Run-time Ink Stability in Pneumatic Aerosol Jet Printing Using a Split Stream Solvent Add Back System

Arjun Wadhwa
R.I.T

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by

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A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Masters in Science in Industrial and Systems Engineering

Department of Industrial and Systems Engineering
Kate Gleason College of Engineering

Rochester Institute of Technology
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Approved by:

Dr. Denis Cormier
(Department of Industrial and Systems Engineering) (Advisor)

Dr. Scott Williams
(School of Chemistry and Materials Science) (Committee Member)

Dr. Marcos Esterman
(Department of Industrial and Systems Engineering) (Committee Member)
Abstract

Aerosol Jet printing is a non-contact process capable of printing nano–ink patterns on conformal and flexible surfaces. Aqueous or solvent nano–inks are pneumatically atomized by the flow of nitrogen gas. The flow of atomizing gas into and out of the cup leads to evaporation and removal of volatile solvent(s). As the solid loading fraction of the ink increases, the rheological changes eventually lead to instabilities in print output. A potential solution to this problem is to moisten the atomizing ink by running it through a bubbler. In this study, neat co-solvent solutions of ethanol and ethylene glycol at 85: 15 and 30:70 mixing ratios were atomized using nitrogen flow rates ranging from 600 to 1000 ccm. It was observed that ethanol, being the more volatile solvent, was depleted from the neat solution. When using a bubbler solvent add-back system, an excessive amount of ethanol was returned to the neat solution. The rate of solvent loss from an ethanol rich neat solution (80%) was higher compared to an ethylene glycol rich neat solution. A mixture of dry and wet (ethanol moistened) nitrogen gas was used to equalize the rate of ethanol evaporation. Ethanol equilibrium in neat solutions with higher ethylene glycol loading (70%) was achieved with a 40-60% wet nitrogen component while neat solutions with higher ethanol loading (85%) were stable with 85 -90% wet nitrogen gas. The results were validated with copper nano ink with similar co-solvent ratios. The solid content of the ink remained constant over four hours of printing when the optimal dry: wet nitrogen gas ratios were used. Copper ink with 85% ethanol being atomized at 1000 ccm exhibited increase in copper loading (3%) despite the dry: wet solvent add back system.
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1. INTRODUCTION

Functional printing of devices directly onto flexible and conformal substrates is rapidly gaining importance in several industries. For example, aerospace components can be made lightweight by printing interconnecting wires directly onto the circuit boards. Smart packaging can include spoilage sensors, displays, and inductive power coils [1]. Printed nano-materials can improve functionality, reduce weight and reduce material costs. Although plating and etching techniques used in conventional circuit board production are widely used, the choice of substrate materials is limited, and there is great interest in development of more environmentally friendly processing approaches. Rather than plating copper and then selectively etching it away, an alternate approach is to print conducting materials (e.g. copper or silver nano-inks) directly onto the substrate only where it is needed in order to eliminate plating, masking, acid etching, and hazardous waste disposal completely. These printed electronic devices meet essential requirements such as high chemical stability, low hysteresis, low temperature processing, and high resolution [2]. Printed electronics have already found a number of industrial applications. For instance, the packaging industry uses printed electronics for making level detectors, temperature and pH sensors, and printed RFID tags [3] [4].

Direct-write printing has been employed to place functional devices directly onto conformal surfaces to reduce material costs and weight. For instance, Yang et al.[5] ink-jet printed electronic circuits onto flexible substrates and then molded the resulting films around 3D surfaces. This approach allows flexible sheets to be molded onto 3D geometries with a single axis of curvature, such as cylinders. Greater challenges occur when surface curvatures are more complex, such as saddle shapes that would result in wrinkles in the film.

Another approach is to add electronic circuitry onto thermoplastic devices during the injection molding process. This is known as the Molded Interconnect Device (MID) approach that can be done in one of two ways. In the first approach, two types of thermoplastics are molded together, one of which is modified such that it can be plated [6]. The second approach uses Laser Direct Structuring (LDS) of a metal-doped thermoplastic. A laser first etches the required circuit pattern on the formed plastic part. The laser-scribed regions are activated such that copper can be selectively plated in a subsequent processing step. The LDS process is effective, although it is limited for use with special thermoplastic formulations and platable metals (i.e. copper).
Solid Oxide Fuel Cells (SOFC’s) are used in the generation of clean energy from a variety of fuels. SOFC’s can be fabricated into portable devices for providing power. They can also be used in integrated hybrid systems for heat and power generation. Direct-write printing of conductive nano-materials (electrodes) and ceramic nano-materials (as the electrolytes) plays an essential role in the fabrication of SOFC’s [7]. There are several researchers who have investigated printing technologies for SOFC’s that are cited in Section 2.4 of this document.

There arises a need for a system that can effectively print nano-inks onto non-planar conformal surfaces with any composition or geometry. Aerosol Jet Printing (AJP) is a mask-less, non-contact direct-write printing technique that can deposit nano-material patterns onto conformal surfaces. This thesis focuses on the study of long-term solvent loss from a nano-ink during the AJP process. Solvent loss leads to changes in the ink’s physical properties and degradation of print quality that is highly undesirable in a high volume production environment. This thesis uses an experimental approach to quantify the rate of solvent loss in the AJP process. and equalize the rate of solvent add-back to maintain solvent equilibrium in the nano-ink.
2. LITERATURE REVIEW

2.1 Classification of Printing Technologies

Printing technologies can be categorized into two groups based on the method of delivery of ink onto the substrate, which are as follows:

![Diagram of Printing Processes]

While contact printing processes are fast and efficient in their output, they pose the following disadvantages that make them impractical for printing micro scale electronic devices and features:

- **Lack of resolution**: Printing fine pitch electronics required high feature resolution, which can be difficult to achieve by contact printing processes.
- **Conformal printing**: Contact printing processes are limited to two axes translation and are not suitable for three-dimensional material deposition. However, direct write processes such as Aerosol Jet and micro-dispensing have Z-axis translation capabilities.

Non-contact Direct Write printing technologies may be used for printing electronic devices, and the advantages and functionality of the same is explained in Section 2.2.

A summary of the operating principles for contact printing processes is summarized as follows:
Table 1: Summary of Contact Printing Processes.

<table>
<thead>
<tr>
<th>Process Name</th>
<th>Operating Principle</th>
<th>Smallest Feature Size</th>
</tr>
</thead>
</table>
| Screen Printing       | • Screen is a fine mesh on which the pattern to be printed is exposed and the rest of it is sealed off.  
                           • The screen is placed on top of the substrate and ink is poured at one end of the screen.  
                           • A rubber squeegee is moved across the stencil with a constant pressure.  
                           • Ink passes through the pores of the mesh and forms the pattern on the substrate.                                                                 | 50 µm                 |
| [8]                   |                                                                                                                                                                                                                      |                       |
| Gravure Printing      | • Substrate passes between the impression and gravure rollers.  
                           • Gravure cylinder has the pattern etched on its surface in the form of dimples  
                           • The Gravure cylinder carries ink from the reservoir in these dimples and a doctor blade removes any excess ink before it reaches the substrate.  
                           • Ink gets deposited where the pattern comes in contact with the substrate.                                                                                                                                 | 50-60 µm              |
| [9]                   |                                                                                                                                                                                                                      |                       |
| Flexography           | • Similar to gravure printing except the pattern is on a rubber sheet that is wrapped around a cylinder.  
                           • Cylinder is immersed in a reservoir of ink and ink is transferred from the raised patterns onto the substrate.  
                           • Process can be done by using flat sheets instead of cylinders.                                                                                                                                             |                       |
| Offset Lithography[10] | • Complex process with series of rollers.  
                           • Inking roller has the pattern etched such that ink adheres only to the pattern to be printed.  
                           • Ink and water are poured onto the roller and ink only sticks to the pattern impression and not to any other part since ink and water and immiscible.  
                           • Ink is transferred onto a roller with a rubber blanket which then transfers the ink onto the substrate which is held by the impression roller.                               | 10 µm                 |

