
<td>50.6</td>
</tr>
</tbody>
</table>

As a result of ink component optimisation with PLS, from the first model it was concluded that:

- 'Resin * Additive' component has the most significant effect
- The effect of the 'Additive' results in different system behaviour

The second model had a high $R^2$ value of 0.994, suggesting a very good model. It shows the maximum 'printed mass' with either low or high phase angle (Paper II). Phase angle and pull-off distance are shown as a response surface in Fig. 12 (a) and the maximum distance in pull-off in Fig. 12 (b). Also, it was concluded that the internal cohesion of the ink should increase with a decrease of the phase angle.
Fig. 12. Effects of 'maximum distance in pull-off' vs. (a) 'phase angle' or (b) 'yield stress' factors to 'printed mass' [Paper II].
3.5 Ag-filled polymer conductor inks

Polymer inks were used in the thesis to create conductors, but similar materials are used as electrically conductive adhesives. Ink contain silver flake shaped particles, are packed in the organic binder material. Conductivity created in such a way is explained by percolation theory [44].

Substrates often limit the highest curing temperatures of the binder. Decrease of curing temperature is often a compromise with other properties, for example, with curing time. Reported curing temperatures vary for different materials from 80 °C [45] to 200 °C [46].

Particles in inks described commonly in the literature are silver, gold, nickel [47], platinum [48] and carbon [49].

In this thesis (Paper VI) gravure offset printing was developed for inks from Coates Electrographics, with low or high (about a 10 wt.-%-unit higher) silver content (Fig. 13), with 2-10 µm flakes. They were studied in order to print conductor lines on plastic substrates. Possible binders for polymer ink components are e.g. bisphenol-F [50], polyarylene ether (PAE-2) [51] or hydroxyethylcellulose [52].

Fig. 13. SEM pictures of polymer ink with low silver content.
4 The ink transfer process in gravure offset printing

The printing process is affected by the parameters of the printer, the offset material and the ink. The correct parameters should be used for each specific ink. The ink transfer mechanism explains how ink is transferred on an offset material from the gravure to the blanket and from the blanket to the substrate. Hydrocarbon resin based inks have been found to comply best with an absorption ink transfer mechanism. The reasoning for this is given in section 4.1. The printing parameter optimisation is described in section 4.2 for ceramic inks, and in section 4.3, for polymer inks. Polymer inks comply best with an evaporation ink transfer mechanism, which makes their case different. Finally for practical printing perspectives, printing problems listed in Paper VII have been discussed in the section 4.4.

4.1 Experimental verification of the absorption mechanism

The absorption ink transfer mechanism suggested has been verified in Paper IV with a variety of experimental data. These justifications are based on the fact that the ink solvent is absorbed into the offset material and the evaporation rate is low (~1 wt.% of all of the solvent in one minute). This is insignificantly small to be related to the evaporation mechanism. Also, ink solvent absorption into the substrate is not a significant factor because the glass substrates are successfully printed. Alumina with about 1 µm Rz_{din} surface roughness has only very minor effects on solvent spreading on the surface of the substrate.

From the perspective of the offset material, it has been found that the silicone polymer can swell by as much as 100 vol.%, when dipped into the solvent for a long time. Also, silicone polymer materials containing residual filler oil from curing, show an increased solvent absorption capability. Furthermore, there are visually observed swelling effects of the offset material, after multiple printings. This shows that solvent absorption is a major issue in ink transfer from the ink to the blanket.

The fact that pressure at the substrate (ps) was found to be significant in the ink transfer is explained by the absorption ink transfer mechanism (Fig. 14). Forced diffusion
is one way to describe the ink solvent transfer from the ink to the blanket. A blanket containing a filler oil resulted in a faster ink transfer, (smaller $t_2$). This can be understood as a more rapid saturation of the blanket surface by the solvent. As there should be no ink solvent transfer to the blanket before the pickup (when there is no ink on the blanket), the effect of the $pg$ parameter was minimal compared to that of $ps$.

![Fig. 14. The effect of $ps$ (a blanket compression thickness over a substrate) on ink G14 transfer from the blanket to the substrate. Data from time range of 7.7 - 8.9 seconds has been used to exclude the effect of $t_2$ [Paper IV].](image)

Different offset silicone polymer materials have different solvent absorption properties. This is shown in Fig. 15 as a plot of the residual mass after printing versus the time $t_2$ with the same ink. The point where the trend line reaches the x-axis gives the minimum $t_2$ for 100% ink transfer. The effect of filler oil content percentage in the blanket has been compared to the minimum value of $t_2$ (Fig. 16). When the observation point was changed from the blanket to the ink, it was found that the ink solvent molecule size was the critical issue for the $t_2$ parameter. The effect of the ink solvent boiling point with similar solvents (highly correlating to solvent molecule size) versus the optimum value of $t_2$ is shown in Fig. 17.
Fig. 15. The mass left on the blanket after printing as a function of $t_2$ (time on blanket). The minimum $t_2$ for 100% ink transfer is expressed as the crossing of the x-axis. The ink G14 has been used for three different blankets [Paper IV].

Fig. 16. The effect of blanket filler oil content on optimum $t_2$ value with two different patches of G14 and one of G32.
Fig. 17. The effect of the ink solvent boiling point on optimum t2 value with tested hydrocarbon resin based inks (Table 3: G14, G25-G28, G31, G32) [Paper IV].

