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## Formulation and Evaluation of Resistive Inks for Applications in Printed Electronics

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**FORMULATION AND EVALUATION OF RESISTIVE INKS FOR  
APPLICATIONS IN PRINTED ELECTRONICS**

by

Sughosh Satish Bhole

A thesis submitted to the Graduate College  
in partial fulfillment of the requirements  
for the Degree of Master of Science  
Chemical and Paper Engineering  
Western Michigan University  
December 2013

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# **FORMULATION AND EVALUATION OF RESISTIVE INKS FOR APPLICATIONS IN PRINTED ELECTRONICS**

Sughosh Satish Bhore, M.S.

Western Michigan University, 2013

In the 21<sup>st</sup> century, it has been shown that printing methodologies can be used to print electrically functional devices on a variety of substrates. In comparison to conventional electronic manufacturing methods, printing is a more cost effective and less complex process. The requirements for manufacturing Printed Electronics (PE) components are much more demanding than graphic printing applications due to the additional requirement of easy electron flow. This additional requirement increases the need for print uniformity and layer-to-layer registration to a much higher degree.

In this work, hybrid UV-curable, water-based, electrical resistive inks were formulated. Inkjet inks were prepared by blending nano silver particles with a UV resin, while screen printable inks were blended from graphite and conductive carbon fillers. After printing, the electrical properties were tested and the results compared to a commercial silver ink, which served as the control. The average sheet resistances of the formulated screen-printed ink blends fell between  $50\Omega/\square$  to  $300\Omega/\square$ . Of all the inks printed, the screen process conductive carbon filler/graphite inks performed the best. The inkjet inks failed to be conductive due to the inability to formulate at sufficient solids for film continuity. Based on the results, these new screen process inks could find application in PE devices where the cost of silver is prohibitive and the high conductivity of silver is not needed.

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# CHAPTER I

## INTRODUCTION

Printed Electronics (PE) is a way of manufacturing electrically functional devices through the use of conventional printing processes. Researchers and companies worldwide are working in the field of PE to try to make it commercially viable. Recent progress has raised the hope that a new age of electronics is beginning in the form of PE. According to Mary Bellis *“PE opens the door to a future of electronic innovations that are lightweight, flexible, and could be produced on cheap materials such as paper or flexible film.”* (1) Table 1 compares the requirements for the traditional printing of graphic inks to the printing of functional materials.

**Table 1. Comparison of Traditional Printing and Electronics Printing. (2)**

Requirements	Traditional	Electronics
Resolution	15 - 100micron	<<20 micron
Registration	Low	High
Edge Sharpness	High	Very High
Uniformity of Layers	Not Really Important	Very Important
Adhesion of Layers to Substrate	Important	Important
Adhesion of Layers to Other layers	Less Important	Very Important
Solvents in Ink	Cost Issues	Functional Issues
Purity of Solution	Not Really Important	Very Important
Visual Properties	Very Important	Not Important
Electrical Properties	Not Important	Very Important

Flexible electronic devices can be produced by depositing single or multiple layers of functional materials, such as conductive, resistive, semi-conductive or dielectric inks, onto a flexible substrate. Today, the application of some of these materials is being performed by high cost, small capacity processes such as physical and chemical vapor deposition, sputtering and spin coating. (3) Although these methods give very controlled and smooth functional layers, they require a dust free, controlled temperature environment, which are expensive to build and maintain, and not viable for high speed production. On the other hand, printing offers a less expensive, high throughput manufacturing process of lesser quality. (3) Along with the advantages of low costs and waste, printing also offers a wider variety of flexible and rigid substrate choices. However, there are many challenges to printing functional electronic devices, such as print quality, smoothness and registration accuracy requirements well beyond what is required for graphic printing. Substrate properties (smoothness, compressibility, porosity and ink receptivity, wettability, etc.) and ink properties (ink chemistry, viscosity, rheological behavior, solvent evaporation rate, drying, etc.) are therefore critical. (4)

PE is not new, but since the early 2000s it has received a lot of attention because of interests in manufacturing low cost electronics through roll to roll additive manufacturing methods. (5) The ability to print low cost flexible electronics is especially of interest to the flexible displays, smart packaging, smart textiles and photovoltaic manufacturers. (5) PE can have many definitions, but in general it is referred to as the printing of electronic devices on flexible substrates known as Polymer Thick Films (PTF). The basic constituents of a PTF conductive ink are metallic particles, resin and solvents. Some of the original use of these materials was in shielding and, membrane touch switch (MTS)

applications. In these applications, screen printable paste silver inks (Resistivity  $\leq 15$  mohm/sq/mil) are used as the conductor. (5) In some cases when a high conductivity is not required, screen printable carbon black ink (Resistivity  $<0.010$  ohm/sq/mil) is used. (6) Printed battery test strips are produced through the screen printing of a carbon resistor and silver electrode onto the side of the battery. The resistivity of the carbon ink used for this application is typically around 70 milliohm/sq/mil. (5) Another example of PTF is RFID tags. In these applications a screen printable silver ink is used to print the antenna. (5) More recently, it has been shown that a blend of copper/silver particles could be used to inkjet print RFID tag antennae. (7) Other applications for conductive inks include thin film photovoltaic's, heaters, in-mold electronics, functional textiles etc. Thin film photovoltaic's use CIGS, a-Si, CdTe, and organic semiconductor materials overprinted with a silver ink. Heaters used in automotive side view mirrors have for decades been made with silver and positive temperature coefficient carbon coatings. (5) For in-mold electronics, a special kind of application where electronic devices are in-molded into plastic, special silver inks having a high crease resistance are used. (5) Textiles or smart clothing is another newly emerging PE field where flexible conductive materials are being used to heat garments or in sensors to sense and react to environment conditions. All such applications are currently based on printing (5)

The development of a UV curable conductive ink is beneficial for low cost flexible electronics because they do not require thermal treatment or sintering, which can cause the distortion of the base substrate. (8) However, current UV conductive inks are less conductivity in comparison to solvent and water based conductive inks; 50% less conductive. (9) This is because conductivity depends upon the # of particle/polymer

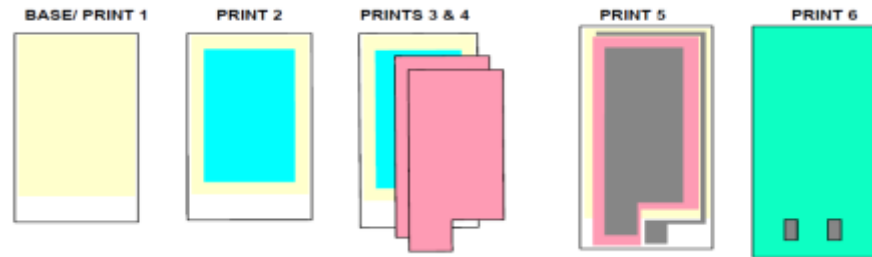
contact points in the ink film. The more particle to particle contact points, the higher the conductivity. (9) Thus, any material that prevents the contact of particles or disrupts particle alignment reduces conductivity; this is why most conductive inks are solvent based. Unfortunately, the polymers in UV inks, which polymerize during the curing process, disrupt the conductive pathways, thus lowering an ink's performance. But on the other hand, the ink films of these inks are highly resistant to solvent attack, which is desirable for overprinting. Another advantage is that these inks do not dry on press and dry immediately upon exposure to UV light, which can result in less ink spreading. Though these advantages make UV conductive inks attractive for PE applications, the most important reason for seeking the development of UV inks is that they offer the ability to print functional materials on film without concern of heat effects. (9)

For the past year, nano colloids, especially silver, have attracted many researchers because of their unique optical and conductive properties (8). This has lead to many promising applications for these inks, (10) (11) (12). As the particle size of a material changes, its interaction with light also changes. When the size of a particle becomes smaller than the wavelength of light, the electromagnetic field of the light can modulate the electrons of the atom. This changes the absorption characteristics of the material. As the absorption characteristic changes, the mobility of the atoms change, resulting in a sufficient rise in temperature when sintering the ink. (13) In addition, a decrease in particle size results in a larger specific surface area, which can result in as much as a 50 % decrease in material consumption. (8) This lowers the sintering temperature requirement for the material and makes possible the use of plastic or other flexible substrates such as paper, as alternative base materials for PE applications.



The use of conductive inks enables electronic devices such as electroluminescent, sensors, membrane switches, flexible circuits, resistance pads, printed heater circuits, additive circuits, etc., to undergo a transition from conventional manufacturing to printing manufacturing. “**Electroluminescence (EL)** is an optical phenomenon and electrical phenomenon in which a material emits light in response to the passage of an electric current or to a strong electric field.” (14) EL was invented in 1930, but was not of any commercial importance until the late 1990s because of the low performance of the raw materials used in their fabrication. (15) These days, ELs are widely used for back light applications and advertising applications such as electroluminescent billboards and signs. ELs are low power consuming devices as compared to other competing lighting technologies such as neon or fluorescent lighting. Plus ELs are flexible, bright, cool to touch, paper thin and shock proof. (15) A sequence for fabricating a printed EL lamp is as shown in Figure 1. (16) As shown, the front electrode is typically a transparent ITO layer followed by a light emitting layer composed of phosphors, a dielectric layer, a base electrode layer and a protective layer. The base electrode is usually silver, but recently silver has been replaced with less expensive carbon for smaller lamps. (16) For larger lamps, carbon is not suitable alone unless it is overprinted with a silver grid, because the resistance of carbon is too high. (16) In these applications, synthetic graphite could serve as a replacement for carbon. Graphite provides an intermediate resistivity between that of silver and carbon. Thus, its use could provide the needed cost benefit and performance by eliminating the need to overprint a silver grid onto the carbon layer. Printed ELs can be combined with membrane switches, back light key pads, instrument panels and medical instrumentation to reduce the overall costs of such products. Due to the vast application

areas for such devices, it is important to review the substrate and conductive ink technology currently being used to print these devices.



**Figure 1. EL build sequence (16)**

### **Materials Used**

According to a report by Electronics Industry Market Research and Knowledge Network, nano markets for electronics could be as high as \$12.6 billion by 2016. (17) To achieve this remarkable target, a need exists for intense research and development in this field. The most important area of development needed is in the formulation of press-ready inks. To print an active electronic device, at least four types of materials are needed; conductor, resistor, semiconductor and dielectric. (18)

### **Conductive Inks**

Metal-based conductive nano inks such as silver and gold have been available for some time, along with carbon black as a resistive ink. However, silver and gold inks are expensive in comparison to copper inks. However, a major problem in using copper is their inherent tendency to oxidize in air, and oxidized copper does not conduct. A recent solution to this problem has been the manufacture of copper-coated particles or copper oxide inks which can be converted to pure copper through their sintering with Intensive Pulse Light (IPL). Although both inks are conductive upon sintering, encapsulation is still needed for long term use. These newly formulated inks are of particular interest for

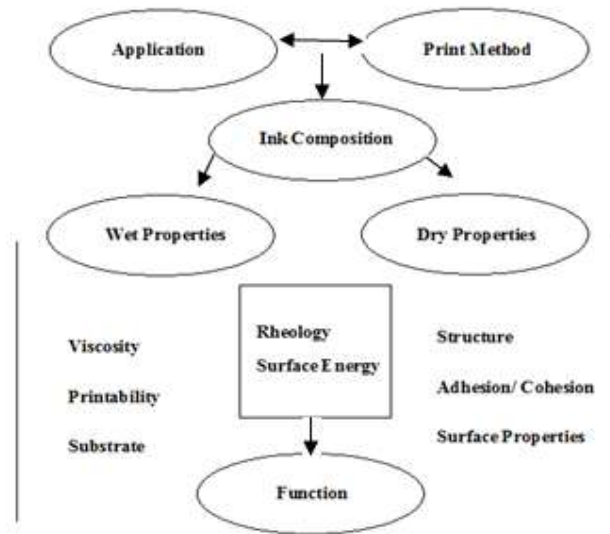
printed capacitors and sensors. Other electronic components that could benefit from these technologies included inductors and diodes. (19)

Inks are specifically designed and formulated to meet the requirements of a printing process. For a given printing process, they are selected upon the performance requirements of the application.. (20) Inks are primarily composed of a filler, binder, solvent(s) and additives. The difference between a graphic ink and conductive ink is the type of filler used. Graphic inks are made from pigments capable of providing color, where as conductive inks are made of conductive materials such as silver or copper to provide the desired electrical characteristic of conductivity. (19)

Conductive inks are manufactured by blending conductive fillers with resin, solvents and additives. In general, there are basically two types of inks; liquid and paste. Liquid inks can be either high or low in solids. Typically, inks that are low in solids contain more solvent and are of low viscosity. Paste inks on the other hand, are high in solids, contain little solvent and are very viscous. Regardless of ink type, when printed, it is important that the solvents evaporate leaving behind sufficient binder for good adhesion and sufficient particle packing to conduct electrons after drying. (19) The conductive fillers are what provide the conductive properties, while the binder provides the needed adhesion to the substrate and cohesion to each other. Thus, the conductivity of an ink depends upon the amount of filler loading, particle size of the fillers, percentage of binder used and continuity of the printed layer after printing and drying. (19)

Therefore when formulating an ink, not only is the percentage of ingredients used important, but the properties of an ink, which contribute to good print quality and performance on press, must also be considered, Figure 2. (20) The important ink

properties required for an ink to perform well are divided into two categories wet and dry properties. The wet properties of an ink affect the printability of an ink. While the dry ink properties affect the roughness, adhesion and surface energy of the printed ink film.

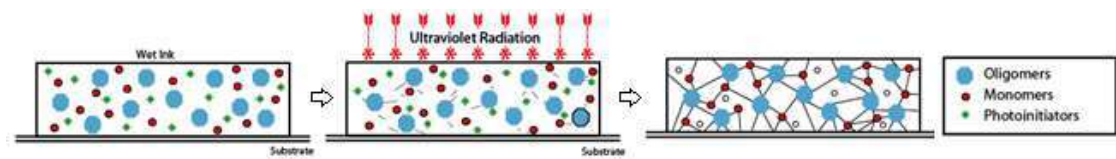


**Figure 2. Various factors governing the properties of a conductive ink. (21)**

### **UV- Curable Resin**

UV-curable inks have been used in the graphic printing and PE industries for many years. They consist mainly of a blend of oligomers, monomers, fillers, photoinitiators, photosynergist and additives. (22) Oligomers are of high molecular weight and serve the same function as a resin used in conventional inks. They are the backbone of a UV cured ink film and responsible for the flexibility, chemical resistance and elasticity of the ink film. After curing, they create a tough and durable ink film. Monomers serve as low molecular diluents. They help to reduce the viscosity and help the ink to flow. After curing, the monomers become part of the polymer matrix. (23) The photoinitiators and photosynergist components of a UV ink serve as catalysts and are usually of a free radical

nature. (23) During the curing process, after absorbing UV energy, they turn into a reactive material, which starts the polymerization reaction process. The need for the addition of additives depends upon the process and print requirements, and end use application, i.e., stabilizer, wetting agents etc. The advantages of using a UV ink over conventional ink are flexibility, solvent and chemical resistance, rapid drying, low temperature cure, no VOC emissions and stability on press. However, they also have the disadvantage of being difficult to clean, thus requiring strong solvents during cleanup. Recycling of the printed samples can also be very difficult and they are skin sensitizers so they must be handled with care. (22)

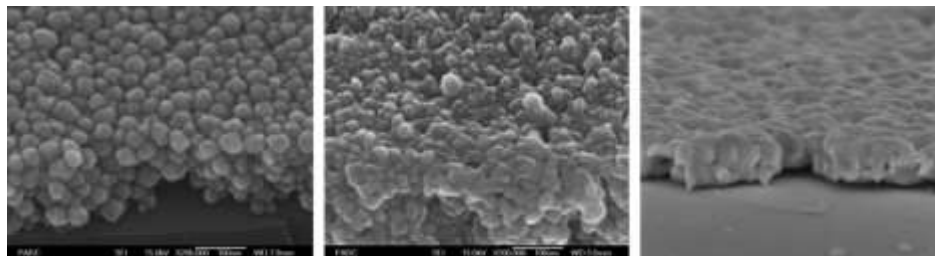


**Figure 3. UV ink reaction to UV radiation. (23)**

## Silver

According to a report by Nanomarket, the amount of silver ink that will be sold in 2013 will be \$4.9 billion. (25) Silver is the most expensive conductive material in-use, but it remains the first choice of end-users because of its high conductivity, even when oxidized (23). Gold is another good conductive metal but because of its high cost, it is less used. Silver can also be easily formulated into inks and its adhesion to substrates is better than copper and nickel. (19) (27) The conductivity of a printed silver layer depends upon the shape and size of the silver particles. Depending upon shape, there are two types of silver inks available; micro sized silver flake inks and nano silver inks. Two dimensional silver flakes are obtained by milling silver powder (27) while silver nano particles are produced by means of chemical reduction, electrochemical, laser ablation or photochemical

processes. Of all these processes just mentioned, chemical reduction is most practiced because of its simplicity in comparison to the others. The basic principle of the chemical reduction process is the reduction of silver nitrate or silver acetate in presence of a stabilizer. By controlling the synthesis and stabilizer conditions, the particle size of the silver particles can be controlled. (19) (28) After synthesizing, the nano particles are encapsulated with an organic material called a capping agent to form a uniform and stable dispersion. The dispersed nano silver particles can then be readily used to formulate an ink. To enhance the performance of the ink, the inks after printing can be heat treated or sintered at 100 to 400° C for 5 to 60 minutes, depending upon the thickness of the ink film, to improve the conductivity of the printed layer. Silver flakes are two dimensional long particles, so they are less conductive than silver nano particle inks. (19) (26) Figure 4 shows the transformation that takes place during the sintering of silver particles. (29) From left to right, the change in nano silver particle shape is shown over the course of being sintered at 150° C from 5 min. to 3 hours. In the initial stages, the encapsulated layer around the silver nano particles break, then the silver particles come together to form interconnected particles and in the final stage of the sintering process, a film is formed. The amount of temperature and time required depends upon how easy the encapsulation breaks and particle size. The smaller the particle size, the lower the temperature required to sinter the particles.