2.2 Direct Write Printing

In order to print conductive inks directly onto thin flexible and/or conformal surfaces, there is a need for non-contact multi axis processes that are broadly classified into Direct Write (DW) Printing. DW printing is a fast and reproducible technology in which the material is deposited onto a substrate without the need of masking or coating the surface, thus saving on production time and material costs.
There are several definitions of these processes, which are listed as follows:

- Any technique or process capable of depositing, dispensing or processing different types of materials over various surfaces following a preset pattern or layout [11].
- A range of technologies, possibly in reconfigurable short production runs, of two- or three-dimensional functional structures using processes that are compatible with being carried out directly onto potentially large complex shapes [12].
- Fabrication methods that employ a computer-controlled translation stage, which moves a pattern-generating device, e.g. ink deposition nozzle or laser writing optics, to create materials with controlled architecture and composition [13].

Direct write printing has been classified as follows [14]:

![Figure 2: Classification of Direct Write Printing Processes.](image)

Salient features of these processes are:

- Feature widths achieved range from sub-microns to a few millimeters.
• Direct write processes are capable of using inks with a wide range of viscosities, surface energies and particle sizes.
• These processes can deposit a variety of materials such as metals, ceramics, polymers and living tissues in chemically dissolved or dispersion form.

2.2.1 Ink Jet Printing

Ink Jet printing is one of the most widely used digital printing methods for commercial printing and printed electronics. The process can be divided into two modes [11]:

Inkjet printing involves the formation and deposition of a sequence of drops of ink onto a substrate. The droplets then dry or solidify by means of heating, evaporation of solvent or a chemical reaction.

In continuous inkjet printing, a jet of ink is generated by pumping the ink into a chamber where a modulating disturbance, such as piezoelectric force, is applied through a transducer, which breaks up the stream into droplets that then exit the nozzle. A charging electrode surrounds the liquid stream and includes an electric charge on every drop. Drops then pass through a continuous field where they are deflected sideways. Charge can be varied on each drop, and this determines the amount of deflection they undergo in the steady field. Undeflected drops go into the catcher (and are recycled) and deflected drops fall onto the substrate.

Figure 3: Classification of Ink Jet Printing Technology.
In drop-on-demand inkjet printing, a droplet is ejected only when needed (avoiding recycle) by means of a trigger signal. Thermal Ink Jet printing employs a small electric heater that is capable of rapid transient heating. This creates a small bubble of vapor in the ink reservoir pushing the ink into the nozzle. Once the bubble collapses, it draws ink into the cavity, and the process is repeated.

Piezoelectric inkjet printing changes the volume of the ink cavity to generate pressure waves that eject droplets of ink out of the nozzle. Releasing the pressure causes ink to be drawn into the cavity, and the process is repeated.

While inkjet printing generally has much higher printing throughput/speed than single nozzle direct-write printing technologies, its primary limitations are:
- It is limited to extremely low viscosity inks, which limits the solid loading fractions and amount of material that can be deposited per pass.

- Inkjet printing is generally limited to use with planar or nearly planar substrates.

**Figure 5: Drop on Demand Ink Jet Printing**

### 2.2.2 Laser Direct Write Printing

Laser DW printing is the process of laser induced deposition of materials such as metals, ceramics, or polymers without the use of lithography or masking processes. This process finds its application in the biomedical field, as well as photonic crystal and MEMS fabrication. Laser DW printing can be carried out in the following ways:

- Laser chemical vapor deposition
- Laser etching electroless plating
- Laser enhanced or activated electroplating
- Laser consolidation of thin solid films
- Laser induced forward transfer
- Matrix assisted pulsed laser direct write
- Laser induced backward transfer
- Multi-photon polymerization
- Laser contact free trapping and transferring of particles in solution
2.2.3 Flow Based Direct Write Printing

Flow based DW printing makes use of positive pressure from either compressed gas or a positive displacement pump to achieve high precision micro-dispensing of ink through a syringe. Flow based systems provide a continuous output of material when actuated, whereas inkjet systems dispense ink in droplet form. The two most established systems for this process are sold by nScrypt® and MicroPen®.

Salient features of the nScrypt® systems are:

- The nScrypt system allows multi-material mixing and dispensing from the nozzle. Mixing is done before extrusion in this case.
- The syringe is the ink reservoir, and positive air pressure is applied from behind. Accurately controlled air pressure, a precise needle valve opening, and high stage motor resolution leads to precision dispensing of material onto the substrate achieving trace thicknesses from approximately 25 microns to 3 millimeters depending on ink formulation and processing conditions.
- A suction system pulls back residual ink from the nozzle tip during non-printing moves to prevent unwanted dispensing.
- The system is capable of processing inks with viscosities as high as 1,000,000 cP and dispensing volumes as small as 20 pL.
- The gap between the nozzle and substrate plays a major role in the dispensing of the ink and thus the final line width and thickness. For this purpose, a laser profilometer may be used to profile the contours of the substrate accurately.
- Similarly, translation speed also influences line geometry and can range from approximately 0.1 – 300 mm/s.
- Material selection is important since the line geometry is determined by the physical properties of the ink (slurry) used.

Flow-based direct-printing is very attractive in the sense that it can be used with perhaps the widest range of printable materials among all printing processes. The print feature sizes are typically larger than those achievable with other dispensing techniques, and the process is very sensitive to the gap distance between the nozzle and substrate.

2.3 Overview of Aerosol Jet Deposition Process

For applications that require fine pitch and high resolution printing of nano materials, Aerosol Jet printing is a relatively new and novel process. Aerosol Jet printing (AJP) is defined as a non-contact, mask-less
printing process for printing fine pitch structures with the capability to process various inks (conducting and non-conducting) containing nano-particles with sizes ranging from 10 – 700 nm and with a viscosity range from 0.7 – 2500 cP [15].

Salient features of this technology are:

- The deposition nozzle is generally kept at a distance of 3 to 5 millimeters from the substrate, hence the process is not particularly sensitive to the gap distance.
- The process employs room temperature operations that give flexibility in choice of substrates.
- Features can be produced with width ranging from 20 to 200 microns.
- The process can be used to print on conformal 3D surfaces as per the CAD geometry assigned.
- Inks used in the system can have a wide range of viscosities from 0.7 – 1000 cP.