Similar observations of absorption are supported in the literature. Silicone polymers are known to absorb solvents of similar polarity [53]. The swelling of offset blankets by the most frequently used solvents is a problem in the lithographic printing [54] and in microcontact printing [55].

The ink viscosity and printed line width affect the ink pickup; for wide grooves and high viscosity inks, the printed line maximum relative height is almost 100 % of the gravure plate groove depth. Conversely, the printed ink height from narrow lines was below 100 %, and the parameters or ink composition had only a minor affect on it. In order to study the effect of gravure plate groove depth on printed line height, a series of gravure plates with different depths (5 - 37 µm) was manufactured.

High and low viscosity inks with 100 % ink transfer from the blanket to the substrate were printed with these gravure plates of different depths. The summary in Fig. 18 (Paper IV) shows that the ink printed and dried relative height of high viscosity inks increases more than that of low viscosity inks (a mixture), with gravure plate grooves deeper than 27 µm. Respectively, with low viscosity ink there was up to 87 % printed relative height for 10 µm deep gravure plate grooves. The studied gravure plate groove widths were, on average, over 100 µm. For narrower lines than that, the optimum is 11 µm deep gravure plate grooves. The reason for such behaviour is in the ink’s internal cohesion: a high concentration of solvents in the inks causes lower internal cohesion, and thus a smaller maximum amount of ink pickup. This behaviour determines the maximum thickness of ink that can be printed from the gravure plate grooves. The result is that a gravure plate groove depth increase above 27 µm does not have a large effect on the relative height of the printed lines. If the objective is to print only wide lines, a high viscosity is preferred. Increased solvent content only decreases the pickup ink thickness. It was also found that
pickup mass decreased (1/4) and most narrow lines were printed imperfectly with blankets containing filler oils. This can be due to ink-blanket interface saturation at the pickup or, alternatively, to decreased blanket hardness (decreased compression pressure with the same compression thickness).

![Graph](image)

**Fig. 18.** Effect of the gravure plate groove depth on relative height of printed and dried ink, average over 100 μm wide lines [Paper IV].

### 4.2 Printing parameter optimisation for conductor inks on ceramics

The most important parameters are the printing speeds, timings (delays) and pressures. The benefit of a laboratory scale printer is its ability to vary these parameters. Manually controlled speed and timing printing parameters were recorded for analysis.

Most of the parameters are inter-dependent. Optimum parameters varied with different inks. Parameter behaviour varied depending on the ink system used: either printing pressure-withstanding (hydrocarbon resin based ink) or pressure-non-withstanding (other resin inks) (Paper VI). In order to study multiple parameters with multiple responses, multivariate methods must be used. This enables the elimination of effects caused by non-controlled printing parameters, such as manually controlled speed, and their separation from those of other controlled parameters. This requires a test series incorporating all relevant variables with high repeatability. Gravure plate groove blocking was the one major factor that decreased repeatability, despite cleaning of the gravure plate. However, gravure plate blocking can then be considered as a factor that increases with run order: as gravure plate groove blocking increased after multiple printing, the
printed mass of the test pattern decreased. To cope with these parameters and multivariate mathematics, Modde 4.0 software was used, utilising MLR and PLS algorithms (Paper II).

Pressure-non-withstanding and pressure-withstanding inks had printing parameters that behaved differently. This is mostly due to the behaviour related to different ink transfer mechanisms: the absorption ink transfer mechanism for pressure-withstanding inks and the evaporation ink transfer mechanism for pressure-non-withstanding inks. Hydrocarbon resin based inks usually had the best ink transfer with the minimum $t_2$ and an increased pickup with increased $p_g$. A summary of hydrocarbon resin based inks printing parameters is shown in Fig. 19 (Paper III).

The optimised ceramic ink, G33, was a non-polar, hydrocarbon resin based ink, with a silver load of 73.6 wt.%. Non-polar blankets were able to absorb the used solvent thus enabling 100 % ink transfer from blanket to substrate. The resulting optimum printing parameters for the final ink G33 are shown in the Table 5.
Table 5. Optimum printing parameters for the optimised ink G33.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect</th>
<th>Optimum values</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_g$</td>
<td>Compression thickness over the gravure plate</td>
<td>400</td>
<td>µm</td>
</tr>
<tr>
<td>$p_s$</td>
<td>Compression thickness over the substrate</td>
<td>400</td>
<td>µm</td>
</tr>
<tr>
<td>$v_1$</td>
<td>Doctoring speed</td>
<td>10 - 20</td>
<td>cm/s</td>
</tr>
<tr>
<td>$t_1$</td>
<td>Time from doctoring to pickup</td>
<td>3 - 5</td>
<td>s</td>
</tr>
<tr>
<td>$v_2$</td>
<td>Pickup speed</td>
<td>5 - 15</td>
<td>cm/s</td>
</tr>
<tr>
<td>$t_2$</td>
<td>Time from pickup to lay down</td>
<td>&gt; 6.5</td>
<td>s</td>
</tr>
<tr>
<td>$v_3$</td>
<td>Lay down speed</td>
<td>~ 5 - 15</td>
<td>cm/s</td>
</tr>
</tbody>
</table>

4.3 Printing parameter optimisation for Ag-filled polymer conductor inks

Printing parameter studies were made with a roller-type gravure offset printer. This equipment enabled the recording of speeds, delays, adjustments of pressures and change of blankets. After development of the ink, pad-printing experiments were made with different pads (Paper VI).