**Figure 4. Progression of silver nano particle contact during sintering. (29)**

## **Carbon**

Carbon is one of the most useful elements used in PE applications. It occurs in several allotropic forms, including diamond and graphite. There are two forms of carbon; graphite (a grey black platelet form) and carbon black (a jet-black amorphous form). (27) Some of the known applications for carbon-based inks are membrane switches, printed circuits and electrodes for sensors. The most important characteristic of carbon inks is their ability to be formulated into inks of different resistivities. Carbon inks that are commercially available are categorized based on the type of resin used, type of carbon used and resistive properties. (27) However, they may also be categorized based on their use: as a printed resistor, as a conductor or as a protective coating for other conductors. (27) Many of the commercial inks available have been formulated for use as screen and inkjet inks. The biggest advantage of carbon over silver is the inert nature of carbon. In most applications, more than one printed layer is deposited. The overprinting of layers can be problematic if the solvents or chemicals used in the inks are not compatible. Since carbon is resistant to virtually any gas or liquid, compatibility issues are of less concern in comparison to silver or other metals. (27) Electromigration is another disadvantage of silver. Electromigration is defined as the movement of metallic material, usually through or across a nonmetallic medium under the influence of an electrical field (31). Carbon does not have a tendency for electromigration. (27) This means a conductor printed with carbon is more stable over time and more chemically resistant.

## Silver-Carbon Blends

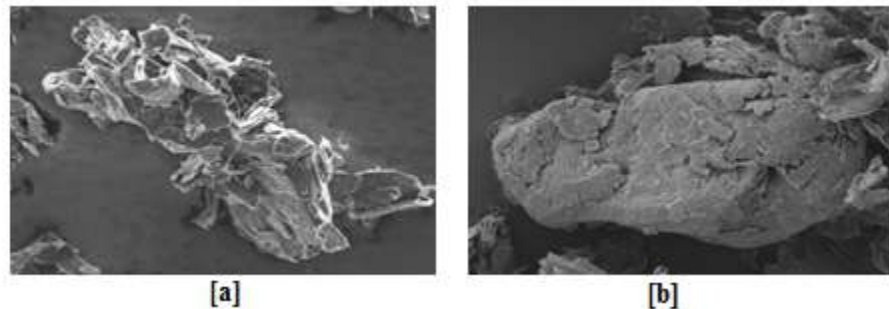
There are several premixed silver-carbon blended inks that are commercially available. The most important reason for blending silver and carbon is to obtain a desired volume resistivity for producing resistive heaters. (27) The volume resistivity for silver is  $\sim 10\text{-}50\text{ m}\Omega/\text{sq}/\text{mil}$  and  $\sim 40\text{-}80\text{ }\Omega/\text{sq}/\text{mil}$  for carbon. (27) Carbon is blended with silver to make a more resistive ink because it is very difficult to make a stable silver ink with resistivity values above  $100\text{ m}\Omega/\text{sq}/\text{mi}$ . (15) As carbon is added to silver, the resistivity of the ink increases slowly. Since the major electrical path occurs by means of silver, the increased addition of carbon results in the disruption of the silver particle, which causes the resistivity of the ink to increase sharply. The more carbon added, the more the ink behaves like carbon as the major pathway of electron transport shifts away from silver-to-silver to carbon-to-silver or carbon-to-carbon. If resistivity is plotted against the ratio of Ag:C the curve will be an extended “S” shape. Another reason to add carbon is to reduce the “switch bounce”. (27) According to literature, membrane switches experience a bounce problem that is best described as the switch bouncing back without functioning if pushed after a few hundred thousand cycles. (27) (32) By adding different percentages of carbon from 0.5% to 12.5% by weight, it has been shown that the switch bounce problem can be reduced. (27) A third reason for adding carbon to silver is to reduce costs. Silver is very expensive in comparison to carbon. As the cost of silver continues to increase with use, this advantage becomes increasingly more important. Carbon can be added to silver in ratios of 1:10 to 3:7. (27) The addition of carbon is useful for reducing costs only when high conductivity is not required. The fourth and last reason to blend carbon with silver is



to prevent or reduce “silver migration”, (27) although some research has shown the addition of carbon to be ineffective in preventing this phenomenon.

### **Graphite**

Graphite is a naturally occurring form of carbon. The word “Graphite” is derived from the Greek word “Graphein”, which means to write. (31) Many commercially available carbon inks contain some graphite and amorphous carbon. (19) (34) Graphite is obtained from the pure form of carbon or carbon containing substances. (33) Graphite is composed of a number of layers of graphene sheets where as graphene is a single sheet made of carbon atoms. (19) The conductivity for graphite is higher in the in-plane direction as compared to the perpendicular direction because the bonding forces between atoms of the same layer is greater than forces between atoms of different layers. (19) (36) Depending upon the source, graphite is classified as being either natural or synthetic, Figure 5. (33) (37) Natural graphite is subdivided into three primary types; amorphous, flake and crystalline. Synthetic graphite is subdivided into many types depending upon the properties of the carbon precursor used during the manufacturing process and the heat treatment used during processing. (33)



**Figure 5. Natural graphite (a), synthetic graphite (b). (37)**

Synthetic graphite is a man made product. Edward Goodrich Acheson first introduced it in 1800's. It is created by processing carbon at high temperature. (33) Depending upon the temperature and the properties of the carbon precursor used, different types of graphite can be formed by *Graphitizing* the carbon. (36) Graphitization is the process in which limited movement and rearrangement of carbon atoms takes place during the heat treatment process. (36) The amorphous carbon used for making graphite can be derived from petroleum, coal and natural or synthetic organic materials. (33) In some cases, graphite can also be manufactured from the direct precipitation of graphite carbon from pyrolysis of a carbonaceous gas such as acetylene (pyrolytic graphite). (33)

Advantages of graphite over other conductive materials are: Silver is an excellent conductor but is expensive and requires high temperatures to sinter. Copper is a good conductor, but it oxidizes rapidly to form an insulating layer that is non-conductive. To deoxidize copper, it must be sintered at high temperature under inert ambient conditions. Nickel and aluminum oxidize under ambient condition to form non-conductive oxides. Carbon nano tubes, CNTs, are excellent conductors, but carcinogenic and toxic in nature. Graphene and graphite are considerably cheaper than silver and copper. Graphite doesn't form an insulating oxide layer. There is no need to sinter graphite, therefore it can be printed on temperature sensitive substrates. Graphite is non-toxic and is readily dispersed in solution. It is flexible, robust, crease resistant and loses little conductivity when folded. Most importantly, graphites are compatible with all printing processes.

## **Resin**

The vehicle of an ink is composed of resins, solvents and additives. Resins can be a naturally occurring substance or man-made material produced in granular or powder form. It is used as a binder in inks. (37) There are various ways to classify a resin; by source, solubility or molecular weight. (40) If classified by source, it can be referred to as natural or synthetic. Rosins, such as cellulosic or cyclized rubber, are two examples of natural resins. Synthetic resins are prepared by the mixing of two or more polymers such as acrylic, vinyl's, polyamides, and epoxide. Classification of resin on the basis of solubility depends upon the solvent compatibility of the resin. Some resins are soluble in water, hence are so called as waterbased resins. On the other hand, some resins are soluble in solvents, such as alcohols and acetates, hence called solvent based resins. Some resins are used for the purpose of grinding the pigments on a three roll mill or in a bead mill. These are known as solution resins. Solution resins are low molecular weight resins and are very good for dispersing pigments while grinding, but are not very good film formers. Emulsion resins are high molecular weight resins, which have excellent film forming properties. (41) Depending upon the customer requirements and end use properties, two or more resins can be blended together. (40) In graphic inks, all the properties except color depend upon the properties of the resin mixture. (40) Commonly used resins are acrylics, alkyds, cellulosic derivatives, rubber resins, ketones, maleics, formaldehydes, phenolics, epoxies, fumarics, hydrocarbons, isocyanate free polyurethanes, poly vinyl butyral, polyamides and shellac. (40)



## Solvents

**Table 2. Volatile printing solvents. (40)**

Name	Structure or Composition	Boiling Point/ °C
Ethyl Acetate	$\text{CH}_3\text{COOCH}_2\text{CH}_3$	77
Isopropanol	$\text{CH}_3\text{CHOHCH}_3$	82.5
N-propyl acetate	$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$	101.6

As the name indicates, solvents are used in the ink as diluents to control the rheological properties of the ink such as viscosity, flow and leveling properties and evaporation rate. They are used to keep the ink in liquid form when applied to the printing plate or cylinder until transferred on to the surface to be printed. (40) Depending upon the drying rate, solvents are classified as fast drying (volatile) or slow drying solvents. The selection of the solvent depends upon various factors such as the printing process, press speed, absorbency of the substrate, compatibility of other raw materials used in the process, toxicity, resin solubility and end use properties. Some printing processes e.g. gravure and flexography requires very high volatile solvents because these processes run at very high speed and the inks dry mostly by evaporation. Some of the common volatile solvents are shown in Table 2. (40)

**Table 3. Examples of solvents used for screen printing. (40)**

Name	Structure or Composition	Boiling Point/ °C
Cyclohexanone		155.6
Butoxyethanol	HOCH <sub>2</sub> CH <sub>2</sub> O(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	171 - 172
Aromatic distillates	mixture of compounds chosen by boiling point	240 - 290
Butyrolactone		89

On the other hand, offset lithography requires a high boiling point solvent such as hydrocarbons, which should be viscous and hydrophobic. Screen printing requires moderately high boiling point solvents (40). Table 3 shows some common screen printing solvents. (40)

### **Additives**

Additives are minor constituents in an ink, but greatly enhance the overall performance of the ink. Different types of additives are plasticizers, wetting compounds, anti set-off compounds, waxes, shortening agents, anti-skinning agents, anti-pin holing compounds. Additives are only considered additives if they individually account for less than 0.2 to 1.0 part of the ink formulation. Additives, when used correctly, can greatly benefit the runnability and functionality of an ink. Plasticizers are used to make the ink softer and improve its flexibility, adhesion and to some extent gloss. Waxes are used to improve the rub resistance of an ink. Wetting agents are used to decrease the surface tension of the vehicle and increase the wettability of pigments. Dispersing agents are beneficial for dispersing the pigment in the vehicle to avoid agglomeration. Additives can vary

depending upon the process; shorting compounds are used in paste inks for lithography and screen printing to minimize print defects such as misting of the ink. Defoamers are used in aqueous liquid inks to reduce foam. Driers are a special kind of additive used in web-offset inks to increase their drying speed. Some commonly used drying agents are manganese and cobalt.

### **Substrates for Printed Electronics**

Another key component in any PE device is the substrate used. For the substrate, the physical properties such as roughness, porosity, and surface energy greatly influence the results, See Table 4. (Sagar, Mater's Thesis 2011)

**Table 4. Comparison between paper and PET polymeric film properties. (2)**

<b>Property</b>	<b>Paper</b>	<b>Polymer film</b>
<b>Stiffness</b>	High	Low
<b>Shrinkage</b>	Low	High
<b>Surface Modification</b>	Possible	Possible
<b>Absorbency</b>	Very high	Low
<b>Biodegradable</b>	Yes	No
<b>Chemical Stability</b>	Low	High
<b>Mechanical strength</b>	Low	High
<b>Surface smoothness</b>	Low	Very high

For most PE applications, a smooth, low porosity and high surface energy (within 10 dynes/cm of the ink) substrate is preferred. Different substrates such as paper and polymer films (Polyester, Polyethylene and Polyimide) can be used (19).

For graphic printing applications, paper is widely used for the manufacture of labels, cartons and rigid packages (19); whereas polymers films are used in the manufacture of labels and packages where high barrier properties are important. Therefore, attempts to explore these two substrates for use in printed electronics are being made (2) (23). High purity, polymer films meet almost all the requirements for electronic printing but have the disadvantage of poor thermal stability and often require some surface modifications such as plasma or corona treatment to improve their ink wetting and adhesion properties. Even though many types of PET films are available, for printed electronics applications, typically heat stabilized and planarized PET substrates are used. Paper on the other hand is thermally stable and recyclable. It is comparatively less expensive than PET and the surface and wetting properties can be modified by the application of coatings (2). Even though both substrates have some drawbacks, they are being extensively researched for use in printed electronics.

## Printing Processes

**Table 5. Specification of different printing processes. (2)**

	Printing Processes				
Property	Lithography	Flexography	Gravure	Screen	Inkjet
Image Carrier	Flat Plate	Relief	Engraved	Stencil	Digital
Substrate	Paper, Board, Polymer	Paper, Board, Polymer	Paper, Board, Polymer	Any Kind	Any Kind
Lateral Resolution ( $\mu\text{m}$ )	15	40	15	100	50
Ink Film Thickness ( $\mu\text{m}$ )	1 to 2	6 to 8	8 to 12	0.02 to 100	1 to 10
Ink viscosity (Pa's)	30-100	0.05-0.5	0.05-0.2	0.5-50	0.001-0.04
Pigment Particle ( $\mu\text{m}$ )	0.2-0.7	0.1-0.5	0.1-0.5	0.8-2.5	0.05-0.5
Material Volume	High	High	High	Medium	Low
Shear Rate ( $\text{sec}^{-1}$ )	Medium-High	Medium-High	High	Low	N/A
Web Speed (m/min)	500	300-1000	1500-3000	300-500	N/A

For the past decade, printed electronic researchers have been trying to find efficient ways to print all the parts of an electronic device and achieve high yield at lowest possible cost.

(2) Depending upon the working principle, printing processes are classified into two types:

- Impact Printing
- Non-Impact Printing



As the name indicates, in impact printing the image carrier comes into direct contact with the substrate to transfer the image onto the substrate under pressure. Impact printing includes offset, gravure, screen and flexography. Non-impact transfers the image onto the substrate without impact or pressure such as inkjet and laser printing processes. Every printing process has its own working principle to transfer ink onto a substrate. Both of these processes have their own specification, advantages and disadvantages. A general summary of the specifications for each of the different printing processes is shown in Table 5. (42) (2)

In this study, only the inkjet and screen-printing processes were used. Thus, only these two processes are described below.

## **Inkjet Printing**

According to Pira International *“Inkjet Printing Market to see Double – Digit Growth”*.

Every year the inkjet printing market grows; by Printing Impression *“The total inkjet print market in 2009 was \$26.8 billion 58.2% higher than in 200, it continuing growth, averaging 10.3% from 2010-15 when it predicts the market will be worth \$46.5 billion”*.

Inkjet is a non-impact printing process, which has been commercially used for decades.

Traditionally, inkjet printers are used for shorter runs in the office, home, and sometimes commercially as well. However today, printers are changing over longer run jobs from conventional printing processes such as gravure, offset, etc., to inkjet printing due to advancements in technology such as speed and flexibility with substrates. In inkjet printing, ink drops are created by using ink from a reservoir to directly print onto a substrate through a printhead. There are a variety of inkjet printing techniques, but Drop on Demand (DOD) is most commonly used. (44)

In DOD inkjet printing, droplets are created using a pressure developed after an electronic signal has been sent to a printhead. Formed droplets are jetted from a small orifice of the head directly on to the substrate. (45) Depending upon the working principle, there are two types of inkjet printers commonly used. One is thermal and the other is piezoelectric. (46) Thermal is a simple form of inkjet printing. The printhead of a thermal inkjet printer consists of several nozzles. Moreover, each nozzle is made of a heater to heat the ink, a chamber to hold the ink, and an orifice through which the ink is jetted. The heater consists of many tiny resistors, through which an electric current is applied, resulting in an increase in temperature inside the chamber. The instantaneous increase in temperature forms a vapor bubble. This bubble forces the ink to be jetted from

the orifice. Next, a vacuum is created causing the ink to flow from the ink reservoir into the chamber to restart the process. This entire process takes place in less than 10 microseconds. (46)

Piezoelectric is another form of inkjet printing. Like thermal, piezoelectric also contains many individual nozzles. Each nozzle has an orifice and piezoceramic material located at the back of reservoir. (46) For safety, a diaphragm is placed between the piezoceramic and printhead. When an electric charge is applied, the flexible piezoceramic material and diaphragm bends inward, forcing the ink to be ejected from the nozzle onto the substrate. After the electric charge is removed, the piezoceramic material bends outward, drawing ink back into the chamber from the reservoir and the process is restarted

### Screen Printing

Screen-Printing (SP) is one of the oldest printing processes known to man. It primarily consists of a screen and squeegee as shown in Figure 6. SP transfers an image by allowing ink to pass through the openings of a stencil that has been applied to a screen mesh. SP has two characteristics that make it distinctive from other forms of printing; versatility and variable ink film thickness (VIFT).

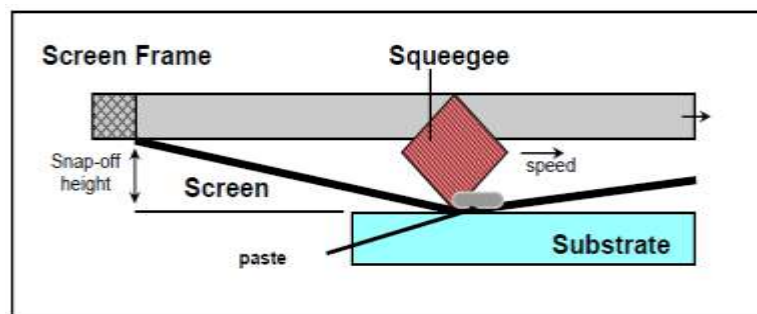


Figure 6. Schematic illustration of screen printing process.(46)

Versatility means that SP can be adapted to print on almost any kind of substrate. By using SP, variable ink film thicknesses, IFT, can be achieved by changing the print parameters of speed, pressure and snap-off. The achievable IFT can be varied from 15  $\mu\text{m}$  to 130  $\mu\text{m}$ . Some other advantages of SP are its cost effectiveness over the other printing processes. (48) SP is a robust, simple and easily automated process. It also produces little waste with little environmental impact. (48) Figure 6 shows a schematic of the screen-printing process. Initially, the ink is spread on the screen by a flood bar or by using a squeegee, which moves from one end to the other with very little pressure applied. During printing, the squeegee moves back across the screen under appropriate pressure to help the ink pass through the open image area of the screen. Inks used for screen-printing are shear thinning, meaning they decrease in viscosity under stress. The squeegee action applies the needed stress to the ink to enable the paste to pass through the patterned area of the screen onto the substrate. As the squeegee stops, the stress is removed and the ink viscosity recovers. After printing, the screen is peeled-off from the substrate. Print defects can be caused by the poor leveling of the ink. Factors affecting peel-off are viscosity, area of print, tension of the screen, squeegee speed, squeegee pressure and snap-off (distance between sample and the substrate). (48) After printing, if the snap-off is too low, the printed sample can't be released from the screen smoothly or it sometimes sticks. If the snap-off is too high, more pressure will be required to transfer the ink: this would decrease the screen tension over time, hence reducing the lifetime of the screen. (48) The squeegee used for screen-printing is usually made of rubber (Polyurethane). It has a square cross section and is mounted at a specific angle, commonly 45 °, as shown in Figure 6. A squeegee that is too soft results in high spreading,

while a squeegee that is too hard results in uneven transfer of ink. (48) The squeegee speed also plays an important role in determining the amount of ink deposited on a substrate. If the speed is too high, the ink has very little time to fill up the opening in the screens. This results in less print weight, which can result in discontinuous printed lines. Low speed results in unnecessary transfer of excess ink. The speed used highly depends on ink viscosity. (48) A low squeegee pressure can result in inconsistent ink transfer, which might cause the ink to dry-in and clog the screen. This is why the optimum squeegee pressure must be set to obtain acceptable prints. (48)

The screen can be made of various materials such as, stainless steel wire, polyester or other types of polymeric materials. They are kept at high tension on a frame. The screen frame is usually made of steel or aluminum. The desired printing image is created on the interwoven mesh by using various techniques, which makes a permeable image area and impermeable non-image area. There are three ways to create an image on a screen; Hand cut, Tusche & Glue and photographic. For the hand cut method, a stencil is prepared by removing the printed image by hand from the base. In the Tusche & Glue method, the image is created using an oil based pigment (Tusche) by drawing it directly onto the screen mesh. Afterwards the non-image area is blocked with a waterbased glue. Photographic stenciling is the latest screen exposing technology in which a thick, light sensitive, gelatin based emulsion is exposed and developed on a supporting film or on the screen itself by using a positive or negative. The photographic stencil process is the most widely used technology for commercial screen making.