A comparison of this process versus traditional ink jet printing is stated in Table 2: [16]

Table 2: Comparision Between Inkjet and Aerosol Jet Printing Processes

<table>
<thead>
<tr>
<th>Properties</th>
<th>Ink Jet</th>
<th>Aerosol Jet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle Diameter (microns)</td>
<td>10 – 50</td>
<td>100 – 300</td>
</tr>
<tr>
<td>Drop Volume (pico liters)</td>
<td>1 – 8</td>
<td>0.001 – 0.005</td>
</tr>
<tr>
<td>Line Width (microns)</td>
<td>20 – 200</td>
<td>5 – 30</td>
</tr>
<tr>
<td>Ink Viscosity (cP)</td>
<td>10-20</td>
<td>0.7-1000</td>
</tr>
</tbody>
</table>
2.3.1 Process Description

The following process parameters contribute to the aerosol stream formation:

Table 3: Aerosol Jet Printing Process Parameters

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Unit</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomization flow rate</td>
<td>Cubic Centimeter</td>
<td>500 – 1200 (recommended)</td>
</tr>
<tr>
<td>Virtual Impactor flow rate</td>
<td>Cubic Centimeter</td>
<td>400 – 1100 (recommended)</td>
</tr>
<tr>
<td>Sheath Gas flow rate</td>
<td>Cubic Centimeter</td>
<td>30 – 100 (recommended)</td>
</tr>
<tr>
<td>Tube Heater Temperature</td>
<td>Deg C</td>
<td>Room Temperature – 90</td>
</tr>
<tr>
<td>Platen Temperature</td>
<td>Deg C</td>
<td>Room Temperature – 90</td>
</tr>
<tr>
<td>Nozzle Diameter</td>
<td>Microns</td>
<td>150, 200, 300</td>
</tr>
<tr>
<td>Z axis height</td>
<td>Millimeters</td>
<td>0 – 50</td>
</tr>
</tbody>
</table>

Atomization:

Atomization is the process of forming an aerosol stream from the ink reservoir in the atomization cup. An incoming stream of nitrogen gas atomizes the ink and then carries the fine mist of droplets out of the atomization container’s exhaust port. Atomization creates a large droplet distribution. Since the larger
droplets have higher moments of inertia, they are not carried out of the atomization cup with the exhaust stream of nitrogen gas. The exhaust stream carries out the small and medium sized droplets.

Two different atomization technologies are commercially available with the Aerosol Jet process

1. **Pneumatic Atomization**: In this process, the aerosol stream is formed by sheering away the ink from a small orifice by a stream of nitrogen gas flowing perpendicular to the ink level. The amount of incoming nitrogen gas is controlled by a mass flow controller, and hence the amount of ink atomized is controlled. Kumar et al [17] studied the effect of the physical properties of the ink such as viscosity, liquid surface tension, liquid flow rate and air velocity on the droplet size range that was formed.

2. **Ultrasonic Atomization**: The process of disintegrating a liquid sheet into fine droplets on a vibrating surface (having frequency (> 20 kHz) is known as ultrasonic atomization. The size of the droplets formed is controlled by the atomization frequency.

Table 4 compares the salient features of the pneumatic and ultrasonic atomization processes [18]:

<table>
<thead>
<tr>
<th></th>
<th><strong>Pneumatic Atomization</strong></th>
<th><strong>Ultrasonic Atomization</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Works well with ink systems having low vapor pressure (≤ 0.1 mmHg) and high boiling point (&gt;180 deg C) solvents</td>
<td>Works well with inks having high vapor pressure and low boiling point solvents (volatile solvents)</td>
<td></td>
</tr>
<tr>
<td>System can handle high viscosity inks ranging from 0.7 – 1000 cP</td>
<td>System can handle low viscosity ranges from 0.5 – 15 cP</td>
<td></td>
</tr>
<tr>
<td>Particle size can be large (&gt; 50 nm)</td>
<td>Particle size should be small (&lt; 50 nm)</td>
<td></td>
</tr>
<tr>
<td>Examples of materials that can be used:</td>
<td>Examples of materials that can be used:</td>
<td></td>
</tr>
<tr>
<td>● Metal inks (&gt;55% SLF by weight)</td>
<td>● Metal inks (&lt;40% SLF by weight)</td>
<td></td>
</tr>
<tr>
<td>● UV curable epoxies</td>
<td>● Aqueous inks</td>
<td></td>
</tr>
<tr>
<td>● Carbon resistor paste</td>
<td>● Organic semiconductors</td>
<td></td>
</tr>
</tbody>
</table>
The Optomec Aerosol Jet system available in the Earl W. Brinkman laboratory (in the Kate Gleason College of Engineering at the Rochester Institute of Technology) has dual pneumatic atomizers that were used for this study. This process is depicted in Figure 7:

![Diagram: Sectional View of the Pneumatic Atomization Unit](image)

Figure 7: Sectional View of the Pneumatic Atomization Unit
Figure 8: Pneumatic Atomization Head

**Bubbler Assembly:**

Continuous flow of nitrogen gas over the ink surface in the atomization cup leads to solvent evaporation, degrading the ink, which affects the print quality. In order to maintain constant solvent content in the ink, solvent loss can be mitigated by passing the nitrogen gas through a bubbler system prior to its introduction to the atomizing cup. The bubbler contains the solvent present in the ink (generally the more volatile solvent). Dry nitrogen gas enters a sponge-like sparger beneath the surface of the liquid solvent. As the gas bubbles out of the sparger and through the solvent, the solvent wets the gas and moves into the vapor phase. This moist nitrogen gas stream then exits the bubbler and is carried to the atomization unit. The intent is for the solvent vapor that is transferred from the bubbler to the atomization cup to replenish the solvent that is lost from the atomizer during operation of the system.

As of yet, there have been no studies to quantify the amount of solvent that a particular ink loses at a particular process parameter setting. The purpose of this study is to quantify the rate at which solvent is lost from ink during atomization. With that basic understanding, one can then attempt to determine how much solvent is added back into the atomization cup when a bubbler is used.
Virtual Impactor:

The aerosol stream that exits from the atomization cup contains a very high quantity of ink droplets that would immediately clog the nozzle. Moreover, the mass flow of ink is too high for producing high-resolution traces. A virtual impactor (VI) is located just after the atomization unit. The VI has a vacuum inlet that draws away a large part of the aerosol stream. As illustrated in Figure 10, vacuum is applied perpendicular to the direction of flow. The fine droplets with low moment of inertia are carried away with the nitrogen gas stream to an activated carbon filter. The medium size droplets that are too large to be diverted through the VI continue downstream to the deposition nozzle. The removal of fine droplets helps reduce over-spray and satellite formation in the printed lines. The vacuum applied is controlled by means of a mass flow controller on the system’s user interface. The difference between the atomization flow rate and virtual impactor flow rate is the amount of ink that makes it to the deposition nozzle. This is referred to as “Delta P” in this study.
In-flight Tube Heater:

The Aerosol Jet system is capable of processing nano-inks with different viscosities. Lower viscosity inks can flow out on the substrate and distorting the feature being printed. An in-flight tube heater is located before the deposition head. This heats up the droplets in-flight, thus promoting evaporation of some of the solvent content of the ink. The tube temperature is an important process parameter and its effect on line quality will be studied.