The studied polymer inks had high viscosity and showed poor flowing properties. Thus, the addition of solvent was one of the parameters studied and optimised. N-pentane and D90-solvent (from Shell) was added as solvent/oil, to improve printing. As far as the n-pentane did not dry in to gravure plate grooves, it was successfully used in high-resolution printings.

When solvent/oil was used, the gravure plate groove blocking was minimal. Blocking was studied with reference to the pickup mass (Fig. 20), or to the narrowest printed line with a minimum relative height of 1 µm. The addition of oils had the drawback of increased resistance of the cured lines. From line height comparison including n-pentane, it was noted that n-pentane prevented gravure plate groove blocking and its mixture with ink gave the best transfer percentages and highest printed mass of the test pattern.
In these experiments it was concluded that the studied ink having low silver content behaved by the evaporation ink transfer mechanism. Addition of non-polar solvents changed the behaviour of the ink to favour the absorption ink transfer mechanism. The critical parameter for successful (almost 100%) ink transfer to the substrate was the pressure on the lay-down ($ps$), as shown in Fig. 21. Only microscopically observed silver flakes were observed on the offset material after the print. Increasing the printing speed reduced the pickup mass. Two different low silver content ink mixtures exhibited good printing properties, and these are shown in Table 6.
Fig. 21. The effect of blanket compression thickness on gravure plate (pg) on ink transfer (with 5 wt.% of D90 oil) from the blanket to the substrate [Paper VI].

Table 6. Optimum printing parameters (Table 1) for two different oil/solvent mixtures (wt.%) to having low silver content [Paper VI].

<table>
<thead>
<tr>
<th>Ink mixture</th>
<th>Compression thickness at substrate</th>
<th>v1</th>
<th>t1</th>
<th>v2</th>
<th>t2</th>
<th>v3</th>
<th>Transfer</th>
<th>Resistance of 150 µm wide lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% D90</td>
<td>800</td>
<td>18.9</td>
<td>3.3</td>
<td>10.9</td>
<td>2.3</td>
<td>6</td>
<td>100</td>
<td>42</td>
</tr>
<tr>
<td>10% n-pentane</td>
<td>800</td>
<td>10.1</td>
<td>3.4</td>
<td>5.4</td>
<td>11.9</td>
<td>4.5</td>
<td>98</td>
<td>28</td>
</tr>
</tbody>
</table>

Traces of lines down to 35 µm were printed with these inks. Line widths of 70 µm were required for successful printing of the resistance measurement pattern used.

The ink having higher silver content gave neither quality printed line resolution nor as good an ink transfer percentage as did ink having a low silver content. However, the printed lines were more rectangular in shape and adhesion to the substrates was higher than that of ink with lower silver content, as shown in Appendix III.

4.4 Printing defects

Each printing method has its own unique printing limitations and problems, which appear in some cases as printing defects. The appearance and magnitude of these defects are dependent on the inks, the printing parameters and the printed patterns. Defects can be so
small that they have no effect on the function of the patterns. The major printing problems studied in Paper VII were:

- **Line Widening:** For pad-printing, line widening has to be considered in the design, as pressure-non-withstanding polymer inks were printed. The second major point was that the pressure-withstanding inks have a property of transferring in printing as a significantly thicker ink layer compared to pressure-non-withstanding inks. Only pressure-withstanding ceramic conductor inks were able to transfer 100% from the blanket to the substrate, as described in section 3.1. Printing angle dependent line widening was, at its maximum, ~15%. Wet on wet multi-printing can cause line widening even for pressure-withstanding inks, especially if a high percentage of solvents is used (Fig. 22).

- **Ink Flow:** In the printing system studied, ink flow into the gravure plate grooves under the doctoring knives was sufficient at the speeds employed. There was no unwanted flow from the gravure plate grooves during pickup at the commonly used pickup speeds. When very low pickup speeds were attempted, there was an outflow from large gravure plate grooves. This caused short circuits to form between probe-pads. A reduced pickup speed resulted in an increased pickup mass for some of the inks. The level of the unwanted flow from the gravure plate grooves can be decreased by increasing the ink yield stress. This, in turn, can be achieved by narrowing the metal particle size distribution [27].

- **Hair-formation:** This is dependent on the printed pattern, the blanket and on many printing parameters. Hair counts often vary depending on the measurement location on the substrate. It was proposed in Paper IV that hairs could be formed due to silicone polymer reformation after the stress caused by compression during the pickup. In micro contact printing, similar silicone polymer deformation is an even greater problem, due to the line widening and compression [56]. On the other hand, industrial users of graphical pad-printers have reported the high significance of air humidity: increased humidity decreased the occurrence of hairs. That would suggest that hairs are formed with graphical inks due to static charges. To study this presumption, printing was attempted with a conductive (sputtered) blanket and conductive substrate with ceramic ink. This experiment still resulted in hairs, which re-enforced the blanket reformation hypothesis presented.

