Materials and Processes for Printed Electronics: Evaluation of Gravure Printing in Electronics Manufacture

Erika Hrehorova
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MATERIALS AND PROCESSES FOR PRINTED ELECTRONICS: EVALUATION OF GRAVURE PRINTING IN ELECTRONICS MANUFACTURE

by

Erika Hrehorova

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Paper Engineering, Chemical Engineering and Imaging
Dr. Alexandra Pekarovicova, Advisor

Western Michigan University
Kalamazoo, Michigan
June 2007

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Erika Hrehorhova
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<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
</tr>
<tr>
<td>AU</td>
<td>Arbitrary units</td>
</tr>
<tr>
<td>AVG</td>
<td>Average</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DOD</td>
<td>Drop-on-demand</td>
</tr>
<tr>
<td>DOE</td>
<td>Design of experiment</td>
</tr>
<tr>
<td>EDOT</td>
<td>Ethylenedioxythiophene</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>F8T2</td>
<td>Poly(9,9’ – dioctyl – fluorine - co – bithiophene)</td>
</tr>
<tr>
<td>FET</td>
<td>Field-effect transistors</td>
</tr>
<tr>
<td>HF</td>
<td>High frequency</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HS</td>
<td>High solids</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated circuit</td>
</tr>
<tr>
<td>JJ</td>
<td>Ink-jet</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LCC</td>
<td>Linear chain conductor</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid crystal display</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>LVR</td>
<td>Linear viscoelastic region</td>
</tr>
<tr>
<td>N/A</td>
<td>Not available</td>
</tr>
<tr>
<td>NTO</td>
<td>Nitrogen tetroxide</td>
</tr>
<tr>
<td>OFET</td>
<td>Organic field-effect transistors</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3 – hexylthiophene)</td>
</tr>
</tbody>
</table>
List of Abbreviations - Continued

PANI Polyaniline
PC Pearson correlation coefficient
PEDOT:PSS Poly (3, 4 – ethylenedioxythiophene) doped with polystyrene sulfonic acid
PET Poly(ethylene terephthalate)
PI Polyimide
PM-acetate Propylene glycol methyl ether acetate
PMMA Poly (methyl-methacrylate)
PPS Parker Print Surf
PS Polystyrene
PSS Polystyrene sulfonic acid
PVP Poly (4-vinyl phenol)
RFID Radio frequency identification
RMS Root mean square
SD Standard deviation
SEM Scanning electron microscopy
UHF Ultra high frequency
UV Ultra violet
VSI Vertical scanning interferometry
CHAPTER 1
INTRODUCTION

Currently, processing and fabrication of organic-based electronics and devices is carried out by using traditional processes such as spin coating, dip coating and thermal vacuum depositions. These techniques are either limited to certain substrate sizes or are very costly and time consuming. It appears that a tremendous advantage can be gained by incorporation of printing technologies into the processing of organic materials and manufacture of electronic devices.

Printing is a new technique for traditional electronic companies and the integration of printing with electronics and material science is nowadays promising to offer low cost and high volume electronic devices. More and more electronics manufacturers are embracing printing technology as a high-potential manufacturing method for mainstream electronic components. The area of printed RFID is expanding rapidly with the increasing trend of integrating RFID tags into supply chains. To fully utilize the benefits of printed electronics, however, manufacturers need advanced materials that are well suited for specific electronic applications and printing systems, and are available in commercial quantities.

Organic electronics is a term that is used not only for systems made exclusively from organic materials, but also for systems that contain at least one organic material, such as an organic semiconductor. The term printed electronics is again not only used for devices fabricated exclusively by using printing technologies, but also for devices manufactured by hybrid technologies, where one of the used technologies is printing. For fully organic
and all-printed systems we need solution processable materials with the highest possible conductivity of conducting polymers, highest possible charge-carrier mobility of semiconductive materials and good insulating properties of dielectrics. Accomplishing the suitable combination of materials and solvents that are compatible and do not attack or dissolve each other is a great challenge. Good electronic, optical, and mechanical properties of thin-film materials could lead to utilizing of roll-to-roll manufacturing to create products, such as low-cost information displays on flexible plastic, and logic for smart cards and radio-frequency identification (RFID) tags.

The present work is divided into several chapters. At the beginning, the current status of printed electronics and the main advantages and disadvantages over conventional manufacture of electronic manufacture will be discussed. Basic components of electronic circuits and materials needed for their production will be considered. Synopsis of available printing technologies is given and then the discussion is focused on gravure printing in greater detail. In the experimental part, an overview of materials and methods used in this study is given. The main goal of this work is to form a starting point for the manufacturing of low-cost electronics by the use of printing methods. Before undertaking full scale gravure printing research, initial screening experiments are required to identify suitable materials and determine other printing concerns. In the Results and Discussion part, it will be shown that conductive inks can be successfully optimized for gravure printing. By using statistical methods, the importance of substrate properties as well as process parameters will be emphasized.
CHAPTER 2

LITERATURE REVIEW

2.1. Overview of Printed Electronics

2.1.1. Why Printing in Electronics Manufacture?

Screen printable conductors, resistors and dielectrics have been known for over 50 years now. These were used to create interconnections and resistive elements of complex circuitry and with further addition of active components to create hybrid circuitry. Nowadays, there is an increasing interest in a number of portable electronic devices; the trend of integrating RFID tags into supply chains is increasing rapidly and this electronics revolution (particularly in wireless and networking technology) has demanded the development of new and optimized materials and processes.

The primary goal of printing electronics is to create structures and devices that are functionally similar to conventional electronics, but at greater speed, lower cost and less production complexity. This might be realized in large part due to the transition from high vacuum and high purity manufacture of integrated circuits (IC) to ambient condition and room temperature processing by printing methods. Technical expertise in printing is already available and with the implementation of printing into electronic manufacture, there is a great opportunity to develop new products and open new markets. Traditional press makers and printers have developed abilities and competencies that can help extend their production beyond printed products addressing the human visual sense. Printing of patterns with inks that are electrically conductive provides the opportunity to print electrical...
circuitry or RFID antennas. Printing patterns with functionalities like semi-conductivity and electrical insulation open routes to print capacitors, polymer transistors and LED's (light emitting diodes).

Current production processes for electronics and integrated circuits manufacturing combines masking, etching, chemical-vapor deposition, thermal diffusion, and sputtering, typically taking place in expensive clean rooms under various high temperature or high vacuum processing conditions. The transition from batch processing in clean rooms at high vacuum and temperature to a press room at atmospheric pressure and ambient temperature would be very appealing, if devices of adequate functionality could be developed.

There are advantages and challenging disadvantages of using printing processes to manufacture electronic devices. The main advantages include high-speed fabrication, low cost manufacturing, and possibility of using flexible substrates, less waste and roll-to-roll capability. On the other hand, each of the available printing processes has its limitations, such as resolution, registration and uniformity of the printed layer. Printing is a microscale production and the lower limitation of resolution is given by the visual capability of the human eye. The eye is limited to about 150 μm and in order to achieve sufficient number of gray levels; the smallest pixels have lateral width of 15 μm. In wafer production, silicon chips with dimensions of 100 nm are becoming common. Another aspect would be that some of the materials needed for electronics are hard to process from solution, without modification of functional properties. Consequently, the performance and function of printed electronic devices is lower when compared to
conventional electronics. The comparison of conventional manufacture of organic electronics and possible manufacture by printing is generalized in Table 1.

Table 1: Comparison of conventional and printed electronics manufacture

<table>
<thead>
<tr>
<th></th>
<th>Solid-State (Conventional)</th>
<th>Organic and Printed Electronics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>Batch</td>
<td>Continuous</td>
</tr>
<tr>
<td>Production Speed</td>
<td>Slow</td>
<td>Potentially Fast</td>
</tr>
<tr>
<td>Capital Cost</td>
<td>Extremely High</td>
<td>Low to Moderate</td>
</tr>
<tr>
<td>Materials</td>
<td>Well Defined</td>
<td>In Development</td>
</tr>
<tr>
<td>Cost</td>
<td>Moderate in High Volume</td>
<td>Low to Moderate</td>
</tr>
<tr>
<td>Substrate</td>
<td>Rigid Silicon</td>
<td>Various, Flexible</td>
</tr>
<tr>
<td>Economic Run Length</td>
<td>Large</td>
<td>Small to Very Large</td>
</tr>
<tr>
<td>Environmental</td>
<td>Acceptable</td>
<td>Friendly</td>
</tr>
</tbody>
</table>

2.1.2. RFID Technology

Figure 1 shows the basic principle of RFID tag operation. Typically, a reader communicates with a tag, which holds digital information in a microchip. Digital data encoded in an RFID tag are transmitted to a reader using radio waves when the correct command is received. The reader converts the radio waves back to a digital form and passes the information to computer systems for processing. In this way, an RFID transponders, consisting of an antenna and integrated electronics, can communicate via radio frequency to an RFID reader that has its own antennas and significant electronic content. The readers can interface through wired or wireless medium to a main computer.

RFID tags typically consist of a metal antenna and a silicon-based microchip. The microchip stores information about the product that it is placed on. The size and shape of the antenna is determined by several factors,
such as frequency range at which it operates, required read range and the type of product, on which the tag will be applied.

In the past few years, the term "low cost RFID" has begun to be used with the potential of using low cost RFID tags in very different, new applications. This alternative to the barcode, magnetic stripe or printed label, has advantages that include tolerance of miss-orientation and obscuration, lower cost over life and ability to "read". Most importantly, they are usually cheap enough to be disposable and thin enough to go in new locations, even inside sheets of paper in some cases. All flat versions, including smart tickets and laminates, are usually called smart labels.

![Figure 1: Principle of RFID tag operation](image)

There are various approaches currently being pursued in order to realize item-level RFID. In conventional approaches, there is an effort to find lower cost technologies of silicon chip attachment on an external antenna. Nowadays, the amount of silicon required for a typical RFID tag is
exceedingly small. This however gives rise to the problems during chip separation and thus, in order to avoid silicon wafer waste or damage to a microchip, very precise separation techniques are necessary. Traditional rotary diamond saw cutting is often inaccurate and produces very rough edges and thus larger spacing is required between individual microchips. Chip separation by etching is a more accurate process improving the silicon usage efficiency. Another issue is the connection of such small chip to HF or UHF antenna. Typically, chips are attached onto a larger strap with appropriate connections. Unfortunately, the cost for attachment technologies does not scale well at this time and it is unlikely that this will help to realize sub one-cent RFID tags. In addition to this, manufacturers are trying to push the operating frequencies to a higher range. However, while high frequency tags are well suited for palette level tracking, they are insufficient in water or metal-contaminated products and therefore this approach is also not attractive for item-level RFID.

The more aggressive approach to the realization of item-level RFID tags is by printing both high-quality passive components and high-performance all-printed transistors. In fact, this approach is one of the greatest driving forces for implementation of printing in electronics manufacture. Printing of passive components and antennas has already been reported. As oppose to etched copper technology for traditional antenna fabrication, printing offers a low cost alternative. In general, the resistivity of printed materials is higher than that of etched copper, and thus printing is used for UHF applications not for HF where the requirements on conductivity are tougher. One of the most popular methods of printing
functional antennas is with the use of silver conductive inks printed on plastics substrates or paper\textsuperscript{15,16,17,18}. Considering integrated circuits, fully printed IC have been already demonstrated\textsuperscript{12}, however the performance is not yet acceptable for RFID applications.

2.2. Electrical Conductivity and Band Theory

Before considering individual components of electronics and materials needed to achieve sufficient functionality, it is necessary to discuss the theory behind electrical conductivity of materials.

Electrical conductivity refers to the transport of charge carriers through a medium under the influence of an electric field or temperature excitation. It is dependent on the number of charge carriers and their mobility. The charge carriers may be generated intrinsically or from impurities, in which case they may be electrons (n-type), holes (p-type), or ions.

Electrical properties of any material are determined by its electronic structure. The theory that most reasonably explains the electronic structure of materials is band theory. In the solid state, atomic orbitals of each atom overlap with the same orbitals of their neighboring atoms in all directions to produce molecular orbitals similar to those in small molecules. When many orbitals are spaced together in a given range of energies, they form what looks like continuous energy bands\textsuperscript{19}. How many electrons these bands have and where the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) are depends on how many electrons the original atomic orbitals contain and the energies of the orbitals. The highest occupied band is
called the valence band (containing $\pi$ bonding orbitals), and the lowest unoccupied band is the conduction band (containing $\pi^*$ antibonding orbitals). The energy gap between the two bands is called the band-gap energy and its magnitude determines whether such a material is a conductor, semiconductor or an insulator (Figure 2)\textsuperscript{20}.

Crucial to the conduction process is whether or not there are electrons in the conduction band. In insulators, the electrons in the valence band are separated by a large gap from the conduction band and such gap is enough to sufficiently reduce conductivity. In conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small well defined gap between the valence and conduction bands that voltage potential or thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically\textsuperscript{20}.

An important quantity in the band theory is the Fermi level, the top of the available electron energy levels at low temperatures. The position of the Fermi level with the relation to the conduction band is a crucial factor in determining electrical properties.
Energy of electrons

Conduction Band

Fermi level in gap.

The large energy gap between the valence and conduction bands in an insulator says that at ordinary temperatures, no electrons can reach the conduction band.

In semiconductors, the band gap is small enough that thermal energy can bridge the gap for a small fraction of the electrons. In conductors, there is no band gap since the valence band overlaps the conduction band.

a. Insulator  b. Semiconductor  c. Conductor

Figure 2: Illustration of the energy bands in insulators, semiconductors and metals

2.3. Basic Components and Materials for Electronic Circuits

Electronic circuits are made of passive and active building blocks and require at least three main material properties for construction. The materials needed are conductors, semiconductors and dielectrics (insulators). Moreover, the substrate, on which the component is constructed, is also an essential part of the system. Figure 3 shows the basic structure of key building blocks and the materials required for their function. Individual components and materials needed for their manufacture will be discussed in more details next.

While the main functional components provide the performance of the device, another material, referred to as a barrier coating, might be necessary in order to increase its lifetime. Such coatings prevent contamination of electronic structures due to water, oxygen, oils, dust or other contaminants.
2.3.1. Conductors

A conductor, or a wire, acts as a conduit for current through a circuit. A wire with sufficiently low conductivity can essentially act as a resistor. In organic transistors, conductive ink can be used to print gate, source and drain electrodes.

Thermal evaporation and sputtering of gold, platinum or aluminum is commonly used in conventional fabrication of organic transistors producing thin metal films for device electrodes. This process is however very slow and requires a high vacuum. Interconnections between conductors and other components can be also produced using printing with conductive inks. Ink conductivity can be achieved by different mechanisms, such as incorporating metallic or other conductive particles into a non-conducting polymer matrix, or by using polymers that exhibit electrical conductivity in a suitable solvent.
Among metallic filled inks for printed transistors, there are reports on the ink-jet printing of nanometalic (Au, Ag) particles to produce contact electrodes for organic transistors\textsuperscript{11, 23}. Additionally, nickel nanoparticle inks that can be printed or coated on dielectric substrates to form conductive films for multilayer electrical contacts and interconnections have also been reported\textsuperscript{24}.

A major breakthrough in the area of conductive polymers was the discovery in 1977\textsuperscript{25} that polyacetylene could be easily oxidized (by electron acceptors) or reduced (by donors). Nowadays, conductive polymers are becoming more and more attractive candidates for use in the field of printed transistors. Polymers become conductive upon partial oxidation or reduction, a process commonly known as doping as an analogy with doping of inorganic semiconductors. However, doping in inorganic semiconductors generates either holes in the valence band or electrons in the conduction band, while polymer doping leads to the formation of conjugated defects (solitons, polarons, or bipolarons) in the polymer chain. It has been demonstrated that the electrical properties of conducting polymers can be reversibly changed over the full range from an insulator to a metallic conductor\textsuperscript{26}. The original oxidative dopants included strong and weak agents such as AsF\textsubscript{5} and I\textsubscript{2}. The list of dopants also includes SbF\textsubscript{5}, AlCl\textsubscript{3}, ZnCl\textsubscript{2}, FeCl\textsubscript{3}, IF\textsubscript{5}, O\textsubscript{2}, WCl\textsubscript{6}, and MoCl\textsubscript{5} and is still expanding\textsuperscript{27}. However, the same dopant cannot always be effective for different polymers; this will depend on its oxidizing ability. Yet, most of the doped conductive polymers have limited solubility. Not a long time ago, it has been discovered that solubility of conductive polymers in their doped form can be improved by use of
appropriate “surfactant-like” molecules as dopants (camphor sulfonic acid or dodecyl benzene sulfonic acid) or attaching alkyl or alkoxy groups onto the polymer chain.

Among commercially available conductive polymers, poly (3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) and polyaniline (PANI) have been used for depositing organic transistor electrodes. Chemical structures of these polymers are shown in the Figure 4. Polyaniline can exist in several structural forms depending on the oxidation stage, which also determine the level of its electrical conductivity.

![Chemical structure of PEDOT:PSS and PANI (Emeraldine Base)](image)

Figure 4: Chemical structure of a) PEDOT:PSS and b) PANI (Emeraldine Base)

In this work, PEDOT:PSS based inks were used to print conductive layers. This conductive polymer is commercially available as a water-soluble polyelectrolyte system with good film-forming properties, high visible light transmittance, and excellent stability. Some applications of PEDOT:PSS
include antistatic coatings, conductive layers in organic light emitting diodes (OLEDs), capacitors and thin film transistors\textsuperscript{35}. PEDOT:PSS complex is prepared by oxidative polymerization of ethylenedioxythiophene (EDOT) in aqueous dispersion using sodium peroxodisulfate as the oxidant. A template polymer (usually polystyrene sulfonic acid – PSS) is present during the polymerization. The PSS in the resulting complex acts as a source for the charge balancing counter ion. Moreover, it keeps the PEDOT chains dispersed in water, forming stable, easy to process, deep blue colored microdispersions\textsuperscript{34}.

It has been reported that electrical conductivity of PEDOT:PSS can be enhanced by the addition of different organic compounds\textsuperscript{36}. The conductivity improvement is strongly dependent on the chemical structure of the compound. Among the alcohols, ethylene glycol and glycerol were found to be the most efficient. Enhancement of conductivity is believed to be a result of an increased inter-chain interaction caused by conformational change of the PEDOT chains from the coil structure into expanded-coil or linear structures\textsuperscript{37}.

2. 3. 2. Semiconductors

As already shown in the Figure 2, semiconductive materials are neither conductive nor insulating. The charge carriers can be influenced by an external electric field and thus such materials will allow diode or transistor functionality.

Elements that build organic semiconductor chemical structures primarily include carbon and oxygen or sulfur. The common feature of these
materials is the presence of conjugated bonds (alternating of single and double carbon bonds) where the presence of mobile \( \pi \)-electrons has the main impact on their electrical performance\(^2\).

There are four classes of organic semiconductors\(^8\):

- small molecules based on (hetero)aromatic rings;
- conjugated polymers;
- hybrid organic-inorganic compounds; and
- molecular semiconductors (such as nanotube like materials and buckyballs).