## **CHAPTER II**

### **PROBLEM STATEMENT**

The typical conductive inks available in the market place for PE applications are formulated using expensive metallic particles. Although there are some other less expensive conductive materials available such as carbon and graphite, these materials are not as efficient conductors as silver or copper. Thus, in some applications where a high performance conductive ink is not required, a carbon or a mixture of carbon and silver could be sufficient for use. UV curing is a non-thermal, fast drying, VOC free process. Not only does UV curing increase product throughput, but it also improves a number of physical properties, such as better scratch resistance, abrasion resistance, chemical resistance, crease resistance, hardness, elasticity, and adhesion or bond strength. The ability to cure inks at low temperatures makes UV inks attractive for use on substrates of low thermal stability, such as PET and paper. The focus of this study is to formulate and evaluate resistive inks of lower cost than silver. Though resistive inks are commercially available, a broad series of resistive inks, specific for one printing process are currently not available. The ability to produce such a series of inks would greatly benefit PE applications where the conductivity of silver is not needed and its price is cost prohibited.

Examples of applications that could benefit from such inks are touch panels

The materials to be used are carbon for the formulation of carbon/silver blended inkjet inks and graphite for carbon/graphite blended screen process inks. The influence of various formulation parameters on the printability and conductive properties of the inks was studied and a cost analysis of the formulated blended inks in comparison to silver performed.

## **CHAPTER III**

### **MATERIALS AND EXPERIMENTAL PROCEDURE**

#### **Phase I**

This work was completed in two phases. In the first phase, the properties of a carbon ink, supplied by Methode Electronics (Chicago, IL), were characterized for viscosity, surface tension and density to enable its z-numbers to be calculated. Next, a hybrid waterbased/UV ink was prepared using a nano silver dispersion supplied by the Department of Chemistry at Western Michigan University and Bayhydrol UV resin. Adjustments to the ink were performed to obtain a z number suitable for printing on a Dimatix DPM inkjet printer. The two inks were then printed, and a waveform created and adjusted, to obtain good jetting and print quality. Lines of different nominal line widths were printed and, their sheet resistivities measured.

#### **Inks and Substrate**

A water-based dispersion of 10 nm nano silver particles was obtained from the department of chemistry at Western Michigan University. The dispersions were prepared according to previously published procedures. (49) Bayhydrol UV 2317, a water-based UV curable resin from Bayer Material Science (Pittsburgh, PA) was used as binder. The photoinitiator used was Irgacure 2959 from Ciba Specialty Chemicals Inc. (Tarrytown, NY). De-ionized water was used as the solvent. From all these materials, a hybrid UV conductive inkjet ink was prepared by mixing the UV resin with the nano silver dispersion, DI water and photoinitiators. The components were mixed well at high speed with a Lab dissolver (Model CM-100, Morehouse Cowles Inc., Chino, CA) to achieve a uniform dispersion. The viscosity of the ink was further adjusted with DI water. For the

successful inkjet printing with a Dimatix printer, Dimatix recommends that the ink viscosity be between 8-12 Cp and surface tension between 32-42 dyne/cm. (48) Keeping this in mind, the hybrid UV silver ink was formulated to meet these specifications by mixing 30% UV resin with 50% of the silver dispersion and 1% photoinitiator into 19% water (weight basis).

The substrate used for print testing was a PET (Melinex ST 505) from DuPont Teijin films. The PET was chosen based on its wide use in PE applications.

### **Experimental Procedure**

All inkjet printing was performed on a Dimatix DMP 2831 printer (Fujifilm Inc, Santa Clara, CA). A picture of the printer is shown in Figure 7. (49) To achieve good jetting, the cartridge temperature, voltage applied to each nozzle, and substrate temperature were adjusted. A typical voltage cycle consists of three segments: 1) A negative voltage period to fill the cartridge 2) A positive voltage period to dispense the fluid and 3) A segment that allows the nozzle to recover to its original shape without drawing in air while doing so. The entire cycle is referred to as the waveform. (50) The waveform used is shown in Figure 8.



**Figure 7. Dimatix inkjet printer. (49)**



Samples were printed at a drop spacing of 10 microns, an angle of 2.3° and cartridge temperature of 30° C. The waveform and cartridge settings used to print the hybrid UV silver ink is shown in Figure 9. The carbon ink was printed using the same waveform and print conditions.

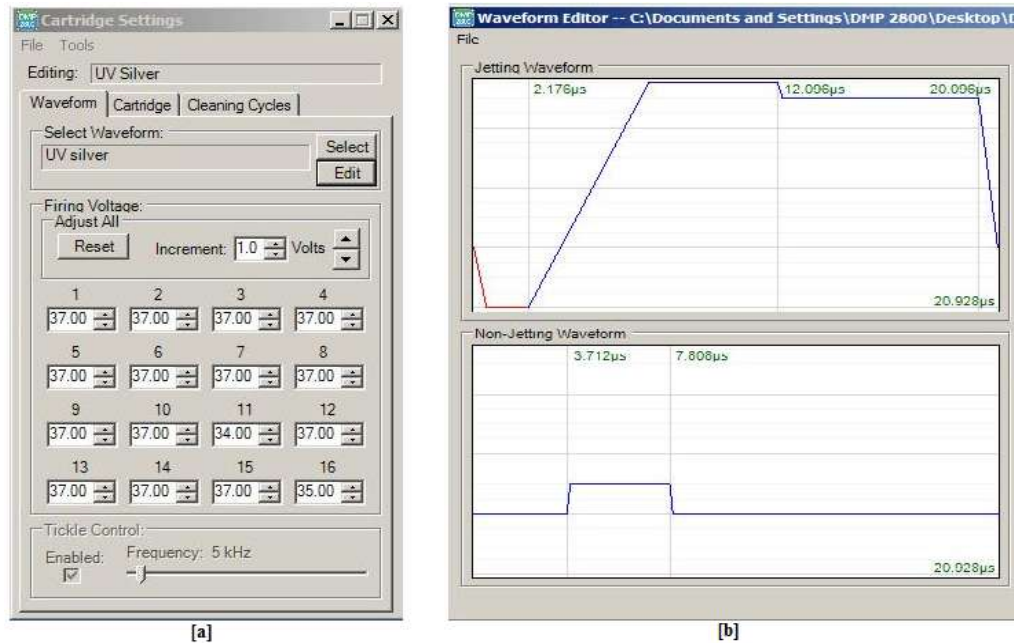


Figure 8. Voltage settings (a) and waveform (b) used for printing UV silver.

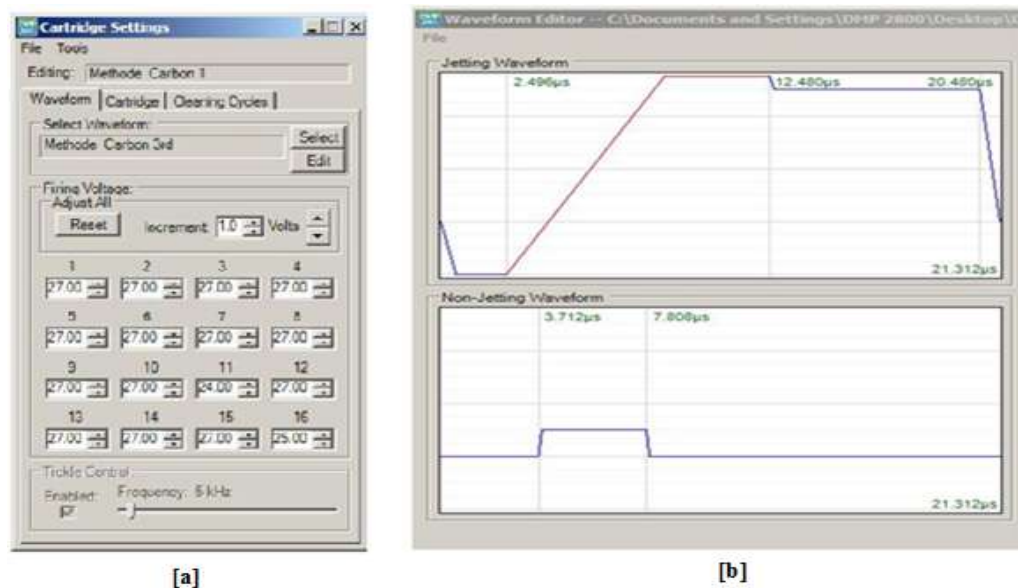
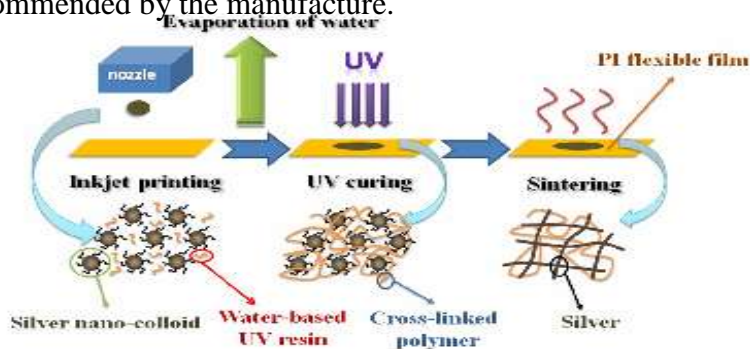


Figure 9. Voltage settings (a) and waveform (b) used for printing resistive carbon ink.

Immediately after printing, the hybrid UV ink was dried for 15 min. in a hot air oven at 60°C to evaporate off the water in the ink. Next, the samples were UV cured for ~ 20 seconds with a Fusion UV drier equipped with a D Lamp (Fusion UV Systems Inc, Gaithersburg, MD). The samples were then sintered at 120° C in a hot air drying oven for 20 min. The electrical resistances of the cured samples were then measured with a Keithley 2602 source-meter. An illustration of the sintering process is shown in Figure 10. (51) The printed carbon ink samples were dried in a hot air convection oven at 60° C for 5 minutes, as recommended by the manufacture.



**Figure 10. Formation process of conductive pattern. (51)**

Unfortunately, the UV silver printed lines were non-conductive, indicating that the silver content within the inks were too low to form a continuous conductive pathway. Since the formulation of the ink resulted in the dilution of the silver nano particle dispersion with resin to the point where it was non-conductive, it was concluded that a higher solid content dispersion was needed. Unfortunately, a higher solid dispersion could not be provided due to stability issues. Therefore, no further formulations were prepared or tested. The results for surface tension, viscosity, density and z numbers for both inks are given in Appendix 1, along with the print analysis of the carbon ink printed lines.

## **Phase II**

### **Inks and Substrate**

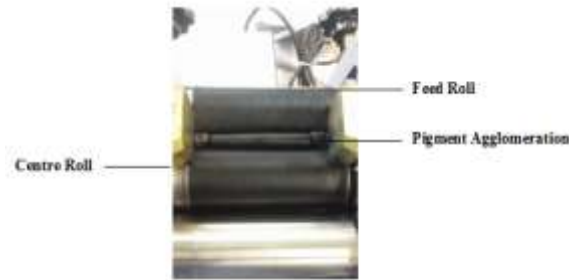
In this phase of the study, a high purity 8 micron synthetic graphite (TC 301, supplied by Asbury Carbons, (Asbury, NJ) was used. Also used was a 3-5 micron amorphous conductive carbon filler supplied from a proprietary source. To bind the pigments, a vinyl resin (Vinol, Wacker Chemical Co, Adrian, MI) was used. The degree of polymerization of the resin, as reported by the supplier, was 40,000 - 50,000. DISPERBYK 111 was used as the dispersant (BYK additives & Instruments, Columbia, MD) and N-Butoxy ethyl acetate (Sigma-Aldrich Corporation, St. Louis, MO) was used as the solvent. The standard inks used for comparison were a silver flake ink (ELECTRODAG 479SS) supplied by Henkel Co., (Irvine, CA) and carbon ink, Dupont 7105, supplied by Dupont, (Wilmington, DE).

The inks were prepared in two steps; 1) the varnish was prepared by dissolving the resin into the solvent, 2) the synthetic graphite, conductive carbon fillers, additives and solvent were blended into the resin and the particles milled on a three roll mill.

*Step 1 - Varnish Preparation:* Four different varnishes were prepared by adding 15 %, 20%, 25% and 30% resin on weight of dry solids into the N-Butoxy ethyl acetate solvent, Varnish 1, Varnish 2, Varnish 3 and Varnish 4, respectively. The resins were dissolved in the solvent with a high speed lab dissolver (Model CM-100, Morehouse Cowles Inc. Chino, CA).

*Step 2 - Pigment Dispersion:* Once the varnishes were made, the graphite, conductive carbon filler, additives and remaining solvent were added. A three roll mill was then used to re-disperse the pigments, Figure 11. The ink was milled (also referred to as grinded)

for ~ 15 minutes during which time solvent was added to account for evaporative losses and to prevent the ink from drying-out onto the rollers.



**Figure 11. Pigment Particles entering a three roll mill.**

### **Design of Experiments, DOE**

Table 6 shows the DOE used. A full factorial design was performed to separate out the main effect variables of varnish type and % carbon solids

**Table 6. Factors and levels used for basic design of experiments.**

Run#	Varnish Type	Carbon (%solids)
1	2	1
2	3	3
3	3	2
4	4	1
5	1	2
6	3	1
7	4	2
8	1	1
9	2	4
10	1	4
11	4	3
12	4	4
13	2	2
14	2	3
15	3	4
16	1	3

According to the DOE, 16 inks were formulated. The influence of the amount of resin and graphite added in the formulation on sheet resistivity was studied. The formulations of the 16 different inks prepared are provided in Table 7. All inks were prepared on a weight basis.

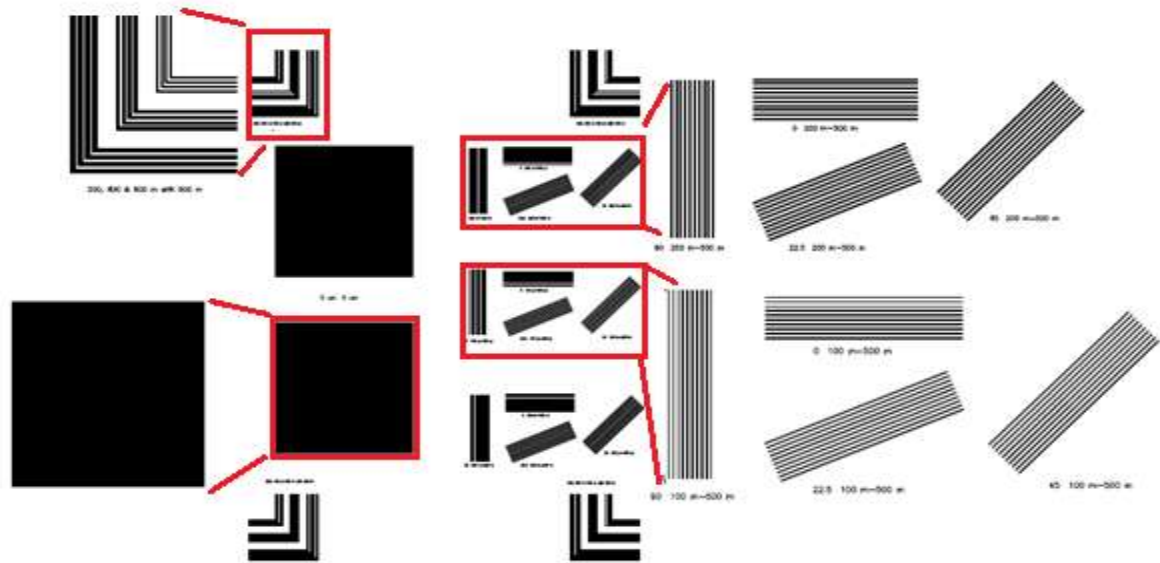
**Table 7. Compositions of formulated inks.**

	Ink 1	Ink 2	Ink 3	Ink 4	Ink 5	Ink 6	Ink 7	Ink 8	Ink 9	Ink 10	Ink 11	Ink 12	Ink 13	Ink 14	Ink 15	Ink 16
<b>Ink ID</b>	V 1 C 0	V 1 C 5	V 1 C 10	V 1 C 15	V 2 C 0	V 2 C 5	V 2 C 10	V 2 C 15	V 3 C 0	V 3 C 5	V 3 C 10	V 3 C 15	V 4 C 0	V 4 C 5	V 4 C 10	V 4 C 15
<b>Ingredients</b>	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
<b>Varnish 1</b>	25	25	25	25												
<b>Varnish 2</b>					25	25	25	25								
<b>Varnish 3</b>									25	25	25	25				
<b>Varnish 4</b>													25	25	25	25
<b>Graphite</b>	50	45	40	35	50	45	40	35	50	45	40	35	50	45	40	35
<b>Conductive Carbon fillers</b>	0	5	10	15	0	5	10	15	0	5	10	15	0	5	10	15
<b>Dispersing Agent</b>	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
<b>Solvent</b>	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24	24
<b>Total</b>	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

## Print Design

Figure 12 shows the test pattern printed. The design consists of lines of various widths and angles to evaluate the fine line printing capability of the ink. Two sets of 200 and 100 micron wide lines, each 500 mm in length, at angles of 90°, 0°, 22.5° and 45° to the print direction are shown. The design also consists of solid blocks that are 5 x 5 cm in dimension. These blocks were used to measure the sheet resistivities of the inks. At the four corners of the design are lines of varying thickness to evaluate the fine line print

performance of the inks. The mesh count of the screen was 230 LPI. The wire diameter of the screen was 0.0011". The thickness of the emulsion applied was 10  $\mu\text{m}$  and wire angle used was 45 ° (MicroScreen, South Bend, IN).