- **Pinholes:** Grooves of the gravure plate are left less than full after doctoring [5] depending on rheological, elastic and surface tension properties of the inks. Pinholes are caused by bad doctoring (insufficient gravure plate groove filling) or by low pressure at pickup ($pg$).

- **Image distortions:** These are caused by the printer and are affected by the printed pattern. A pattern with a small image area can make the problem irrelevant.

- **Ribbing:** This effect is characteristic of gravure-type printing over a large area. It is dependent on pattern size and ink viscosity. Multiprinting creates cumulatively a more uniform layer. SCG reduces the problem because, with the SCG method, there is a counter pressure at the bottom of the gravure plate grooves at pickup (Paper V).
- Scooping: This is caused during doctoring when the doctoring knife is not at a 90° angle. It is dependent on the ink doctoring device and the pattern (Fig. 29).
- Streaking: This is affected by the motion of the doctor blade.
- Gravure plate groove blocking: This is a major limitation that can be affected by a decrease of solvent or oil in the ink. Alternative solutions are effective gravure plate groove cleaning methods or the adoption of the SCG-method presented in section 6.1.

### 4.5 Multiprinting

With the hydrocarbon based ceramic inks, there is 100% ink transfer from blanket to substrate, so immediately after one print the next can be done (wet on wet). Square resistance values of two prints are usually less than half those of single prints. Square resistances below 1 mΩ/sq. were measured for 10-times multiprinted lines (Paper VII). Requirements for multiprinting are: there has to be 100% ink transfer from blanket to substrate, ink should not be reverse picked up (by the blanket from the substrate), the printer has to have a high placing accuracy from print to print and line widening must be controlled.

With multi-printing, the relative line height is in direct relation to the number of prints. Wet on wet printing causes line widening which is dependent on the rheological properties. The effect of line widening as a function of multiple printings, with high concentrations of solvent is shown in Fig. 22. With the addition of solvent this decreased the required doctoring pressure and increased the speed as well as minimum pickup speed (without ink flow). There will be decreased gravure plate blocking, and narrower lines can be printed. Drawbacks are increased line widening and thinner printed layers.

![Fig. 22. Line widening of G32 + 7-10 wt.% of its specific solvent vs. number of prints with different line widths [Paper VII].](image-url)
5 Firing / curing and properties of printed films

5.1 Firing of conductor inks on ceramics

In order to make printed ceramic inks conductive, vehicle (solvents and organic material) must be removed and the metal particles must form a uniform trace of sintered particles (conductor path). If solvent removal is sufficiently effective in the firing oven, the separate drying stage can be omitted to improve the speed of the industrial manufacturing process. A problem associated with a too rapid increase in temperature is bubble formation, because the surface layer is sintered before removal of the organic material. An extreme case where bubbles are left in the ink, as in the case of a twice multiprinted sample, is shown in Fig. 23.

Fig. 23. Bubble formation in twice multiprinted and fired silver on alumina.
Decreasing the firing temperature below 850 °C had only a minor effect on the square resistance, as shown in Fig. 24. Square resistance of single printed 300 µm wide line was minimum 4.6 mΩ/sq. for ink G29.

![Graph showing square resistance as a function of line width from samples of ink G14 and fired at different temperatures. Printed with the gravure pattern A.](image)

**Fig. 24.** Square resistance as a function of line width from samples of ink G14 and fired at different temperatures. Printed with the gravure pattern A.

Glass frit reduces the fired ink trace conductivity because it blocks some paths and can diffuse at metal interfaces. The conductivity of the silver conductors is based on the sintering together of solid particles. With the used ink, the conductivity for most thick lines was about 2/3 of the bulk silver conductivity. If these particles are large and the printed layer is thin, this can cause the metal trace to be porous or rather network-like (Fig. 25). The Fig. 11 suggests that less than 2.5 mg of ink, printed from the gravure pattern A, would not result in a conductive trace. With small particles and a smooth substrate, the obtained thin traces are more uniform after firing.
5.2 Curing of Ag-filled polymer conductor inks

In order for polymer inks to become conductive, the polymer has to bind the metal particles together. The change of organic material from the liquid to the hardened state is called curing, which is generally a polymerisation reaction or solvent removal. At temperatures lower than the recommended temperature, the curing time is longer. In a slowly increasing temperature, the studied polymer inks had an optimal curing temperature of 140 °C, and a dwell time of 15 min. After reaching this temperature, the resistance did not decrease. For 300 and 150 µm wide lines, square resistances as low as 20 and 28 mΩ/sq., respectively, were measured in < 7 - 8.5 µm thick lines (calculated from cross section area). The minimum line width was 70 µm (ink having low silver content) with a square resistance of about 50 mΩ/sq. (Paper VI). Appendix III shows, by means of software developed during the work, surface profiles of polymer inks. The surface profiles show the more rectangular line shape and larger cross section area for high silver content ink than for low silver content ink, with 300 µm wide line. The latter has a lower printed mass of the test pattern, as narrow lines are not printed. Also, the obtained square resistance was about twice as high because the ink contained oil.
5.3 Processed samples of conductor inks on ceramics

Conductor line resistance is an accumulated effect of a variety of the ink properties and several factors in printing and firing. Because for gravure offset printing the square resistance is dependent on line width, limitations of resistance measurements are overcome by surface profiling. Printed patterns contain lines of different width, which can be measured separately with surface profiling. Since there are variations on measured profiles depending on the measured place, a better alternative is to use the average of the line cross section area. The profiling device used was a Dektak 3D, which has Z-axis theoretical accuracy of 10 Å.