Among small molecules, pentacene (Figure 5a) is the most studied organic semiconductor due to its availability and well understood processability. Unfortunately, pentacene is insoluble in almost all organic solvents. However, one report\(^9\) showed the possibility to process pentacene from a soluble precursor solution, which is heated upon deposition to convert to pentacene. The conversion temperature to a polycrystalline film of pentacene will determine which substrate can be used with such material. The anneal temperature influences performance of the final device and can be varied from 120°C to 205°C. Another work\(^40\) reported on improved solution processing and high performance of pentacene through modification of pentacene with silane and mobility as high as 1 cm\(^2\)/Vs was achieved.

\( C_{60} \) or other fullerenes are examples of conjugated molecular semiconductors. Due to their chemical structure (closely packed molecules) the valence and conductive bands overlap, resulting in a semimetal. For polymers, the valence electrons are delocalized along the polymer chains. Delocalization promotes intrachain charge transport easier than interchain,
which is, however, still required for the usual size range of devices made from polymer semiconductors.

Polymeric semiconductors exhibit structural stability, tunable electrical properties, and solubility. These properties can be achieved by designing and optimizing of polymer chain structures. From polymeric semiconductors, several have proved the suitability for usage in organic transistors. These are mostly from polythiophene family, such as poly(3-hexylthiophene) (P3HT), poly(9,9'-dioctyl-fluorene-co-bithiophene) (F8T2) shown on the Figure 5a and 5b, and recently poly(3,3-diethyl-quaterthiophene) with enhanced stability and processability.

![Figure 5: Structure examples of semiconducting materials, a) pentacene, b) P3HT and c) F8T2](image)

The majority of organic semiconductors are of p-type, transporting holes (h⁺) rather than electrons. As already discussed, the ability of materials to transport charge is due to the p-orbital overlap of neighboring molecules.
providing their semiconductive and conductive properties. Higher degree of crystallinity of organic materials enhances this p-orbital overlap and it is a key to improvements in carrier mobility. Research efforts on organic semiconductive conjugated materials have led to improvements in the mobility of these materials by five orders of magnitude (Figure 6). However, the polycrystalline character of organic materials makes it more difficult to achieve the mobility of the single-crystal silicon used in high-performance devices. For example, measurements on single organic crystals of p-type pentacene marking the upper limit of performance show mobility of 2.7 cm² V⁻¹ s⁻¹, whereas mobility of single-crystal silicon and polysilicon is in the range from 300 – 900 and 50 – 100 cm² V⁻¹ s⁻¹, respectively⁴³.

Figure 6: Mobility improvement of organic semiconductors⁴⁴

Overall, semiconductor materials and their properties have a tremendous effect on device performance and characteristics. Two critical properties of solution-processed polymer semiconductors are needed to
enable printing low-cost electronics. One is the ability to self-organize into a higher structural order for efficient charge carrier transport; and second is the sufficient stability to permit processing under ambient conditions without a costly protective environmental setup. Moreover, there is a need to study how the properties and performance of organic semiconductors are influenced by process parameters during printing and drying.

Formulation of polymeric semiconductors into printing inks will be determined by the solvent selection, rather than by the chosen printing process. In some cases, there is a need for aggressive, corrosive and caustic solvents that are used to dissolve these materials. This puts constraints on the printing processes and thus compatibility of the ink with the image carrier and with the whole printing system.

2.3.3. Dielectric Materials

The function of a dielectric material is to isolate conductive and semiconductive layers. Dielectric materials lack the charge carriers and thus prohibit the flow of electric current. For dielectric layers, it is very important that they are uniform and smooth, defect-free (pin-holes and cracks) and impurity-free and capable of sufficient separation of charge without breakdown. Pinholes can occur either due to air bubbles trapped in the ink film and ruptured during drying, or due to mismatch between surface tension of ink and surface energy of the substrate and thus insufficient wetting. Therefore, good wettability properties and compatibility with semiconductive and conductive layers are also required. Uniform thickness of dielectric is necessary in order to avoid breaking of the layer and causing the
creation of possible paths for charge to travel through. This may be in the form of surface conductivity or from migration of atoms from electrodes through the voids in dielectric layer or filling the voids with conductive material during manufacture. All of this can cause a short-circuit.

Two categories of dielectric materials are used in organic transistors: inorganic (ceramics) and organic (polymer). Inorganic dielectric materials include silicon dioxide (SiO₂) and silicon nitride (SiNₓ). Although these ceramic materials have high dielectric constants, they suffer from being rather inflexible and brittle materials, and due to lack of solution processability they are very difficult to incorporate into printing processes.

Some examples of polymer dielectrics include poly (methylmethacrylate) (PMMA), poly (4-vinyl phenol) (PVP), polystyrene (PS), or polyimide (PI). Reports on nanocomposite materials that are composed of high dielectric constant inorganic oxide core/polymer shell nanoparticles (TiO₂ in PS shell) are promising solution processable materials. These also provide better charge mobility of a pentacene semiconductor, due to good compatibility with the nanocomposite and improved orientation of the pentacene film.

2.3.4. Printed Organic Transistor

Transistors using silicon require a complicated and high precision manufacturing process that creates electronic circuits by starting with a single-crystal silicon substrate and applying a variety of processes such as oxidation, the addition of impurities (ion implantation), chemical-vapor deposition, thermal diffusion, annealing, metallization, photolithography and
etching. Large scale and expensive equipment, such as clean rooms and vacuum systems, are required. In contrast, with organic transistors, one can take advantage of the features of organic materials and, by dissolving them in a solvent, use printing technologies such as rotary press or inkjet printing to create circuits simply. Since these are low-temperature processes, they have excellent compatibility with plastic substrates.

The printed organic transistor revolution started in 1994. The first organic transistors were manufactured by combination of screen printing, laminating and organic vapor deposition techniques. Although, the field-effect transistors (FET) based on organic semiconductors have been reported prior to this work, they used robust gold electrodes requiring vacuum deposition. Electrodes for the first printed organic transistor were made by screen-printing of graphite-based conductive ink.

2.3.4.1. Organic Field-Effect Transistors Design

Organic field-effect transistors (OFET) can be designed in several different ways depending on gate electrode position (top gate and bottom gate) and placement of semiconductor (top contact and bottom contact). Figure 7 shows different architectures of organic transistors. For bottom gate transistor, the gate electrode is deposited on the substrate and for the top gate setup; the gate electrode is deposited on the top. Considering the semiconductive layer, for the top contact layout, the semiconductor is deposited on the insulator, then the source and drain contacts are placed. Finally, in the bottom contact transistor layout the semiconductor layer is deposited on the contacts. The bottom contact device is easier to fabricate.
However, the device performance is limited due to the poor quality of organic semiconductor film deposited at the interface of the contacts and the channel. However, a design concept of OFET utilizing a vertically stacked structure with promising performance has been reported\textsuperscript{50,51}.

![Illustration of different types of horizontal OFET architectures](image)

Figure 7: Illustration of different types of horizontal OFET architectures, a) bottom gate, bottom contacts b) bottom gate, top contacts c) top gate, bottom contacts and d) top gate, top contacts

2.3.4.2. Principle of Operation

In principle the basic function of an organic transistor is comparable to that of conventional transistor. Figure 8 illustrates the basic operation principle of OFET. Without a gate voltage applied, the semiconductor layer is not doped and thus insulating; no current will flow between source and drain electrodes and transistor is in the OFF position. Applying an electric field across the dielectric layer through control of gate voltage induces the accumulation of minority charge carrier sites at the interface of the organic semiconductor and the dielectric forming a channel. The channel supports charge transport (flow of current) between the source and drain electrodes.
The extent of the current depends on applied gate voltage and the semiconductive material characteristic, which determines the depth of the channel and the number of minority charge carriers sites\textsuperscript{29,41}.

Figure 8: The principle of basic operation of an organic FET (bottom gate bottom contact architecture)

The quality of the semiconductor layer, insulator-semiconductor interface and the device geometry are important factors that affect the transistor characteristics. As already mentioned earlier, ordering of the semiconductor contributes to an increase in mobility and this can be altered by optimizing the deposition process. Additionally, the larger the grains, the lesser the trap states, therefore the mobility can be increased\textsuperscript{49}.

Successful manufacture of fully printed organic transistors has been already reported\textsuperscript{42,52} and even a low voltage all-printed transistor was also reported\textsuperscript{53}.

2.4. Potential of Printing in Electronics Manufacture

Different discoveries and inventions made in engineering, computer science, information technology, physics and chemistry have contributed to
development, improvement and the current status of today’s printing technologies. With implementation of available printing methods to electronics manufacturing, a new value can be added to already established technology. From the previously discussed material properties required to produce electronic devices, it might seem easy to implement printing into the manufacture by simple substitution of regular printing ink with functional ink possessing conductive, semiconductive or insulating properties. Unfortunately, the whole transition is not so simple. Conventional printing techniques have been optimized to be seen by human eyes, for which the resolution of 100 - 150 μm is sufficient. Additionally, the printed image consists of printed dots that are printed side by side or they are slightly overlapping. On the other hand, for the printing of polymer chips, continuous lines are required for conductive electrodes with resolution in the micrometer range. Very thin, homogeneous, defect free layers of semiconductor, dielectric and gate electrode must be deposited onto source and drain electrodes as accurately as possible in order to create properly functioning devices. Furthermore, the presence of additives that are commonly added to regular printing ink formulations in order to meet process requirements (such as viscosity, wettability, and end-use properties, etc.) may cause undesired change of the electrical properties of the materials and consequently performance of the final device.

2. 4. 1. Available Printing Technologies

Printing technologies can be divided into two main groups, conventional printing (with master) and non impact printing technologies
The former is based on image carrier or master, from which the information is transferred onto the substrate. The later does not require a fixed image carrier and it is digitally controlled. It can produce different printed information per print. The classification of printed technologies is given in Figure 9. Basic principles and a more detailed description of the two groups and their subgroups are discussed separately in further text.

Figure 9: Overview of printing technologies

2. 4. 1. 1. Conventional Printing Technologies

There are four basic groups of conventional printing methods. These include flexography, gravure, lithography and screen printing.

Flexography and gravure are based on different surface relief of image
and non-image areas. Printing elements are raised above the non printed elements in the case of flexography or recessed in the case of gravure printing. Flexography uses low viscosity inks and resilient or soft, flexible printing plates. This printing technology requires only a slight contact pressure to enable reliable ink transfer from printing plate to substrate. Because of the flexible printing plates, which are now made mostly from photopolymeric plastic, printing can also be done on materials with relatively rough surfaces. Gravure printing also uses fluid ink with lower viscosity than those used in flexography. The image carrier is a steel-based cylinder electroplated with copper, engraved and chromium plated. Due to the hardness of gravure cylinders, high printing pressure and a smooth compressible substrate is required in order to sufficiently transfer ink from the cells to the printing substrate. Gravure printing and image carrier preparation will be discussed to a great extent later (Chapter 2.5).

Lithography is also known as planography, due to the nature of the image carrier, on which the information is defined by the difference in wetting (surface tensions) of a plane surface. Printing inks for lithography are mostly oil-based and thus the image areas are oleophilic and non-image areas are oleophobic.

Finally, screen-printing is based on pushing the ink through the openings in meshed image carrier defining the printed information.

2.4.1.2. Non-Impact Printing Technologies

The predominating technologies among non-impact printing technologies are electrophotography and ink-jet printing. However also other
methods are used including ionography, magnetography, thermography, and photography. New physical processes that could be incorporated in non-impact printing are constantly being discussed and developed in special fields.\textsuperscript{54}

Electrophotography is based on selective discharging of photoconducting drum by a laser or LED. The drum is then toned by charged ink (pigment particles). Special inks are used for electrophotography. These may be powder or liquid toners, which may vary in structure according to their composition, and contain the colorant in the form of pigments. The toner charge is configured in such way that the charged areas of the photoconductor surface accept the toner. Therefore, the latent image on the photoconductor drum becomes visible where the toner is applied and can be then transferred onto the substrate via electrostatic forces and fused using heat and contact pressure.

Ink-jet printing, on the other hand, does not require any intermediate image carrier such as a photoconducting drum in electrophotography. There are two general categories of ink-jet printing: continuous mode and drop-on-demand mode. Whereas in the continuous ink-jet process, only part of the continuously generated flow of small ink droplets is directed onto the paper during printing in accordance with the image, in drop on demand ink jet processes drops of ink are generated only if the information to be printed demand them. Drop-on-demand (DOD) ink-jet processes can be further classified according to the way that the individual ink drop is generated to the following categories: thermal (bubble jet), piezo ink-jet and electrostatic ink-jet. Thermal ink-jet uses the heating of the liquid ink until it vaporizes,
and ink drop is ejected from the nozzle as a result of the pressure exerted by the vapor bubble. In piezo ink-jet systems, the drop is generated as a result of a change of volume within the ink chamber due to piezoelectric effects. The pressure waves are converted to fluid velocity and this leads to the drop of ink being ejected from the nozzle system. Electrostatic ink-jet is based on existence of electrical field between the ink-jet system and the surface to be printed. The ink drop is generated due to field forces. Withdrawal of ink from the nozzles is prepared via the electrical field and a control pulse (e.g., electric signal or the supply of heat) then enables the release of a drop.

2. 4. 2. Specifications of Printing Processes

In the past, printing of visual images was the only application of printing and technologies were very well optimized to meet these requirements. Recent efforts are pushing toward the use of printing technologies as a manufacturing platform for electronics production. The potential of different printing technologies is yet very often not known.

Several challenging issues must be overcome for successful incorporation of printing as a platform for electronics manufacture, such as resolution, accuracy (registration tolerances), continuity and uniformity of the printed layers. General advantages of printing over conventional manufacture of electronics were already implied in the Table 1. Detailed specifications of individual printing processes are summarized in Table 2. The data presented were collected from various sources and are considered to be most important to be taken into account when incorporating into electronics manufacture.
The limiting factor for source and drain electrodes would be the resolution of the printing technique. The source drain current is inversely proportional to the channel length. Channel length less than 10 microns, providing relatively high switching speed of organic transistor was already reported. A semiconductive layer is usually applied over the whole device surface and its thickness is typically around 100 nm or less. As for the insulating layers, a thin homogeneous layer, without voids, is required. Surface roughness and voids have to be minimized because it might limit the charge transport in the transistor channel. Printing of the semiconductive layer only in the channel areas of the transistor would be optimal, in order to avoid leakage current between transistors in the integrated circuit. This would require very precise overprinting and registration when using printing technologies. The last part of a transistor is the gate electrode, which should be printed only on the top of the channel area in order to minimize gate capacitance. At this point, the requirements for resolution are the same as for source and drain electrodes.

2.4.3. Challenges in Printing of Electronics

Patterning issues that are crucial to electronics manufacturing include resolution, design rules, accuracy, registration, and yield. A truly challenging task for printing techniques would be to achieve one micron accuracy level, in order to become relevant to microelectronics. However, single-layer printing with reduced lateral-accuracy requirements and replication with overlay of larger patterns (micrometer scale) may soon be applied in niche markets.
Table 2: Basic specifications of main printing processes

<table>
<thead>
<tr>
<th></th>
<th>Screen</th>
<th>Gravure</th>
<th>Flexography</th>
<th>Lithography</th>
<th>Ink-jet</th>
<th>Electrophotography</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lateral Resolution [µm]</td>
<td>100</td>
<td>15</td>
<td>40</td>
<td>15</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>Viscosity of Ink [Pa. s]</td>
<td>0.5 - 50</td>
<td>0.05 - 0.2</td>
<td>0.05 - 0.5</td>
<td>30 - 100</td>
<td>0.001 - 0.04</td>
<td>10 - 20 (Liquid Toner)</td>
</tr>
<tr>
<td>Functional Fraction* [wt %]</td>
<td>15 - 25</td>
<td>5 - 20</td>
<td>12 - 20</td>
<td>20</td>
<td>3 - 10</td>
<td>5 (Powder)</td>
</tr>
<tr>
<td>Pigment Particle Size [µm]</td>
<td>0.8 - 2.5</td>
<td>0.1 - 0.5</td>
<td>0.1 - 0.5</td>
<td>0.2 - 0.7</td>
<td>0.05 - 0.5</td>
<td>6 - 20 (Powder) 1 - 2 (Liquid)</td>
</tr>
<tr>
<td>Amount of Material</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Shear Rate</td>
<td>Low</td>
<td>High</td>
<td>Medium - High</td>
<td>Medium - High</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Web Speed [ft/min]</td>
<td>300 - 500</td>
<td>1500 - 3000</td>
<td>300 - 1000</td>
<td>500</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*Typical pigment content in traditional printing inks
Triggered by promising applications with intermediate accuracy requirements, improvements might drive printing technologies to reduce pattern sizes from 20 µm to 100 nm and to improve overlay from 20 µm to sub-micron levels.

In printing, adequate wetting and surface adhesion are necessary for sufficient ink film integrity. Overlaying of colors to achieve required color is basically controlled by thickness of the ink film. In electronics, the quality of interface between individual layers is crucial, because it functions as a conveyor of charge carriers across or along the interface. Additionally, chemical interaction between individual layers is very important. For visual appearance of color, the intermixing of ink layers is not a problem, but for electronics it might not be the same. Further problems can arise when different materials needed for multi layer fabrication require different solvents and thus possibly different printing processes. There is a need to research the area of interfaces created during printing of materials and their effect on device performance.

As already mentioned, high smoothness and uniformity of printed semiconductor and dielectric is essential for optimal device performance. During printing, shear forces are applied to the substrate and inks, increasing the chance to create texture or roughness of the printed layer. Additionally, substrate and ink properties influence quality of the printed interface. Variations in surface smoothness, surface energy and absorption properties of substrate or poorly dispersed pigment and variation in surface tension of an ink lead to poor ink transfer and mottle (non-uniformity) problems of a printed ink film. Morphology of the printed surface and contour definition strongly depend on ink properties that determine integrity and uniformity of printed films (such as
ink film splitting, wetting and spreading, and ink adhesion). Better understanding of these issues can lead to fabricating of more uniform and reliable printed structures.

Shrinkage of the substrate plays a very important role in the production of smaller structures. Substrates face mechanical stress as they travel through the press or during the transfer of liquids on the substrate by rollers, especially polymer foils. The hygroscopic properties of papers can also cause dimensional changes and other problems (such as curled, waved or tight edges).

Electrical conductivity of a printed layer is generally dependent on its thickness. Film thickness will depend mostly on the printing process, ink rheology and substrate absorbance. In order to increase conductivity, the printing can be adjusted so that a thicker ink layer is deposited, or simply by increasing the number of passes. However, this might be limited by the integrity of the printed film. In many electronics applications, the thickness of the ink film must be reduced even below the known limits of today's printing methods, e.g. printing of thin uniform dielectric layers.

Another important factor affecting the choice of printing method is suitable ink chemistry and viscosity. From the viscosity point of view, lithography uses mostly oil-based paste inks, whereas flexography and gravure need fluid ink to assure adequate ink flow out from anilox roll or gravure cylinder cells. With ink-jet printing, it is very important is to employ low viscosity inks. The particle size of materials used needs to be smaller than nozzle dimensions, in order to avoid clogging. Furthermore, some ink formulations include various additives improving ink working and end use properties. This might change the electrical properties of functional inks and thus influence the
overall performance of electronic structures.

Printing press settings and process parameters also significantly influence final quality of a printed layer. However, there is not enough knowledge about the relationship between printing process parameters and their influence on printed layer morphology and resulting electrical behavior.