Deposition Head:

The aerosol stream is carried from the VI to the ceramic deposition nozzle through polypropylene or polyethylene tubing with an internal diameter of 1/8 of an inch. The deposition head has a sheath gas of nitrogen which pinches, or aerodynamically focuses, the aerosol stream as it enters the ceramic nozzle. The sheath gas flow rate can be controlled through an independent mass flow controller (unit: ccm). The nozzles typically used have internal diameters of 150, 200 or 300 microns. The formation of the aerosol stream is a continuous process. To make complex patterns that require breaks or step overs, a mechanical shutter attached to a stepper motor (known as the drip catcher system) obstructs the flow of the aerosol stream to the substrate when deposition needs to be stopped. This is illustrated in Figure 11.
Figure 11: Sectional View of the Deposition head and catcher assembly

Figure 12: 200 micron ceramic nozzle

**Heated Platen:**

The moving substrate platen is capable of translation in the X and Y directions. The substrate is secured onto the platen by means of vacuum. The X and Y translation motors have a step resolution of 1/4000 of an inch that allows the system to have high precision motion control while printing micro-features. The Z height of the nozzle is adjusted relative to the platen. The nozzle is generally placed 3 – 5 millimeters above the substrate upon which ink is printed. The platen is equipped with a heater system that maintains the substrate at an elevated temperature to facilitate the drying of ink.
The operation of the AJP system can be summarized as follows:

**Figure 13** Aerosol Jet Printing Process Schematic

- **Nitrogen Cylinder**: Provides pressurized nitrogen for atomization and sheath gas.
- **Bubbler Assembly**: Used for atomization of the ink.
- **Pneumatic atomization**: Transfers the aerosol into the deposition head.
- **Virtual Impactor**: Reduces fine aerosol particles.
- **In-flight tube heater**: Heats the aerosol stream inflight.
- **Sheath Nitrogen Gas inlet**: Supplies sheath gas to focus the aerosol stream.
- **Deposition Head**: Controls the direction and concentration of the aerosol stream.
- **Catcher system**: Collects any unused material.
- **Substrate**: Receives the deposited material.

**Figure 14**: AJP process flowchart

- Atomization of Ink
- Extraction of exhaust aerosol stream
- Transfer of aerosol into deposition head
- Inflight heating of aerosol stream
- Aerodynamics focusing of stream by sheath gas
- Deposition of stream onto substrate through nozzle
2.4 Real World Applications of AJ Printing

Several researchers have used the AJP system to fabricate devices such as solid oxide fuel cells, conducting pads, fine pitch electronics etc. The literature describing some of these applications is summarized in the Table 5.

Table 5: Summary of application of Aerosol Jet Printing

<table>
<thead>
<tr>
<th>Author</th>
<th>Objective</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rui Liu et al. [19]</td>
<td>Carbon based Field Effect Transistors were printed</td>
<td>Sheet Resistance obtained was in the range of $600 - 800 \ \Omega \ \text{m}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>High and low concentration Graphite Oxide (GO) inks were used and a layer of soluble MWNT was printed to form a conducting film.</td>
<td>Surface coverage and flatness obtained was good.</td>
</tr>
<tr>
<td></td>
<td>AJP was used to print the source and drain electrodes.</td>
<td>Feature resolution of $40 - 80$ microns was obtained.</td>
</tr>
<tr>
<td></td>
<td>Samples were reduced with hydriodic acid for 10 min at 100 deg C</td>
<td>Field Effect mobility of the FET was recorded to be $\sim 350 \ \text{cm}^2 \ (\text{V} \cdot \text{s})^{-1}$</td>
</tr>
<tr>
<td>A. Mette et al. [20]</td>
<td>Process was used to print the first layer for a contact structure on a silicon solar cell.</td>
<td>Fine lines of 14 micron width were obtained.</td>
</tr>
<tr>
<td></td>
<td>Modified screen printing organic metal ink was used for this application</td>
<td>Energy conversion efficiency of 17.8% was obtained.</td>
</tr>
<tr>
<td>Palvi Kopola et al. [21]</td>
<td>Indium Tin Oxide is replaced with a PEDOT: PSS layer in combination with a silver grid by means of AJP.</td>
<td>For a single pass, coverage of 5.8 – 11.9% was obtained with sheet resistance of 8.9 – 1.5 $\Omega$.</td>
</tr>
<tr>
<td></td>
<td>Optimizing the printing parameters helps determine the coverage and effective sheet resistance.</td>
<td></td>
</tr>
<tr>
<td>Mary Sukeshini et al. [22]</td>
<td>Printing of Anode supported layer of SOFC using AJP</td>
<td>Material Deposition rate (mg / min) for both materials with different combinations of atomization and VI flow rates were examined.</td>
</tr>
<tr>
<td></td>
<td>Dual pneumatic atomization system was used to make a graded layer or YSZ and NiO</td>
<td>The cells had stable voltages around 1.2 V with a maximum power density of 200 mW / cm$^2$.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Although performance was low, obtaining functional grading and reproducibility make AJP a viable option for this technology.</td>
</tr>
<tr>
<td>Chunhe Yang et al. [23]</td>
<td>Preparation of active layers of polymer solar cells by AJP of organic inks.</td>
<td>Optimal results were obtained by using poly (3 – hexyliophene) and a $C_{60}$ providing coverage of 67% and power conversion</td>
</tr>
</tbody>
</table>
were tested while preparing the organic inks
- Effect of surface treatment by heat and solvent vapor annealing were also studied.

### Rui Liu, Haiyan Ding et al. [16]
- Platinum decorated Single walled carbon nano tubes (SWCNT’s) are prepared using the AJP process.
- Low material consumption, and application of nano particles makes AJP a feasible and reproducible process for printing SWCNT’s

### J. Hoerber and C. Goth et al. [2]
- Aerosol Jet Printing is an interesting approach to apply circuit tracks on three-dimensional thermoplastic circuit carriers used for Molded Interconnect Devices.
- Four thermoplastics were used as substrates (PA6.6, spec PA6, PA6, PBT/ASA) having different surface roughness.
- Silver nano-inks were used for the printing process (Bay Ink TP S 50 and Cabot CSD 66)

### Andreas Lesch, Dmitry Momotenko
- Soft linear gold microelectrode arrays for high throughput scanning electrochemical microscopy (SECM) imaging were fabricated

### Efficiency of 2.53% without surface treatment.
- Also, using PCBDTPP and C_{70} devices provided 3.92% power conversion efficiency for 0.03 cm² and 3.14% for 1 cm².
- Stable aqueous solutions of the SWCNT’s are printed onto the substrate with various passes.
- It was observed that the density of the SWCNT’s networks increased with increasing the number of passes.
- Controlling the number of layers controlled the electrical properties and homogenous nature of the layers.
- Three samples of each substrate were created by grinding, milling and polishing the samples.
- Eight trace lines were printed on the surfaces of the plastics and the effect of the surface roughness on the pitch of the printed lines and the resistance obtained was studied after sintering at 80 deg C for 240 min.
- 50 and 100 micron pitch lines produced the lowest resistance while 300 micron pitch produces pinholes in the printed lines.
- Thermal shock treatment (at 0, 250, 500, 750 and 1000 deg C) resulted in no change in resistance for 0, 50 and 100 micron pitch printed lines while there is a marginal increase in resistance for 300 micron pitch lines.
- Exposure to humidity heat loading had little effect on the electrical conductivity of all the samples.
- Sintering and thermal shock treatment improved the adhesion to the substrate and humidity heat loading has little to no effect.

---

High throughput SECM imaging in contact mode of a large sample area with resolved details in the micrometer scale was achieved.
2.5 Process Parameter Characterization

Aerosol Jet printing technology is a relatively new and novel technology for making high precision printed electronic devices on two-dimensional and conformal surfaces. Several researchers have put this technology to use as illustrated in Table 5. The process of ink atomization and deposition onto a substrate is a complex process with several process parameters as well as ink properties that determine the quality of the printed lines. Process characterization is determining best-fit process parameter settings for a particular application.

Goth et al. [15] describe the use of AJP for printing of fine pitch electronics. The authors:
• Printed electronic features onto a 3D printed object (termed as 3D-MID prototyping). The part was first manufactured using Stereolithography, and the fine pitch electronic components were printed by Aerosol Jet Printing.
• Studied the effect of AJP process parameters and sintering parameters on the line width, thickness, resistivity and adhesion to substrate.
• Used Cabot CSD-32, Bay Ink TP S 50, MicroCat conductive inks.
• Worked with Somos Nanotool, Accura Bluestone, PPS-GF40, and PBT-PET substrates.