A response factor correlation matrix (Table 7) has been used to compare different analysis methods for evaluation of printed results: printed mass of the test pattern, (maximum) line height, cross section area and square resistance (Paper III). The response to be measured, depends on the particular parameter under optimisation; the used pattern or the ink. Selected responses were:

- Printed mass of the test pattern can describe ink transfer when the same pattern is used with the same ink, and the printed pattern has line widths suitable for optimisation.
- Average line height (cross section area divided by line width) can be used to estimate conductivity. For gravure offset printed lines with pressure-withstanding inks, the printed and fired line cross section behaves linearly as a function of line width, unlike line height as shown in Fig. 26.
- For high yield repeatable printings, square resistance measurement, preferably from the Kelvin structure (4-point measurement pattern), is the easiest alternative. Then all effects such as random printing errors are included in the result.

Table 7. Correlation matrix of response values: printed mass (Mass, mg), and for two different designed line widths: printed line height maximum (Height, μm), printed line cross section area (C-s-area, μm²) and square resistance (Sq. resistance, mΩ/sq.) using ink G14 [Paper III].

<table>
<thead>
<tr>
<th></th>
<th>Mass</th>
<th>Height</th>
<th>C-s-area</th>
<th>Sq. resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 μm wide lines</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass</td>
<td>1.00</td>
<td>0.80</td>
<td>0.90</td>
<td>-0.89</td>
</tr>
<tr>
<td>Height</td>
<td>0.80</td>
<td>1.00</td>
<td>0.94</td>
<td>-0.85</td>
</tr>
<tr>
<td>C-s-area</td>
<td>0.90</td>
<td>0.94</td>
<td>1.00</td>
<td>-0.88</td>
</tr>
<tr>
<td>Sq. resistance</td>
<td>-0.89</td>
<td>-0.85</td>
<td>-0.88</td>
<td>1.00</td>
</tr>
<tr>
<td>150 μm wide lines</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass</td>
<td>1.00</td>
<td>0.57</td>
<td>0.69</td>
<td>-0.96</td>
</tr>
<tr>
<td>Height</td>
<td>0.57</td>
<td>1.00</td>
<td>0.93</td>
<td>-0.68</td>
</tr>
<tr>
<td>C-s-area</td>
<td>0.69</td>
<td>0.93</td>
<td>1.00</td>
<td>-0.76</td>
</tr>
<tr>
<td>Sq. resistance</td>
<td>-0.96</td>
<td>-0.68</td>
<td>-0.76</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Fig. 26. Cross section area and line height vs. line width with best-fit equations of ink G28.

Visual confirmation of the printed trace is an effective way to study printings. A light from the top result (bright-field illumination) is shown in Fig. 27 (a). A light-through substrate (transmission illumination) picture, as shown in the Fig. 27 (b), will show places of even partial ink coating. Before firing, the view is often optimistic compared to a fired sample, as shown in Fig. 27 (c) and Fig. 25 (different sample, light from the top). For uniform conductor trace thickness evaluation, multiple scans with a surface profiler have been used. Novel confocal- and interference-microscopy solutions can also be used to obtain results faster (Paper II).
Fig. 27. G14 ink on alumina with 9 - 70 μm wide printed lines. Dried ink (a) light from the top, (b) light through the substrate and (c) light-through substrate with fired ink.
The quality of the pattern is in most cases measured by pattern conductivity. When comparing sample treatments, the largest effects on the obtained square resistance were achieved by firing the samples in an \( \text{O}_2 \) atmosphere, the use of 'high silver-loaded' (85 wt.\%) inks and with multi-printings, as shown in the Fig. 28.

![Fig. 28. Effects of firing of samples in \( \text{O}_2 \) atmosphere (G14), use of high silver-loaded ink (G29) and with different numbers of printings (1-4 prints, G14) for 300 \( \mu \text{m} \) wide lines are shown [Paper VII].](image_url)
6 Uses of gravure offset printing

The main advantages of gravure offset printing are the ability to transfer large substrate surface areas of ink onto various surfaces with small distortions and at high speed. Ink has been successfully printed onto alumina, glass, LTCC-green sheet and metal substrates in this work. Materials for the ink are cost effective. Conductors and integrated components demanding high resolution printing are included in a number of plans for electronics miniaturisation, such as NEMI [1].

The best printing of narrow lines with ceramic inks is achieved with low viscosity inks. Uniform printing over large areas, for wide and narrow lines, was achieved with an n-pentane mixture of ink (G14, Table 3), as shown in Fig 29. Compared with the gravure pattern in Appendix II, it shows that all narrow lines in the pattern are included with the difference of a scooping effect (section 4.4) in large areas. However, this highly volatile solvent sets high requirements for both the ink doctoring container and the blanket. The narrowest printed line traces were 9 µm wide (Fig. 27). The minimum line width for the conducting test pattern was 35 µm wide with a single print. When a large printed thickness is required, wide lines should be preferred; with high metal content ink, 300 µm wide lines can be deposited up to 8 µm high (relative height) after firing. The obtained square resistances are shown in the Fig. 28.
Fig. 29. Gravure pattern B (the gravure pattern in Appendix II) printed with G14 (Table 3) + 5-10 wt.% n-pentane for 2” x 2” alumina substrate [Paper II].