2.5. Gravure Printing as a Manufacturing Platform

Gravure printing is the premier printing process, due to its very high quality and ability to print at very high speeds. Robustness of its image carrier is also advantageous, contributing to very good printing stability over time. Moreover, gravure printing has the ability to deposit variable film thicknesses in one print unit, a feature that is a limitation in both flexography and offset printing. These advantages of gravure printing make it a very promising process for electronics manufacture, smart packaging and RFID.

2.5.1. Basic Principles of Gravure Printing

Gravure printing is mechanically simpler when compared to the other printing processes. It has four basic components to each printing unit: an engraved cylinder, ink fountain, doctor blade, and impression roller. Gravure can print on a broad range of substrates and the widest range of ink formulations can be applied. It is typically associated with high print quality output and low variation throughout the printing run.

The heart of a gravure press is the gravure cylinder, which carries the image design to be printed. A gravure cylinder is composed of a thick-walled steel base with flanged steel journals. It is electroplated with copper and then
polished to a predetermined diameter. Precise diameter of gravure cylinders is critical because any variances in diameter, as little as two thousandths of an inch, can significantly affect the print registration. Once engraved, cylinders are electroplated with a thin layer of chromium to ensure hardness of surface that protects softer copper against scratches and abrasion by the doctor blade during printing.

The doctor blade is a simple device used to shear the ink from the surface of an engraved cylinder. Pressure is applied to the doctor blade to assure uniform contact along the length of the cylinder. The blades must be angled to cut the surface of the ink, but pressure and angle must be carefully adjusted to prevent premature wear of the cylinder. The doctor blade oscillates back and forth to prevent accumulation of ink particles or blade chips underneath the doctor blade, as well as a premature wear. Much of the wear on a gravure printing cylinder is caused by doctor blade wiping action. This wear may be abrasive, fatigue or corrosion wear. Abrasive wear occurs whenever hard foreign particles are present between the blade and cylinder as they rub against one another. Some pigments are more abrasive than others are. More examples of abrasive particles include insoluble ink vehicle particles, dried ink, rust, paper dust, particles of clay coating, doctor blade particles or chromium chips from the print cylinder.

The elastomer covered impression roll brings the substrate in contact with the engraved cylinder, resulting in proper ink transfer. The impression roll also acts to adjust the tension between print units and helps move the substrate through the press.

There are many factors influencing gravure print quality, such as
substrate properties (smoothness, compressibility, porosity and ink receptivity, wettability, etc.) and ink properties (ink chemistry, viscosity, rheological behavior, solvent evaporation rate and drying, etc.). Furthermore, process parameters, such as doctor blade angle and pressure, impression pressure and speed, have tremendous effects on quality of printed ink films. Very important is also the preparation of the image carrier by different engraving methods, because ink release from engraved cells will depend on the width and depth of cells and their overall shape. Different factors affecting print quality in gravure printing are summarized in Figure 10.

<table>
<thead>
<tr>
<th>INKS</th>
<th>CYLINDER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry (solvent and binder type)</td>
<td>Engraving method</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Cell geometry</td>
</tr>
<tr>
<td>Temperature</td>
<td>Cylinder type</td>
</tr>
<tr>
<td>Surface tension</td>
<td>Image composition</td>
</tr>
<tr>
<td>Functional properties (color)</td>
<td>Coating</td>
</tr>
<tr>
<td>Overprinting</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SUBSTRATE</th>
<th>PROCESS PARAMETERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type (paper or plastic)</td>
<td>Doctor blade</td>
</tr>
<tr>
<td>Surface finish properties (coating)</td>
<td>- (material, type, pressure, angle)</td>
</tr>
<tr>
<td>Thickness</td>
<td>Printing speed</td>
</tr>
<tr>
<td>Compressibility</td>
<td>Impression roller</td>
</tr>
<tr>
<td>Response to humidity and temperature</td>
<td>-(material, geometry, pressure)</td>
</tr>
<tr>
<td>Operational (drying) temperature</td>
<td>Environmental conditions</td>
</tr>
<tr>
<td>Dimensional stability</td>
<td>-(humidity, temperature, solvents)</td>
</tr>
<tr>
<td></td>
<td>Electrostatic assist</td>
</tr>
<tr>
<td></td>
<td>Web tension</td>
</tr>
<tr>
<td></td>
<td>Registration</td>
</tr>
<tr>
<td></td>
<td>Drying</td>
</tr>
<tr>
<td></td>
<td>Cooling</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PREPRESS</th>
<th>GR AV U R E</th>
<th>P R IN T IN G</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin of information</td>
<td>Engraving method</td>
<td>Cell geometry</td>
</tr>
<tr>
<td>Resolution</td>
<td>Cylinder type</td>
<td>Image composition</td>
</tr>
<tr>
<td>Gamut compression</td>
<td>Coating</td>
<td></td>
</tr>
<tr>
<td>Colors used</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transfer algorithms</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 10: Overview of different factors affecting print quality in gravure printing

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2. 5. 2. Gravure Cylinder Engraving

In gravure printing, the image is almost always broken up into separate cells and a solid image is then created by the ink spreading on the substrate. Walls between individual cells provide a supporting surface for doctor blade as it wipes the ink off the non-image areas of the gravure cylinder.

There are several different methods of image carrier preparation. These include chemical etching, electromechanical engraving and laser engraving. Very recently, a new engraving method, based on indirect laser ablation combined with electrolytic copper removal, has been introduced by Creo and Acigráf - Thermal Gravure Technology (EXACTUS™)*. Each of these techniques produces different type of cells. Even though the electromechanical engraving dominates the engraving industry, for electronics the indirect laser ablation combined with chemical etching or direct laser might be more suitable.

2. 5. 2. 1. Chemical Etching

Traditionally, in chemical etching, a thin layer of water-soluble photopolymer is coated onto the copper plated base cylinder. Image areas are prepared by imaging of photopolymer through black and white positive film so that image area is not exposed with UV light and thus can be easily removed by dissolving in water. While the nonimage areas are protected by exposed photopolymer, copper in the image areas is etched away with ferric chloride of very precisely controlled concentration and temperature*9. After etching, the photopolymer is removed from the cylinder and once the engraved cylinder is tested and approved, it is chrome plated and polished.

Improvements in photoresist imaging were made in 1995 by combining...
laser technology and chemical etching. In this case, a photoresist is evaporated by the laser, leaving the image areas unprotected so it can be chemically etched. This process is also known as laser ablation and it provides the highest degree of precision, accuracy and cell quality. For this process, spot size and maximum resolution is typically 10 microns and 5081 lpi.

Figure 11: Detail of an etched gravure printing cylinder (100 l/cm)

2.5.2.2. Electromechanical Engraving

Electromechanical engraving is the most common method in gravure cylinder imaging. It is based on cutting the cells into the copper-plated cylinder by using a diamond stylus. The amount of ink transferred is controlled by various sizes and depths of the cells obtained by varying the cutting angle and the amplitude of cutting stylus. The speed of the rotating cylinder will determine the screen angle of the cells.

With this method, all lines and shapes are composed of discrete cells resulting in lines and text having ragged edges typical for gravure, due to the diamond shape of the cells. In order to reduce this effect visually, quite often partial cells are added in the adjacent nested rows of cells to provide the softening of ragged edge. Still, discrete cells resulting in ragged edges and poor
contour definition are disadvantageous for electronic printing, where uniform and straight fine lines are required.2

Recently, HELL Gravure Systems introduced Xtreme™ Engraving technology. It is able to engrave at a very high resolution (up to 2000 l/cm for security applications). It is very promising new technology, retaining the advantages of electromechanical engraving, being a simple, stable and inexpensive process for high-quality reproducible cylinder engraving. In addition to the high write resolution and the possibility of engraving outlines, Xtreme™ Engraving has another advantage that contours, which run vertically or horizontally, are always engraved as closed, continuous lines. This is also beneficial for gravure printing of very fine lines for electronics manufacture. However, no work considering such application has been reported yet. The packaging sector was already tested for application of Xtreme™ technology and it is predicted that it will also succeed in security printing.

Max Daetwyler Corporation also introduced a new engraving system called transScribe™, capable of producing both fine line art and process works with one engraving head, while Xtreme™ Engraving, on the other hand, requires two heads. Both systems use a special screening technique whereby the engraving stylus is controlled only via a computer signal. Daetwyler’s transScribe™ would be more suitable for engravers looking for a versatile solution, while Hell’s Xtreme™ Engraving seems to evoke interest in niche applications.
2.5.2.3. Laser Engraving

Laser engraving of gravure cylinders was first introduced by Max Daetwyler Corporation in 1996. It is based on focusing the laser beam onto gravure cylinder surface and local vaporization of the image-carrier material. Since copper does not absorb laser energy efficiently, a zinc layer is added to copper surface and used as a layer for engraving. Thermal energy of the pulsating laser beam evaporates the zinc material and thus produces the grooves. Laser engraving allows for larger variability in cell shapes and sizes. Typically, the cells are around 35 µm or less in depth and have a round shape. A spherical section shape of cells is believed to be better at ensuring ink release. These new shapes actually provide for higher print density and it is possible to use higher viscosity inks than with traditional electromechanically engraved cylinders. That may be also due to the fact that laser engrave cells are shallower (maximum depth 35 micron) compared to electromechanically engraved cells with up to 60 micron depth. It was shown that uniformity of the printed layer (in terms of print mottle) is better with a laser engraved cylinder.
2.5.2.4. Thermal Gravure Technology – Exactus

The thermal gravure technology process is very similar to chemical etching method, except for the copper removal procedure. The thermal gravure process consists of the following steps: applying a thermal layer to a standard rotogravure copper cylinder; imaging by direct exposure; developing the resist layer; removing the copper by an electrolytic process; and stripping of the remaining resist material. Electrolytic copper removal is controlled through an electrical current. The cylinder acts as the anode and a steel (or titanium) mesh acts as the cathode. The electrolytic solution can be also recovered. Use of direct laser imaging again brings sharp and accurate images. Cylinders imaged with thermal technology exhibit better ink release, resulting in a decrease in skipping dots on paper. It is possible to implement screening without the physical limitations of the diamond stylus in the electromechanical process. Furthermore, thermally imaged cylinders distribute a uniform layer of ink on the paper, which means a reduction in the “fish eye” effect (Figure 13); better ink coverage; smoother and sharper text reproduction. This technology is also not explored to a full extent yet. Possible further applications might include engraving for printing of features for electronic devices.

Figure 13: Illustration of “fish eye” effect for electromechanically engraved cells (a) and cells produced by thermal gravure (b)

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2.5.3. Substrates for Gravure Printing

Paper smoothness is one of the most critical substrate properties for gravure printing. It promotes optimal contact between a paper surface and engraved cells for ink transfer. It also affects the ink spreading and overall quality of the printed ink layer. Printing on rougher substrates can result in numerous missing dots, and therefore low print quality. Uneven contact between the ink filled cells and the paper surface is a reason for variation of ink film thickness causing a variation in ink optical density, also known as print mottle. Topographical studies of substrates showed that missing dots in gravure printing are caused mainly by large fibers and fiber crossings, or non-uniform filler or coating distribution causing the local roughness of the substrates, resulting in skipped dots\(^8\).

Another important substrate property is compressibility, which can somewhat compensate for roughness, meaning that contact between ink and substrate is improved under pressure in the printing nip. Both, smoothness and compressibility can be measured with a Parker Print Surf instrument, which is based on air leak method (amount of air passing through annular ring)\(^8\).

Penetration of ink into the substrate is also very important. It is determined by substrate absorptivity, permeability, and porosity\(^8,8^3\). In high speed gravure printing, ink spreading and penetration happen within a fraction of a second (dwelling time can be as low as 1 millisecond). The more absorbent the substrate, the more readily ink transfers from gravure cells onto the substrate. The narrower is distribution of pores and their size, the more uniform is the printed ink film. Dwelling time is determined by printing speed and thus the higher the speed, the less ink gets transferred onto the substrate.
In addition to smoothness and penetration, other surface properties, such as wettability and ink adhesion are very important, especially with plastic substrates, where the non-porous character inhibits penetration of ink into the substrate structure. Surface chemistry of the substrates must be compatible with ink chemistry. Solvent-based inks have lower surface tension when compared to water-based inks, which usually require addition of co-solvents and surfactants to decrease surface tension and improve wettability. Paper chemistry (surface or internal sizing and coating) also has an important effect on surface properties. Internal sizing reduces the paper hydrophilicity and wettability restraining the penetration of water-based inks. Surface sizing increases the contact angle between water based ink and paper substrate, resulting in reduced ink transfer. Substrate and ink interactions are very often studied by using contact angle measurements.

2.5.4. Inks for Gravure Printing

Generally, gravure printing requires inks to be mobile, low in viscosity and fast drying. Low viscosity allows the ink to properly fill the recessed gravure cells in the cylinder and then transfer onto the substrate. The typical operating viscosity of gravure inks ranges from 50 – 200 mP.s (or cP), depending on the speed and the pressure applied during printing, as well as product application of gravure printing. Publication gravure inks are less viscous than packaging gravure inks. Among packaging inks, white inks have typically higher viscosity than colored inks.

Gravure inks can be solvent or water based. The majority of solvent based packaging inks utilize alcohol/ester mixes, except some more specialized
applications, where hydrocarbon and ketone solvents can be used more readily than in flexography, where strong solvents can cause distortion of flexo plates. A wide range of resins can be used with gravure inks and these include nitrocellulose, acrylics, polyurethanes, polyamides, etc. Water-based acrylic ink chemistry is also well established and widely used mainly in product gravure printing (such as wall coverings, floor coverings, gift-wraps, etc.). UV-curable and hot melt inks for gravure printing were also reported.

Fluid gravure inks may contain up to 65% of solvent resulting in printing of thin ink layers. This is advantageous for printing of organic semiconductors, which require high load of solvents. On the other hand, it might not be ideal for inks using conductive metal particles, where particle content can be up to 75% by mass and subsequently they may be of too high viscosity. Higher viscosity generally leads to higher ink transfer, but with such high loadings of particles, it may cause integrity problems. Additionally, low content of solvents may cause poor adhesion to the substrate.

2.5.5. Conductive Inks and Percolation Threshold

The term conductive polymer ink is used to generally characterize printing inks that are used for printing of conductive layers, such as electrodes or wires. Conductivity can be achieved by different mechanisms, such as incorporating metallic or other conductive particles into a non-conducting polymer vehicle, or by using polymers that exhibit electronics conductivity in a suitable solvent. Metal particles in conductive inks include silver, gold, copper, nickel or platinum. The benefit of silver is that it has a low resistance and a thin oxide layer. The oxide is also a good conductor, so the natural oxidation in air
does not degrade performance. Different types of carbon black are also used as a filler material in inks for printed conductors and resistors. From conductive polymers, solvent based (xylene, toluene) polyaniline inks and water based polythiophene and PEDOT:PSS inks are under study for gravure printing of conductors. Conductive polymers are very sensitive to some solvents and their electronic properties can be negatively influenced due to interaction of solvent with dopant. On the other hand, in some cases addition of co-solvent can significantly enhance conductivity.

Conductivity of bulk metals is naturally higher than that in printed layers composed of metal particles. This is due to the presence of numerous gaps between conductive particles in non-conductive media. The essential condition for a printed layer to be conductive is creation of at least one conductive path, by packing of particles so that they are in contact, allowing electrons to pass when voltage is applied. Conductivity created in such way is often explained by percolation theory that characterizes the minimum load of conductive filler (percolation threshold) needed to create a continuous pathway (Figure 14). At this point, resistivity rapidly decreases and electrons can travel without restrictions along the path. The percolation threshold differs for different shapes of particles. With more structured particles, it is more likely to create a contact with neighboring particles and form a continuous network. Perfectly spherical fillers, which arguably have the least elaborate and least structured shape, can require as much as 40% loading in order to reach the percolation threshold. Silver flake load in conductive inks can be as high as 80%, in order to achieve sufficient conductivity for particular application. Carbon black particles are more irregularly shaped and often have long branches reaching out from the
main body of the particle. These moderately structured particles can require anywhere from 5-35% loading to reach the percolation threshold. Additionally, the amount of carbon black, required to obtain desired surface resistivity, is resin dependent\(^{101}\). Finally, fillers of elongated shape randomly oriented in space (sticks like or tubes), such as carbon nanotubes or fibers, may be present in as little as a few percent by volume in order to achieve low resistance\(^{102}\). The concentration of carbon nanotubes can be as low as 0.01\(^{\circ}\)\(^{103}\). There are discrepancies between different studies of percolation threshold for carbon nanotubes, most likely caused by different orientation of nanotubes inside the composite with respect to contacts used for measurements of electrical behavior\(^{104}\).

![Illustration of percolation theory](image)

Figure 14: Illustration of percolation theory\(^{105}\)

In addition to the particle shape incorporated into the printing ink, their size is very important and it significantly influences rheological behavior of the final ink. From the point of view of particle size, it is very important to produce stable dispersions with low settling or agglomeration rate of particles. Micro particles have relatively low surface area and thus reduced agglomeration. However, settling and sedimentation of particles is higher than with smaller particles\(^{106}\). However, with nanoparticles, higher agglomeration resulting from high surface area is disadvantageous. In order to avoid agglomeration,
nanoparticles have to be stabilized. There are two mechanisms of stabilization, electrostatic (with charged functional groups – sulfonate, carboxylate) or steric (with polymers – acrylic, polystyrene, etc.)\textsuperscript{107}. The functional groups are adsorbed on the surface of particles providing the necessary barrier for preventing further attraction either by formation of electric double layers or by physical barriers.
Successful implementation of printing into electronics manufacture requires optimization of current printing processes, in order to meet new requirements, mainly the comparable functionality of printed devices to those produced by conventional methods. To achieve such a challenging task, development of functional solution processable materials is necessary, as well as evaluation of factors affecting the quality of printed features with respect to their electrical behavior. New requirements for quality of printing electronic layers differ from those for visual images and thus the full potential of individual printing processes is very often not yet known.

The main objective of this work is materials testing and their optimization for gravure printing of functional conductive traces and layers for printed electronics. Different conductive inks, their properties and printability by gravure were studied. In order to fulfill the main objective of this work, the following tasks were performed:

**Task 1:** Evaluation of rheological behavior of commercially available silver-based inks and correlation of their rheology to printability. Simulation of the printing process using oscillatory testing for prediction of printability. Printability here means all properties that can help to increase printed feature conductivity and thus functionality, such as trace fidelity, edge sharpness, and ink film thickness uniformity.

**Task 2:** Optimization of silver based conductive ink for gravure printing and evaluation of factors affecting conductivity with the main focus on printing
on paper substrates. Evaluation on how paper properties affect printed traces conductivity.

**Task 3:** Characterization and optimization of conductive polymer (PEDOT:PSS) based inks for printing of conductive layers for printed circuits. Suggestion of conductive polymer ink formulation for improved printability and performance.

**Task 4:** Investigation of factors influencing sheet resistivity of gravure printed conductive polymer layers. Comprehensive evaluation of paper properties and suggesting the most important paper properties and/or their combinations affecting electrical behavior.