The PCM process parameters for the Optomec system were varied, and their effect on the line width and thickness were studied.

• Line width increased with increase in atomization and sheath flow rates (keeping a constant Delta P of 20 ccm) and increasing the sheath pressure.
• Line width and height increased with increasing the number of passes.
• Line width decreased with increasing the translating speed.

Results for each ink used are summarized in Table 6.

Table 6: Results obtained by C. Goth et al

<table>
<thead>
<tr>
<th>Ink Used</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>MicroCat</td>
<td>• Trace width: 90 -130 microns depending on the substrate used and 200 microns after plasma treatment.</td>
</tr>
<tr>
<td></td>
<td>• Feature thickness: 0.2-0.4 microns</td>
</tr>
<tr>
<td></td>
<td>• Resistivity: 4 – 4.5 µΩcm depending on the substrate.</td>
</tr>
<tr>
<td>Bay Ink TP S 50</td>
<td>• Trace width: 62 – 68 microns depending on the substrate and up to 87 microns after plasma treatment.</td>
</tr>
<tr>
<td></td>
<td>• Feature thickness: 1.1 – 2.1 microns and 1 – 1.5 microns after plasma treatment</td>
</tr>
<tr>
<td></td>
<td>• Resistivity: 5.75 µΩcm.</td>
</tr>
<tr>
<td>Cabot CSD-32</td>
<td>• The ink de-wetted the substrates by forming droplets and flakes.</td>
</tr>
<tr>
<td></td>
<td>• After plasma treatment trace width ranged from 67- 110 microns with no change for Accura Bluestone.</td>
</tr>
<tr>
<td></td>
<td>• Feature thickness: 0.8 – 1.4 microns before plasma treatment and 0.3 – 0.7 microns after.</td>
</tr>
<tr>
<td></td>
<td>• Resistivity: 27 µΩcm.</td>
</tr>
</tbody>
</table>

M. Sukeshini et al. [27] investigated the use of AJP for printing solid oxide fuel cell layers. The cathode and electrolyte layers of Solid Oxide Fuel Cells were printed using Aerosol Jet Printing. A composite of YSZ (Yttrium Stabilized Zirconia) and LSM (Strontium doped lanthanum manganate) was used for printing the cathode and electrolyte interlayers on standard anode supported substrates by means of a dual atomization system.
Process parameters used were:

- Atomization flow rate: 1500 ccm
- Virtual Impactor flow rate: 1350 ccm
- Sheath gas flow rate: 3000 ccm
- Number of passes: 20
- 1:1 mixing ratio of both materials.

The effect of changing Z height (distance between the substrate and deposition nozzle) and Delta P (difference in flow rate of nitrogen gas between the atomizer and virtual impactor by keeping atomization constant) on the amount of material deposited was studied.

- The Z height was varied from 5 to 12 mm, and the results were illustrated by means of Scanning Electron Microscopy images for each sample.
- For YSZ, it was observed that as Delta P increased, the amount of material deposited increased to a maximum and then decreased because the density of droplets having the optimum size and momentum decreased.
- For LSM, the deposition rate was sluggish, and a definite maximum could not be determined.

This preliminary study indicated that the rate of material deposition could be controlled by means of controlling the process parameters for AJP. The AJP cathode and electrolyte interlayers provided a stable voltage of 1.16 – 1.20 Volts at 700 – 850 Deg C.

Verheecke et al [28] studied the use of AJP to print silver interconnects for embedded electronic applications. The objective of this research was to determine a process parameter window that influences the geometry, electrical properties and adhesion of printed silver lines. The researchers found that:

- Controlling process parameters and ink formulation helped control the printed line quality and minimize over spray. Also, surface preparation and cleanliness prevented contamination and helped reduce the formation of over sprays.
- Cabot CSD-32 silver nano-ink was used for printing the conducting lines. The process parameters used were:
  - Atomization flow rate range: 550 – 800 ccm
  - Delta P range: 20 – 40 ccm
  - Sheath gas flow rate range: 20 – 110 ccm
- Nozzle Diameter: 150 microns
- Z height: 3 mm
- Platen Temperature: 80 Deg C
- Ink Temperature: 22 – 37 deg C
- Tube heater Temperature: 22 – 37 deg C
- Translation speed: 1 – 5 – 10 mm/sec

- The quality of the printed lines was rated on a scale of 1 – 10 based on visual inspection, and a model for determining the rough line quality was developed.

- Line width and edge smoothness were used as the parameters in determining a 3D scatter plot to estimate the optimum process window to obtain the desired line quality.

**Optimization of Aerosol Jet Printing for High Resolution, High Aspect ratio Silver lines.**
Mahajan et al [28] specifically studied AJP of high aspect ratio conductive silver lines. UTDAg40X (UT Dots Inc.) silver nano-ink was ultrasonically atomized, and the effect of process parameters on the line quality (thickness and width) was studied.

Process parameters considered were:

- Focusing ratio (Sheath gas flow rate / carrier gas flow rate)
- Nozzle diameter
- Translation speed
- Carrier gas flow rate

The effect of varying each process parameter on the width and thickness of the printed line and the resistance per unit length was plotted. A rough process window (of carrier gas flow rate, focusing ratio and stage speed) with the least over-spray and good line quality was determined from the previous plots. It was observed that line width decreased with an increase in the focusing ratio and stage speed. Line thickness increased with increase in the focusing ratio, but it decreased with increasing stage speed.

**2.7 Current Challenges**

In a production environment, nano-ink printing systems must be capable of consistently printing with known and stable process parameter values to maintain repeatability and high quality standards. Most nano-inks are colloidal dispersions in a solvent (single solvent or co-solvent). Surfactants are optionally included to lower the surface tension of the ink, and dispersants are often used to prevent particular coagulation. Ink manufacturers select solvent systems depending on the application the ink will be used
for. For example, in order to achieve small feature sizes (20 microns or below) nano-inks contain a high percentage of the high volatility solvent; this promotes fast drying of the aerosol droplets in flight leading to narrower width of ink deposition. Conversely, for coating and low porosity applications, the low volatility solvent is in higher percentage; leading to slower drying of the ink on the substrate, facilitating uniform ink spread.

Barnes et al [29] classified commonly used solvents by ink manufacturers into two categories (High and Low volatility) depending on their rate of evaporation.

Table 7: Classification of Solvents as Per Volatility

<table>
<thead>
<tr>
<th>Material</th>
<th>Vapor pressure @ 20°C, mmHg</th>
<th>Evaporation rate @ 40°C, % mass loss per min</th>
</tr>
</thead>
<tbody>
<tr>
<td>GROUP 1: High Volatility Solvents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopropyl Alcohol</td>
<td>32.40</td>
<td>1.85</td>
</tr>
<tr>
<td>DI water</td>
<td>17.54</td>
<td>0.39</td>
</tr>
<tr>
<td>Amyl Acetate</td>
<td>4.00</td>
<td>0.85</td>
</tr>
<tr>
<td>GROUP 2: Low Volatility Solvents</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMP</td>
<td>0.3</td>
<td>0.036</td>
</tr>
<tr>
<td>DEGMEA</td>
<td>0.1</td>
<td>0.018</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>Terpineol</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>DEGBE</td>
<td>0.01</td>
<td>0.008</td>
</tr>
<tr>
<td>Texanol</td>
<td>0.01</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Long term nano-ink stability within the Aerosol Jet atomization cup while printing is strongly affected by solvent evaporation. When a nano–ink is atomized, the flow of nitrogen gas over the ink surface in the atomizing cup causes a loss of solvent through evaporation. Additionally, during atomization the larger droplets have a higher moment of inertia and hence fall back into the ink reservoir; since droplets have a very large surface area to volume ratio, solvent evaporation is further increased. This is depicted in Figure 15.
As solvent is lost over time, the physical properties of the ink such as viscosity and solid loading fraction change. Prolonged solvent evaporation eventually leads to ink that is so dry that further printing is difficult. Sludge formation at the bottom of the atomization cup and ink sludge deposition on the inside walls of the virtual impactor assembly, deposition head and nozzles as depicted in Figures 16, 17 and 18 can occur if excessive ink drying is not prevented.