It was observed that gravure plate groove blocking is the most significant limiting factor when considering the repeatability of the printings. In this respect, the printer defines the level of repeatability and yield. Multiprinting can be used to improve yield significantly, as it improves the printed ink height and thus reduces breaks in fired conductors. When gravure plate groove blocking is not a problem, high volumes (compared to screen-printing) can be produced.

Paper VII describes the printing of inductor coils with 56 $\mu$m lines and 28 $\mu$m spaces and also interdigital capacitors with 30 $\mu$m lines and 10 $\mu$m spaces respectively. Circuitry printed on glass for a novel laser application was also presented. This required the printing of contact pads having holes/conductor widths of 28/28 $\mu$m (Paper VII).

In some applications the line thickness should be independent of the line width. There are three methods of approach to this. Firstly, narrow gravure plate grooves can be made deeper compared to the wide ones. Secondly, narrow lines can be printed incrementally with different gravure plates. Thirdly, very low viscosity (diluted) inks can be used to produce width independent line thickness. Multiprinting may then be applied.

A higher resistance for thin printed layer thicknesses may be accepted for some applications. This can make thin layer printed by gravure offset printing, a better choice than screen printing [57]. Reduced usage of materials such as palladium can also be the criterion for selecting the method of printing thin layers.

Pad printing of polymer inks provides a conductor manufacturing method for non-planar surfaces. Investment in manufacturing equipment is low because graphical pad-printers are widely available. Radar components and consumer electronics printed on
inexpensive polymers are potential applications for polymer inks. Furthermore, ceramic inks can also be printed on non-planar surfaces with pad-printing.

The benefits of gravure offset printing are also to be found in large volume, low cost applications, which do not require such a high resolution as do state of the art circuitry boards. The main criteria for selection of this method over other methods are the ability to transfer patterns quickly and cost-effectively onto hard surfaces. A potential industrial printer can have a printing area of 0.5 m$^2$ with a printing cycle time of approximately 18 seconds, thus producing approximately 100 m$^2$/h. As the printed components can have sizes down to 2 mm$^2$, this would result in a manufacturing throughput of approximately 50 million components per hour.

The results of this work have been used by the related HiReCiPri-project partners and in research projects. Gravure printing of ceramic inks from soft silicone polymer gravure, direct gravure printing (DGP), has been a result of the research related to the thesis [58].

Roller-type gravure offset printing has a large potential for cost-effective mass-production of electronics. Potential applications are printed high-density circuitry, metal patterned glass, displays, plastic and paper. The two latter are the subjects of study in a Finnish national PRINTO-project, where the goal is to produce demonstration samples of printable electronics on consumable product packages. A well known application is stripping voltammetry, which requires printed electrodes [59]. For such applications, the essential benefit of inexpensive large-scale production is obvious. Offset printing offers the property of printing on a hard surface. This makes it a superior reproduction method for LCD-colour filters compared to screen printing, flexo-graphic, and gravure printing methods [60].
7 Conclusion

The aim of this thesis was to study and develop the roller-type gravure offset printing process. During the work, methods for ink evaluation have been established. The physical parameters affecting printing and the principle properties of gravure offset printing have been determined. The absorption ink transfer mechanism has been established as the main factor controlling the transfer of the best-printed inks. Also the printing properties of polymer inks have been studied. A novel Self-Cleaning Gravure method has been researched and proposed for improved printing. Finally, a summary of the printing properties and applications of the ceramic ink has been presented, for such as a novel laser soldering application.

In the printing process, a single printing of ceramic ink was capable of producing up to 8 \(\mu\)m (relative high) conductor lines after firing for 300 \(\mu\)m wide conductors. It was possible to print down to 35 \(\mu\)m wide conductor lines with a single print. Tested patterns realised with a single print were interdigital capacitors, inductor coils and laser soldering contact pads. The latter were successfully realised down to 28/28 \(\mu\)m line/space resolution. To improve printing quality with minimum artefacts there should be smaller (<2 \(\mu\)m) metal particles in the ink, high precision printing equipment, high-quality blankets, closed ink containers and a clean room facility.

Polymer inks were printed with a resolution down to 70 \(\mu\)m and 20 m\(\Omega\)/sq. square resistance for 300 \(\mu\)m wide lines after curing at 140 °C for 15 min dwell time, with both roller type gravure-offset and pad-printer technologies.

In order to obtain low resistance conductors from ceramic inks, 10-times multiprinting of high metal content ceramic ink produced square resistances down to 1 m\(\Omega\)/sq. (for 300 \(\mu\)m wide conductors). Multiprinting improves the printed quality, increases the manufacturing process yield and reduces printing problems.

In this thesis, the requirements of an industrial environment have been met in such respects as \(t_2\) (the time ink has to remain on the blanket for 100 % transfer to substrate). This time has been decreased from 30 seconds to 3 seconds. Sources of printing problems have been studied and correction measures are suggested. Further background research of the selection of printing parameters, inks, gravures and blankets is detailed in this thesis.