**Task 5:** Designing a gravure print form consisting of different features needed for printed integrated circuits and evaluation of engraving quality. Drawing attention to the most important issues and critical concerns of engraving quality when printing functional devices.
CHAPTER 4
MATERIALS AND ANALYTICAL METHODS

4. 1. Materials and Preparation Methods

4. 1. 1. Silver Based Conductive Inks

Conductive silver based inks used in this work are commercially available and their main components are presented in the Table 3. Two solvent based, one water based and one UV-curable ink was used in this work. Solvent based inks, SB1 and SB2 are very similar in the formulation; the only difference is the evaporation of the solvent used. Evaporation rate of n-propyl acetate is 0.39 as oppose to PM-acetate (propylene glycol methyl ether acetate) with the value of 2.3 when compared to relative evaporation rate of butyl acetate (BuAc = 1.0)\textsuperscript{108}.

Table 3: Basic composition of studied silver based inks

<table>
<thead>
<tr>
<th>Ink ID</th>
<th>Conductive Component</th>
<th>Binder</th>
<th>Solvent</th>
<th>Preferred Printing Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>WB</td>
<td>Silver</td>
<td>Acrylic Resin</td>
<td>Water</td>
<td>Flexo, Gravure</td>
</tr>
<tr>
<td>UV</td>
<td>Silver</td>
<td>Urethane Acrylic</td>
<td>N/A</td>
<td>Flexo</td>
</tr>
<tr>
<td>SB1</td>
<td>Silver</td>
<td>Vinyl Resin</td>
<td>N-propyl acetate</td>
<td>Gravure</td>
</tr>
<tr>
<td>SB2</td>
<td>Silver</td>
<td>Vinyl Resin</td>
<td>PM acetate</td>
<td>Flexo, Gravure</td>
</tr>
</tbody>
</table>

4. 1. 2. Conductive Polymer Inks Based on PEDOT:PSS

Firstly, conductive polymer ink sets were prepared from Baytron\textsuperscript{°} P (H. C. Starck GmbH & Co). This solution contains 1.2 - 1.4% of PEDOT:PSS in water.
Three different types of PEDOT:PSS based inks were prepared. Ethylene glycol, ethanol and TWEEN80 (nonionic surfactant) were purchased from Sigma Aldrich. Ethylene glycol was used in the formulation of PEDOT:PSS based inks to enhance conductivity. Ethyl alcohol and TWEEN80 were used to decrease surface tension of the PEDOT:PSS dispersion. Table 4 shows the tested ink compositions and ink IDs' that will be used throughout this work.

Table 4: Composition of tested PEDOT:PSS based inks

<table>
<thead>
<tr>
<th>Ink ID</th>
<th>Ink Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>Pure PEDOT:PSS (Baytron® P)</td>
</tr>
<tr>
<td>EG-PEDOT:PSS</td>
<td>Ethylene Glycol in PEDOT:PSS (50% v/v)</td>
</tr>
<tr>
<td>EtOH-EG-PEDOT:PSS</td>
<td>Ethanol in EG-PEDOT:PSS (25% v/v)</td>
</tr>
<tr>
<td>TWEEN80-EG-PEDOT:PSS</td>
<td>Surfactant Tween80 in EG-PEDOT:PSS (0.31 wt%)</td>
</tr>
</tbody>
</table>

Secondly, Baytron® P HS was purchased from H. C. Starck GmbH & Co. This aqueous solution of PEDOT:PSS contains higher solids (2.6 - 3.2%) of conductive polymer complex. Conductive ink was formulated from BAYTRON® P HS by addition of 50% v/v of ethylene glycol and then ethanol 25% v/v.

4.1.3. Substrates

A wide variety of substrates was used in this work. Table 5 summarizes label stock paper and packaging paperboard substrates used for gravure printing with silver based inks and Table 6 presents the substrates that were employed with PEDOT:PSS based inks. Paper and paperboard substrates were used as received. PET was treated using a corona treater (SOA, Inc.) to increase the
surface energy and thus improve its wettability with ink.

Table 5: Paper (P) and board (B) substrates used with silver based inks

<table>
<thead>
<tr>
<th>Substrate ID</th>
<th>Basis Weight [g/m²]</th>
<th>Thickness [μm]</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>54.6</td>
<td>44.7</td>
<td>Labels</td>
</tr>
<tr>
<td>P2</td>
<td>72.8</td>
<td>64.5</td>
<td>Labels</td>
</tr>
<tr>
<td>P3</td>
<td>68.8</td>
<td>63.0</td>
<td>Labels</td>
</tr>
<tr>
<td>P4</td>
<td>77.8</td>
<td>73.2</td>
<td>Flexible packaging</td>
</tr>
<tr>
<td>B1</td>
<td>251</td>
<td>251</td>
<td>Flexible packaging</td>
</tr>
<tr>
<td>B2</td>
<td>396</td>
<td>499</td>
<td>Flexible packaging</td>
</tr>
<tr>
<td>B3</td>
<td>395</td>
<td>509</td>
<td>Flexible packaging</td>
</tr>
</tbody>
</table>

Table 6: Label (L) paper substrates used with PEDOT:PSS based inks

<table>
<thead>
<tr>
<th>Substrate ID</th>
<th>Basis Weight [g/m²]</th>
<th>Thickness [μm]</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>N/A</td>
<td>70</td>
<td>Flexible packaging</td>
</tr>
<tr>
<td>L1</td>
<td>73</td>
<td>70</td>
<td>Flexible packaging</td>
</tr>
<tr>
<td>L2</td>
<td>74</td>
<td>69</td>
<td>Pressure sensitive labels</td>
</tr>
<tr>
<td>L3</td>
<td>81</td>
<td>71</td>
<td>Pressure sensitive labels</td>
</tr>
</tbody>
</table>
4.1.4. Laboratory Scale Gravure Printing

A K Printing Proofer, by RK Print-Coat Instruments Limited (Figure 15), was employed in this study. Ink is transferred from an engraved plate directly onto the substrate, which is attached to the rubber covered impression roller. Doctor blade and roller adjustments were made via micrometers allowing repeatable settings. A fine micrometer control (0.01 mm) was used to adjust impression and doctoring settings. Variable printing speeds up to 40 m/min (=130 feet/min) enabled the use of press viscosity inks110.

![K Printing Proofer with gravure head attachment](image)

Figure 15: K Printing Proofer with gravure head attachment

Different types of standard plates are available for this proofer. In addition, special plates with custom design can be also used. Plates are typically engraved similarly to production cylinders. In this work, three different plates were used for printing conductive layers and various features.

A standard plate (1 + 4 Wedge) was electromechanically engraved with 45 deg compression angle cells at 150 lpi (60 lines/cm) resolution with following
densities: half area 90% tone and adjacent step wedges 100-90-80-70%. This plate was used in printing of silver-based as well as PEDOT:PSS based inks.

It was found that the standard plate (at 150 lpi) deposited insufficient ink film thickness when printing with silver-based inks and thus another plate was used. The second plate was also electromechanically engraved, however, at lower resolution (80 lpi) allowing for larger amount of ink volume to be deposited onto the substrate.

Additionally, a special plate was custom designed for printing of PEDOT:PSS based inks. The plate design was created in order to get as much information as possible about the capability of the chosen engraving method to engrave uniform cells over large areas as well as fine lines and features needed in electronics manufacture. The design of the gravure print form used in this work and its manufacture is discussed next.

4.1.5. Designing Gravure Print Form

Gravure printing tends to be a directional process when fine lines are printed. The basic layout components used in designing a gravure print form, the line and wire dimensions used and their position to print direction, are presented in Table 7. Two plate designs were created in Adobe Illustrator CS2. The spacing between lines is designed as two times the line width in all cases. Different line widths, line spacing and angles to print direction are included in the plate design, as well as testing patterns for conductivity.
Table 7: Basic design components of gravure print form

<table>
<thead>
<tr>
<th>1) Line block (30 mm long):</th>
<th>![Line block image]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line Widths: 300 to 10 µm</td>
<td></td>
</tr>
<tr>
<td>Gap Widths: 600 to 20 µm</td>
<td></td>
</tr>
<tr>
<td>Angles to print direction: 0°, 30°, 45°, 60°, 90°</td>
<td></td>
</tr>
</tbody>
</table>

| 2) S-Curve printability pattern                               | ![S-Curve image]   |
| Trace widths: 250, 200, 150, 100, 50 µm                        |                     |
| Trace spacing: 500, 400, 300, 200, 100 µm                      |                     |
| Angles to print direction: 0°, 45°, 90°                        |                     |

| 3) Conductivity testing pattern I.:                           | ![Conductivity pattern I image] |
| “d” values: 10, 20 mm                                         |                     |
| “w” values: 5, 10 mm                                          |                     |
| “l” values: 30 mm                                            |                     |
| Angle to print direction: 0°                                  |                     |

| 4) Conductivity testing pattern II.:                          | ![Conductivity pattern II image] |
| Wire Widths: 300, 150, 75, 37.5 µm                            |                     |
| Angles to print direction: 0°, 45°, 90°                       |                     |

| 5) Interdigitated electrodes design:                          | ![Interdigitated electrodes image] |
| Electrode widths: 150, 100, 50 µm                             |                     |
| Electrode spacing: 300, 200, 100 µm                           |                     |
| Angles to print direction: 0°, 90°                           |                     |

| 6) Simple antenna design:                                    | ![Simple antenna image] |
| Trace width: 150 µm                                           |                     |
| Trace spacing: 300 µm                                         |                     |
4.1.6. Preparation of Image Carrier for Gravure Printing

Custom designed gravure plates for this work were engraved by Schepers GmbH & Co. KG, Germany, using the laser imaging of the mask resist followed by chemical etching. The DIGILAS system (MAX Daetwyler Corp.) was employed for laser ablation of the mask resist. This system uses a quad-beam system. Four beams are coming from the same laser source and therefore are of equal power. The beam splitting improves the productivity of the machine since it works with 4 beams simultaneously compared to just a single beam. A Ytterbium fiber laser was used with the beam size of 10 microns\(^1\). Therefore, the minimum line width was also about 10 microns, or a little more due to the sidewall etching.

![Illustration of laser beam splitting and DIGILAS system](image)

Figure 16: Illustration of laser beam splitting (left), indirect laser system used by DIGILAS system in Shepers, Germany (right)

The engraving process was performed in the following steps:

1) Coatings with black lacquer (spray or ring coating).
2) Laser Imaging with DIGILAS (laser ablation).
3) Spray etching with appropriate etchant.
4) Removal of lacquer.
After engraving, the cylinder was chromium plated by traditional methods. In order to produce a flat plate for the K-printing proofer, non-adhesive copper plating was used, also known as Ballard shell. With such a method, the engraved and chromium plated copper can be peeled off and glued onto flat aluminum plate of required thickness. Total thickness of the plate for K-printing proofer was 1.5 mm.

4.2. Analytical Methods

4.2.1. Rheological Behavior of Conductive Inks

The rheological behavior of the silver-flake inks was studied using a TA AR 2000 Dynamic Stress Rheometer together with Rheology Advantage software. Concentric cylinder geometry was employed to measure the ink samples. This geometry is advantageous for measuring thin dispersions with limited stability and large particle sizes. In order to eliminate any possible shear history effects from loading, each sample was pre-sheared at 2000 s\(^{-1}\) for 5 seconds and then allowed to equilibrate for 5 minutes. The geometry was maintained at a constant temperature using a circulating water bath (25 °C). Steady state flow test and oscillation measurements were performed (stress sweep, frequency sweep and time sweep).

4.2.1.1 Steady State Flow

Steady state flow is a measurement of viscosity at different shear rates. The sensitivity of a sample to changing shear rates can be evaluated in terms of shear thinning, thixotropy, hysteresis, etc. During printing, an ink experiences a broad range of shear rates and the shear thinning of printing ink plays an
important role in the ink transfer process. Shear rates investigated in this work ranged from 0.001 to 2000 s\(^{-1}\) in both an increasing and decreasing mode. During this test, a shear rate is applied and viscosity measured when the material reaches steady state flow (Figure 17). After the viscosity is measured, the shear rate is again increased and the process repeated yielding a viscosity flow curve. There are several different flow models available. The best fit using the viscosity vs. shear rate curve was found with the help of Rheology Advantage Data Analysis software (version 5.3.1).

![Figure 17: Steady state flow test](image)

4.2.1.2. Oscillation Stress Sweep Test

During oscillation tests, a sample is subjected to a sinusoidal stress wave and the resultant strain of this waveform is measured. Viscoelastic parameters of tested samples are monitored as a function of increasing stress, strain or frequency. In the stress sweep test, a material’s response to increasing oscillation stress (amplitude of deformation) is measured at a constant frequency and temperature (Figure 18). Stress sweep tests are typically used to find the linear viscoelastic region (LVR), which is needed for subsequent frequency sweep tests.
4. 2. 1. 3. Oscillation Frequency Sweep Test

Frequency sweeps are used to investigate time-dependent shear behavior since the frequency is the inverse of time. Short-term behavior is simulated at higher frequencies (rapid motion) and long-term behavior at small frequencies (slow motion). During frequency sweeps, an increasing frequency (deformation rate) is applied at constant stress amplitude (Figure 19) and the response is monitored. Stress amplitude is typically chosen within the LVR.

Figure 18: Oscillation stress sweep test

4. 2. 1. 4. Oscillation Time Sweep Test

In oscillatory time sweeps, both frequency and amplitude are kept at constant value during each time interval. Such tests can be used to simulate the deformation of the ink during the printing process, such as while in the ink pan, during doctoring and transfer of the ink onto the substrate and finally leveling.
The settings used for five time sweeps performed are presented in Table 8.

Table 8: Parameter settings during oscillation time sweep tests

<table>
<thead>
<tr>
<th>Time Sweep Steps</th>
<th>Applied Stress [Pa]</th>
<th>Duration [s]</th>
<th>Simulated action during printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>5</td>
<td>60</td>
<td>in ink pan</td>
</tr>
<tr>
<td>Step 2</td>
<td>3000</td>
<td>1</td>
<td>doctoring</td>
</tr>
<tr>
<td>Step 3</td>
<td>5</td>
<td>1</td>
<td>between doctoring and transfer</td>
</tr>
<tr>
<td>Step 4</td>
<td>1800</td>
<td>1</td>
<td>ink transfer</td>
</tr>
<tr>
<td>Step 5</td>
<td>1</td>
<td>60</td>
<td>leveling</td>
</tr>
</tbody>
</table>

4.2.2. Surface Tension of Conductive Inks

There are a few different methods for surface tension measurement, such as Wilhelmy plate, Du Noüy ring, sessile drop, pendant drop, maximum bubble pressure method and others. Although the static surface tension is widely used in the printing industry to predict wetting behavior of printing inks, especially water based printing inks, it is also important to characterize interfacial surface tension under dynamic press conditions where the ink is under constant compositional change.

4.2.2.1. Static Surface Tension

Measurement of the static surface tension of conductive inks was done using the FTA200 from First Ten Angstroms. The values of ink surface tension were calculated from the pendant drop shape of the ink (Figure 20). The final results reported are an average value of at least five values of surface tension.
measured for five individual drops.

Figure 20: Illustration of pendant drop shape method (drop shown for Baytron® P)

4.2.2. Dynamic Surface Tension

A SensaDyne Tensiometer was used to measure dynamic surface tension of conductive inks based on PEDOT:PSS during addition of ethylene glycol, ethanol and surfactant. This test uses the maximum differential bubble pressure method based on creation of air bubbles in the fluid at the end of two orifices with different diameters. The differential pressure of the formed bubbles is measured and the surface tension of the liquid is directly proportional to the pressure difference. Basic principle of this method is shown in the Figure 21, where \( \Delta P \) is differential maximum bubble pressure; \( r \) is capillary tip radius; \( \rho \) is density; \( h \) is immersion height; \( g \) is gravitational constant; and \( \gamma \) is surface tension of measured liquid. Subscripts 1, 2 designate properties at capillary tubes 1 and 2.
Figure 21: Principle of maximum differential bubble pressure method

4.2.3. Substrate Testing

4.2.3.1. Contact Angle Measurements

In general, the wetting process is reflected by the contact angle, defined as the angle that a liquid makes with a solid surface\(^{117}\). The equilibrium relation of a three phase system can be described by the Young – Dupre equation\(^{118,119}\):

\[
y_h \cos \Theta = y_{sv} - y_{sl}
\]

where \(\Theta\) is the contact angle and \(\gamma\) is the surface/interfacial tension at the liquid-vapor interface (lv), solid-vapor interface (sv) and solid-liquid interface (sl).

Wetting behavior of inks on the substrates was evaluated by measuring dynamic contact angle using the FTA200. The values of contact angle were calculated using the sessile drop method\(^{120}\) (Figure 22). FTA 32 software was used for data acquisition and analysis. The results are the average values of at least ten contact angle measurement values obtained from ten individual drops.
In addition to contact angle, drop volume change was also recorded, which gives and indication of ink absorption into the paper substrate.

![Illustration of sessile drop method for contact angle measurements](image)

**Figure 22:** Illustration of sessile drop method for contact angle measurements (water drop on label paper substrate L3)

4.2.3.2. Estimation of Surface Energy

Surface energy of some selected substrates were calculated using the Owens-Wendt method\textsuperscript{121}, the most widely used method in industrial research\textsuperscript{122}. Water and methylene iodide were selected as testing liquids as they are commonly used with this method. According to their model, the surface tension is the sum of disperse and polar fractions. This extends the Fowkes model of interfacial tension calculation to the following form:

\[
\gamma_{12} = \sigma_1 + \sigma_2 - 2\sqrt{\sigma_1^D \times \sigma_2^D} + \sqrt{\sigma_1^P \times \sigma_2^P}
\]

where \(\gamma_{12}\) stands for interfacial tension between two phases 1 and 2, \(\sigma\) is the surface tension of individual components, \(D\) denotes dispersive and \(P\) polar character of interactions. The constant value (equilibrium) of contact angle was used in the estimation of the substrate surface energy.

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4.2.3.3. Parker Print Surf Testing

A Parker Print-Surf (PPS) tester is used in the paper industry to measure roughness and porosity of solid substrates under conditions similar to printing conditions. The sample is clamped between a measuring head and a specifically designed backing assembly. Properties that can be measured or calculated from PPS tester include roughness, compressibility, PPS porosity and permeability coefficient1 2 3.

Roughness was measured at two different clamping pressures (500 and 1000 kPa), which was consequently used in the calculation of compressibility of tested substrate. Compressibility is a very important property, especially in rotogravure printing, where a more compressible substrate ensures better contact with gravure cylinder1 2 4. PPS surface compressibility (K) was calculated as follows, K = R1000/R500, where K is the surface compressibility coefficient, R1000 and R500 are roughness values at clamp pressures 1000 kPa and 500kPa, respectively.

4.2.3.4. Mercury Porosimetry

Mercury porosimetry is a widely used technique for measuring the pore size distribution of paper coatings. The principle of this method is based on the fact that liquid mercury has a high surface tension (γ) and thus does not wet most of the solids (high contact angle Θ). Therefore, mercury does not penetrate pores by capillary action and penetration requires application of pressure (P), which is in inverse proportion to the pore diameter (D), according to following equation1 2 5:

\[ D = \frac{-4\gamma \cos \Theta}{P} \]

A Micromeritics AutoPore IV was used to determine the pore size
distribution of the substrates. Because all substrates were only one-side-coated, some modifications to the substrates needed to be done in order to isolate the pore distribution of the coating layer from the base sheet. This was accomplished by taping the backside of the board with a transparent backing tape.