**Figure 12. Test design used for phase II**

## Printing Experiments

Printing was performed on a MSP-485 AMI screen printer, Figure 13. The substrate used was a 130 micron PET film (Melinex, ST 505) supplied by DuPont Teijin Films. The pressure of the squeegee, speed and snap-off distance was varied until an acceptable print quality was obtained. The samples were printed using the “Print to Print” mode on the AMI printer. This enabled each sample to be printed twice. The snap-off was maintained at 1.52 cm. The distance of the squeegee from the screen was set to 0.51cm, and the pressure and speed of the printer was held constant throughout all print runs.



**Figure 13. Laboratory screen printer. (AMI MSP-485 W).**

### **Curing and Sheet Resistivity Measurement**

Once printed, the samples were immediately dried in a 100° C hot air oven for 5 minutes to evaporate-off the solvent in the ink. After cooling, the sheet resistivities were measured with a Keithley 2400 digital multimeter. A picture of the multimeter and drying oven are shown in Figure 14.



**Figure 14. Keithley 2400 digital multimeter (a) and Conventional hot air drying oven (b).**

### **Resistance, Sheet and Bulk Resistivity**

Resistance is the property of a conductor that opposes the flow of current through it. Resistance not only depends upon the chemical composition of the material, but on the

length, cross sectional area and shape of the device. (2) The resistivity of a material is the reciprocal of the conductivity and is usually reported in Ohm/meter or Siemens/meter.

Sheet resistance is a measure of the resistance of a thin film of nominal uniform thickness. The resistance of each sample was measured using a Keithley 2400 digital multimeter in the 4-wire sensing mode. The measured resistance values were then used in the following equation to calculate sheet resistivity. (2)

$R_s = R (L/W)$  where:

$R_s$  is Sheet Resistivity [ $\Omega/\text{sq}$ ]

$R$  is Resistance [ $\Omega$ ]

$L$  is Length [mm]

$W$  is Width [mm]

Sheet resistance is applicable for only two dimensional systems, in which it's assumed that the current is flowing only along the plane. In actuality, current also flows perpendicular to a plane. Therefore it is important to also determine and compare the bulk resistivity of the printed samples. To enable the bulk resistivity to be determined, the thickness of each sample was measured with a thickness gauge (Technidyne Co, New Albany, IN) and the results used in the following equation: (52)

$P = R_s \times t/25$  where:

$P$  is Bulk Resistivity [ $\Omega\text{-cm} \times \text{mil}$ ]

$R_s$  is Sheet Resistivity [ $\Omega/\text{sq}$ ]

$t$  is thickness [ $\mu\text{m}$ ]



## **Rheological Studies**

The rheological properties of the inks were measured with a TA AR 2000 dynamic stress rheometer equipped with a 20 mm parallel plate geometry. Parallel plates are usually used for high viscosity, high solids materials containing large particles. This is because, unlike a cone and plate geometry, parallel plates do not require a defined gap to be set. Since large particles can damage the surface of a cone and plate geometry parallel plates are better suited for such inks. (53) In order to eliminate any shear history within the samples, all samples were pre-sheared at  $1000 \text{ sec}^{-1}$  for 30 seconds, then equilibrated at rest for 1 minute prior to running each test. The temperatures of the inks were maintained at  $25^\circ \text{C}$  throughout all experiments.

### **Step-Change Tests with Controlled Stress**

Step change tests were performed on the inks to simulate conditions similar to what would be experienced on press, and to study the time dependency of the inks under a periodic change of stress and time. A step change test is a shear and time dependent test. First an increasing stress is applied to the ink. After a period of time, the stress is removed and the recovery of the ink measured. This cycle is repeated sequentially to observe the time dependency of the ink to cyclic change. (54) Controlled stress tests were also performed to characterize the flow properties of the ink under varying rates of shear. Tests were performed over a shear rate range of  $2\text{-}500 \text{ sec}^{-1}$ . All tests were performed at a temperature of  $25^\circ \text{C}$ . (55) The shear rates were selected to be representative of shear rates encountered on press. The lower shear rates represent the time just after ink transfer

on press and the higher shear rates represent the ink metering step where the ink is pushed through the screen by the squeegee.

### **Steady State Flow**

Printing inks are fluid or semi fluid materials of high thixotrophy. In this test, ink is subjected to a continuously increasing shear rate. Lower shear rates simulate storage conditions whereas higher shear rates simulate conditions on press. Steady state flow tests are commonly used to understand the flow characteristics of inks at different shear rates. Typically, all printing inks exhibit shear thinning properties, which means their viscosity decrease with increased shear. The shear rates applied were from 0.1 to 100 sec<sup>-1</sup> because screen-printing is a slow printing process in comparison to other printing processes such as gravure and flexography. (46) Testing was performed at 25 °C.

### **Print Analysis**

The line width and line raggedness of the printed samples were measured with an ImageXpert (KDY Inc.) image analysis system comprised of a motion table for sample positioning, two calibrated cameras for image capture and ImageXpert image analysis software (IX 10.0b63). Five readings were taken for every feature measured on each sample

### **Contact Angle Measurements**

Contact angle and surface tension measurements were performed using a FTA200 dynamic contact angle measurement device. The change in contact angle with time was measured for DI water and methylene iodide on the PET substrate and printed ink films

to enable their surface energies to be determined by use of the Owen's Wendt method. The equilibrium contact angle for each liquid (contact angle where no further change with time was observed) was used in these calculations. (2) (56)

### **Adhesion Test**

Adhesion tests were performed with Scotch tape to determine the adhesion of the ink film to the PET substrate. The effect of binder and carbon content on adhesion was studied. Tests were performed manually by placing the tape on the printed samples and pulling the tape by hand.

## **CHAPTER IV**

### **RESULTS AND DISCUSSION**

#### **Effect of Conductive Carbon Fillers on Sheet Resistivity**

Initial resistivity studies were performed by preparing drawdowns with a #26 Mayer rod (Gardco, Gardner Company Inc.) with each ink. Five Samples for each ink were prepared and the resistivity measured in five different places on the sample. Five ink film thicknesses were measured with a thickness gauge (Technidyne Co, New Albany, IN) for each sample. Different ink film thicknesses were obtained for each ink by altering the % solids in the ink. Figure 15 shows the variation in ink film thickness with % resin added. The thinnest ink film was obtained for the ink containing 15% resin. It is believed this is because of ink spreading as a results of the lower ink viscosity, The spreading of the ink and thinning of the ink film resulted in fewer contact points between conductive particles. Though spreading can be controlled by increasing the amount of binder in the ink, excess binder disrupts electron flow. This explains the higher resistivity observed for the 25% and 30% resin formulations. Their higher viscosity resulted in less ink spreading. After curing, the resin forms a polymeric network structure to enable a solid ink film to form. This network can disrupt the flow of electrons, ultimately lowering the conductivity of the ink. (59) Thus, when formulating a functional ink, an optimum percentage of resin is required to maximize the performance of the ink in terms of printability, robustness and conductivity. The resistivity of the 20% and 15% resin conductive carbon filler inks were lower than the other inks.

As shown in Figure 15, ink V20C15 has the lowest resistivity, while inks containing no conductive carbon, V1C0, V2C0, V3C0 and V4C0, are of higher sheet resistivity. Inks

V1C15, V2C15, V3C15 and V4C15 have the lowest sheet resistivity respectively in their group. The resistivity significantly increased with decreasing amounts of carbon filler added. Because the lowest resistivity was found for the V20C15 ink, this ink was carried forward for additional print studies.

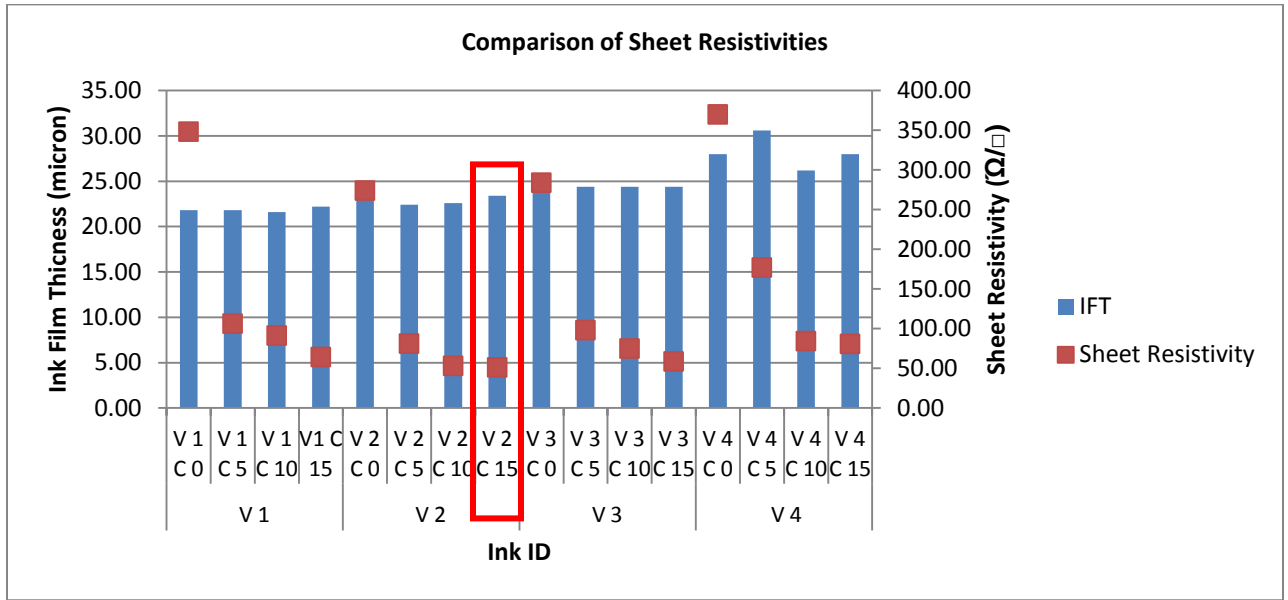


Figure 15. Effects of conductive carbon fillers on sheet resistivity.

### Statistical Analysis

Table 8 shows the results of the ANOVA analysis performed on the data. The P-values obtained indicate that both the varnish type and carbon (% solids) significantly impacted sheet resistivity. The R-Sq value for the analysis was 97.75%.

Table 8. ANOVA table for sheet resistivity

Source	DF	SS	MS	F	P
Varnish Type	3	9223	3074.3	6.7	0.011
Carbon (% solids)	3	170019	56673	123.42	0.000
Error	9	4133	459.2		
Total	15	183375			

## Rheological Behavior of Inks

### Step-Change Tests with Controlled Stress

In Figure 16, the rheology of the formulated graphite/carbon ink is compared to a commercial silver and carbon ink. All the inks decrease in viscosity with shear, but the recovery of each ink vary significantly. The silver ink recovers very quickly, compared to other two inks, where as the recovery for the graphite ink is moderate. The carbon ink recovered the least. The step change test is shear and time dependent; as shear is applied to the ink, the ink decreases in viscosity. Upon removing the shear, the ink regains its viscosity, but the recovery of the ink depends upon the elastic property of the ink. A high recovery rate has been reported to reduce the potential for print defects. (54) Among all the inks tested, the silver ink recovered the quickest and reached a significantly higher viscosity. This behavior is favorable for fine line printing because the quick recovery would prevent slumping (spreading). The carbon ink recovered to a much lower viscosity, which would make it suitable for the printing of solids where coverage is needed. The graphite/carbon blend's intermediate viscosity makes it suitable for fine line, as well as solid printing.

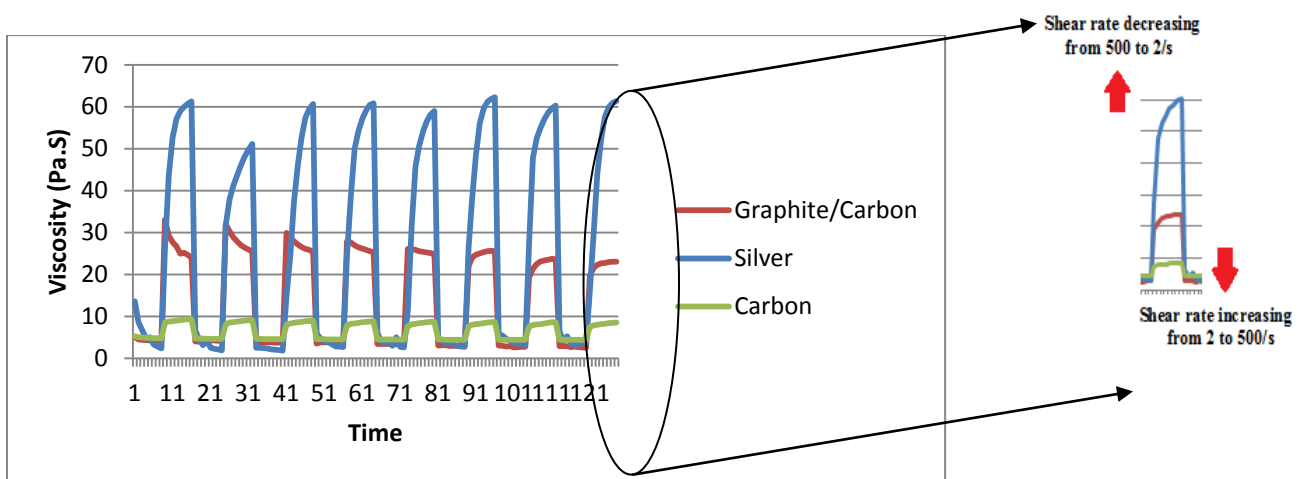


Figure 16. Step-change test results obtained using a controlled stress rheometer.

### The Steady Test Flow

The flow properties of the inks under shear are shown in Figure 17. All inks are shear thinning. The shear thinning properties of the graphite/carbon and silver inks are similar as indicated by the slopes of their curves. The initial viscosity of the carbon ink is lower than that of the silver and carbon/graphite ink, but it is less shear thinning. The viscosities of all the inks leveled off at a shear rate  $\sim 50 \text{ sec}^{-1}$ . The viscosities at this shear rate are all approximately the same.

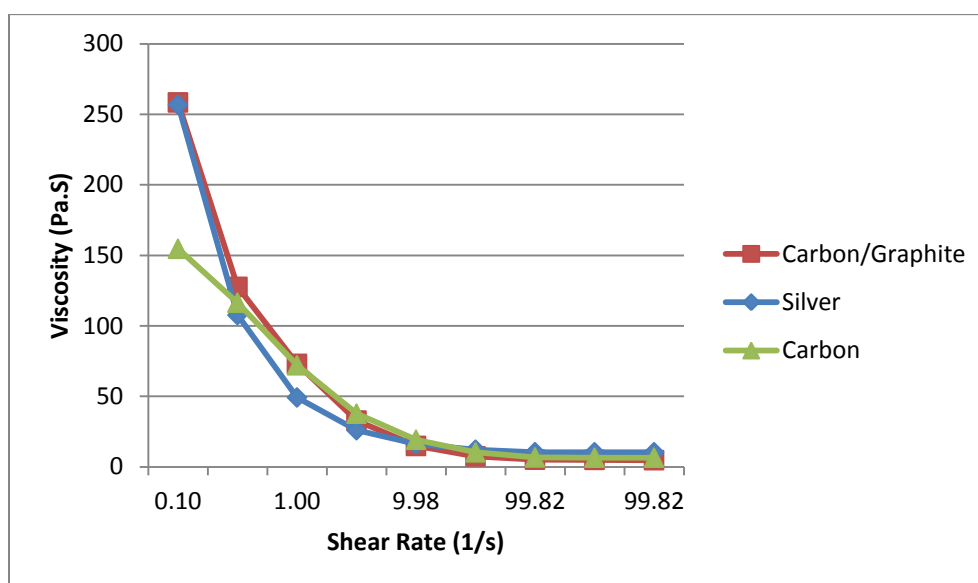


Figure 17. Steady State Test results.

### Effect of Conductive Carbon Fillers on Bulk Resistivity

Figure 18 shows the influence of conductive carbon filler loading on the bulk resistivity of the ink containing varnish 1. The ink film thicknesses were measured with a thickness gauge (Technidyne Co, New Albany, IN). The bulk resistivities were calculated from the ink film thickness values obtained by image analysis. The equation for the best model fit is provided. The R-Sq value obtained for the model fit shown was 0.9466.

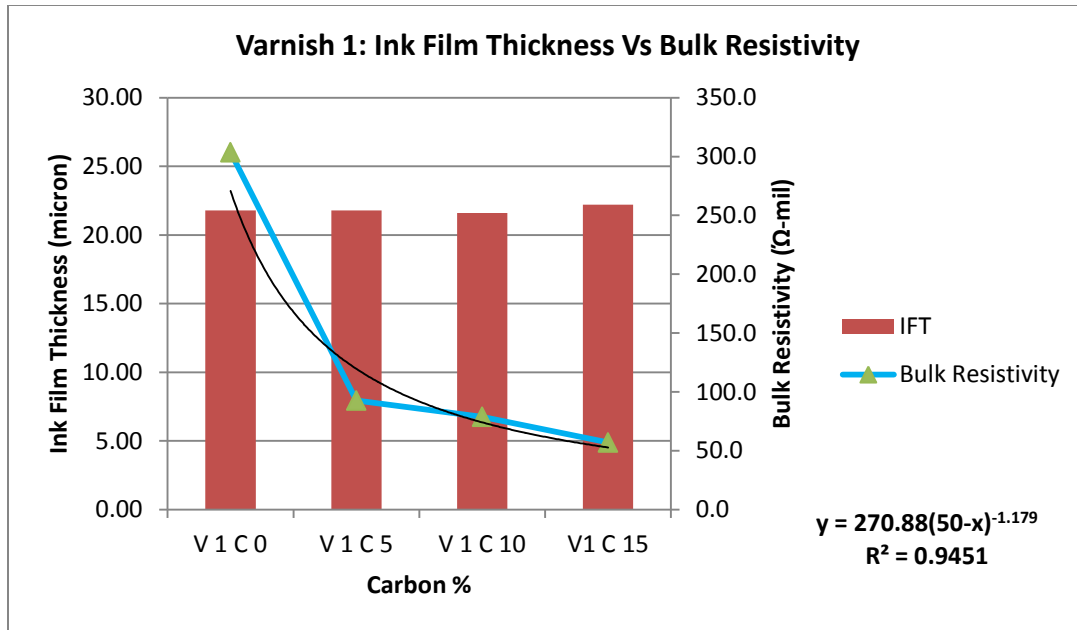


Figure 18. Equation for bulk resistivity at different carbon percentages for Varnish 1.