It has been shown that gravure offset printing can offer a cost effective manufacturing method for electronic circuitry. With industrial printing equipment it is possible to
produce 100 m²/h with the demonstrated printing properties. The minimum line width with the studied inks depended mainly on the printer, the substrate roughness and the ink particle size. Ink transfer mechanisms were studied and the absorption ink transfer mechanism was established, through detailed experiments, as a major factor for the best-printed inks. The existence of other printing related problems is dependent on the printed patterns, the printing environment and the required product quality. The gravure offset printing method is dependent on many parameters, which makes it more complicated than, for example, screen printing. It has however a high potential, but continued research and development is required of materials such as offset blankets.

The printing of ceramic- and polymer inks has been successfully demonstrated. A pilot stage production with the method has been enabled. The method enables, upon realisation, a rapid and cost effective manufacturing method for increased line resolution with low VOC emissions.
References


Appendix I Other printing methods for electronics

In this thesis, gravure offset printing method for electronics manufacturing is analysed. However, in order to understand the related printing processes and effects, other printing methods used in the manufacture of electronics are referred to in the text. The following list and Fig. A I.1. give a short description of these printing methods that use inks.

In direct writing systems, the ink is deposited under the computer controlled printing head. Such methods produce the pattern based on software commands and thus each printed sample can be different.

<table>
<thead>
<tr>
<th>Non-patterned</th>
<th>Fine-patterned</th>
<th>Derived methods</th>
<th>Direct writing</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Doctoring</td>
<td>- Screen printing</td>
<td>Stencil printing</td>
<td>- Ink-jet printing</td>
</tr>
<tr>
<td>- Spinning</td>
<td>- Lithography</td>
<td>Offset lithography</td>
<td>- Dispensing</td>
</tr>
<tr>
<td>- Meniscus</td>
<td>- Electrostatic Printing</td>
<td>Gravure offset printing</td>
<td>- Dip-pen</td>
</tr>
<tr>
<td>- Ink spraying</td>
<td>- Flexography</td>
<td>Microcontact printing</td>
<td>- Pad-printing</td>
</tr>
<tr>
<td></td>
<td>- Letter press</td>
<td></td>
<td>- Roller-type printing</td>
</tr>
<tr>
<td></td>
<td>- Gravure printing</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. A I.1. Division of printing methods.

Doctoring is an ink spreading method that rapidly forms a uniform layer of ink. Ink is simply spread over a substrate and excess ink is removed with the doctor knife. The resulting ink on the substrate can be non-patterned, or patterned with a single use solution, such as adhesive (Scotch-) tape. The aim of this method is to apply the ink to
large areas without any patterning or else with simple rough patterns. The doctoring method has been widely used for making test-strips and uniform metallised areas [61].

Spinning (spin casting) is a method to create a coated area with a very uniform thickness of ink. Stereo lithographic photo-resists, widely used in the die-patterning processes, are commonly spread using this method. Spinning consists of pouring the ink onto a rapidly rotating substrate disk. The spinning momentum spreads the ink over the substrate. Inks may also be spread onto different substrates using this method, in order to create uniform layers [62].

Meniscus coating can be applied to low viscosity materials e.g. photoresist, on level outer surfaces. Low viscosity ink (0.1 - 10 Pas at ~10 1/s) is caused to flow from a porous or slotted pipe onto the surface. As the substrate material is moved over it, the contacting substrate surface will be coated to a thickness dependent on the ink’s surface energetic properties [63].

Ink spraying (spray-printing) is used for graphic inks, usually under the influence of high pressure air. This causes the ink droplets to flow onto a large targeted area. The use of such a method for coating non-planar surfaces has obvious benefits. Spraying of graphite ink has been reported for the production of electrodes [64].

Screen printing has been used traditionally in electronics pattern manufacturing, especially in hybrid microelectronics. The ink is based on a binder, a solvent and the functional material to be printed. Such materials are, for example, metals, metals with a polymer binder, and polymers. A screen (steel or polymer wire mesh) is first coated with a uniform layer of photo-emulsion. After photo patterning and developing this will form a selectively penetrable printing screen. In the printing process, the ink is then placed on top of this screen and squeezed through it with a squeegee. This causes the ink to pass through mesh openings onto the substrate as a uniformly thick layer. Thus the mesh count limits the obtained resolution. The thixotropic rheological property, required from the inks, forces it to form a uniform structure after printing. This creates a uniform patterned layer over the printed area. As the screen is the key patterning component, it must be in good condition for successful high-resolution printing. During the industrial manufacturing process, the mesh becomes loosened and has to be replaced after a few thousands of prints. Also, in some cases the screen needs to be cleaned from time to time and this can require its removal. Screen printing enables the printing of a number of materials with a rheologically correctly formed vehicle. However, solid particles of the ink must be small enough to pass through the screen and they must not damage the emulsion layer.

Stencil printing is a specific form of screen printing. In this method, the patterned screen is replaced by a uniform plate of metal or polymer containing the hole patterns to be printed. For instance, solder pastes are industrially printed by stencil printing.