4.2.3.5 Dynamic Liquid Penetration

An Emco Dynamic Penetration Tester DPM30 was employed to measure dynamic liquid penetration of tested paper substrates. The construction of the measuring cell is shown in the Figure 23. For the measurement, the transmitter sends ultrasound waves every 40 milliseconds through the liquid medium and the submerged paper sample to the receiver. The power of the ultrasound signal received by the receiver changes with the time based upon the wetting characteristics of tested sample. Testing liquids used in this experiment were deionized (DI) water and solvent system used in PEDOT:PSS ink formulated from BAYTRON® P HS, which contains DI water, 50% v/v of ethylene glycol and 25% v/v ethanol.

![Figure 23: Construction of the measuring cell in dynamic penetration tester Emco DPM 33](image)

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4.2.4. Image Analysis

Image analysis system by ImageXpert (KDY Inc.) was used to evaluate the quality of printed layers, lines and other features\textsuperscript{126}. The quality of gravure plate engraving was also evaluated using this method. ImageXpert system is a high precision optical measurement system comprised of a motion table for sample positioning, two calibrated cameras for image capture and ImageXpert image analysis software (IX 10.0b63). The system was calibrated using a ceramic target that has photolithographically deposited features on the fine-polished ceramic surface\textsuperscript{127}.

4.2.5. Atomic Force Microscopy

An Atomic Force Microscope (AFM) utilizes the tip at the end of a cantilever, which bends in response to the force between the tip and the sample. A laser beam is focused onto the cantilever and as the cantilever flexes, the beam is reflected onto the photodetector (Figure 24). By measuring the difference signal, changes in the bending of the cantilever can be measured. Since the Cantilever obeys Hooke's Law for small displacements, the interaction force between the tip and the sample can be found. In our case, the cantilever is stationary and the sample is mounted onto the moving platform, which is controlled by high precision positioning device made from piezo-electric ceramics.

Surface topography of PEDOT:PSS films was characterized using the AFM microscope Autoprobe CP (Thermomicroscopes, USA), with Proscan version 1.3 software operating in a tapping mode to study the morphological features at different levels of structural organization and depending on the preparation.
conditions of the samples. Typical scan sizes range from $30 \times 30 \ \mu m^2$ down to $2 \times 2 \ \mu m^2$. Root mean square (RMS) roughness was then calculated as a deviation of the surface heights from the mean surface plane expressed by following equation:

$$RMS = \sqrt{\frac{1}{n} \sum_{i} (z_i - \bar{z})^2}$$

where $z$ is the distance of the point $(i)$ from arbitrary plane.

![Figure 24: Basic principle of AFM](image)

**4.2.6. White Light Interferometry**

White Light Interferometry (WYKO RST-Plus microscope) was used to study topography of the resulting conductive ink films. White light interferometry is a non-contact method for optical surface profilometry of various surfaces. The principle of operation is based on the beam of polychromatic white light being split into two parts. One part travels to a reference mirror and the other to the surface under study. In the vertical scanning interferometry (VSI), the white-light is filtered through a neutral density filter, which preserves only short coherence lengths of the light. The

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interferometric lens scans the surface at varying heights by vertical movement through the focus and capturing frames of interference data at fixed intervals. The interference signal for each point of the sample surface is recorded, providing information about the fringe modulation, which is consequently used to calculate the surface height profile\textsuperscript{129}. It is possible to obtain the height profile of a surface in the course of one measuring procedure.

Figure 25: Principle of vertical scanning interferometry

4.2.7. Conductivity Testing

In this work, the printed layers were measured using a Keithley multimeter model 2400 in a four-probe sensing mode. Electrical conductivity of printed films was studied in planar configurations\textsuperscript{130}. Measured resistance, $R$, cross-sectional area, $A$, and length of tested film samples, $l$, can be used to calculate volume resistivity, $\rho$ (Ω-cm). The inverse of resistivity yields conductivity, $\sigma$ (S/cm). In four-probe mode, small current is applied between the outside electrodes, while the voltage drop is recorded between the middle electrodes. The property of sheet resistance ($\rho_s$) can be obtained from these
measurements, assuming that the film thickness, d, is much smaller than its lateral dimensions (length, l and width, w). Sheet resistivity can be then calculated from the equation below and the typical units are Ohms per square (Ω/sq or Ω/□):

\[ \rho_s = \frac{Rw}{l} \quad \text{or} \quad \rho = \rho_s \times d \]

4.2.8. Statistical Analysis

In this work, various statistical methods were used to evaluate the effects of printing parameters and substrates on electrical conductivity of printed conductive layers with both silver and conductive polymer based inks. Minitab 14 software was used to design an experiment and statistically evaluate and analyze results.

4.2.8.1. Pearson Correlations

Correlation coefficients are widely used to evaluate how two variables are related to each other. There are two main characteristics describing this relationship and these are direction and strength. The Pearson correlation measures the strength of the linear relationship between two variables and it can range from 1 to -1, where -1.0 is a perfect negative (inverse) correlation, 0.0 is no correlation, and 1.0 is a perfect positive correlation.

4.2.8.2. Design of Experiment and ANOVA

A full factorial design of experiment (DOE) was carried out to determine the effect of substrate (3 levels - L1, L2, L3), printing speed (3 levels - 5, 7, 10) and tone step (4 levels - 70, 80, 90, 100%) on sheet resistivity of PEDOT:PSS gravure printed layers. The total of 36 trials was performed (Table 9). Two dependent
variables were measured, average sheet resistivity and uniformity of printed layer in terms of standard deviation of sheet resistivity. Average and standard deviation were calculated from five replicates.

The overall objective is to identify the important factors and to determine how they interact and their effect on the response. The main effect and interaction plots were used to determine the most significant factors and their combinations in order to optimize the process for printing of conductive layers. The measured data were examined using ANOVA (Analysis of Variance) techniques. As the name implies, the ANOVA analyzes the variation in the response and assigns appropriate proportions of this variation to each of the factors.
Table 9: Full factorial DOE for three factors at multiple levels

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Substrate</th>
<th>Speed</th>
<th>Tone Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L2</td>
<td>7</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>L3</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>L3</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>L3</td>
<td>7</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>L1</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>L1</td>
<td>7</td>
<td>90</td>
</tr>
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<td>L3</td>
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<td>L2</td>
<td>7</td>
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<td>L2</td>
<td>7</td>
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</tr>
<tr>
<td>36</td>
<td>L3</td>
<td>7</td>
<td>90</td>
</tr>
</tbody>
</table>
CHAPTER 5
RESULTS AND DISCUSSION

5.1. Silver-Based Inks for RFID Antennae Printing

5.1.1 Rheological Behavior of Silver-Based Inks

Silver based inks for antennae printing typically consist of silver particles dispersed in an appropriate mixture of binder and solvent. The rheological behavior of inks depends on many factors and has an enormous impact on printing performance, quality of printed layers, line edge definition and resolution. Factors influencing flow characteristics include silver content, particle shape and size distribution, binder system and other additives used in ink formulation. Particles can be of different shape and size and particle size distribution. The flake shape is used the most in today’s silver inks, but the combinations with other shapers are also possible. The load of silver particles in the ink formulation is usually very high (40 - 80 wt. %) depending on intended printing application method. Table 10 summarizes the basic properties of the tested silver-based inks relevant to their rheological behavior.

Table 10: Basic composition and properties of inks for printed antennae

<table>
<thead>
<tr>
<th>Ink ID</th>
<th>Binder</th>
<th>Solids [wt. %]</th>
<th>Density [kg/l]</th>
<th>Particle Size [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>WB</td>
<td>Acrylic</td>
<td>85</td>
<td>N/A</td>
<td>&lt;3</td>
</tr>
<tr>
<td>UV</td>
<td>Urethane acrylic</td>
<td>100</td>
<td>2.7</td>
<td>&lt;7</td>
</tr>
<tr>
<td>SB1</td>
<td>Vinyl Resin</td>
<td>69</td>
<td>2.2</td>
<td>&lt;7</td>
</tr>
<tr>
<td>SB2</td>
<td>Vinyl Resin</td>
<td>64</td>
<td>2.1</td>
<td>&lt;7</td>
</tr>
</tbody>
</table>

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5.1.1.1. Rotational Tests Results

For antennae printing, it is important that the ink can be printed easily and produces uniform deposits with high edge definition, required fine but thick lines and preserves the narrow gaps where the microchip is placed. For this purpose, the ink must exhibit shear-thinning behavior, meaning viscosity reduction with increasing shear rate. However, after printing, it is desirable that ink regains its structure quickly, preventing the excessive spreading or slumping.

The flow properties of silver based inks were tested using rotational viscometry. Viscosity curves (viscosity vs. shear rate) can provide information about ink’s processing and performance and thus they are very important to monitor. Low shear rates can be related to storage conditions of material, such as sedimentation, phase separation and structure retention. High shear rates give information about performance on the press.

Viscosity curves of tested inks are shown in the Figure 26. It can be seen that all tested inks exhibit a shear thinning behavior. The UV ink initially shows a shear thinning behavior, however, the rate of shear thinning decreases in the range of 0.05 -0.15 s\(^{-1}\), where a plateau is observed, after which the shear thinning continues again. WB ink shows a shear thinning behavior instantaneously upon application of stress and the viscosity decreases gradually. Solvent based inks, SB1 and SB2, show a slower rate of shear thinning in the beginning, but it increases at higher shear rates. The only difference between SB1 and SB2 is the solvent used and solids content. The slightly lower % solids in the SB2 ink results in a lower viscosity at both the low and high shear rates.
Figure 26: Steady state viscosity curves for tested silver-based inks as measured during increasing shear rate

There are several different flow models available, but the best fit for viscosity vs. shear rate curves was found using the M. Cross model in the following form[^12]:

\[
\eta = \frac{\eta_0 - \eta_\infty}{1 + (K \gamma^m)} + \eta_\infty
\]

The Cross model combines the low shear viscosity, \( \eta_0 \), the high shear viscosity, \( \eta_\infty \) and the shear thinning part of the curve by a two parameter power law relationship. Other parameters of the model shown bellow include \( K \), known as the characteristic time of the material and \( m \), degree of shear thinning. Results from the Cross model fitting are summarized in the Table 11.
Table 11: Parameters of Cross model for the tested silver-based inks as calculated from viscosity vs. shear rate curves

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>WB</td>
<td>3050</td>
<td>0.41</td>
<td>2115</td>
<td>0.70</td>
<td>11.1</td>
</tr>
<tr>
<td>UV</td>
<td>4.97x10⁵</td>
<td>0.18</td>
<td>9.16x10⁷</td>
<td>0.58</td>
<td>40.6</td>
</tr>
<tr>
<td>SB1</td>
<td>478</td>
<td>0.50</td>
<td>244</td>
<td>0.80</td>
<td>16.4</td>
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<tr>
<td>SB2</td>
<td>266</td>
<td>0.29</td>
<td>91</td>
<td>0.82</td>
<td>16.8</td>
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</tbody>
</table>

The model fitting software calculates standard error of the fit. A reasonable fit gives a value of less than about 20. From Table 11, the highest standard error was found for the UV-curable and was best for the water-based ink. Figure 27 illustrates the model fitting results for the water-based and UV-curable inks. The high standard error for the UV-curable ink comes from the presence of the plateau causing deviations from the model fit (Figure 27b). Such behavior can be due to absence of solvent and it is solely dictated by the flow properties and interactions of silver flakes and urethane acrylic binder system and other additives used in ink formulation.

![Figure 27: Illustration of Cross model fitting, a) the best fit for WB ink and b) the worst fit (UV ink)](image-url)

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Ideal shear-thinning behavior assumes that the rate of structure breaking (disruption) in the material when stress is increasing is instantaneous and is identical to the rate of structure rebuilding when stress is removed. However, most structured fluids do not follow ideal Newtonian behavior, but instead exhibit a time dependence for structure breaking as well as structure rebuilding i.e., hysteresis\textsuperscript{134}. Such materials are known as thixotropic materials.

The thixotropy of the inks was tested using a steady state flow test by applying first an increasing, then decreasing shear rate. Figure 28 presents the thixotropic behavior of the silver-based inks. Hysteresis is most evident for the solvent based ink SB2 at low shear rates, indicating slower rebuilding of its structure.

Figure 28: Thixotropy testing of silver-based inks, a) WB, b) UV, c) SB1 and d) SB2
5.1.1.2 Oscillatory Tests Results

The viscoelastic properties studied by oscillation tests include elastic ($G'$) and viscous moduli ($G''$) and phase angle ($\delta$) or its tangent (tan$\delta$) as a function of stress and frequency. The elastic or storage modulus, $G'$, represents the amount of energy from the oscillation that can be stored within the sample structure. It reflects both the strength of each interaction and the number of interactions. The viscous modulus or loss modulus, $G''$, represents the energy lost as frictional heat between the constituents of the sample during the oscillation sweep. These two properties fully describe the dual nature of a viscoelastic material and together they give the total resistance made by the sample in oscillatory motion known as the complex modulus\textsuperscript{135}. Considering the phase angle, if the material is purely elastic, then the applied stress and measured strain waves will be in-phase and follow Hooke’s law. However, if the material is purely viscous (more fluid) then the stress and strain will be 90° out-of-phase\textsuperscript{136}. Most materials exhibit a behavior between these extremes. Tan$\delta$ is a key property in oscillatory tests for relative comparison of tested materials, as it expresses the ratio of energy dissipation (viscous modulus) and storage mechanism (elastic modulus). It is measure of material damping (such as vibration or sound damping). It does not provide information about the actual values of elastic and storage modulus only their ratio.

$$\text{Tan} \delta = \frac{G''}{G'}$$

During an oscillation stress sweep, the material is subjected to increasing stress at a fixed frequency of oscillation and the resulting strain is measured. This test is used to determine the LVR and critical stress (onset point) of nonlinear
behavior. A frequency sweep at fixed stress amplitude is typically performed below the critical stress and it generates information on the materials structure. Frequency sweeps for the tested inks were performed at stresses found in the LVR of Figure 29.

![Graph showing linear viscoelastic region (LVR) and non-linear region.]

Figure 29: Illustration of material's response to increasing oscillation stress showing the LVR and non-linear region and determination of critical stress (stress sweep test results for WB ink at 10 Hz)

Figure 30 shows the results from oscillation frequency sweep tests in terms of tanδ vs. oscillation frequency. Generally, extremely high values of tanδ indicate predominantly viscous flow and particles that are only weakly associated. Thus, sedimentation is driven by gravity for these materials. A decrease in tanδ value (increasing in elasticity) indicates the presence of strong inter-particle interactions. However, extremely low values can indicate coalescence and the formation of large aggregates, which might settle with time.
It has been reported that optimal storage stability is obtained if tanδ is between 1 and 1.5\textsuperscript{13}. It is evident from Figure 30 that the WB ink exhibit tanδ values lower than 1 for most of the tested range of frequencies indicating strongly associated particles and a domination in the elastic properties. At longer times (frequency < 0.05 Hz), the viscous modulus is larger than the elastic. Even though the tanδ values do not exceed 2 within the measured frequency range, the trend is obvious. On the other hand, both solvent based inks show tanδ < 1 only at very short times (frequency higher than 0.8 Hz for SB1 and 5.5 Hz for SB2) indicating weaker interactions among particles and thus a higher rate of sedimentation.

![Figure 30: Oscillation frequency sweep test results for tested silver-based inks](image)

Oscillatory stress sweeps were performed at two different frequencies, 1 and 10 Hz. Tanδ results for both frequencies are presented in the Figure 31. It is evident that the higher oscillation frequencies resulted in the lower starting
values of tanδ measured. This signifies that strong inter-particle interactions dominate the system until a critical stress is reached, after which the tanδ increases rather significantly.

Figure 31: Oscillation stress sweeps for silver-based inks at a) 1 Hz, b) 10 Hz
The critical stress (onset point) was calculated from the $G'$ curves (illustrated in the Figure 29) by first applying a straight line to the initial plateau and then to the main drop in elastic modulus. The cross-section of the two straight lines gives the critical stress and the value of $G'$ in the LVR. Two onset points were observed for all four tested inks at a frequency of 1Hz, however the second plateau disappears at a frequency of 10 Hz (Figure 32). The calculated onset points for each ink are summarized in Table 12.

![Figure 32: Oscillation stress sweeps for SB2 ink at different oscillation frequencies (1 and 10 Hz)](image-url)
Table 12: Critical stress and elastic modulus at critical stress as calculated from $G'$ vs. oscillation stress at different frequencies (1 and 10 Hz)

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>WB</td>
<td>2.81</td>
<td>1082</td>
<td>68.4</td>
<td>2.07</td>
<td>3.54</td>
<td>1377</td>
</tr>
<tr>
<td>UV</td>
<td>0.30</td>
<td>9500</td>
<td>49.8</td>
<td>3.70</td>
<td>0.69</td>
<td>12050</td>
</tr>
<tr>
<td>SB1</td>
<td>0.77</td>
<td>595</td>
<td>48.7</td>
<td>0.81</td>
<td>0.79</td>
<td>2022</td>
</tr>
<tr>
<td>SB2</td>
<td>1.20</td>
<td>256</td>
<td>33.1</td>
<td>0.28</td>
<td>0.84</td>
<td>2641</td>
</tr>
</tbody>
</table>

5.1.1.3. Effect of Rheology on Printed Line Dimensions

It was reported\textsuperscript{138} that rotational viscometry could be used as a first predictor of ink performance during printing. However, it cannot be used to predict the slumping behavior. Thus, oscillation times sweep tests were performed to simulate the printing conditions as the application of high stresses that take place for very short times. There are several different levels of shear stress that an ink experiences during printing, such as low stress while in the ink pan that rapidly increases during doctor blade wiping from the anilox roll or gravure cylinder. After doctoring, ink slumps to the trailing edge of the cells and levels as the cells pass the doctor blade\textsuperscript{139}. In gravure printing, the next step is the ink transfer from the cells directly onto the substrate. Finally, after printing, the ink film is subjected to a minimal stress as the ink levels and dry. The rate of recovery is dependant on the viscous forces of the printing ink. Figure 33 shows the results of individual steps used to simulate the printing process by means of phase angle vs. time at various levels of applied stress (Table 8).

It can be seen that during the initial phase of low stress the phase angle
does not change with time. During simulated doctoring and also ink transfer, significant change can be observed and all inks exhibited complete viscous flow. The biggest relative change in phase angle was observed with WB ink. Next, the stress was again lowered and the ink structure starts to rebuild. Lower \( \delta \) indicates fast structure recovery.

![Figure 33: Time sweep test results by means of phase angle changes with time at various levels of applied stress](image)

In order to evaluate the effect of ink rheology on printing characteristics, three of the tested inks were printed using flexographic printing. A Comco Commander narrow-web inline flexographic printing press, located at Western Michigan University’s Printing Pilot Plant, was used for printing. Solvent based ink SB1 was not used for flexographic printing due to high evaporation rate of the solvent and possible drying in the cells of the anilox roll or on the flexographic plate.
The aim of this work was not to print the optimal line, but rather to be able to compare different ink and influence of rheology on printing behavior, and thus the printing conditions were kept constant for all inks. The line of specified width 1 mm was printed in parallel to printing direction and the width and thickness was measured using ImageXpert and Scanning Electron Microscopy (SEM), respectively. Moreover, line raggedness was evaluated using ImageXpert and it was determined by the displacement of the black-white boundary line from the ideal boundary line. The ideal boundary line is determined by calculating the best-fit line through the boundary points. Measured results are summarized in the Table 13. The aspect ratio was calculated as the ratio of average line width and average line thickness print after drying. The lower ratio indicates thicker ink film, which is desirable for higher conductivity.