Figure 19 shows the influence of carbon filler percentage for the ink containing Varnish 2. The best model fit and R-Sq value 0.9702, obtained for the model fit is shown. The model fit for the Varnish 3 ink is shown in Figure 20. The R-Sq value obtained was 0.9635.

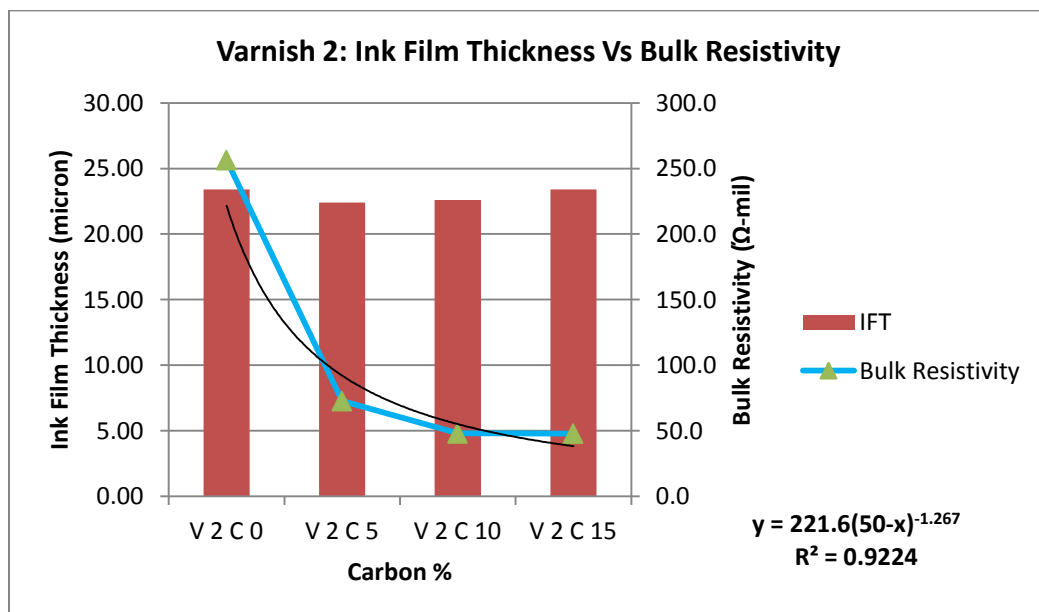


Figure 19. Equation for bulk resistivity at different carbon percentages for Varnish 2.



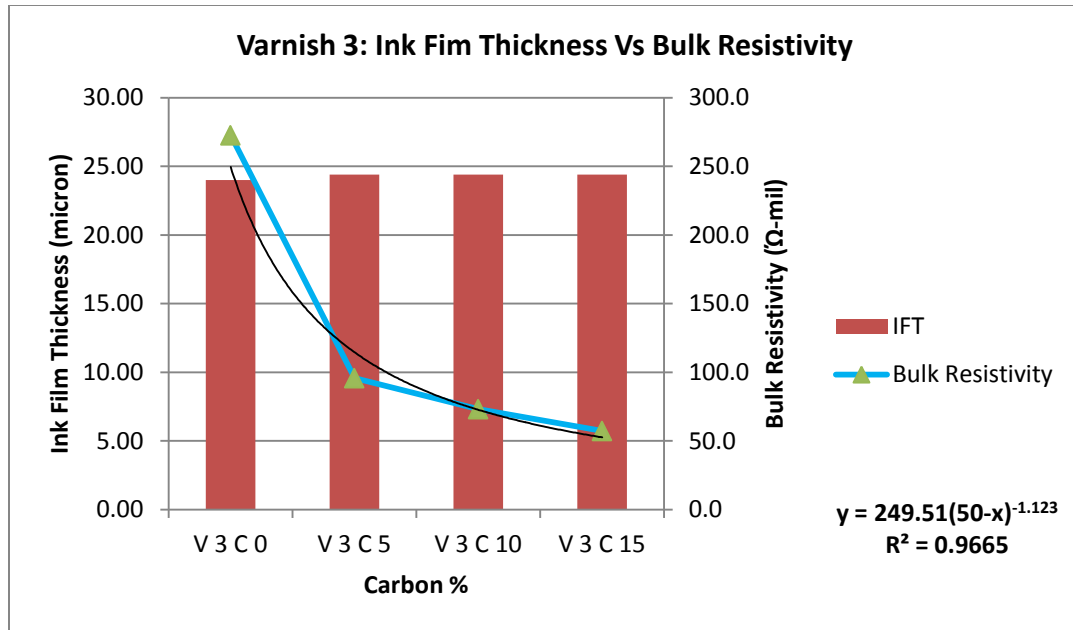


Figure 20. Equation for bulk resistivity at different carbon percentages for Varnish 3.

Figure 21 shows the influence of carbon filler percentage for the ink containing Varnish 4. The best model fit and R-Sq value 0.9974, obtained for the model fit.

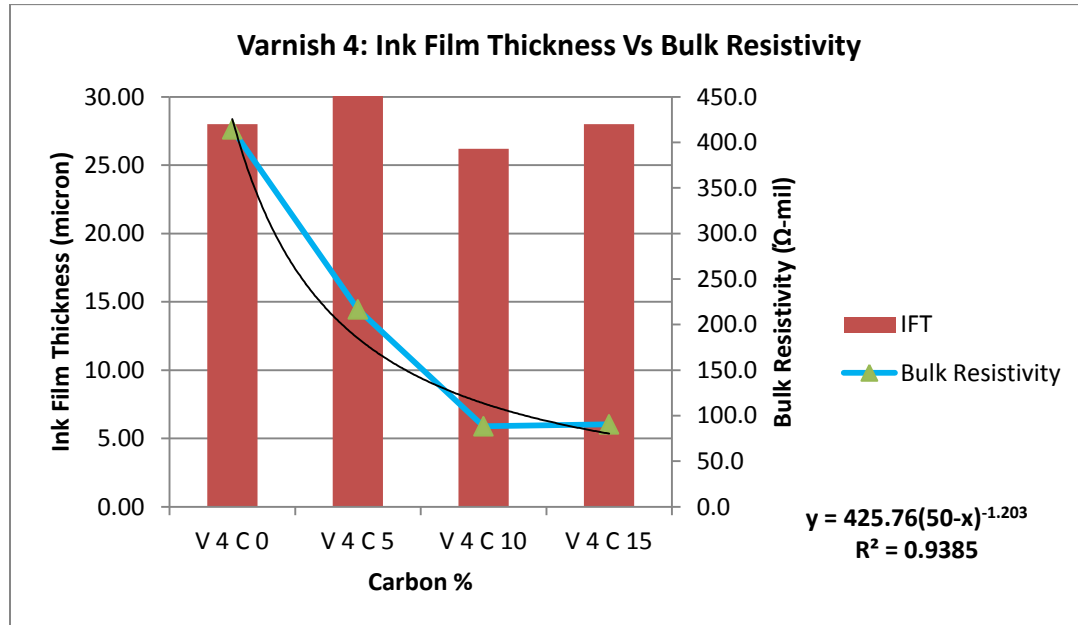


Figure 21. Equation for bulk Resistivity at Different Carbon Percentages for Varnish 4.

A comparison of Figure 18, Figure 19, Figure 20 and Figure 21 shows a decrease in resistivity with carbon filler loading. Graphite has a platelet structure, which aligns in the

print direction when sheared But it is very hard to create a uniform ink film, because graphite does not melt at high temperature. As a result, fillers are needed to fill in the open areas within the film so a conductive network-like structure can be created. (58) The network structure increases the number of contact points, which results in a significant increase in conductivity. This is supported by the findings of this study.

### Contact Angle Measurement

The surface energy of the printed ink films were calculated from the contact angles shown in Figure 22. The surface energy of the graphite/carbon ink (V 20 C15) was determined to be 49.71 dyne/cm for silver 35.1 dyne/cm and for carbon 50.66 dyne/cm. A high surface energy is preferred if another ink is to be sequentially overprinted.

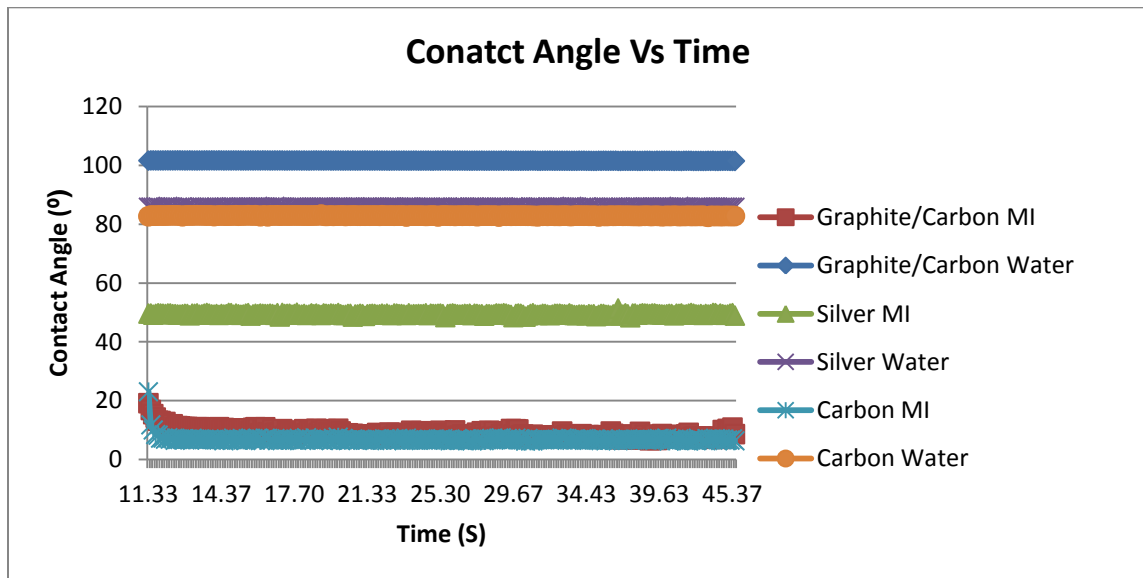


Figure 22. Change in Contact Angle for Printed Ink Film with Water and Methylene Iodide (MI).

### Print Analysis

Figure 24 compares the line raggedness of the graphite/carbon ink, commercial silver ink and commercial carbon ink at different line angles. Three samples were measured per angle at five different sampling points. As the angle increased from 0 degree to 22.5 degrees, the raggedness increased, but it then decreased from 22.5 to 90 degrees. The graphite/carbon lines are much smoother in the 0° print direction, in comparison to the other print angles. The commercial silver ink printed well at all angles as did the carbon ink.

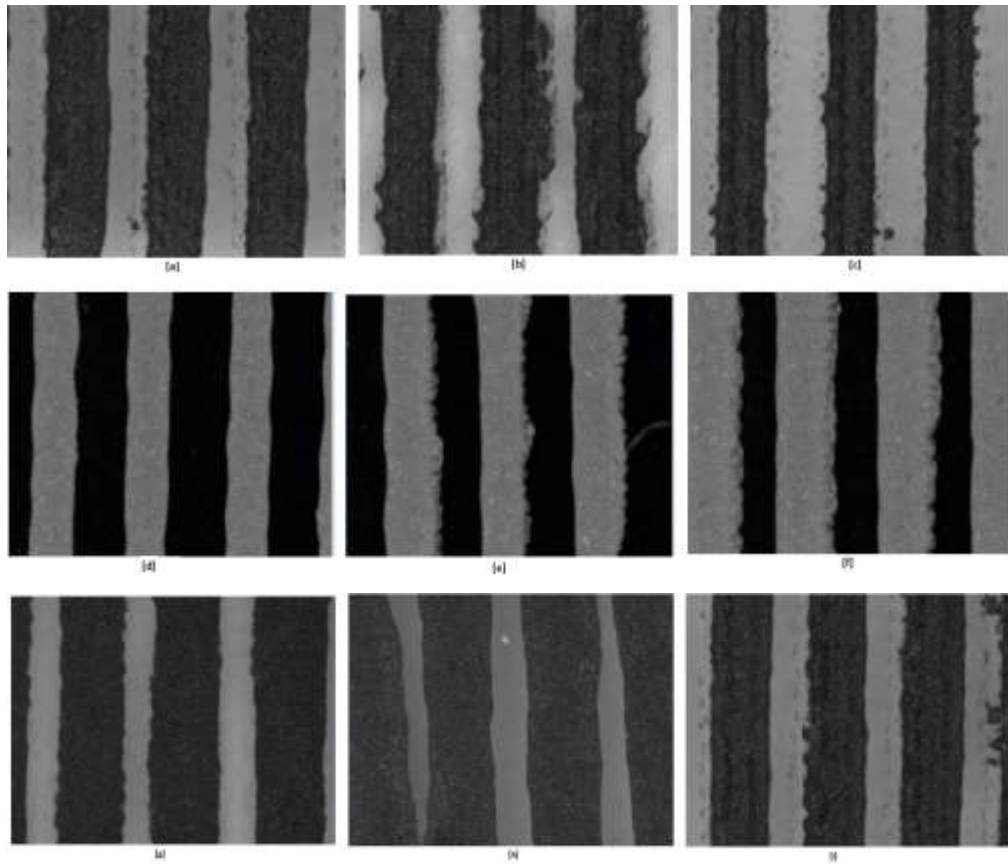
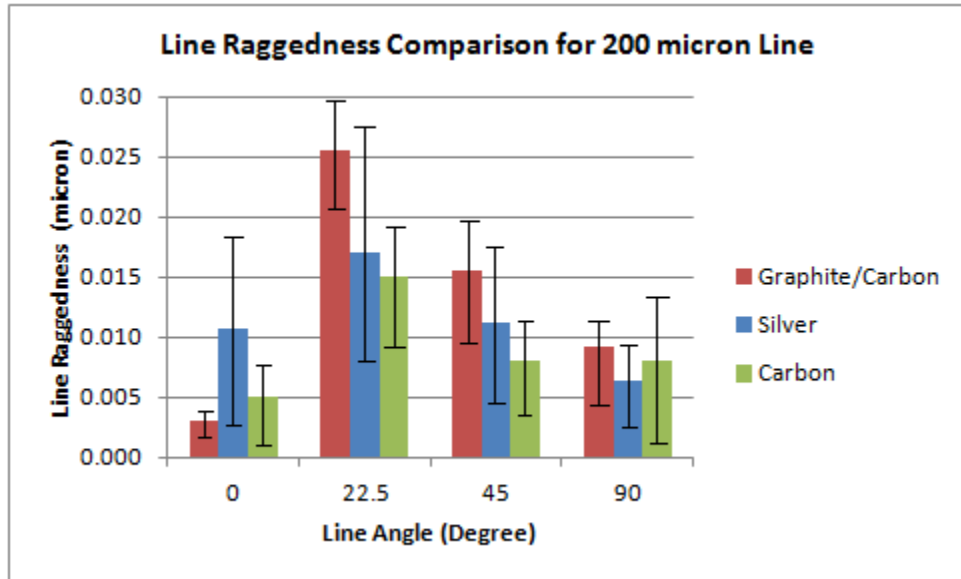


Figure 23. Images of Graphite/Carbon, Carbon and Silver printed lines



**Figure 24. Line raggedness comparison for Ink 5 at different print angles.**

The average line widths for the graphite/carbon (V20C15) commercial silver and commercial carbon ink are shown in Figure 25. The nominal width of the line was 200 micron. For the graphite/carbon lines, at all angles, a gain in the width was observed except at the 22.5° angle. For the 0° line, the gain is ~ 25% whereas for 45° line gain it's ~23% and for 90 degree line gain its ~10%. The increase in line width is attributed to the viscosity of the ink and pressure exerted by the squeegee during printing. Only the 200 micron lines were analyzed because the 100 micron lines did not transfer completely. For the commercial silver ink, line gains were observed at all angles. The line gain at 0° is ~40%, for 22.5° the gain is ~45%, for 45° the gain is ~60% and for 90° the gain is ~50%. For the commercial carbon ink, the line gains observed at 0° was ~2%, for 45° the gain was ~5% and for 90° the gain was ~10% except 22.5° as shown in Figure 25.

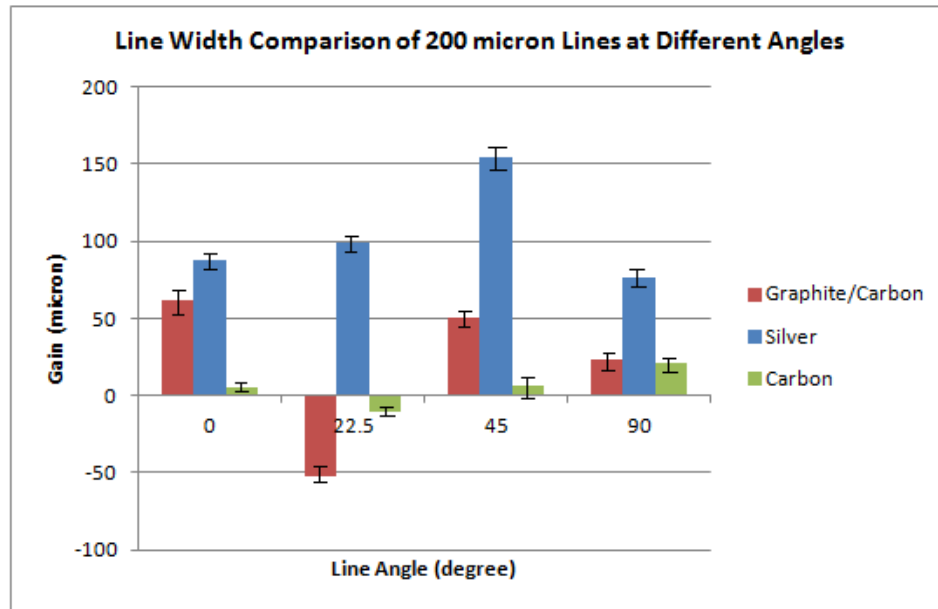
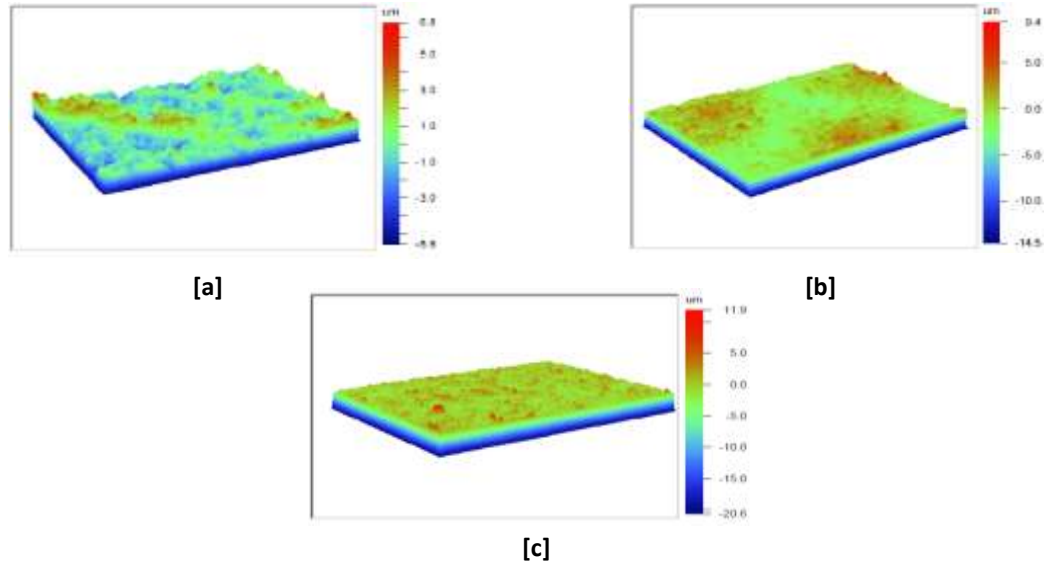


Figure 25. Line Width Comparison for Ink 5 at Different Angle.