Figure 16 shows silver ink sediments at the bottom of the atomization cup on the left and copper ink deposited on the outlet of the atomization cup on the right.
Figure 17: Clogging In Virtual Impactor

Figure 17, shows clogging in the exit point of the virtual impactor on the left and copper ink deposition on the internal components of the virtual impactor on the right.

Figure 18: Clogging In the Deposition Nozzle

Figure 18, shows balling up of copper ink on the tip of the nozzle, which disrupts the aerosol flow. The right image shows an internal view of a nozzle with ink deposits on the inside walls. This causes turbulence in the aerosol stream as it passes through the nozzle leading to over spray formation. The effect of clogging is also reflected in the quality of the printed feature, which is depicted in Figure 19. Periodic pulsing in the aerosol stream can be caused by a number of different factors, one of which is nitrogen streaming that dislodges the accumulated ink in the tubing system. This sudden change in feature dimensions adversely affects the feature resolution and bulk conductivity.
One proposed method to compensate for the loss of solvent from the atomization cup is through wetting of the incoming nitrogen gas with solvent vapors in a bubbler add-back system prior to the atomization cup as previously described. The idea is that moist atomizing gas will "add back" solvent into the atomizing cup in an attempt to compensate for the solvent loss due to atomization. To date, the effectiveness of this solvent add-back approach has not been quantitatively assessed. The aim of this thesis is to study the impact of the solvent add-back approach on ink stability, and to then make recommendations on further process enhancements.

2.6 Research Scope

The recent work that has been summarized in this chapter illustrates the evaluation of a process parameter window for optimal quality of printed features specific to the conductive ink(s), substrates, or application being studied. However, variability in the ink properties over print time has a severe effect on the desired output. Industrial applications require repeatability of printing, which is not yet well established with the Aerosol Jet printing process.

The bubbler system replenishes the solvent in the ink system, but the rate of solvent loss and the rate of feedback has not yet been quantified. The purpose of this study is to quantify the rate of loss and feedback of the more volatile solvent, and to attempt to establish equilibrium between the two to maintain a constant ratio of co-solvents throughout the printing time.
3. EXPERIMENTAL METHODOLOGY

3.1 Research Objective
The purpose of this study is to quantify the rate of solvent loss from a co-solvent neat solution system during Aerosol Jet printing. We will also quantify the rate of solvent add-back achieved when nitrogen atomizing gas is passed through a bubbler. The ultimate research objective is to equalize the rate of solvent loss and add-back, and to experimentally verify the best parameter settings to maintain co-solvent equilibrium in the atomization cup.

3.2 Materials
Commercial ink manufacturers generally keep their formulations a trade secret. Moreover it is difficult to accurately quantify the change in solid loading fractions of ink over time. In this research, a “neat solution” (e.g. pure co-solvent ink without any nanoparticles) is therefore used whose composition is known and whose index of refraction can be quickly and accurately be measured when subjected to various process parameter settings. It is assumed here that the nano-particles, surfactants and dispersants that are present in a nano-ink have relatively low effect on the evaporation rate of solvents in the inks. Hence a stripped down version of a conventional nano-ink is used for ease of experimental quantification.

In order to study Aerosol Jet ink stability as a function of process parameter values, two types of neat co-solvent solutions of ethylene glycol (lower vapor pressure) and ethanol (higher vapor pressure) were prepared. This co-solvent blend is used in a number of commercial nano-inks. The low volatility neat solution consisted of 30 wt.% ethanol and 70 wt.% ethylene glycol. The high volatility neat solution consisted of 85 wt.% ethanol and 15 wt.% ethylene glycol.

For validation purposes; commercially made copper nano inks (prepared by Intrinsiq Materials, Rochester, NY) using ethylene glycol and ethanol as the co-solvents were prepared. Two inks were prepared including a more volatile ink with approximately 80 wt.% ethanol and 20 wt.% ethylene glycol, and a less volatile ink with approximately 20 wt.% ethanol and 80 wt.% ethylene glycol to establish solvent equilibrium over both extremes of ink volatilities.

3.3 Proposed Approach
The experimental approach was divided into two stages.

1. Rate of solvent loss, add-back and optimal bubbler settings determination with the neat solutions
2. Testing solvent equilibrium for the copper inks using optimized process parameters from Part 1.

Stage 1: Experiments with Neat Solutions

A. Solvent Loss

1. Co-solvent mixtures of ethylene glycol and ethanol were prepared as described in Section 3.2.

2. The neat solution was atomized in the pneumatic atomizer with a nitrogen flow rate of 600 ccm and the virtual impactor set to 575 ccm nitrogen flow to maintain a constant Delta P of 25 ccm for 210 minutes (8 data points).

3. Approximately 0.5 ml of neat ink solution was withdrawn directly from the atomization cup at 30-minute intervals using a 6 inch long, 0.125 inch diameter stainless steel needle through an inlet port sealed with a septa.

4. An Abbe refractometer was used to measure the refractive index of the sample. Three repeats per sample were measured and the average values were reported.

5. It is assumed that the neat solution follows the rule of mixtures (i.e. the refractive index of the neat solution is proportional to the mixing ratio of the two solvents).

6. The refractive index of the sample was converted to ethanol wt.% by:

\[
\%\text{Ethanol} = \frac{RI_{EG} - RI_S}{RI_{EG} - RI_{Eth}}
\]

Equation 1: Converting refractive index to ethanol wt.%

Where,

\(RI_{EG}\) = refractive index of ethylene glycol (=1.4293)

\(RI_S\) = refractive index of ink sample extracted from cup at any given time interval

\(RI_{Eth}\) = refractive index of ethanol (=1.3616)

7. The average refractive index was plotted against time to observe the change in solvent content with time.

8. Steps 1-5 were repeated again with 700, 800, 900 and 1000 ccm nitrogen atomization flow rates and a constant Delta P of 25 ccm for 210 minutes.
B. Solvent Add Back

9. The bubbler system was connected between the nitrogen source and atomization cup such that the incoming nitrogen gas would be wetted by ethanol vapors.

10. Steps 1-6 were repeated for 600 and 1000 ccm atomization flow rates, this time with the bubbler in place.

11. Results from parts A and B for 600 ccm and 1000 ccm were plotted and compared.

C. Bubbler Optimization

During experimentation, it was found that a 100% bubbler system actually added too much ethanol into the atomization cup under certain conditions. It was determined that a method was needed to reduce the ethanol vapor content coming in. The solution was to use two incoming nitrogen gas streams – one moist from a bubbler, and one dry. These two streams were merged into a single nitrogen gas stream by means of a Y connector and static mixer. By independently controlling the mass flow rates of the wet and dry nitrogen streams, it become possible to regulate the overall ethanol content in the nitrogen gas. The following steps were followed to determine the optimal wet: dry ratio of nitrogen gas.