Table 13: Characteristics of flexo printed line using different silver based inks

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>UV</td>
<td>1.20 ± 0.01</td>
<td>7-8</td>
<td>0.005</td>
<td>0.16</td>
</tr>
<tr>
<td>SB2</td>
<td>1.26 ± 0.03</td>
<td>6-7</td>
<td>0.012</td>
<td>0.19</td>
</tr>
<tr>
<td>WB</td>
<td>1.23 ± 0.05</td>
<td>10-15</td>
<td>0.025</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The widest line was printed with SB2, and then WB and UV-curable ink. Figure 34 shows the optical images of printed lines. It can be seen that line printed with UV-curable ink prints has the smoothest edge and the sharpest definition. The standard deviation of line width for solvent and water based inks comes from the line raggedness, being the highest for water based ink. From the
line thickness value, it is evident that the water based ink produced the thickest ink film.

As discussed earlier, it was predicted that WB ink will produce the highest aspect ratio due to very fast structure recovery after application of high shears during ink transfer. According to Figure 33, SB2 ink is recovering better than UV-curable ink, however the aspect ratio was found to be slightly lower for UV-curable ink. Possible reasons for such behavior can be caused by differences in viscosity and viscoelastic properties of studied inks. It can be seen from Figure 31 that tanδ for solvent based ink SB2 is always higher than UV-curable ink indicating dominance of viscous over elastic properties. Moreover, the viscosity of SB2 ink is lower than that of UV-curable ink, which generally leads to more broadening and slumping after the printing.113

![Figure 34: Comparison of lines printed with different silver-based inks using flexography on paper board substrate (B2)](image-url)

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5.1.2. Silver Ink Optimization for Gravure Printing

Rotogravure printing trials for printing with silver based inks were performed using K Printing Proofer (RK Print-Coat Instruments Limited). The typical operating viscosity of gravure inks ranges from 50 – 200 mP.s. Available conductive inks have much higher viscosities (Figure 26) due to the high load of silver particles. Thus, it was necessary to add solvent to allow the ink to flow in and out of engraved cells and transfer onto the substrate. Because this proofer does not have an inking system and cylinder rotating continuously in inking pan, printing plate needs to be cleaned after each and every print. Therefore, SB2 was chosen for gravure proofing. This ink is solvent based with slower evaporation rate of the solvent and thus allowed for better cleaning of the printing plate as opposed to SB1 with faster evaporative solvent or WB ink with limited resolubility of the ink dried in the cells. UV-curable inks are rarely used in gravure printing due to very high viscosity, thus the UV ink was not considered for gravure proofing.

Doctor blade settings were kept constant for all substrates and the impression pressure was adjusted by using a fine micrometer control (0.01 mm) according to the thickness of to be printed substrate. Two different print forms
were used, both electromechanically engraved at 150 and 80 lpi (Figure 36). It was found that with 150 lpi plate it was possible to print uniform layers, however conductivity was minimal. This is due to (i) lower concentration of silver flakes caused by dilution of ink and (ii) insufficient volume of the ink deposited onto the substrate to create a continuous path. Among tested gravure plates, only plate with engraving resolution of 80 lpi transferred the required amount of ink for electrical conductivity.

![Comparison of electromechanical engraving at 150 lpi (left) and 80 lpi (right) used for gravure printing](image)

First, the ink was adjusted by stepwise addition of solvent and subsequent printing until a continuous layer of silver ink was deposited. It was found that a uniform and continuous layer of SB2 ink film was printed after addition of 10% wt/wt (solvent/initial ink) of solvent, in this case PM acetate. Figure 37 shows the effect of viscosity adjustment on ink coverage. Significant improvement of ink coverage was achieved by addition of solvent and decreasing ink solids content from initial 73% to 60%.

85
Figure 37: Comparison of gravure printed ink SB2 on paper substrate (P4) before (left) and after (right) adjustment of viscosity

Evidently, viscosity has a tremendous impact on how much ink will be transferred onto the substrate. Viscosity curves of initial and adjusted SB2 ink are shown in the Figure 38. The viscosity of adjusted ink at higher shear rate, for instance at 100 s⁻¹ is 0.52 and 0.23 Pa.s for initial and adjusted ink, respectively. The viscosity of adjusted ink is in the upper range of press ink viscosity, but further diluting of the ink could lead to lowering the conductivity of printed layers due to lower concentration of silver filler.

Figure 38: Viscosity curves of initial and adjusted SB2 ink
Another concern when diluting the ink down is dispersion stability. Therefore oscillation frequency sweeps were performed and compared with initial ink (Figure 39). The shape and slope of the $G'$ and $G''$ curves are similar for both inks, however the values of moduli are higher for the initial ink indicating higher number and higher strength of interactions than in the adjusted ink. There is a cross-over point of $G'$ and $G''$ curves at frequency 5.3 and 9.0 Hz for initial and adjusted ink, respectively. At higher frequencies, elastic behavior dominates the viscous one, which is a result of intermolecular forces within the system forming a three dimensional network of forces. In this state, more energy can be stored within the system due to reduced relative motion between particles and polymer binder at high frequencies (fast motion) and hence higher $G'$. On the other hand, below the frequency of cross-over points, viscous properties dominate over the elastic ones. The structure is showing more mobility and more energy is lost by friction and thus the sedimentation is more possible.

![Figure 39: Oscillation frequency sweeps for initial and adjusted ink SB2](image-url)

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5.1.3. Effect of Substrates on Sheet Resistivity

Substrates used in this part of the work are summarized in the Table 5. These were gravure printed using laboratory scale K-printing proofer with adjusted SB2 ink. After printing, samples were heat treated for 20 minutes at 105 °C to assure complete curing of the ink. Consequently, the resistivity was measured using the four-probe method and sheet resistance was calculated from measured resistivity and sample dimensions. Width and length of printed samples used for calculations was measured by using ImageXpert optical imaging system.

Table 14 summarizes tested substrate properties for two main groups of the paper substrates used (papers and paperboards) and Figure 40 shows the sheet resistivity of gravure printed silver ink on these substrates. It can be seen that the resistivity values somewhat group together. The two substrates (P3 and B1) have the highest resistivity and the difference between the remaining substrates is not very obvious.

Table 14: Summary of substrates properties used for gravure printing

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Emveco Roughness [μm]</th>
<th>Surface Energy [mN/m]</th>
<th>Hg Porosity [%]</th>
<th>Compressibility [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1.26</td>
<td>44.2</td>
<td>36.6</td>
<td>0.35</td>
</tr>
<tr>
<td>P2</td>
<td>0.83</td>
<td>49.3</td>
<td>40.7</td>
<td>0.31</td>
</tr>
<tr>
<td>P3</td>
<td>0.77</td>
<td>59.8</td>
<td>40.2</td>
<td>0.33</td>
</tr>
<tr>
<td>P4</td>
<td>1.33</td>
<td>41.8</td>
<td>40.3</td>
<td>0.33</td>
</tr>
<tr>
<td>B1</td>
<td>0.84</td>
<td>31.1</td>
<td>31.7</td>
<td>2.41</td>
</tr>
<tr>
<td>B2</td>
<td>0.73</td>
<td>34.5</td>
<td>43.2</td>
<td>1.15</td>
</tr>
<tr>
<td>B3</td>
<td>1.41</td>
<td>39.5</td>
<td>44.0</td>
<td>1.11</td>
</tr>
</tbody>
</table>

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In order to evaluate the correlation between substrate properties and sheet resistivity of printed silver ink layers, the Pearson correlation (PC) coefficient was calculated using Minitab 14.0. It is evident from the Table 15, that there is no strong linear correlation between any of the substrate properties. The best correlation was found for porosity, however it is also not statistically significant at $\alpha=0.05$.

Table 15: Pearson correlation coefficients for individual substrates properties and sheet resistivity

<table>
<thead>
<tr>
<th>Emveco Roughness [µm]</th>
<th>Surface Energy [mN/m]</th>
<th>Hg Porosity [%]</th>
<th>Compressibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>-0.479</td>
<td>0.087</td>
<td>-0.589</td>
</tr>
<tr>
<td>p-value</td>
<td>0.276</td>
<td>0.852</td>
<td>0.164</td>
</tr>
</tbody>
</table>

When considering boards and label stock papers separately, strong and significant correlation of Hg porosity (PC/p-value=-0.99/0.08) and compressibility (PC/p-value=0.99/0.10) to sheet resistivity was found for board substrates at $\alpha=0.1$. Among boards, the highest resistivity was found for B1, then B2 and B3.
From Hg porosity values, B1 has the lowest porosity, however the pore size distribution (Figure 41) indicates that it has a narrow distribution of pores with the maximum peak for pore diameter around 2.5 µm as opposed to B2 and B3 with wide distribution and maxima for lower pore size diameters. Thus, it is possible that more ink penetrated into the structure of B1 than into B2 or B3 causing lower conductivity of the printed film.

![Figure 41: Pore size distribution of tested substrates](image)

For label stock papers, there was no significant correlation found, the strongest being for surface energy (PC/p-value=0.79/0.21). Let's consider the highest (P3) and the lowest (P2) resistivity among paper substrates. These two substrates have similar roughness, porosity, pore size distribution and compressibility and only surface energy is different, being higher for P3. Even though, higher surface energy generally leads to better surface wetting and ink spreading, in this case it might have caused a decrease in conductivity due to
better wetting of the pores and thus increased penetration of the ink into the paper structure.

5.2. Conductive Inks Based on PEDOT:PSS

Conductive polymers have a disadvantage of lower conductivity when compared to metallic conductors. However, on the other hand, they are easier to process from solution and it was also reported that they create a better interface with organic semiconductor for hole injection\textsuperscript{141}. Among all conductive polymers, the one that has been used very widely as a conductor is probably PEDOT:PSS. This polymer was developed and patented by Bayer in 1989\textsuperscript{142} and it is maintained soluble by using the water-soluble polyelectrolyte polystyrene sulfonate (PSS) as a dopant. The water based character of the polymer is advantageous for subsequent semiconductor layers typically processed from organic solvents\textsuperscript{143}. The following sections will discuss some properties of PEDOT:PSS inks and their printability characteristics in general and specifically using gravure printing.

5.2.1. Surface Tension of PEDOT:PSS Based Inks

As already mentioned, PEDOT:PSS is commercially available as aqueous dispersions. The water-based nature of this polymer system gives rise to the issues of substrate wetting and ink spreading. Water has a high surface tension and thus water based inks are very often formulated with alcoholic co-solvents and/or surfactants in order to lower surface tension for printing. The addition of alcohols lowers the surface tension monotonically with increasing concentration, due to a preferential adsorption of the organic molecule at the liquid-air interface. Surfactants, however, quickly reduce the surface tension at very low
concentrations up to the critical micelle concentration (CMC), due to a strong adsorption of the surfactant at the liquid-air surface. At concentrations higher than the CMC, the surface tension is practically constant, because any additional amount of surfactant will form micelles in bulk.

In this part of this work, the effect of addition of ethylene glycol, ethanol and surfactant on dynamic and static surface tension of PEDOT:PSS dispersions was studied. Conductive polymer inks formulations are given in the Table 4. Firstly, ethylene glycol was added to the PEDOT:PSS dispersion. This addition caused decrease of static surface tension of PEDOT:PSS ink from 70.7±0.7 to 59.3±0.2 mN/m as measured by the pendant drop method. However, the surface tension of EG-PEDOT:PSS measured under dynamic conditions is higher than the static (equilibrium) surface tension and depends strongly on time of interface existence - surface age. For shorter surface age, the alcohol molecules have less time to migrate onto the newly created interface and thus the surface tension is higher than that measured under equilibrium conditions (Figure 42).

![Figure 42: Dynamic surface tension of EG-PEDOT:PSS ink](image-url)
Figure 43: Surface tension and bubble frequency changes during addition of ethanol (top) and TWEEN80 (bottom) to EG-PEDOT:PSS ink

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Figure 43 shows the change in dynamic surface tension and bubble frequency of EG-PEDOT:PSS ink during addition of ethanol and nonionic surfactant TWEEN80, respectively. It can be seen, that addition of alcohol into the system caused gradual decrease in surface tension within the measured range of ethanol addition. It has been reported that the surface tension decreases relatively slow or is almost constant when the ethanol content in ethanol/water mixture is exceeding 20 vol%. Therefore, and also due to low concentration of polymer, only up to 20 vol% of ethanol has been used in this work. In the case of the surfactant TWEEN80, the initial drop in surface tension is more dramatic and further addition of surfactant caused rather slow decrease in surface tension, indicating that the system is above the CMC of the tested surfactant at the measured bubble frequency. This conclusion is also confirmed by a steady bubble frequency observed.

Static surface tensions of the tested inks are shown in Table 16. The “rule of thumb” in the printing industry is to have the surface tension of ink at least 10 mN/m lower than the surface energy of the substrate to be printed on. Typical values of static surface tension for water-based inks used in gravure or flexo printing are in the range of 28 - 45 mN/m. The lowest surface tension was found for EtOH-EG-PEDOT:PSS ink. However, printing of such ink might be still problematic for some polymeric substrates with lower surface energy.

5.2.2. Dynamic Contact Angle

The dynamic contact angle was measured for all prepared inks on corona treated PET substrate. As expected, the lowest contact angle was found for the ink with the lowest surface tension (EtOH-EG-PEDOT:PSS).
Table 16: Static surface tension of tested PEDOT:PSS based inks

<table>
<thead>
<tr>
<th>Ink ID</th>
<th>Static Surface Tension [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>70.7 ± 0.9</td>
</tr>
<tr>
<td>EG-PEDOT:PSS</td>
<td>59.3 ± 0.2</td>
</tr>
<tr>
<td>EtOH-EG-PEDOT:PSS</td>
<td>37.4 ± 0.2</td>
</tr>
<tr>
<td>TWEEN80-EG-PEDOT:PSS</td>
<td>41.8 ± 0.1</td>
</tr>
</tbody>
</table>

It can be seen from Figure 44 that contact angle of pure PEDOT:PSS ink and inks containing only alcohols stabilizes after a short time (around 1.5 sec), corresponding to initial spreading of the ink drops on the substrate. In the case of the surfactant-containing system, the contact angle has not reached the stable value even after 30 seconds. Figure 45 shows the contact angle of TWEEN80-EG-PEDOT:PSS ink on PET substrate after 2, 5 and 10 minutes of observation.

Figure 44: Dynamic contact angle of tested PEDOT:PSS based inks on corona treated PET substrate

95
During printing, however, there is only a very short time available for ink to spread on the substrate before it goes into the drying station. Thus, the dynamic contact angle is more important than contact angle at equilibrium conditions. Therefore, it is reasonable to look at contact angle measurements only for short time periods (Figure 46). It can be seen, ethanol is more efficient than the surfactant (TWEEN80) at short time scale. This is valid for both static and dynamic conditions for the tested system.

Figure 46: Dynamic contact angle of PEDOT:PSS based ink at short time scale
5. 2. 3. Rheological Behavior

The flow properties of a polymer solution depend on polymer concentration, molecular weight, temperature and the applied stress. Polymer solutions of higher concentrations deviate from Newtonian behavior more than diluted solutions due to higher number of chain entanglements per unit volume.

Figure 47 shows the flow curves of four different PEDOT:PSS based inks. Initial polymer solution (PEDOT:PSS) first shows increase in viscosity with increasing shear rate. This can be due to orientation of polymer chains with applied shear and thus increasing the polymer-polymer interaction up to the point of maximum viscosity, after which it slowly shear-thins. Addition of EG to PEDOT:PSS solution lowers the concentration of the polymer, however, as already mentioned, it causes the polymer chains to expand, resulting in stronger interchain interactions. This effect results in increased viscosity at lower shear rates. Addition of surfactant caused even further viscosity increase at lower shear rates. The possible explanation for such behavior is that because the concentration of surfactant in the ink formulation was above the CMC (3 g/l), there is a possibility of formation of rod-like micelles of surfactant molecules and generation of additional entanglements within the polymer system.
5.2.4. Surface Topography

In order to avoid effect of the substrate and study only the effect of ink formulation on surface topography, conductive polymer films were first solution casted onto glass slides. It can be seen from Figure 48 that addition of alcohols into the PEDOT:PSS system significantly improves uniformity of the film surface at the millimeter scale (2.5x1.9 mm²) as measured by VSI. On the other hand, AFM scans made at micrometer scale (10x10 μm²) show smoother surface of PEDOT:PSS films. EtOH-EG-PEDOT:PSS film show the presence of some larger domains, which can be a result of conformational change of polymer chains and swelling of the PEDOT:PSS complex indicating stronger interchain interactions caused by alcohol addition\textsuperscript{37}. It was found that the RMS roughness of PEDOT:PSS film measured by VSI was reduced from 902 nm down to 67 nm by addition of ethylene glycol and ethanol. Simultaneously, the RMS roughness measured by AFM shows only 2.3 nm for PEDOT:PSS and 12.9 nm for EtOH-EG-

Figure 47: Flow curves for different PEDOT:PSS based inks
PEDOT:PSS. A similar effect on RMS roughness measured by AFM was found for addition of glycerol into the PEDOT:PSS system\textsuperscript{149}.

Topography of the PEDOT:PSS film on label stock paper substrate L2 was also measured. The EtOH-EG-PEDOT:PSS ink was printed using K-printing proofer on L2 substrate. The RMS roughness of polymer film on paper increased to 76.9 nm as oppose to 12.9 nm when casted onto the glass substrate. RMS results for all tested inks are summarized in the Table 17. Good correlation of VSI RMS roughness and conductivity was found (Figure 49).

![Figure 48: Surface topography of PEDOT:PSS and EtOH-EG-PEDOT:PSS ink film on glass substrate as studied by a), c) VSI and b), d) AFM](image)

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Table 17: RMS roughness for polymer films as measured by VSI and AFM

<table>
<thead>
<tr>
<th>Ink</th>
<th>Substrate</th>
<th>RMS (VSI) [nm]</th>
<th>RMS (AFM) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>glass</td>
<td>902</td>
<td>2.3</td>
</tr>
<tr>
<td>EG-PEDOT:PSS</td>
<td>glass</td>
<td>52.7</td>
<td>10.6</td>
</tr>
<tr>
<td>TWEEN80-EG-PEDOT:PSS</td>
<td>glass</td>
<td>51.2</td>
<td>17.8</td>
</tr>
<tr>
<td>EtOH-EG-PEDOT:PSS</td>
<td>glass</td>
<td>67.1</td>
<td>12.9</td>
</tr>
<tr>
<td>EtOH-EG-PEDOT:PSS</td>
<td>label paper (L2)</td>
<td>N/A</td>
<td>76.9</td>
</tr>
</tbody>
</table>

5.2.5. Electrical Conductivity

The electrical conductivity of the PEDOT:PSS based inks was calculated from resistance measurements on casted films. As it was previously reported, addition of ethylene glycol to PEDOT:PSS dispersion enhances conductivity of the resulting films up to 200 S/cm\textsuperscript{3}. In our case, addition of 25 vol% of ethylene glycol resulted in conductivity increase from 5.3 to 92.1 S/cm. Addition of ethanol to EG-PEDOT:PSS caused a decrease in conductivity. On the other hand, the presence of surfactant TWEEN80 in EG-PEDOT:PSS has led to slightly increased conductivity (Table 18). Figure 49 shows the relationship of measured VSI roughness and resulting conductivity of PEDOT:PSS films. Higher smoothness of polymer film leads to higher conductivity.