### Roughness Measurement

A WYKO Rough Surface Tester (RST) white light interferometer microscope was used to measure the roughness of the printed ink films. The average roughness reported was obtained from measurements take from two different samples tested at 3 different positions. The average roughness obtained from the printed ink film was  $\sim 1.11 \mu\text{m}$  for the graphite/carbon ink. The average roughness obtained from the printed ink film was  $\sim 1.29 \mu\text{m}$  for the commercial silver ink. One of the measurements for both the inks is shown in Figure 26. By observing different topographical plots of different graphite/carbon samples, it was observed that the ink films were rougher at the edges as compared to the center. The higher roughness values at the edges indicate that the leveling properties of the ink need to be improved. The smoothness of the ink film can be improved by increasing the recovery of the ink via blending in another resin, which is a

good film former and elastic in nature. The commercial silver ink printed with no trouble, but the recovery of the ink was too fast to allow for good leveling. A fast recovery is good for printing fine lines, but the poorer for leveling.

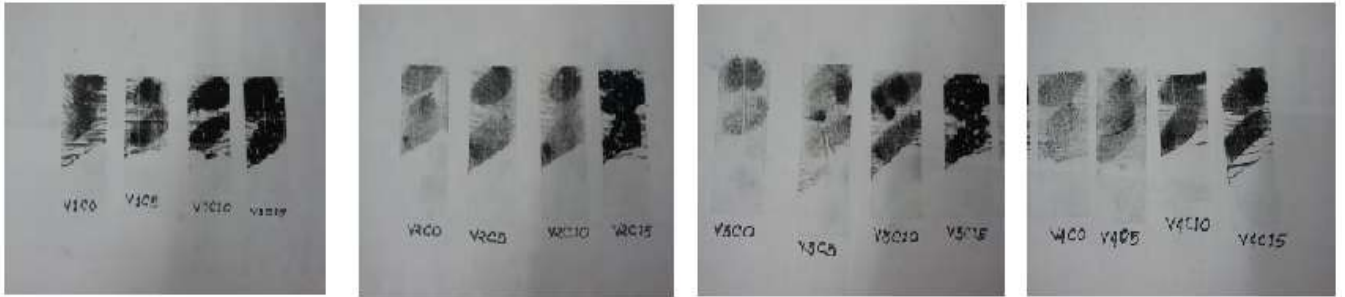


**Figure 26. WYKO images of ink film topography for carbon/graphite ink (a), silver Ink (b) & carbon ink (c)**

### **Adhesion Test**

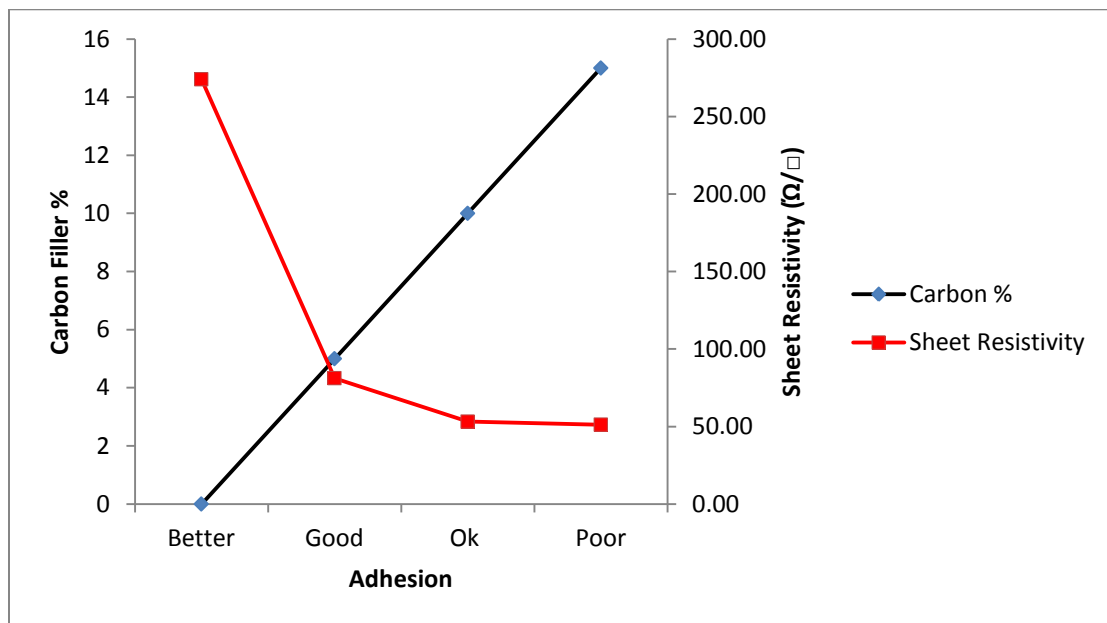
The results of the adhesion test performed using Scotch tape are shown in Figure 27. Ink V3C0 and V4C0 showed the best adhesion and ink V1C15 showed the poorest adhesion among all the inks. The results support what is commonly known; that the adhesion of an ink depends upon the amount of binder added. A comparison of V1C0, V2C0, V3C0 and V4C0 inks show much better adhesion with binder content. Adhesion also depends upon the amount of carbon conductive filler added. The higher the amount added, the lower the adhesion.

Figure 27 shows inks formulated using Varnish 1 having different adhesion properties based on the amount of fillers added. Ink V1C0 (no fillers) adhered much better to the PET film than the V1C15 ink (highest amount of fillers).



**Figure 27. Adhesion Test Results from left to right for V1C0 to V4C15.**

Figure 28 shows the relationship between the adhesion, conductive carbon filler percentage and sheet resistivity. It's clear from the results that there is a huge impact of carbon filler on adhesion. The intersection of two curves shows the “sweet spot” where optimum resistivity can be achieved with satisfactory adhesion.



**Figure 28. Effect of filler addition on adhesion and sheet resistivity of Varnish 2.**

## Cost Analysis

Knowing the approximate cost of 1 gm of silver, 1 gm of graphite and 1gm of carbon and amount of ink required to print an ink film of known thickness, a rough cost analysis can be performed. The approximate cost for silver powder used in the ink formulation is ~\$ 0.353/gm (59), synthetic graphite is \$0.002/gm (60) and conductive carbon fillers is 0.024/gm (61). These values may change day-to-day and company-to-company. The total cost may also vary depending upon the ingredients used in the ink formulation and processing methods used to make the inks. In this study, the cost for the polymer, solvent and additives are equally considered for both inks. The approximate cost of the polymer used is \$0.018/gm, solvent is \$0.0007/gm and additives are \$0.0007/gm. (59)

**Table 9. Costs required to print inks of different film thicknesses.**

IFT (microns)	Sheet Resistivity		Cost (\$)	
	Silver ( $\Omega/\square$ )	Graphite/Carbon ( $\Omega/\square$ )	Silver	Graphite/Carbon
10	0.045	115.062	0.291	0.018
20	0.036	106.002	0.585	0.036
30	0.014	68.403	0.880	0.054
40	0.009	51.642	1.174	0.072
50	0.009	38.505	1.469	0.091
60	0.005	28.539	1.763	0.109
70	0.004	24.462	2.058	0.127
80	0.004	21.744	2.352	0.145

Based on these values, a comparison in ink cost with sheet resistivity for the silver and graphite/carbon ink at different ink film thicknesses was made. The results are shown in Figure 29. This information is extremely useful because in some applications a highly conductive ink is not required for certain applications. So the use of a silver ink will unnecessarily increase the cost of the product. In these applications, a low cost graphite/carbon ink capable of providing a moderate conductivity would result in



significant cost savings. Figure 29 also shows the resistivity of silver is very low and doesn't change to a large extent with ink film thickness. Different resistivity's can be obtained using graphite/carbon by changing ink film thickness where as for silver other resistive inks must be added to obtain a desired specific resistivity.

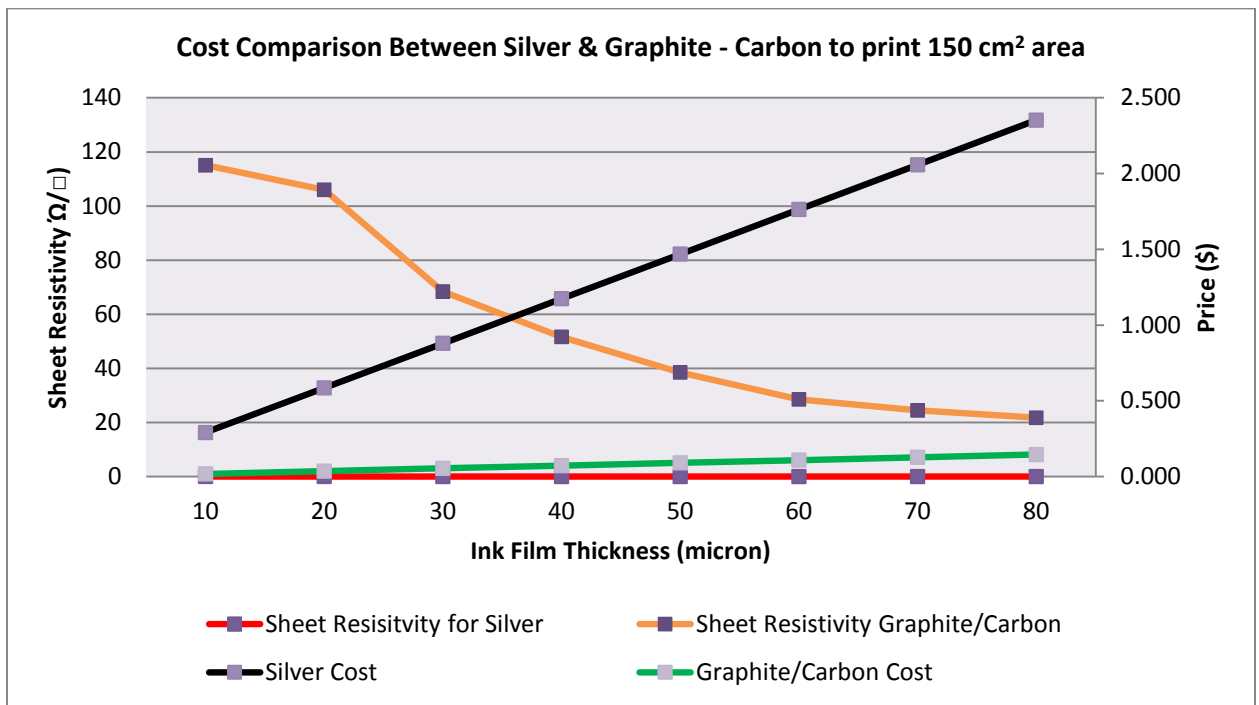


Figure 29. Cost analysis comparison of a commercial silver and graphite/carbon ink.

## **CHAPTER V**

### **CONCLUSION**

In this study, formulated conductive inks and factors affecting their functionality were studied. In Phase I, hybrid UV curable conductive inks were formulated and characterized on the basis of z-number to check their print performance on a Diamatix Inkjet printer. A commercial carbon resistive ink was used as a basis of comparison for matching the z-number, surface tension, density and viscosity properties. Both inks were jettable, however the low solids of the hybrid UV curable ink prevented it from being conductive.. A resistive carbon ink was successfully inkjet printed and showed excellent resistance. Blends of the two inks was not performed due to the inability of the silver ink to conduct and inability to increase its silver content. As future work, it is recommended to obtain a water silver dispersion having solids ~25-30% or nano silver powder for in house dispersion using dispersing agents.

Graphite and graphite/carbon composite conductive inks for screen printing were formulated and studied for their electrical properties, rheological properties and screen printability. Sixteen different inks were formulated by mixing conductive carbon fillers with graphite. The printed ink film of graphite was not highly conductive, but the addition of conductive carbon increased the ink's conductivity significantly. The sheet resistivity was found to be significantly dependent upon the amount of graphite and carbon fillers added to the ink. The effect of different resin solids on conductivity was also determined to be significant. A correlation between the amount of resin added and resistivity of the ink was obtained. The ink containing a moderate resin percentage, 20% (VOC15) had the lowest resistivity. A significant effect of conductive fillers was seen on the sheet and bulk resistivity of formulated inks. Four different levels of conductive

fillers were considered and the ink containing 15% filler showed the lowest sheet resistivity. It is believed that the high percentages of carbon filler added improved ink conductivity due to the formation of network-like structures formed between the carbon filler and graphite. The inks showed reasonable print quality but some difficulty in printing fine lines especially under different angles to print direction occurred. The adhesion of some inks were satisfactory. The inks containing lower percentages (VOC0) of carbon filler had better adhesion than the inks containing higher percentages (VOC15) of carbon filler. Adhesion was also found to depend on the amount of binder added. The higher the binder content (V4C15) the better the adhesion. The cost analysis of the inks enabled a “sweet spot” for these blended ink formulations to be found.

### **Recommendations for Future Work**

Knowing the effect of conductive fillers and by looking at the cost of the material, as future work it is recommended to look at morphology of the ink using SEM's to evaluate the distribution of graphite and carbon particles in the ink film. Different fillers such as Ni can be mixed with the graphite along with conductive carbon to further change the resistivity values. Different kinds of resins can be mixed together to improve adhesion while maintaining good conductivity and leveling. Finally, the formulated inks could be tested in an actual device, such as an EL as its base electrode material or in membrane switches as a means to validate the performance of the ink.

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## **Phase I Results**

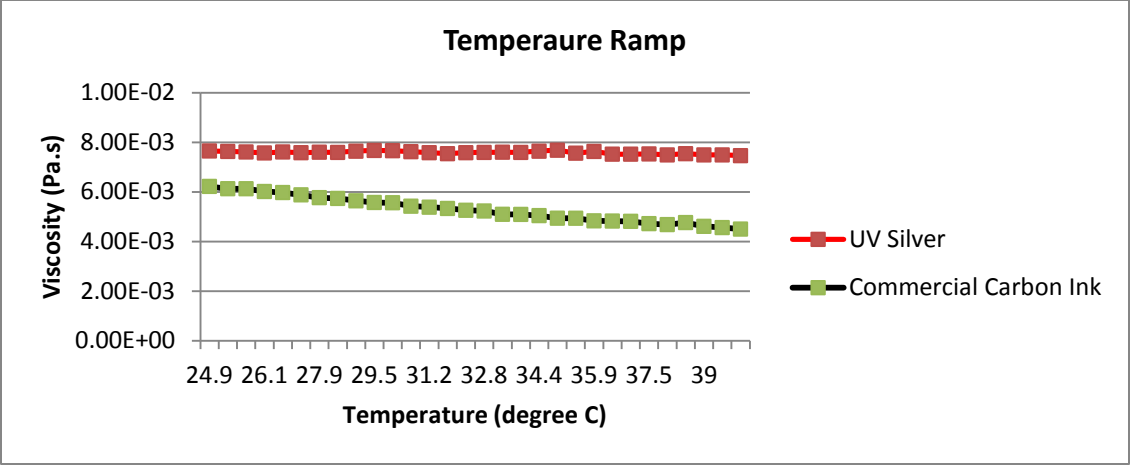


Figure A1.1. Temperature Ramp of UV Silver Ink and Commercial Carbon Ink.

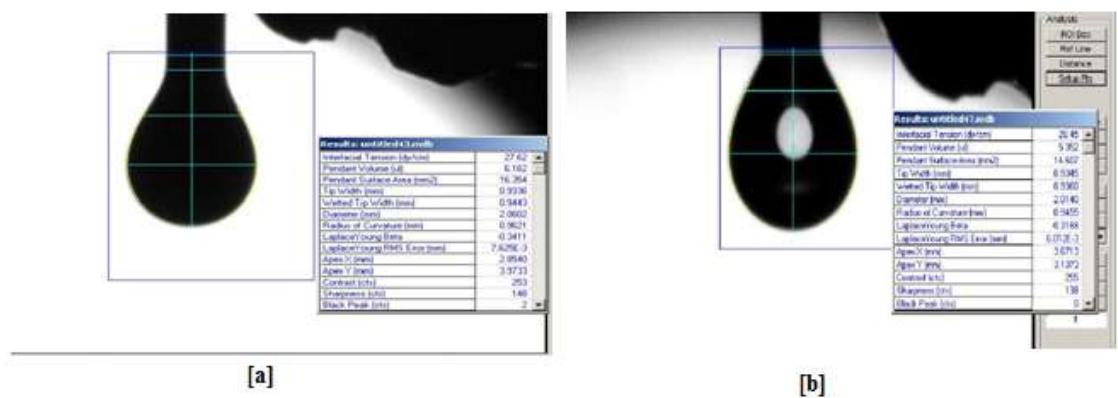


Figure A1.2. Surface Tension measurement of Commercial Carbon Ink (a) and UV Silver Ink (b).