12. Both the low volatility neat solution (30 wt.% ethanol and 70 wt.% ethylene glycol) and the high volatility neat solution (85 wt.% ethanol and 15 wt.% ethylene glycol) were atomized at 600 and 1000 ccm atomization flow rates at various wet: dry nitrogen ratios as listed in Table 8.

<table>
<thead>
<tr>
<th>Combination No</th>
<th>% wet nitrogen gas</th>
<th>% dry nitrogen gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>

13. Ethanol wt.% graphs were plotted for both the high and low volatility neat solutions being atomized at 600 and 1000 ccm.

14. Root Mean Square (RMS) ethanol wt. % values for each experimental run were calculated.
15. For each experimental run, RMS – average ethanol wt.% (at time = 0) versus % wet nitrogen gas were plotted.

16. The % wet nitrogen value at which the RMS – average ethanol wt.% (at time = 0) values closest to zero were selected as the optimal values for each experimental run. Simply put, this was the % wet nitrogen value that gave a stable ink whose ethanol content remained steady.

Stage 2: Validation with Copper Nano Ink

17. Copper nano-inks fabricated by Intrinsiq Materials as mentioned in Section 3.2 were printed using optimum results obtained from the Stage 1 bubbler optimization trials.

18. Approximately, 0.5 ml of ink was withdrawn from the atomization cup at 30 minute intervals for 4 hours, and the solid loading fraction of each sample was measured using a TA Q2050 rheometer.

19. Solid loading fraction was plotted against time to determine change from original loading fraction at time = 0.

3.4 Tools Used

Hardware:

- Optomec® Aerosol Jet Deposition System.
- Fisher Scientific 60 Sonic Dismemberator (Ultrasonic mixer).
- Branson 5510 Ultrasonic Cleaner
- T.A Q2050 Rheometer
- Bausch and Lomb Abbe Refractometer

Nano Inks: Intrinsiq Materials Copper nano-inks.

Substrates: Kapton.
4. EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1 Ethanol Add-Back Simulation

Using ethanol as a representative solvent with an atomizing cup pressure of approximately 10 psi (69 kPa), Figure 19 illustrates the loss of ethanol from the atomizing cup via evaporation at different nitrogen flow rates and temperatures. This is obtained by using a mass flow estimation Equation 2:

\[
Q_E = Q_{N2} * \left( \frac{P_E}{P_T - P_E} \right)
\]

Equation 2: Determining Mass Flow Rate of Ethanol at a Particular Atomization Flow Rate.

Where,

- \( Q_E \) = mass flow rate of solvent vapors (ccm)
- \( Q_{N2} \) = mass flow rate of atomizing gas (ccm)
- \( P_T \) = total pressure (kPa)
- \( P_E \) = vapor pressure of ethanol (kPa)

The vapor pressure of ethanol is dependent on temperature. Since all experiments were run at room temperature, \( P_E \) has been calculated at 25 °C for all cases. The vapor pressure is calculated using Antoine’s equation (Equation 3):

\[
P_E = 10 ^ {(A - B / (C + T))}
\]

Equation 3: Antoine’s Equation

Where,

- \( P_E \) = vapor pressure of ethanol (kPa)
- \( A, B, C \) = Antoine’s constants dependent on temperature determined from Table 9.
- \( T \) = process temperature in °C

<table>
<thead>
<tr>
<th>No.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>( T_{\text{min}} ) [°C]</th>
<th>( T_{\text{max}} ) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.20417</td>
<td>1642.89</td>
<td>230.3</td>
<td>-57</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>7.68117</td>
<td>1332.04</td>
<td>199.2</td>
<td>77</td>
<td>243</td>
</tr>
</tbody>
</table>

Table 9: Antoine’s Equation Constant Values
Since the vapor pressure of ethylene glycol is significantly lower than that of ethanol, the rate of ethylene glycol loss during atomization is approximately 1% of that of ethanol. In this study, it was therefore assumed that the rate of ethylene glycol loss was not significant. In co-solvent inks with both low and high vapor pressure constituents, one can effectively concentrate on the high vapor pressure solvents when trying to control ink stability.

Figure 19. Ethanol Flow Rate Versus Temperature Curve at Different Atomization Flow Rates

4.2 Baseline Solvent Loss Rate Without Solvent Add-Back

The rate of solvent loss for each solution was first determined by atomizing the neat solution at different atomization flow rates (600 – 1000 ccm) without the bubbler add-back system (i.e. with dry nitrogen). The refractive index of the neat solution was measured at 30 minute intervals for 3 hours and 30 minutes in order to determine the weight percentage of ethanol remaining. Refractive index values measured while atomizing at 600 ccm are shown in Table 10. As expected, the neat solution loses ethanol, and hence the ethanol wt.% reduces. The same experiments were repeated at 600 – 1000 ccm atomization flow rates for both low and high volatility inks. Figure 20 shows results of experiments for the low volatility and high volatility inks respectively run without the solvent add-back system.
Table 10: Refractive Index and Weight Percent of Ethanol for a 30% Ethanol 70% Ethylene Glycol Co-Solvent Mixture Atomized at 600 ccm Flow Rate Without Bubbler Add-Back

<table>
<thead>
<tr>
<th>TIME (min)</th>
<th>REFRACTIVE INDEX</th>
<th>ETHANOL wt.%</th>
</tr>
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<td>R2</td>
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<td>1.4165484</td>
<td>1.4165483</td>
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<td>1.417549</td>
</tr>
<tr>
<td>60</td>
<td>1.419495</td>
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</tr>
<tr>
<td>90</td>
<td>1.420501</td>
<td>1.4205000</td>
</tr>
<tr>
<td>120</td>
<td>1.421506</td>
<td>1.4215507</td>
</tr>
<tr>
<td>150</td>
<td>1.422514</td>
<td>1.4225512</td>
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<tr>
<td>210</td>
<td>1.4255224</td>
<td>1.425523</td>
</tr>
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</table>

Figure 20. Weight Percent of Ethanol Versus Time Plot for Atomization of a 30% ethanol 70% Ethylene Glycol Co-Solvent Mixture Without Bubbler Add-Back
Figures 21 and 22 plainly demonstrate that atomization with dry nitrogen led to substantial ethanol loss in a relatively short amount of time (3½ hours). For the 30% ethanol ink, nearly half of the ethanol was lost. In practice, Aerosol Jet printed nanoparticle inks include blends of low and high vapor pressure co-solvents. The high vapor pressure solvents (e.g. ethanol) allow droplets of ink to dry rapidly on the substrate. As the high vapor pressure co-solvent is depleted in the ink, the drying speed and surface energy of the ink changes – sometimes dramatically. Practically speaking, this means that the quality of the printed lines, as indicated by line width, thickness, and over-spray, will change as the high vapor pressure solvent is depleted. Figures 21 and 22 point towards a strong need for an alternative approach to atomization with high vapor pressure co-solvent blends. The aforementioned solvent add-back system is a relatively simple approach.