Table 18: Conductivity of tested PEDOT:PSS based inks

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Conductivity [S/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>5.3 ± 0.1</td>
</tr>
<tr>
<td>EG-PEDOT:PSS</td>
<td>92.1 ± 0.1</td>
</tr>
<tr>
<td>EtOH-EG-PEDOT:PSS</td>
<td>62.4 ± 0.2</td>
</tr>
<tr>
<td>TWEEN80-EG-PEDOT:PSS</td>
<td>115.6 ± 2.1</td>
</tr>
</tbody>
</table>

100

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 49: Relationship of VSI RMS roughness and conductivity of PEDOT:PSS based ink films casted on glass

The best printability among studied PEDOT:PSS based inks was found for EtOH-EG-PEDOT:PSS. Only with this ink, was it possible to deposit layers with measurable conductivity. Two label stock papers (L1 and L2) were used to print the chosen ink, using the gravure K-printing proofer. The sheet resistivity of printed layers was calculated from resistance measurements. It was found that substrate significantly influences the measured resistance. Sheet resistivity on L1 was measured to be 11.3±2.8 and on L2 it was 88.5 ± 21.8 MΩ/□. The higher resistivity of film on L2 is caused by improper wetting and not complete coverage (Figure 50). In order to achieve higher conductivity required for conductors in electronic devices, higher concentration of PEDOT:PSS was used and the effect of some substrate properties as well as printing parameters is discussed next.
5. 3. Paper Substrates for Printed Electronics

The vast majority of organic transistors has been prepared using doped silicon wafers as the substrate, basically with the purpose to demonstrate the concept of utilization of organic materials in electronics\textsuperscript{143}. However, to realize large scale and roll-to-roll production of printed electronics, flexible substrates will be required. With the technology of flexible electronics becoming closer to device prototyping and commercial production, it is clear that the choice of substrates with desirable properties is essential in order to make this technology viable. Different applications, such as displays, disposable electronics or intelligent packaging, will demand different sets of substrate properties.

Flexible substrates pose a number of challenges. Dimensional stability of the substrate is very important in order to ensure precise registration and resolution. Many types of substrates are also incompatible with some solvents used for organic materials\textsuperscript{150}. Surface smoothness and cleanliness of the flexible substrate are both essential to ensure the integrity of subsequent layers and formation of a high quality interface for better device performance.

Of the flexible plastic substrates, the most commonly used are polyesters\textsuperscript{151,152} (PET, PEN) and polyimides\textsuperscript{31}. Although paper is of big interest
for printed electronics, there are very few reports to date\textsuperscript{153,154}.

5.3.1 Factors Affecting Sheet Resistivity

In this work, the printability of PEDOT:PSS ink was tested on commercially available label stock papers (Table 6). Conductive ink was formulated from BAYTRON\textsuperscript{®} P HS by addition of 50% v/v of ethylene glycol and then ethanol 25% v/v. A full factorial DOE (Table 9) was carried out to determine the effect of substrate, printing speed, and tone step on sheet resistivity of PEDOT:PSS gravure printed layers. Consequently, ANOVA analysis was used to investigate and model the relationship between a response variable and independent variables, at multiple levels, as well as the interaction of these factors (Table 9). The printing speed is expressed in arbitrary units (AU) and represents the setting on laboratory proofer used for printing.

Table 19: Tested factors and their levels

<table>
<thead>
<tr>
<th>Independent Variable</th>
<th>Levels</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>3</td>
<td>L1, L2, L3</td>
</tr>
<tr>
<td>Speed [AU]</td>
<td>3</td>
<td>5, 7, 10</td>
</tr>
<tr>
<td>Tone Step [%]</td>
<td>4</td>
<td>70, 80, 90, 100</td>
</tr>
</tbody>
</table>

The response variable was sheet resistance and it was tested using ANOVA analysis. Substrates were printed using a K-printing proofer with testing plate engraved at 150 lpi. The most important statistic in the analysis of variance table is the p-value (P). The p-value for a term tells whether the effect for that term is significant at a chosen level of significance, in this case $\alpha = 0.05$. ANOVA analysis for sheet resistance (Table 20) shows several statistically significant factors ($P \leq 0.05$). These include substrate, speed and tone step. In addition, the interaction between substrate and speed and substrate and tone
step is also significant. The R-Sq for this analysis is 97.18%.

Table 20: ANOVA table for sheet resistance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>2</td>
<td>45.2169</td>
<td>22.6084</td>
<td>88.93</td>
<td>0.000</td>
</tr>
<tr>
<td>Speed</td>
<td>2</td>
<td>6.2185</td>
<td>3.1093</td>
<td>12.23</td>
<td>0.001</td>
</tr>
<tr>
<td>Tone Step</td>
<td>3</td>
<td>27.1423</td>
<td>9.0474</td>
<td>35.59</td>
<td>0.000</td>
</tr>
<tr>
<td>Substrate*Speed</td>
<td>4</td>
<td>9.2990</td>
<td>2.3247</td>
<td>9.14</td>
<td>0.001</td>
</tr>
<tr>
<td>Substrate*Tone Step</td>
<td>6</td>
<td>14.2495</td>
<td>2.3749</td>
<td>9.34</td>
<td>0.001</td>
</tr>
<tr>
<td>Speed*Tone Step</td>
<td>6</td>
<td>3.0387</td>
<td>0.5065</td>
<td>1.99</td>
<td>0.146</td>
</tr>
<tr>
<td>Error</td>
<td>12</td>
<td>3.0506</td>
<td>0.2542</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>35</td>
<td>108.2156</td>
<td>2.5556</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To look closer into the strength of individual significant factors, the main effects plot and interactions plot are displayed in the Figure 51. In main effects plot, a horizontal line is drawn at the grand mean and the effects are the differences between the means and the reference line. The dependence of sheet resistivity on tone step is expectable, since the lower tone step is printed from smaller engraved cells and thus it delivers less ink onto the substrate. The lowest sheet resistivity was found for L3 and it can be seen that the effect of the substrate type is rather dramatic. Increasing the printing speed resulted in lower resistivity, though further increase did not change the response considerably.

From the ANOVA analysis, interaction substrate-speed and substrate-tone step were also found to be significant. This indicates that these factors are not acting completely independently. From the interaction plot, it is evident that each of the substrates responds to the changes in speed at different extent. For instance, the best speed for L2 was 7 AU, however for L1 it was 10 AU. In addition, the sheet resistivity for 70% percent tone step was the most sensitive to changes in printing speed.
Figure 51: Main effects (top) and interaction plots (bottom) for sheet resistance
5.3.2 Effects of Paper Substrate Properties on Sheet Resistivity

By considering paper substrate type, a significant effect on sheet resistivity was observed. The lowest sheet resistivity was measured for L3, and then L1 and L2. For example, at speed 7 AU and 100% tone step, the sheet resistivity for L3 was $4.8\pm0.2 \ \text{k}\Omega/\square$. The L1 and L2 have significantly higher sheet resistivity, $459\pm92$ and $784\pm85 \ \text{k}\Omega/\square$, respectively, which means at least 100 fold increase of resistivity by using different paper substrate.

Among paper substrate properties, the two most important in gravure printing are roughness and compressibility. Table 21 presents some basic properties of the tested substrates, such as PPS roughness and compressibility calculated from roughness values taken at two different clamping pressures and permeability coefficient calculated from PPS porosity. Basis weight, thickness and bulk are also shown in the table bellow.

It can be seen that in terms of roughness, L1 and L3 are very similar and L2 has higher roughness. In terms of compressibility, all three substrates are very similar. Considering the bulk of tested papers, it can be seen that L3 is the least bulky or in other words, it is the densest since the bulk is just the inverse of density.
Table 21: Properties of tested label stock papers

<table>
<thead>
<tr>
<th>Substrate ID</th>
<th>PPS Results</th>
<th>CP [kPa]</th>
<th>AVG</th>
<th>SD</th>
<th>Compressibility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Roughness [μm]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L1</td>
<td></td>
<td>500</td>
<td>1.28</td>
<td>0.05</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>1.02</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>L2</td>
<td></td>
<td>500</td>
<td>1.47</td>
<td>0.03</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>1.20</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>L3</td>
<td></td>
<td>500</td>
<td>1.25</td>
<td>0.03</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>1.02</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Porosity [ml/min]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L1</td>
<td></td>
<td>500</td>
<td>2.54</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>L2</td>
<td></td>
<td>500</td>
<td>2.67</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>L3</td>
<td></td>
<td>500</td>
<td>2.28</td>
<td>0.15</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Basis Weight [g/m²]</th>
<th>Thickness [μm]</th>
<th>Bulk [cm³/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>73</td>
<td>70</td>
<td>0.96</td>
</tr>
<tr>
<td>L2</td>
<td>74</td>
<td>69</td>
<td>0.93</td>
</tr>
<tr>
<td>L3</td>
<td>81</td>
<td>71</td>
<td>0.88</td>
</tr>
</tbody>
</table>

The above discussed paper properties do not give a clear explanation of such strong dependence of measured sheet resistivity on substrate type. Therefore, further evaluation was needed. It is typical with water based systems that the surface energy of the substrate as well as the ink is very important for proper wetting and spreading. Surface energy of the tested substrates was measured with FTA200 and sessile drop method and Owens-Wendt approach was used to calculated surface energy from contact angles with two testing liquids, water and methylene iodine. Estimated values of surface energy are shown in the Table 22. The highest value was found for L2 and the other two substrates have comparable surface energy.
Table 22: Estimated values of surface energy for tested substrates

<table>
<thead>
<tr>
<th>Substrate ID</th>
<th>Surface Energy [mN/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>42.6</td>
</tr>
<tr>
<td>L2</td>
<td>49.7</td>
</tr>
<tr>
<td>L3</td>
<td>43.3</td>
</tr>
</tbody>
</table>

During the measurements of contact angle for estimation of surface energy, different changes in water drop volume were observed for the tested substrates. Figure 52 shows that L2 absorbs the water the most and L3 the least. This is in good correlation with PPS porosity values and might be one possible explanation of significantly higher conductivity of printed polymer film on L3 substrate.

![Figure 52](image)

Figure 52: Change in water drop volume with time for tested substrates

Another test that has been performed on used paper substrates is dynamic liquid penetration. Two testing liquids were used, DI water and solvent system containing DI water, 50% v/v of ethylene glycol and 25% v/v of ethanol. Results are shown on the Figure 53 and Figure 54.
Figure 53: Dynamic water penetration curves for tested substrates

Figure 54: Dynamic solvent penetration curves for tested substrates
It can be seen that L3 substrate exhibits the lowest penetration of both testing liquids. Dynamic penetration curves for the L1 substrate initially show a hold out and then liquid absorption. Substrate L2 shows immediate liquid penetration in both testing liquids. This test is a good indication of ink absorption into the paper surface structure and, based on the sheet resistivity measurement, it can be used as one of the testing methods for selecting of the best substrate for printing of functional inks.

Figure 55 shows the optical images of gravure printed PEDOT:PSS based ink on the tested substrates. Polymer film does not cover the substrate completely and it can be seen that printed layers exhibit a branched inhomogeneous morphology. Such morphology is typically observed due to the phenomenon known as “viscous fingering instability”\textsuperscript{155}. This occurs when a viscous fluid (in our case polymer solution) is displaced by lower viscosity fluid (air). Similar branched structures were observed with offset printed PEDOT:PSS on a plastic substrate\textsuperscript{156} and it was reported that the size of the fingers can be optimized by printing speed and amount of ink volume. In this case, morphology of printed layers is also significantly influenced by choice of substrate. Evidently, the widest fingers, or best polymer spreading occurs on L3 and the narrowest for L2 substrate, which also had the highest sheet resistivity. It can be also seen that shear forces during printing induced the fingers orientation preferably in print direction. For printing of integrated circuits, sufficient conductivity of contact electrodes as well as their surface morphology is very important for higher performance\textsuperscript{157}. Possibly, low absorptivity of the L3 substrate allows for better polymer spreading resulting in higher conductivity.
5.4. Evaluation of Gravure Print Form for Printed Electronics

The first step in evaluation of gravure printing as a manufacturing platform for electronics manufacture is to determine the capability and limits of available engraving methods. High quality engraving of basic electronic components and features is crucial in the production of functional electronic devices. The simplest feature to be considered is a line. Various lines can function as interconnects between active blocks of integrated circuits or as contact electrodes for individual transistors. Requirements for line dimensions (such as width and length) as well as line spacing (gaps) used in integrated circuits are many times very strict. In order to increase the performance of printed integrated circuits the active channels between source and drain electrodes in transistor structures should be very small. These parameters are affected by engraving method, ink and substrate properties, as well as process parameters.

Different engraving methods for preparation of gravure cylinder have been discussed (Chapter 2.5.2). Each of these methods produces different size and shape of engraved cells, which influence the ink release. Resolution,

Figure 55: Optical images of printed PEDOT:PSS ink on different substrates illustrating the viscous fingering effect (arrow on the left indicates the print direction)
determining the line width, is limited by the engraving process used. Electromechanical engraving produces lines as a row of dots. Substrate wetting and ink spreading are very important here in order to produce continuous lines. Ragged edges are very common with this type of engraving. With the direct laser system, a minimum beam size of about 40 microns is used and therefore the minimum line width is about 40 microns. Indirect laser systems use a lower energy laser source than direct laser systems. Fiber lasers are relatively new and were only available with very low power output when they came on the market and were therefore not suited for direct laser engraving where more power is needed to locally evaporate zinc layer. Today, fiber lasers are available with considerably more power output so that we will see fiber lasers used for direct laser engraving soon\textsuperscript{158}.

There are several different methods to characterize and evaluate the quality of engraving. These include optical microscopy, fluid volumetrics, replicates, confocal microscopy and white light interferometry. In addition, atomic force microscopy and scanning electron microscopy can be used in evaluation of gravure cells; however these are performed off line and are more complex\textsuperscript{159}. White light interferometry is a widespread method for optical surface profilometry and it has already shown its applicability in the printing industry, more specifically in measuring of anilox rolls for flexographic printing\textsuperscript{160}, engraved cells for gravure\textsuperscript{159} as well as screen printed lines and patterns\textsuperscript{161}.

Gravure print forms for this work were engraved by Schepers GmbH & Co. KG, Germany, using the laser imaging of the mask resist followed by chemical etching. The processes involved in the manufacture are described in Chapter 4. 1. 6. Design of the print form included larger solid areas to evaluate
the cell dimensions uniformity, various line blocks at five angles to the print direction and patterns for measuring conductivity if used for printing with conductive inks. Line blocks incorporated into the design were designed in such a way, so that the widest specified lines (300 microns) were at the edges and the narrowest lines (15 microns) are in the center. Figure 56 illustrates different positions of line blocks with regard to the print direction. The red boxes in Figure 56 demonstrate the areas that were investigated in this work.

![Figure 56: Line blocks of different line widths and at different angles to the print direction](image)

5.4.1. Engraving Quality of Large Solid Area

With white light interferometry, it was possible to obtain accurate 2D and 3D profiles of engraved forms. Typical results from vertical scanning are presented in Figure 57. In order to extract the actual dimensions of engraved cells and analyze their uniformity, X- and Y- cross-sections were made across multiple cells and rows of cells. A total of 40 individual cells was taken into account when calculating the average cell depth and diagonal width in both X- and Y- cross-
sections. The scaling of X and Y axes in cross-sections in Figure 57 is not uniform - the lower row differs, thus it does not provide a real representation of width to depth ratio. For a better illustration, a detailed image of gravure cells showing its shape in 3D perspective and in cross-section is given in Figure 58.

Figure 57: 2D contour (a) and 3D profiles (b) of solid coverage area (100% tone) gravure cells engraved at 400 l/cm and the cross-sections made in X (c) and Y (d) axes (Note different scaling of X and Y axes in cross-section profiles)
Figure 58: Detailed image of engraved cells showing the shape in 3D perspective (left) and in cross-section (right)

It was found that the average depth calculated from X- and Y-cross-section profiles for solid coverage area gravure cells engraved at resolution 400 l/cm is very uniform. The average depth of the cell extracted from X-profile and Y-profile was found to be 21.45 ± 0.31 μm (1.5%) and 21.72 ± 0.45 μm (2.1%), respectively. The diagonal dimensions for measured cells calculated from X- and Y-cross-sections are very similar, implying the square shape of engraved cells on the top surface. The diagonal length was measured to be 100.2 ± 3.6 μm (3.6%) as calculated from X - cross-section and 102.6 ± 2.4 μm (2.3%) from Y - cross-section.

When calculating dimensions using pixel data from the VSI scans, one must take into account the roughness of chromium surfaces, which can lead to variations when defining the cell dimensions\textsuperscript{159}. Moreover, the wall roughness is also a factor contributing to cell volume variations and thus the amount of ink transferred onto the substrate (Figure 59). In this work, the top surface height mean was used in calculation of cell parameters.
Surface characteristics of measured chromium layer of gravure print form are as follows: average roughness $R_a = 92 \text{ nm}$, root mean square (RMS) roughness $R_q = 115 \text{ nm}$, average maximum peak-to-valley height $R_z = 836 \text{ nm}$ and maximum peak-to-valley height $R_t = 1.2 \mu\text{m}$. In gravure printing, it is typical that chromium layer has so called cracks providing a beneficial lubrication for the doctor blade. However, there are no reports to date on the effects of cracks in chromium on printing of functional materials.

5.4.2 Quality of Engraved Lines

In gravure printing, the smoothest edges are typically produced in the print direction. Printing in the perpendicular direction often results in more pronounced "sawtooth" edges and poor line contours, when printing from electromechanically engraved print forms.

In this work, the quality of engraved grooves was evaluated in terms of line depth and top and bottom width uniformity. The effect of line orientation...
with regard to the laser imaging direction was first studied by measuring lines (specified width of 37.5 μm) imaged in parallel, perpendicular and in 45° angle to the imaging direction. Figure 60 and Figure 61 show the 2D and 3D plot of engraved lines and their cross-section.

Engraving the lines as continuous grooves might lead to increased uniformity of the printed line width and thus reduced edge roughness. However, the uniformity of width and depth along the groove is essential in order to assure consistent amount of ink being deposited onto the substrate.