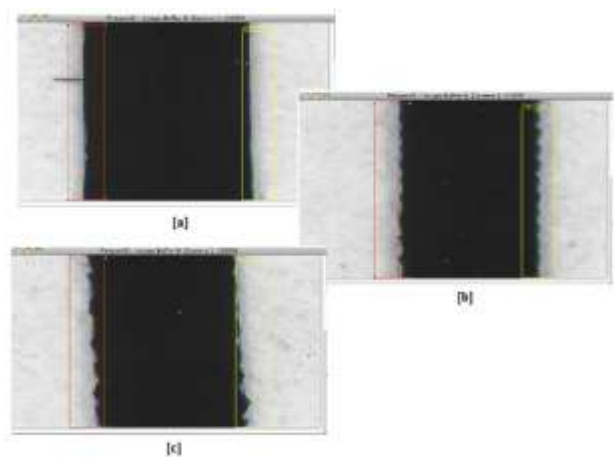
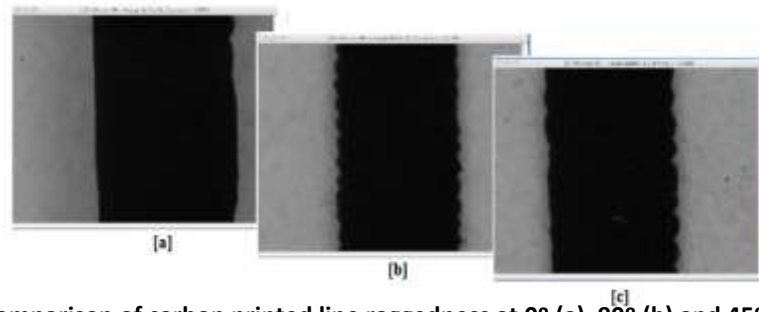


Figure A1.3. Images of Carbon Printed lines at 0° (a), 90° (b) and 45° (c) angle used for Raggedness comparison.



FigureA1. 4. Comparison of carbon printed line raggedness at 0° (a), 90° (b) and 45° (c) print angles

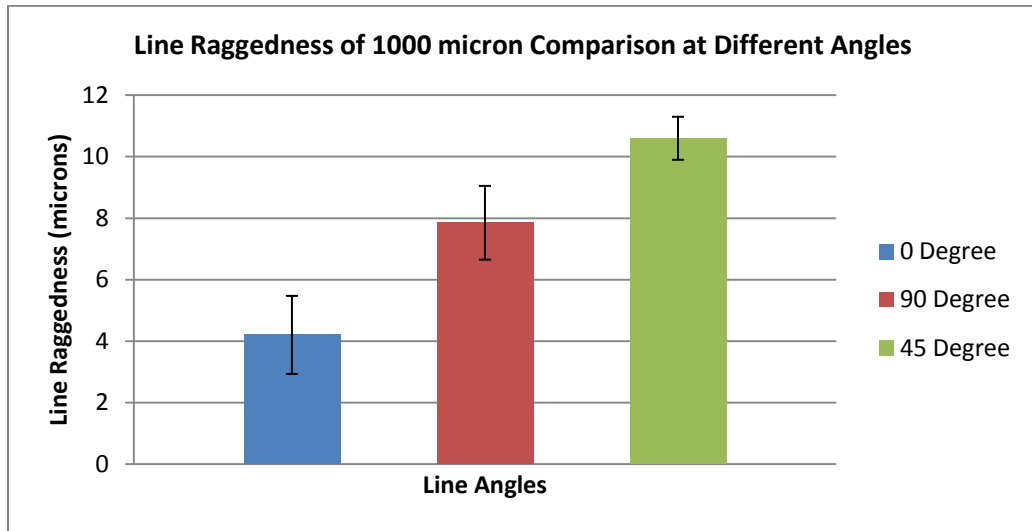


Figure A1.5. Comparison of carbon ink line raggedness at varying print angles.

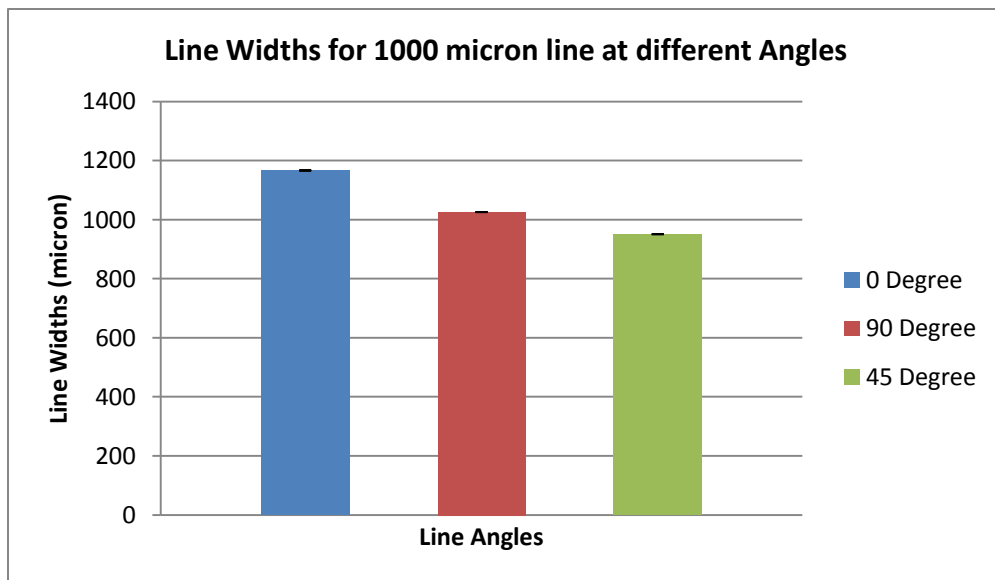


Figure A1.6. Line Width Comparison for Carbon ink at Different Print Angle.

## **Phase II Results**



**Table A1. 1. Ink Film Thickness (IFT) and Sheet Resistivity ( $\Omega/\square$ )**

V1C0		V1C5		V1C10		V1C15	
IFT	Resistivity	IFT	Resistivity	IFT	Resistivity	IFT	Resistivity
22	361.6	20	151.9	24	86.0	21	67.1
20	386.7	24	91.6	22	85.6	23	63.3
24	309.1	21	81.5	22	96.7	23	62.5
23	318.6	24	110.1	20	96.9	21	66.1
20	365.2	20	96.7	20	91.5	23	62.3
23	341.6	21	150.9	25	86.0	20	68.0
21	376.7	25	92.6	23	85.0	24	63.3
24	309.1	20	81.5	21	96.7	23	62.5
23	318.6	23	112.1	21	96.9	21	67.1
22	355.2	21	96.7	21	92.1	23	62.3
21	361.6	20	151.9	25	86.0	21	68.0
24	386.7	25	92.6	23	85.6	24	63.3
25	310.1	21	81.5	21	96.7	23	63.5
21	318.6	24	111.1	19	96.9	20	66.1
20	365.2	21	96.0	20	92.0	22	63.0

V2C0		V2C5		V2C10		V2C15	
IFT	Resistivity	IFT	Resistivity	IFT	Resistivity	IFT	Resistivity
23	273.3	23	94.0	23	53.2	22	51.3
23	259.0	23	85.0	21	56.0	27	52.0
22	280.2	22	75.9	23	54.7	24	48.1
25	273.0	22	72.9	22	45.9	25	51.3
24	284.3	22	78.1	24	57.0	20	53.3
23	274.0	22	94.0	22	53.2	23	51.3
22	260.0	22	84.0	22	56.0	27	52.0
23	280.2	23	76.9	23	54.7	24	48.1
26	274.0	21	72.9	22	46.0	25	51.3
23	285.7	22	79.1	23	56.0	21	53.3
23	273.3	23	94.0	22	53.2	22	51.3
23	260.1	23	85.0	22	56.0	28	52.0
23	280.2	22	75.9	23	54.7	24	48.1
23	274.0	22	73.1	22	45.9	24	51.3
24	284.3	22	78.1	23	56.0	24	53.3

V3C0		V3C5		V3C10		V3C15	
IFT	Resistivity	IFT	Resistivity	IFT	Resistivity	IFT	Resistivity
24	304.0	22	104.8	24	82.5	24	64.2
25	247.8	24	94.0	25	80.1	25	59.6
23	258.7	21	93.8	24	65.7	24	56.8
26	303.1	28	95.6	26	82.7	26	55.4
22	306.3	27	102.3	23	63.9	23	57.4
24	204.0	21	105.0	24	83.0	24	64.2
25	248.0	24	95.0	24	80.3	24	60.0
22	257.7	24	93.8	24	66.0	24	56.9
27	303.0	24	96.6	27	83.0	27	55.4
23	306.3	24	102.3	22	64.6	23	58.0
21	303.6	23	105.0	24	83.0	23	64.0
25	248.0	25	95.0	25	80.1	23	60.0
23	277.0	21	93.8	24	66.0	23	56.8
26	304.0	27	96.0	25	82.7	26	55.3
22	306.8	27	102.6	24	64.0	23	58.0

V4C0		V4C5		V4C10		V4C15	
IFT	Resistivity	IFT	Resistivity	IFT	Resistivity	IFT	Resistivity
28	362.9	30	203.2	26	79.3	30	82.4
27	314.8	31	168.7	27	85.2	30	83.8
29	351.1	32	173.0	26	89.2	31	79.7
28	408.2	31	175.2	26	84.3	25	77.5
28	412.7	29	165.1	26	83.8	24	80.6
28	362.9	31	203.2	26	80.0	31	83.0
27	315.0	31	169.0	26	85.4	30	84.2
28	351.1	32	173.0	27	90.0	30	80.0
28	409.0	31	173.1	26	84.3	26	77.6
28	412.7	30	166.0	26	84.0	25	81.0
28	363.0	30	203.2	26	79.1	30	83.0
27	314.8	31	169.0	26	85.7	30	84.0
29	351.1	31	173.0	27	89.2	30	80.0
28	408.2	31	173.1	26	85.0	26	77.6
28	412.7	30	165.0	26	84.0	25	80.7

**Table A2.2. Step Change Test with Controlled Stress**

Shear Rate (1/s)	Time (S)	Viscosity (Pa.S)		
		Graphite/Carbon	Silver	Carbon
499	18	5.133	13.54	5.288
499	20	4.47	8.727	5.043
499	22	4.411	6.703	4.957
499	24	4.348	4.697	4.9
499	26	4.297	5.052	4.854
499	28	4.228	3.301	4.819
499	30	4.191	2.788	4.788
499	32	4.179	2.38	4.756
2	34	33.03	25.86	8.524
2	36	29.22	43.56	8.795
2	38	27.71	52.68	8.876
2	40	26.69	57.09	8.983
2	42	24.96	58.98	9.1
2	44	25.16	59.93	9.188
2	46	24.66	60.7	9.279
2	48	24.06	61.24	9.363
499	50	4.053	6.665	4.739
499	52	3.922	4.455	4.712
499	54	4.411	3.118	4.695
499	56	4.348	4.201	4.681
499	58	4.297	2.544	4.665
499	60	4.228	2.28	4.649
499	62	4.191	2.091	4.637
499	64	4.179	1.895	4.629
2	66	31.94	31.75	8.117
2	68	30.28	37.92	8.534
2	70	28.81	41.22	8.641
2	72	27.85	43.69	8.761
2	74	27	45.96	8.868
2	76	26.41	48.04	8.96
2	78	25.96	49.77	9.063
2	80	25.5	51.08	9.142
499	82	3.768	2.481	4.626

499	84	3.78	2.493	4.608
499	86	3.79	2.451	4.598
499	88	3.789	2.335	4.589
499	90	3.78	2.097	4.579
499	92	3.743	2.023	4.567
499	94	3.71	2.001	4.558
499	96	3.7	1.81	4.555
2	98	29.9	14.89	7.981
2	100	28.85	24.57	8.326
2	102	27.89	37.05	8.473
2	104	27.19	45.84	8.585
2	106	26.54	52.63	8.703
2	108	26.05	57.35	8.806
2	110	25.84	59.41	8.903
2	112	25.34	60.67	8.991
499	114	3.485	5.859	4.555
499	116	3.78	4.776	4.541
499	118	3.79	4.064	4.536
499	120	3.789	3.959	4.524
499	122	3.78	3.34	4.516
499	124	3.743	2.82	4.513
499	126	3.71	2.789	4.505
499	128	3.7	2.687	4.499
2	130	27.92	24.57	7.841
2	132	27.6	38.66	8.203
2	134	26.96	50.03	8.31
2	136	26.48	54.22	8.451
2	138	26.13	57.17	8.577
2	140	25.89	59.09	8.681
2	142	25.58	60.4	8.775
2	144	25.33	60.83	8.862
499	146	3.42	6.104	4.504
499	148	3.437	3.94	4.493
499	150	3.435	3.558	4.485
499	152	3.391	4.337	4.476
499	154	3.381	2.955	4.468
499	156	3.358	5.037	4.468
499	158	3.341	2.717	4.463
499	160	3.328	2.555	4.453
2	162	26.07	11.36	7.706
2	164	26.09	31.45	8.095

2	166	25.85	45.69	8.216
2	168	25.56	50.51	8.365
2	170	25.37	53.97	8.475
2	172	25.25	56.45	8.592
2	174	25.12	58.14	8.702

2	176	24.89	58.95	8.783
499	178	3.034	4.585	4.462
499	180	3.155	4.198	4.456
499	182	3.143	3.498	4.443
499	184	2.992	3.9	4.439
499	186	3	3.282	4.439
499	188	2.971	2.948	4.432
499	190	3.341	2.832	4.429
499	192	3.328	2.715	4.427
2	194	22	26.4	7.643
2	196	24.01	37.96	7.992
2	198	24.74	48.49	8.125
2	200	25.04	56.1	8.242
2	202	25.34	59.48	8.372
2	204	25.53	61.16	8.504
2	206	25.62	61.89	8.611
2	208	25.59	62.29	8.676
499	210	3.017	5.776	4.433
499	212	2.952	5.396	4.422
499	214	2.831	4.652	4.417
499	216	2.858	4.114	4.415
499	218	2.56	3.624	4.41
499	220	2.688	3.516	4.404
499	222	2.759	3.491	4.404
499	224	2.725	3.079	4.403
2	226	19.27	27.2	7.611
2	228	21.33	47.81	7.958
2	230	22.53	52.49	8.065
2	232	23.1	55.04	8.17
2	234	23.37	57.06	8.297
2	236	23.52	58.5	8.439
2	237	23.71	59.56	8.576
2	239	23.67	60.3	8.616
499	241	2.91	6.448	4.409
499	243	2.897	4.133	4.396

499	245	2.867	5.273	4.391
499	247	2.656	3.576	4.393
499	249	2.802	3.187	4.386
499	251	2.661	3.192	4.381
499	253	2.597	3.85	4.382

499	255	2.535	3.716	4.378
2	257	19.75	16.15	7.553
2	259	21.55	29.98	7.878
2	261	22.27	43.82	7.998
2	263	22.62	52.22	8.12
2	265	22.71	57.64	8.2
2	267	22.94	59.88	8.392
2	269	23.05	60.85	8.492
2	271	23	61.31	8.573

**Table A2.3. Steady State Flow**

Shear Rate (1/s)	Viscosity (Pa.s)		
	Graphite/Carbon	Silver	Carbon
0.10	258.4	256.8	154.6
0.32	127.6	107.6	116.4
1.00	72.99	49.18	72.01
3.16	32.78	25.96	37.69
9.98	14.81	16.16	19.2
31.57	7.438	12.12	10.28
99.82	5.08	10.35	6.636
99.81	4.922	10.34	6.484
99.82	4.721	10.34	6.484

**Table A2.4. Bulk Resistivity**

Ink ID	Thickness 1 (micron)	Thickness 2 (micron)	Thickness 3 (micron)	Thickness 4 (micron)	Thickness 5 (micron)	Avg. Thickness (micron)	Std.dev
V 1 C 0	22	20	24	23	20	21.80	1.79
V 1 C 5	20	24	21	24	20	21.80	2.05
V 1 C 10	24	22	22	20	20	21.60	1.67
V 1 C 15	21	23	23	21	23	22.20	1.10
V 2 C 0	23	23	22	25	24	23.40	1.14
V 2 C 5	23	23	22	22	22	22.40	0.55
V 2 C 10	23	21	23	22	24	22.60	1.14



<b>V 2 C 15</b>	22	27	24	24	20	23.40	2.61
<b>V 3 C 0</b>	24	25	23	26	22	24.00	1.58
<b>V 3 C 5</b>	22	24	21	28	27	24.40	3.05
<b>V 3 C 10</b>	24	25	24	26	23	24.40	1.14
<b>V 3 C 15</b>	24	25	24	26	23	24.40	1.14
<b>V 4 C 0</b>	28	27	29	28	28	28.00	0.71
<b>V 4 C 5</b>	30	31	32	31	29	30.60	1.14
<b>V 4 C 10</b>	26	27	26	26	26	26.20	0.45
<b>V 4 C 15</b>	30	30	31	25	24	28.00	3.24

<b>Resistance 1 (ohms)</b>	<b>Resistance 2 (ohms)</b>	<b>Resistance 3 (ohms)</b>	<b>Resistance 4 (ohms)</b>	<b>Resistance 5 (ohms)</b>	<b>Avg. Resistance (ohms)</b>	<b>std. dev.</b>	<b>Bulk Resistance (ohms/square)*mil</b>
<b>361.58</b>	386.68	309.08	318.59	365.16	348.22	32.99	303.6
<b>151.89</b>	91.55	81.54	110.08	96.72	106.36	27.46	92.7
<b>85.98</b>	85.62	96.72	96.94	91.51	91.35	5.52	78.9
<b>67.13</b>	63.28	62.51	66.14	62.29	64.27	2.22	57.1
<b>273.34</b>	259.03	280.23	273.02	284.35	273.99	9.64	256.5
<b>93.95</b>	85.03	75.88	72.93	78.05	81.17	8.42	72.7
<b>53.23</b>	55.99	54.68	45.93	55.99	53.16	4.20	48.1
<b>51.32</b>	52.00	48.11	51.28	53.32	51.21	1.92	47.9
<b>303.96</b>	247.79	258.66	303.06	306.27	283.95	28.33	272.6
<b>104.82</b>	94.04	93.77	95.58	102.29	98.10	5.11	95.7
<b>82.49</b>	80.09	65.69	82.72	63.87	74.97	9.38	73.2
<b>64.19</b>	59.57	56.81	55.40	57.44	58.68	3.43	57.3
<b>362.85</b>	314.84	351.08	408.15	412.68	369.92	41.02	414.3
<b>203.17</b>	168.74	173.05	175.18	165.07	177.04	15.12	216.7
<b>79.28</b>	85.16	89.24	84.26	83.81	84.35	3.56	88.4
<b>82.45</b>	83.81	79.73	77.46	80.63	80.82	2.45	90.5