Lithography is an ink printing method, where a planar printing plate is first wetted with ink. The printing plate has hydrophilic and hydrophobic areas, and after the inking process only one type of these areas is left eventually coated with ink. Then the printing plate is pressed against the substrate to transfer the ink. Printed resolution is one of the limitations of the method [65]. Offset lithography is a lithography process with an offset-step. It has been used for the fabrication of capacitors [66].

Electrostatic (toner) printer works on the principle of an electrostatically (selectively) charged drum that pulls ink particles (toner) on to its surface. From there the ink is
transferred onto the substrate and adhered by heating. Laser printers and photocopy machines are electrostatic printers. The ink particles are carbon in an ordinary copier, but they can be replaced by different materials. Insulator materials [67] and etching masks [68] have been produced with this method for electronics manufacturing.

In flexography (flexo-printing), ink is first doctored to a densely dot patterned roller called an Anilox-roller. Then, a topographically patterned polymer surface picks up the ink from this roller. The ink is only transferred to higher areas of the polymer and from there eventually to the substrate. Printing resolution can be limited by the Anilox roller and the printed thickness is limited by the ink pickup property of the polymer material. This method enables very high printing speed and efficiency and is becoming an increasingly popular method for the production of a variety of graphic printings. This method has been used to print copper ink on alumina [69]. Versions of this method have been shown to be capable of producing lines down to 20 µm wide on hard patterned surfaces [70].

In Letterpress, ink is applied to the raised surface of the image plate (or cylinder). This plate is then pressed against the substrate to transfer the ink. This method has only a limited printing thickness due to the requirement that the ink should adhere to the raised area of the image plate. The method has been applied in the printing of magnetic inks containing one micrometer particles [71].

Microcontact printing (stamping) is a method used to produce thin, high-resolution patterns. With catalytic materials or with self-assembly (molecular) monolayers (SAM), only a thin layer is needed for patterning. Letterpress type printing is then suitable for this purpose. Microcontact printing is a specific version of letterpress used for microelectronics. In microelectronics manufacture, there is often no ink solvent absorption in the substrate and the pressures used cannot be high. A silicone polymer surface in microcontact printing has spreading problems even with low pressures [72]. This defines one of the major differences between letterpress and microcontact printing. With microcontact printing, catalytic materials or SAM are transferred with very high-resolution (<1 µm) to substrates such as silicon. Microcontact printing is a potential method to solve the problem of the line resolution on silicon, limited only by the wavelength of light [73].

Ink-jet printing is a widespread method of colour image printing used with home computers. This, in turn, has generated markets and research for this technology. Different versions of ink-jet printing are based on the jet flow of droplets of ink from an ink head directly to the substrate. This generates thin layers made of dots. Due to the small size of the droplets and the technology used, nano-particles from metals such as silver are needed [74].

Dispensing is essentially a process where an ink-syringe (pen) or pump moves over the substrate producing the pattern of ink. Varieties of dispensing equipments are available for the printing of different inks for electronics, e.g. solder paste. One unique state-of-the-art equipment, for the continuous contact printing of conductor and other ink patterns, is Micropen (tm) [75], which enables the printing of line widths down to 25 µm. The main benefit of the method is the ability to print thick and at the same time narrow lines. Obviously, this method is significantly slower than the mass production methods presented above.
The Dip-pen has a sharp hard tip, running on the substrate material structure similar to an Atomic Force Microscope (AFM). The ink flows down to the contact point of the substrate, thus making an ink trace. Nano-structures have been produced with this method [76].
Appendix II Gravure patterns

The gravure patterns used in the thesis for printings, where the printed mass and most other values were measured are shown in the Figs. A II.1 (a) and (b). Pattern sizes are 50 mm * 50 mm. Pattern A has lines from 300 to 20 µm at angles of every 18° and a dot/grid array of same dimensions. Pattern B has lines at four different angles having line widths of 280 to 9 µm and a dot/grid array of from 300 to 20 µm, 4-point measurement patterns of 25-300 µm wide line and large ink areas.
Fig. A II.1 (a) and (b). 50 mm * 50 mm size gravure patterns A and B used in the thesis to print patterns, from which the mass was measured.
Appendix III Surface profiles analysis

An analysis program was made for the measurement of the printed line cross section area. Its function was also to make a summary and graphical presentation of measured surface profiles. As the resistance of the conductor line can be considered to be related to line cross section areas along the line, the software shows the minimum, maximum and average outer surface from the measurements. The software also calculates the average width and height of the line based on user definitions. From that data the standard deviation of the width and line cross section area is calculated. Furthermore, a value called 'Rectangular Deviation' has been added to describe how far the data cross section is from the ideal rectangle (height * width). This information is useful in comparison of, for example, the RF-simulation data with the measured samples. Examples of polymer inks with low and high silver content are given in Figs. A III.1 (a) and (b). These show the different behaviour of these inks after double prints: high silver content ink enables printing of more rectangular lines with higher cross section area than low silver content ink, for the studied 280 μm wide line.
Fig. A III.1 (a) and (b). Surface profiles of 280 μm wide lines (average of 10 lines), printed twice with a) low and b) high silver content inks. Highest printed cross section area and more rectangular line shapes is obtained when printed with high solid content ink having 5% of D90 [Paper III].