![Figure 60: Contour (a) and 3D plot (b) of engraved lines used for evaluation of width and depth of the grooves](image)

Figure 60: Contour (a) and 3D plot (b) of engraved lines used for evaluation of width and depth of the grooves

![Figure 61: Cross-section of engraved lines used for evaluation of width and depth of grooves](image)

Figure 61: Cross-section of engraved lines used for evaluation of width and depth of grooves
Table 23 presents the average values for groove depth and top and bottom width of measured grooves. The values are given in the form of average, standard deviation and percent of standard deviation in brackets. It is evident that all the measured parameters are affected by the orientation of the line with respect to the laser imaging direction. The smallest depth was found for parallel orientation of the lines and the largest for 45° oriented lines. Generally, the depth of the grooves depends on the active etchant concentration, its temperature and the etching time. From the Table 23, it can be seen that with increasing groove width, the depth of etched groove is also slightly increasing. The widest lines were engraved in 45° angle and the narrowest lines were measured for lines parallel to imaging direction. Considering uniformity of measured parameters based on standard deviation of depth and width, it is obvious that depth and top surface width dimensions of the grooves have standard deviation of around 6%. However, the bottom width varies more along the grooves with standard deviation of 23 to 28%. Figure 62 shows a more detailed image of engraved grooves. Decreased uniformity in dimensions along the line might lead to variations of ink transfer. The varying amount of functional material transferred from the grooves can result in non uniform conductivity of printed traces. More extensive research is necessary in order to find how such variations affect the functionality of printed functional features.
Table 23: Calculated dimensions of engraved grooves as measured with Vertical Scanning Interferometer

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>19.35 ± 1.15 (5.9%)</td>
<td>50.69 ± 3.39 (6.7%)</td>
<td>19.07 ± 4.39 (23.0%)</td>
</tr>
<tr>
<td>90°</td>
<td>21.46 ± 1.39 (6.5%)</td>
<td>55.92 ± 3.47 (6.2%)</td>
<td>18.82 ± 5.10 (27.1%)</td>
</tr>
<tr>
<td>45°</td>
<td>22.12 ± 1.38 (6.2%)</td>
<td>59.41 ± 3.83 (6.4%)</td>
<td>19.67 ± 5.60 (28.5%)</td>
</tr>
</tbody>
</table>

Figure 62: Detailed image of engraved grooves

In order to study the widening effect of the engraving method in parallel and perpendicular orientations, specified line widths of 15, 25, 37.5, 50, 75, 100, 150, 250 and 300 μm were measured. It was found that the increase in line width is not consistent for different specified line widths and higher width gain was observed for finer lines. Figure 63 shows the relationship between width gain and specified line width in parallel and in perpendicular orientation to imaging direction. Evidently, there is a significantly higher increase in line width for lines below 100 μm and the finer the line, the more width it will gain during engraving. For example, the specified line width of 15 μm was measured to be
29.1±3.0 μm in parallel and 31.6±1.9 μm in the perpendicular direction. This corresponds to the average width gain of 94% and 111% for parallel and perpendicular direction, respectively. Width gain for parallel orientation of lines was always lower than that for perpendicular; however this difference lessened for higher line widths. Experimental results fit very well with power law function, which can help in predicting the widening effect for different specified line widths.

![Graph showing width gain results for different line widths](image)

Figure 63: Width gain results for different line widths

So far, only perpendicular and parallel orientations of lines and their effects on width gain have been shown. However, integrated circuit designs may require conductive traces at various angles to the print direction. Figure 64 shows the width gain results for engraved fine lines (below 100 μm) at different angles to imaging/print direction. It can be seen that finer lines are more sensitive to changes in orientation than coarser lines. Width gain is the highest for the 15 μm specified line at 45 degree angle to the print direction.
Figure 64: The width gain for fine line widths at different angles to imaging direction

There are several possible causes of such widening effects during the gravure print form manufacture. These may include the scattering of the laser beam during laser ablation of the mask resist and sidewall etching. In order to determine the widening effects of individual processes involved in manufacture, further study is necessary.

5.4.3. Concerns of Engraving Quality for Electronic Components

As already reported, the width of engraved lines differs from the width specified in electronic files. This consequently leads to reducing the distance (gap) between designed lines. Let us consider the interdigitated electrodes design for source and drain electrodes for printed transistor (Figure 65).
For instance, lines width was specified to be 50 μm and the distance between electrodes was set to 100 μm both parallel and perpendicular to the imaging direction. The engraved line width was measured to be 68.3±4.2 and 73.2±3.1 μm in parallel and perpendicular direction, respectively. The widening of lines affected the gaps and logically resulted in narrower gaps for the perpendicular direction (Table 24). Controversially, the reduction of gap width is more valued than widening of the lines when considering printing of contact electrodes for transistor structures, because the performance of transistor increases with decreasing of channel length (distance between source and drain electrodes) and thus decreasing the distance that the charge carriers need to travel.

Table 24: Measured values for specified line of 50 μm and gap of 100 μm

<table>
<thead>
<tr>
<th>LINE</th>
<th>Parallel</th>
<th>Perpendicular</th>
<th>GAP</th>
<th>Parallel</th>
<th>Perpendicular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width [μm]</td>
<td>68.3</td>
<td>73.2</td>
<td>Width [μm]</td>
<td>88.8</td>
<td>83.7</td>
</tr>
<tr>
<td>SD [μm]</td>
<td>4.2</td>
<td>3.1</td>
<td>SD [μm]</td>
<td>2.6</td>
<td>3.4</td>
</tr>
<tr>
<td>% of Gain</td>
<td>36.6</td>
<td>46.3</td>
<td>% of Reduction</td>
<td>11.2</td>
<td>16.3</td>
</tr>
</tbody>
</table>

Figure 65: Interdigitated electrodes design optical image and detailed 3D visualization
Similarly to the relationship between line width gain vs. specified line width, gap width reduction fit the power law function very closely. Again, the highest gap width reduction was observed for the narrower gaps. Figure 66 shows the results for gap width reduction in the parallel direction. The uniformity of the gap width is however the lowest with finer gaps. The crucial requirement in the production of electronics is to avoid circuit shortage by printing clean and uniform gaps. The variation of gap width for the narrowest gap on tested gravure print form was measured to be 14.5% (gap width = 18.5±2.7 µm). Figure 66 on the right shows the engraved grooves and the quality of the spacing between them. Such engraving would not be acceptable for printing of conductive traces due to possible failure of the final device.

![Graph showing gap width reduction](image)

\[ y = 2394.7x^{1.2061} \]
\[ R^2 = 0.9698 \]

Figure 66: Gap reduction for different gap widths (right) and illustration of undesirable engraving of very narrow gaps

5.4.4. Line Printing from Engraved Grooves

It has been reported that when the substrate comes in contact with the
fluid in the groove a strong eddy currents can be observed and as the substrate exits the groove, a recirculation region attaches to the moving substrate and follows it\textsuperscript{163} (Figure 67). Thus, when printing the lines oriented perpendicularly to print direction, it is more likely that they will be wider than the lines printed in parallel with print direction. It was also reported\textsuperscript{164} that the strength of recirculation depends on the groove orientation relative to the print direction. As the angle increases from 0° (parallel) to 90° (perpendicular), the strength of recirculation also increases.

![Figure 67: Formation of recirculation region when the moving substrate comes in contact with the groove perpendicular to the movement direction, a) recirculation region is formed, b) recirculation region follows the moving substrate and moves toward the edge of the groove\textsuperscript{163}](image)

A PEDOT:PSS based ink was printed using gravure K-printing proofer to evaluate the printing from engraved grooves. The substrate used was label stock paper L2. The printability of an ink is influenced by many properties. Rheological properties play an important role in gravure printing as they govern the flow in and out of engraved cells. Typically, lower viscosity inks flow and
print more easily, but on the other hand it can cause an ink to be dragged out from the cells and be deposited in undesired areas. Table 25 shows dimensions of a line as it changes from specified 300 μm throughout engraving process and then printing at different angles to imaging/printing direction.

Table 25: Changes in line width during engraving and printing

<table>
<thead>
<tr>
<th>Angle</th>
<th>Engraved Width [μm]</th>
<th>Printed Width [μm]</th>
<th>Width Gain [μm]/[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>AVG 333.3 ± 4.2 SD</td>
<td>AVG 434.7 ± 22.4 SD</td>
<td>101.4/30.4</td>
</tr>
<tr>
<td>45°</td>
<td>AVG 339.1 ± 2.7 SD</td>
<td>AVG 456.5 ± 17.1 SD</td>
<td>117.4/34.6</td>
</tr>
<tr>
<td>90°</td>
<td>AVG 336.5 ± 1.8 SD</td>
<td>AVG 624.1 ± 16.3 SD</td>
<td>287.6/85.5</td>
</tr>
</tbody>
</table>

During engraving the line increased in width from 33 to 39 μm, which represents around 11-13% of width gain depending on the angle to imaging direction. During printing, width gain was more significant. It can be seen around 100 μm width increase in parallel and almost double width in perpendicular direction. This supports the previously discussed effects of recirculation strength on line widening. Moreover, viscosity of used ink was lower than typical gravure inks (Figure 47 – curve for EtOH-EG-PEDOT:PSS), especially at shear rates higher than 100 s⁻¹. This might also have contributed to extensive widening of the line in the perpendicular direction.
CHAPTER 6

SUMMARY

The aim of present work was to review and evaluate available materials suitable for use in rotogravure printing of functional electronic elements and layers. The main tasks performed in this work (Chapter 3) and the most significant findings can be summarized into the following parts:

**Task 1:** Rheological behavior of commercially available silver-based ink was tested. Flow characteristic viscoelastic properties of studied inks were measured using rotational viscometry and oscillatory tests, respectively. Four different silver-based inks were evaluated, including water based ink, UV-curable ink and two solvent based inks. It was found that all tested inks exhibit shear thinning behavior as measured by steady state flow tests. The water-based ink showed a shear thinning behavior instantaneously upon application of stress and it fits chosen flow model (Cross Model) the most accurately among the tested inks. Oscillation stress sweeps showed that UV-curable ink exhibit the highest number of interactions within the system (the highest elastic modulus). However, the critical oscillation stress was the smallest among tested inks, indicating that these interactions can be disrupted easily at low stresses (0.3 Pa). This is due to the character of binder system in UV-curable inks, which consist mainly of short chain monomers or oligomers, rather than long-chain and entangled polymers and thus creating weaker structures. From oscillation frequency sweeps, it can be concluded that all of the tested inks have a tendency for sedimentation at long times, being the highest for tested solvent based inks. Oscillation time sweep test was used to simulate the printing process. Ink was
subjected to various levels of shear stress to predict ink performance while in ink pan, during doctoring and ink transfer and finally leveling after being deposited onto the substrate. It was found that the thickest ink film was deposited with water based ink, which showed the highest relative change in measured phase angle as well as fast recovery once the stress was removed.

**Task 2:** In gravure printing, ink flow characteristics play a crucial role in governing sufficient ink transfer. Solvent based silver ink was optimized for gravure printing by addition of solvent and thus reducing its viscosity. The adjusted silver ink was gravure printed on various substrates including paper boards and label stock papers and the sheet resistivity of printed ink film was tested. There was no strong correlation of sheet resistivity and tested substrate properties found when considering all substrates together. However, when considered separately in group of paperboards and label stock papers, it was found that porosity and compressibility are the most important for paperboards and surface energy for label stock papers. Even though, higher surface energy generally leads to better surface wetting and ink spreading, it might have caused increase in sheet resistivity due to better wetting of the pores and thus increased penetration of the ink into the paper structure.

**Task 3:** Conductive polymers are just one class of organic materials that can be used for active components of low-cost electronic devices. This part of work was focused on modification of PEDOT:PSS aqueous solutions by addition of alcohols (ethylene glycol and ethanol) and non-ionic surfactant. Addition of 25 vol% of ethylene glycol to PEDOT:PSS solution lowers the static surface tension by 11 mN/m. Further decrease can be achieved by addition of ethanol or surfactants. Dynamic contact angle measurements have revealed that the
surfactant-containing ink did not reach an equilibrium contact angle within the time of measurement and continued to decrease. On the other side, ethanol was more efficient under dynamic conditions, which is more important, since the ink is under contact compositional change during printing. Surface topography studies revealed that addition of alcohols into PEDOT:PSS solution helped in improving the resulting film roughness on a millimeter scale, however the opposite effect was detected at the micrometer range. Additionally, it was observed that the addition of ethylene glycol increased the conductivity of the films almost 20 times. Good correlation of RMS roughness on millimeter scale and sheet resistivity was found. Higher smoothness of the ink film resulted in lower sheet resistivity.

**Task 4:** Based on the findings from the previous task, PEDOT:PSS ink formulation was optimized and consequently gravure printed on label stock paper substrates. Effects of printing process parameters and paper properties were evaluated using statistical methods. In summary, all of the tested factors (printing speed, tone step and substrate) were found to be statistically significant and even their interaction existed and played important role in resulting sheet resistivity values. Among paper properties, it was observed that absorptivity and ink penetration had negative effect on conductivity. The higher the ink penetration into the substrate surface the lower the conductivity. Moreover, surface energy of the substrates needs to be in balance with surface tension of the conductive inks.

**Task 5:** Another area of gravure printing investigated in this study was the quality of engraved print forms. Ideally, it would be beneficial to be able to produce sub 5 μm features along with sub 5 μm gaps, which would allow the
required performance of the transistors building higher functional components. The most promising engraving technique is the indirect laser method. With this process, it is possible to engrave lines as continuous grooves as opposes to a row of individual cells as in traditional electromechanical engraving. Vertical scanning interferometry was employed to evaluate the quality of engraved print form. It was found that the width of engraved lines is higher than the line widths specified in electronic file sent to laser imager. There are several possible causes for line widening effects during the gravure print form manufacture. These may include the scattering of the laser beam during laser ablation of the mask resist and sidewall etching during the engraving step. In order to determine the widening effects of individual processes involved in manufacture, further study is necessary. The highest width gain was observed for the narrowest lines. Furthermore, the effect of line orientation with regard to print direction was studied. It was found that the finer the line, the more sensitive it is to changes of orientation. The finest line that was engraved by the studied engraving method was 29.1±3 microns in orientation parallel with the print direction. The narrowest gap on tested gravure print form was measured to be 18.5±2.7 μm. Widening of the lines was dominant in perpendicular direction. Considering printing from engraved grooves, the directionality of gravure printing is an important factor to be taken into account when depositing functional layers or fine features.
CHAPTER 7
CONCLUSIONS

Successful incorporation of printing techniques into electronics manufacture can lead to reduced cost of conventional electronics. This is mainly due to the transition from high cost clean room based IC manufacturing to ambient conditions, reduced waste and higher throughput. The applications that will be affected by lower cost of electronics include RFID tags, solar cells, displays, chemical sensors, etc. The initial goal of this work was to form a starting point to a larger picture of the printing of low cost electronics by reviewing available materials and printing processes as well as pointing out challenging issues to overcome. The specific objectives of this work have been to evaluate printable materials needed for conductive layers and features and to optimize these for deposition by gravure printing.

One of the developments in the field of printable electronics has been the ability to print antennae that are utilized in RFID tags. There is a wide variety of conductive inks available, both for interconnects or for antennae printing. Though they are typically formulated for use with screen or flexographic printing, they can be modified and optimized for gravure printing as well to increase production rate.

It was shown that rheological behavior of inks is very important in predicting printability of silver based inks. Flow properties of silver based inks depend on several factors, such as silver load, binder system, additive and solvent type. Oscillatory tests were performed in order to find a correlation between rheological behavior and ink's performance on the press. By proper
adjustments to ink formulation, it is possible to print highly conductive layers that can be used for RFID tag antennae printing.

For interconnects and contact electrodes of printed transistors, however, there are still concerns about the roughness of printed silver layers due to high particle size of silver flakes. Therefore, conductive polymers are being studied extensively for the use in printable electronics. The present work focused on properties of PEDOT:PSS based polymer inks. Applicability of the PEDOT:PSS ink to printing process was addressed with consideration of surface tension, surface roughness of the deposited films and their electrical conductivity depending on the ink formulation. Based on these results, an alcoholic co-solvent is more efficient in lowering the surface tension of water based polymer system as well as it provides improved substrate wetting under dynamic conditions. In addition, it was found that addition of ethylene glycol improves conductivity of printed ink film. Surface roughness was found to be in good correlation with measured sheet resistivity; the higher the smoothness of printed polymer films the better the electrical conductivity.

Paper substrates are of interest in printed electronics, however, they possess a number of challenges. This work focused on comprehensive study of paper properties and their effect on sheet resistivity of gravure printed PEDOT:PSS ink. There is need for better understanding of functional ink-paper interaction and novel paper substrates with optimized surface structure and chemistry for better performance of final printed electronic components. Some of the methods that correlate well with experimental results, and thus can be used to evaluate ink-paper interactions and predict printing behavior, include dynamic contact angle and dynamic liquid penetration tests.

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The last area explored in this work considers the quality of engraved print form. The most promising engraving technique is indirect laser ablation of a mask resist followed by chemical etching. This method is capable of engraving very fine grooves that can be used to print contact electrodes and interconnects in printed circuits. There are few issues remaining to be solved when considering engraving of very fine features, such as widening of the specified lines during engraving and printing and orientation of lines to imaging/printing direction.
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APPENDIX

LIST OF PUBLISHED WORK


IV. E. Hrehorova, R. Kattumenu, "Evaluation of Gravure Print Form for Printed Electronics", GravurEzine, March 2007, 10-17


VII. E. Hrehorova, V. N. Bliznyuk, A. A. Pud, V. V. Shevchenko, K. Y. Fatyeyeva, "Nonlinear Electrical Properties and Fractal Behavior of Polyurethane Elastomer/Polyaniline Composites under Mechanical Deformation," Polymer,
Accepted for publication, May 2007


Paper I considers the suitability of gravure printing in electronics manufacture. Different engraving methods are described in terms of resolution and quality. The properties influencing printability of conductive polymer inks, more specifically surface tension and substrate wetting are discussed in greater detail.

Paper II focuses on properties of PEDOT:PSS based polymer inks. Applicability of the PEDOT:PSS ink to printing process was addressed with consideration of surface tension, surface roughness of the deposited films and their electrical conductivity depending on the ink formulation. The mechanism of surface tension reduction under dynamic conditions was studied during addition of alcoholic co-solvent as well as non-ionic surfactant.

Paper III studies the interactions between commercially available materials for manufacturing of electronic components and paper substrates. Materials employed in this study include organic conductors, semiconductors and insulators. Label grade paper for gravure printing was used as the substrate.

Papers IV-VI discuss different methods used for engraving of gravure print forms. The most promising engraving process when considering printing of fine lines for circuitry is chemical etching, which nowadays uses laser ablation of the mask resist. This process is capable of engraving fine lines as continuous grooves. This work evaluates the quality of a gravure print form in terms of
uniformity of individual cell dimensions as well as parameters of fine grooves.

Paper VII reports on electrical properties of polyurethane elastomer/polyaniline (PU/PANI-HCl) composite films under tensile deformation. Two types of surface modified and one type of volume modified composite of PU and PANI-HCl were prepared. Surface modification of PU film was performed by swelling the parent film in aniline followed by its contact with the acidified oxidant solution to polymerize aniline and form PANI-HCl distributed inside surface/subsurface layer of the film. Volume modified PU was prepared by mixing of the polymer components in a joint solution and then solution casting. Nonlinear current-voltage characteristics were observed for surface modified samples while linear ones were typical of volume-modified samples. Deformation of the polymer composites caused partially reversible decrease of their conductivity characteristics, which could be described mathematically with a power law function of the strain with an exponent being dependable on the type of PU modification. Such behavior was interpreted in terms of deformation of a fractal percolation network formed in the system during its formation and chemical synthesis.

Paper VIII deals with the preparation and properties of a conductive polymer and effect of paper properties on printed conductive inks. The use of renewable natural materials to develop or improve existing materials or technologies is one of the most important ideas of research. Lignin is a complex natural polymer, which can be isolated from lignocellulosic materials. Polyaniline was prepared using template guided polymerization in the presence of different lignosulfonic acids. The resulting product is a complex of polyaniline and lignosulfonates.