**Table A2.5. Contact Angle Measurement**

<b>Time</b>	<b>Graphite/Carbon</b>		<b>Silver</b>		<b>carbon</b>	
	<b>MI</b>	<b>Water</b>	<b>MI</b>	<b>Water</b>	<b>MI</b>	<b>Water</b>
11.33	19.15	101.61	49.61	85.77	23.03	82.68
11.43	16.83	101.67	49.62	85.83	11.79	82.93
11.53	15.41	101.68	49.24	85.76	10.05	82.92
11.63	14.25	101.66	49.51	85.9	8.5	82.88
11.73	13.19	101.66	49.71	85.87	8.27	82.93
11.83	13.09	101.66	49.62	85.7	7.25	82.96
11.93	12.66	101.66	49.56	85.67	7.3	82.92
12.00	12.76	101.68	49.46	85.76	6.91	82.93

12.10	11.79	101.68	49.64	86.05	7.42	82.96
12.20	11.2	101.67	49.66	85.85	6.93	83.01
12.30	11.98	101.67	49.42	85.78	7.22	83.02
12.40	11.04	101.68	49.41	85.44	6.53	83.01
12.50	11.36	101.70	49.3	85.82	6.8	82.98
12.60	11.29	101.69	49.25	85.78	6.8	82.94
12.70	11.05	101.67	49.37	85.86	6.9	82.68
12.83	11.02	101.65	49.51	85.67	6.68	82.97
12.93	11.04	101.66	49.47	85.76	6.92	82.93
13.03	10.6	101.68	49.01	85.8	6.65	83
13.13	10.88	101.65	49.58	85.67	7.22	82.94
13.23	10.89	101.64	49.51	85.44	6.98	83.02
13.33	10.96	101.64	49.67	85.14	6.94	83.03
13.43	10.99	101.66	49.24	85.82	7.01	83.01
13.53	10.45	101.65	49.33	85.8	6.82	83
13.63	10.61	101.68	49.59	85.72	6.76	82.99
13.73	10.69	101.68	49.81	85.72	6.66	82.92
13.83	10.44	101.67	49.58	85.82	6.94	82.99
13.93	10.67	101.69	49.32	85.82	6.78	82.96
14.07	10.33	101.67	49.25	85.79	6.73	82.74
14.17	10.5	101.66	49.45	85.77	6.68	82.91
14.27	10.99	101.69	49.16	85.63	6.62	82.94
14.37	10.1	101.67	49.48	85.75	6.89	82.98
14.47	10.72	101.64	49.29	85.79	6.39	82.93
14.60	10.57	101.66	49.39	85.82	6.88	82.9
14.70	10.19	101.66	49.83	85.45	6.6	82.89
14.80	10.49	101.65	49.76	85.88	6.85	82.97
14.90	10.04	101.67	49.23	85.83	7.26	82.96
15.00	10.55	101.65	49.6	85.82	6.86	83.03
15.13	9.84	101.67	49.37	85.8	6.6	82.87
15.23	10.14	101.64	49.2	85.88	6.68	82.98
15.33	9.96	101.64	49.29	85.81	6.65	82.95
15.43	10.6	101.64	49.59	85.85	6.45	83
15.57	10.53	101.65	49.76	85.8	7.08	83.05
15.67	9.64	101.66	48.92	85.83	7.07	82.99
15.77	10.77	101.65	49.32	85.86	7.07	82.95
15.90	10.98	101.66	49.54	85.75	6.68	83.04
16.00	10.53	101.67	49.39	85.85	7.24	82.91
16.10	8.84	101.64	49.62	85.85	6.45	82.69
16.23	10.53	101.68	49.5	85.82	6.67	82.97
16.33	10.96	101.66	49.46	85.83	7.24	82.95



16.43	9.22	101.66	49.44	85.75	7.2	82.66
16.57	9.11	101.64	49.58	85.84	6.73	83
16.67	10.22	101.64	49.45	85.76	6.62	82.96
16.77	9.01	101.66	49.2	86.06	7.14	82.97
16.90	8.96	101.65	49.74	85.83	6.54	83.02
17.00	8.91	101.66	48.62	85.82	6.76	82.89
17.13	10.32	101.66	49.83	85.83	6.42	82.96
17.23	7.97	101.62	49.46	85.75	6.74	82.96
17.37	9.82	101.63	49.51	85.31	7.05	82.94
17.47	9.3	101.64	49.57	85.53	6.82	82.92
17.57	8.99	101.63	49.23	85.79	6.69	82.98
17.70	9.08	101.64	49.46	85.73	6.64	82.98
17.80	8.53	101.65	49.9	85.83	6.67	82.95
17.93	9.75	101.65	49.29	85.8	7.2	82.96
18.03	9.18	101.62	49.25	85.8	6.49	82.93
18.17	10.31	101.64	49.49	85.8	6.73	82.93
18.27	8.85	101.62	49.15	85.8	7.41	82.93
18.40	9.84	101.62	49.26	85.79	6.8	82.89
18.53	9.31	101.63	49.68	85.82	6.94	82.96
18.63	9.63	101.64	49.39	85.81	6.51	82.94
18.77	10.45	101.67	49.61	85.74	6.86	82.99
18.87	8.94	101.63	49.32	85.81	6.77	83
19.00	9.64	101.64	49.13	85.82	6.82	83.26
19.10	8.74	101.62	49.66	85.81	6.59	82.87
19.23	10.3	101.65	49.52	85.78	6.86	82.82
19.37	9.45	101.65	49.42	85.81	6.72	82.85
19.47	8.92	101.62	49.63	85.74	6.46	82.97
19.60	9.09	101.62	49.51	85.73	7.21	82.83
19.73	9.2	101.63	49.42	85.77	6.65	82.89
19.83	10.45	101.63	49.8	85.79	7.6	82.91
19.97	9.54	101.62	49.37	85.87	6.45	82.95
20.10	8.77	101.62	49.12	85.84	7.19	82.99
20.20	8.89	101.61	49.18	85.76	6.57	82.8
20.33	8.91	101.63	49.48	85.85	6.68	82.93
20.47	8.26	101.60	49.51	85.76	6.67	82.87
20.57	8.72	101.63	48.59	85.82	6.95	82.98
20.70	8.58	101.61	49.3	85.87	6.83	82.93
20.83	8.51	101.61	49.32	85.71	6.59	82.87
20.97	8.48	101.62	49.54	85.75	6.77	82.86
21.07	8.4	101.63	49.41	85.69	6.65	82.95
21.20	8.53	101.64	48.82	85.83	6.57	82.87

21.33	8.18	101.63	49.38	85.84	6.63	82.95
21.47	8.32	101.61	49.45	85.8	6.9	82.87
21.60	8.09	101.62	49.53	85.86	6.62	82.94
21.73	8.53	101.61	49.47	85.78	6.47	82.92
21.83	9.02	101.64	49.24	85.86	6.89	82.92
21.97	8.37	101.61	49.35	85.79	6.81	82.84
22.10	8.35	101.61	49.59	85.78	6.69	83.03
22.23	8.13	101.60	49.31	85.79	7.02	82.91
22.37	8.7	101.61	49.59	85.77	6.42	82.89
22.50	9.14	101.58	49.22	85.79	6.58	82.88
22.63	7.56	101.61	49.11	85.84	6.68	82.95
22.77	8.02	101.61	49.65	85.8	7.01	82.86
22.90	9.07	101.62	49.59	85.78	7.02	82.91
23.03	8.11	101.61	49.42	85.78	6.68	82.89
23.13	8.38	101.60	49.45	85.69	6.94	82.93
23.27	8.38	101.62	49.29	85.66	6.46	82.95
23.40	8.66	101.60	49.13	85.88	7.26	82.59
23.53	8.74	101.60	49.7	85.86	6.59	82.93
23.67	9.77	101.60	49.27	85.85	6.7	82.91
23.80	8.85	101.62	49.41	85.73	6.62	82.91
23.93	8.84	101.62	49.36	85.85	6.58	82.89
24.10	9.12	101.58	49.47	85.75	6.58	82.88
24.23	9.61	101.60	49.38	85.82	6.98	82.91
24.37	8.77	101.61	49.44	85.71	6.58	82.87
24.50	8.65	101.60	49.7	85.81	6.7	82.82
24.63	9.43	101.62	49.1	85.79	6.7	82.85
24.77	8.59	101.58	49.57	85.75	6.72	82.93
24.90	8.39	101.57	49.47	85.73	6.8	82.93
25.03	8.63	101.62	49.45	85.69	6.62	82.88
25.17	8.51	101.62	49.54	85.71	6.69	82.62
25.30	9.77	101.60	49.6	85.75	6.98	82.89
25.47	8.82	101.63	49.41	85.75	7.07	82.96
25.60	8.68	101.62	48.41	85.71	6.59	82.95
25.73	8.45	101.63	49.42	85.82	6.74	82.88
25.87	8.45	101.60	49.52	85.53	6.39	82.86
26.00	8.2	101.59	49.67	85.84	6.48	82.9
26.17	9.89	101.62	49.49	85.82	6.64	82.81
26.30	8.04	101.60	49.34	85.83	6.72	82.88
26.43	7.89	101.61	49.25	85.81	6.56	82.91
26.57	8.54	101.60	49.34	85.75	6.52	82.85
26.73	8.25	101.59	49.5	85.82	6.85	82.94

26.87	8.19	101.59	49.4	85.7	6.97	82.9
27.00	7.56	101.57	49.57	85.81	6.53	82.86
27.17	8.09	101.57	49.09	85.77	6.33	82.91
27.30	7.59	101.59	49.57	85.78	7.17	82.9
27.43	9.11	101.58	49.49	85.73	6.62	82.71
27.60	7.87	101.59	49.32	85.82	6.76	82.83
27.73	9.61	101.60	49.39	85.83	6.43	82.9
27.87	8.66	101.57	48.9	85.76	6.43	82.92
28.03	7.64	101.57	49.43	85.73	6.97	82.91
28.17	9.77	101.58	49.39	85.78	6.87	82.9
28.33	7.77	101.58	49.25	85.86	7	82.87
28.47	9.6	101.58	49.34	85.75	6.82	82.9
28.63	7.65	101.57	49.67	85.79	7	82.88
28.77	7.76	101.57	49.56	85.72	7.23	82.57
28.93	8.6	101.61	49.54	85.76	7.38	82.89
29.07	8.72	101.56	49.74	85.82	6.72	82.9
29.23	8.47	101.63	49.59	85.71	6.75	82.86
29.37	7.48	101.58	49.33	85.59	6.7	82.89
29.53	10.37	101.56	49.15	85.7	6.59	82.84
29.67	8.49	101.55	48.41	85.81	6.75	82.93
29.83	10.3	101.58	49.48	85.8	7.24	82.87
29.97	10.23	101.56	49.62	85.78	6.74	82.89
30.13	8.1	101.55	49.53	85.87	6.86	82.87
30.27	8.5	101.57	49.18	85.71	6.74	82.95
30.43	8.1	101.57	48.57	85.74	6.27	82.87
30.60	7.82	101.56	49.03	85.55	7.16	82.85
30.73	8.22	101.61	49.49	85.9	6.31	82.88
30.90	8.43	101.60	49.74	85.75	6.33	82.79
31.07	8.02	101.59	49.27	85.79	6.78	82.81
31.20	7.9	101.54	49.15	85.75	6.69	82.65
31.37	8.09	101.53	49.23	85.84	6.78	82.89
31.53	8.22	101.56	49.53	85.7	6.73	82.85
31.70	7.95	101.57	49.48	85.73	6.72	82.89
31.83	7.83	101.57	49.25	85.76	6.82	82.83
32.00	7.94	101.59	49.05	85.78	6.78	82.9
32.17	7.69	101.56	49.25	85.86	6.7	82.89
32.33	7.73	101.55	49.53	85.77	6.81	82.83
32.47	7.92	101.57	49.52	85.77	6.89	82.85
32.63	7.85	101.55	49.57	85.9	6.81	82.82
32.80	9.5	101.56	49.38	85.87	7.28	82.91
32.97	7.81	101.54	49.36	85.7	7.17	82.92

33.13	8.24	101.56	49.24	85.67	6.56	82.9
33.30	8.37	101.54	49.68	85.76	6.79	82.79
33.43	8.01	101.53	49.35	86.05	6.56	82.78
33.60	7.62	101.54	49.12	85.85	6.79	82.89
33.77	7.67	101.53	49.08	85.78	6.7	82.93
33.93	8.28	101.58	49.28	85.44	6.69	82.88
34.10	8.61	101.56	49.26	85.82	7.02	82.9
34.27	7.9	101.57	49.25	85.78	7.14	82.87
34.43	7.53	101.53	49.02	85.86	6.59	82.9
34.60	8.31	101.54	49.4	85.67	6.59	82.84
34.77	7.33	101.52	49.25	85.76	6.74	82.84
34.93	7.78	101.51	49.39	85.8	6.74	82.87
35.10	7.25	101.51	48.74	85.67	6.8	82.85
35.27	7.51	101.56	49.16	85.44	6.56	82.62
35.43	7.84	101.53	49.49	85.14	6.43	82.85
35.60	8.27	101.58	49.47	85.82	7.07	82.82
35.77	7.36	101.55	49.18	85.8	6.39	82.8
35.97	7.96	101.54	49.19	85.72	6.79	82.82
36.13	9.51	101.56	48.93	85.72	6.56	82.91
36.30	8.73	101.55	49.33	85.82	6.78	82.83
36.47	8	101.58	49.47	85.82	6.58	82.85
36.63	7.32	101.51	51.34	85.79	6.4	82.88
36.80	6.9	101.49	49.1	85.77	6.71	82.89
36.97	6.87	101.54	49.28	85.63	6.57	82.84
37.17	8.32	101.53	49.69	85.75	6.72	82.86
37.33	7.63	101.53	49.36	85.79	7.01	82.85
37.50	8.4	101.53	48.35	85.82	6.62	82.84
37.67	8.47	<b>101.53</b>	49.61	85.45	6.74	82.82
37.87	6.77	101.55	49.62	85.88	6.87	82.82
38.03	6.99	101.50	49.24	85.83	6.79	82.81
38.20	9.4	101.51	49.51	85.82	6.88	82.77
38.40	7.32	101.52	49.71	85.8	6.86	82.86
38.57	8.36	101.54	49.62	85.88	6.83	82.84
38.73	7.18	101.55	49.56	85.81	6.63	82.88
38.93	6.54	101.54	49.46	85.85	6.7	82.81
39.10	8.04	101.50	49.64	85.8	6.68	82.78
39.30	8.44	101.51	49.66	85.83	6.57	82.86
39.47	6.64	101.56	49.42	85.86	6.88	82.83
39.63	7.64	101.53	49.41	85.75	7.12	82.82
39.83	8.66	101.54	49.3	85.85	6.84	82.71
40.00	8.16	101.55	49.25	85.85	6.95	82.77

40.20	7.94	101.54	49.37	85.82	7.27	82.84
40.37	8.29	101.53	49.51	85.83	6.28	82.78
40.57	8.37	101.53	49.47	85.75	6.78	82.81
40.73	7.68	101.49	49.01	85.84	6.88	82.87
40.93	7.95	101.52	49.58	85.76	6.49	82.83
41.13	7.89	101.52	49.51	86.06	7.03	82.75
41.30	7.87	101.47	49.67	85.83	6.7	82.8
41.50	7.61	101.53	49.24	85.82	6.61	82.81
41.67	8.54	101.54	49.33	85.83	6.44	82.8
41.87	9.06	101.55	49.59	85.75	6.37	82.87
42.07	7.29	101.53	49.81	85.31	6.63	82.77
42.23	7.69	101.48	49.58	85.53	6.6	82.83
42.43	7.75	101.50	49.32	85.79	6.41	82.78
42.63	7.53	101.49	49.25	85.73	7.22	82.85
42.80	7.82	101.50	49.45	85.83	6.78	82.8
43.00	7.45	101.48	49.16	85.8	6.46	82.88
43.20	7.64	101.49	49.48	85.8	6.38	82.68
43.40	7.53	101.53	49.29	85.8	6.87	82.5
43.60	7.8	101.51	49.39	85.8	6.95	82.82
43.77	7.05	101.55	49.83	85.79	6.84	82.8
43.97	7.23	101.49	49.76	85.82	7.09	82.76
44.17	7.69	101.49	49.23	85.81	6.87	82.82
44.37	7.04	101.52	49.6	85.74	6.99	82.74
44.57	10.02	101.53	49.37	85.81	6.79	82.77
44.77	7.37	101.55	49.2	85.82	6.47	82.8
44.97	10.41	101.53	49.29	85.81	6.66	82.81
45.17	9.83	101.51	49.59	85.78	6.58	82.76
45.37	10.84	101.49	49.76	85.81	7.03	82.79
45.53	8.63	101.48	48.92	85.74	6.36	82.76

**Table A2.6. Line Width Measurement at Different Angles.**

Graphite/Carbon				Silver				Carbon			
0	22.5	45	90	0	22.5	45	90	0	22.5	45	90
61.5	-52.9	50.1	23.4	87.3	99.5	154.3	76.3	5.5	-10.3	6.2	20.6
60.1	-53.6	51.2	23.4	87.6	99.3	155.4	77.4	5.4	-11.4	6.5	20.8
61.3	-52.5	50.6	22.5	88.6	99.4	155.3	76.4	5.5	-10.5	6.4	21.0
61.4	-51.4	51.4	23.6	87.3	99.3	155.6	77.4	6.0	-11.1	6.3	20.6
62.0	-52.6	50.7	22.8	88.6	99.1	156.0	76.0	5.4	-10.4	6.7	20.3

**Table A2.7. Line Raggedness Measurement at Different Angles.**

<b>Graphite/Carbon</b>				<b>Silver</b>				<b>Carbon</b>			
0	22.5	45	90	0	22.5	45	90	0	22.5	45	90
0.003	0.026	0.016	0.009	0.011	0.017	0.011	0.006	0.005	0.015	0.008	0.008
0.003	0.026	0.016	0.009	0.011	0.009	0.011	0.007	0.004	0.015	0.008	0.008
0.004	0.027	0.017	0.01	0.012	0.0016	0.012	0.006	0.006	0.012	0.007	0.007
0.003	0.003	0.018	0.013	0.009	0.0017	0.013	0.006	0.007	0.013	0.009	0.006
0.005	0.026	0.016	0.009	0.011	0.0018	0.011	0.008	0.005	0.015	0.008	0.009