4.3 Solvent Add-Back Rate Using A Bubbler

In order to quantitatively assess effectiveness of the solvent add-back system on ink stability, the next set of experiments were run using the solvent add-back system to determine the effectiveness of this technique at maintaining a constant volume percentage of ethanol in the neat solution. The bubbler contained the more volatile ethanol, since the rate of evaporation of ethylene glycol at room temperature
is substantially lower than that of ethanol. The rate of solvent loss for each solution was determined by atomizing the neat solution at different atomization flow rates (600 – 1000 ccm) using the bubbler add-back system (i.e. saturated nitrogen gas). The refractive index of the neat solution in the atomizing cup was measured at 30 minute intervals for 3 hours and 30 minutes in order to determine the weight percentage of ethanol remaining. Figures 23 and 24 show results of experiments for the 30% and 85% ethanol inks respectively at 600 (low flow) and 1000 (high flow) ccm nitrogen atomization flow rates respectively. The dry nitrogen (no solvent add-back) results are also plotted for comparison.

Figure 22. Weight Percent of Ethanol Versus Time for Atomization of 30% Ethanol 70% Ethylene Glycol Co-Solvent Mixture With Solvent Add-Back

Figure 23. Weight Percent of Ethanol Versus Time for Atomization of 85% Ethanol 15% Ethylene Glycol Co-Solvent Mixture With Solvent Add-Back

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Figure 23 shows the ethanol concentration for the low ethanol (30 wt.%) solution. The ideal outcome is obviously a horizontal line indicating that the ethanol concentration remains constant over the 3½ hours of atomization. At relatively low ethanol concentrations shown in Figure 23, the rate of ethanol loss without solvent add-back was essentially the same at both low (600 ccm) and high (1000 ccm) nitrogen atomization flow rates. When the nitrogen gas was passed through the bubbler on its way to the atomizing cup, Figure 23 illustrates that the ethanol concentration actually increased. Under these experimental conditions, more ethanol was transferred to the atomizing cup than was lost during atomization.

Figure 24 plots the same information for the high (85%) ethanol ink solution. When the ink consists primarily of a high boiling point solvent, that solvent is rapidly lost during atomization. As expected, the rate of ethanol loss with dry nitrogen is greatest at high atomization flow rates (1000 ccm). When the solvent add-back bubbler technique is used, the ethanol concentration is nearly stable. The fact that the solvent add-back technique is able to compensate for the loss of high boiling point solvents during atomization is very encouraging. Figure 23, however, points out the need for further development work to overcome excessive solvent add-back under certain printing conditions.

It is worth commenting on the fact that Figure 23 indicates that the rate of ethanol add back at a 600 ccm nitrogen atomization flow rate was higher than the rate of add back at 1000 ccm nitrogen flow rate. This may seem counterintuitive, since one would think that bubbling nitrogen through ethanol solvent at higher flow rates would transfer more solvent to the atomization cup. There are several possible explanations for this phenomenon.

Kazakis et al. [30] observed that the mechanism of bubble formation and initial bubble size distribution (in the bubbler add back system) from a metal sparger submerged under a liquid strongly depend on the liquid properties, sparger design and gas flow rate. A sparger is a fine pore sponge like structure that allows maximum contact between the gas and liquid phase. Two stainless steel spargers were used in the experimental setup. In this study, all physical properties of ethanol and sparger mean pore diameter were fixed; hence the mass flow rate of the incoming nitrogen gas governed the bubble size formation.

Further, the size distribution of bubbles changes as the bubbles rise in the liquid column (3 – 40 cm tall) after detachment from the sparger surface due to the influence of viscosity and surface tension [31]. However, the height of the ethanol column above the sparger surface is approximately equal to or less than 3cm, hence the initial mean Sauter diameter $d_{32}$ (unit: meters) is considered as the average bubble diameter. It is observed that as the mass flow rate of nitrogen gas increases, more pores in the sparger are activated and hence more bubbles are formed. According to Equation 3, the capillary pressure is smaller for large pores, hence at low gas mass flow rates (600 ccm), only large pores are activated producing
larger bubbles than one would observe at higher gas flow rates. This is known as a homogeneous regime where the mean bubble diameter distribution is small. Larger bubbles are also more buoyant and will rise through the solvent more quickly, effectively reducing contact time between the gas and liquid for wetting / mass transfer.

\[ \Delta p = \frac{2\sigma l}{r_p} \]


Where,
- \( \Delta P \) = Capillary pressure
- \( \sigma L \) = Surface tension of the liquid
- \( r_p \) = Pore radius (microns)

As the mass flow rate of gas is increased, pores that were already activated produce larger bubbles and smaller pores that were not activated are now activated and produce smaller bubbles. This is because, as gas flow rate is increased, the pressure under the porous sparger increases, overcoming the capillary pressure for smaller pores. This is known as a heterogeneous regime with the increased bubble size distribution and the overall number of smaller bubbles. Intuitively, less buoyant smaller bubbles in the heterogeneous regime take longer to float up out of the liquid ethanol, thus producing higher mass transfer of methanol. However, due to the low surface tension of ethanol, (20 mN/m at 20°C) the activation of new pores preponderates over the formation of larger bubbles from already activated pores leading to a reduction in mean bubble diameter. Further, at high flow rates (1000 ccm), larger bubbles with higher rise velocity than small bubbles are formed by coalescence [32]. Hence, the bubble size distribution at a certain height in the bubbler is strongly different from the bubble size distribution near the sparger whose influence on the flow is reduced. These phenomena could potentially explain why we see distinct large bubbles at 1000 ccm (which might be formed due to coalescence), whereas smaller bubbles are observed at 600 ccm flow. Images of the bubbler at both 600 and 1000 ccm were captured (Figure 25 (a) and (b)). The diameters of twenty distinctly visible bubbles were measured and it was observed that the mean bubble diameters for 600 ccm and 1000 ccm nitrogen flow rates were 1.01 mm and 1.66 mm respectively.

- At high nitrogen gas flow rates through the bubbler, larger bubbles are formed.
- Larger bubbles have less surface area to volume ratio than smaller bubbles, hence there is potentially less nitrogen bubble surface area exposed to liquid solvent at higher flow rates.
• Larger bubbles float to the top of the solvent more quickly than smaller bubbles and are therefore exposed to solvent for a shorter period of time.

• However, a larger number of bubbles is obviously formed at higher nitrogen flow rates. Even though larger bubbles are less effective at solvent transfer than smaller bubbles, the higher number of bubbles will tend to counteract the lower transfer efficiency of larger bubbles.

When one takes all of the preceding discussion into account, it is clear that more detailed study of this point is needed to fully explain the observed phenomena. High speed video of the bubbler at different flow rates would allow one to accurately measure the size distribution, overall quantity, and velocity of bubbles generated at different flow rates. Unfortunately, a high speed camera was not available during the course of this research.

Figure 24. Bubble Formation At (a) 600 ccm and (b) 1000 ccm Nitrogen Flow Rates
4.4 Split Stream Solvent Add-Back

Allowing all the nitrogen to be wetted by ethanol from the bubbler before atomization leads to overcompensation of ethanol especially in a low volatility neat solution. Whether the ratio of co-solvents in an ink decreases due to solvent drying or increases due to excessive solvent add-back, the end result is that the ink’s physical properties (viscosity, surface energy etc) change. Either case is unacceptable, as changes in ink properties generally leads to changes the print quality. One way to mitigate this is to regulate the amount of co-solvent that is transferred from the bubbler to the atomization cup such that the amount of co-solvent added back is in equilibrium with the amount of solvent lost during atomization.

To accomplish this experimentally, the high and low volatility neat ink solutions were once again atomized at 600 and 1000 ccm atomization flow rates by partially wetted nitrogen gas according to wet: dry ratios as determined in Table 8. The split stream bubbler set-up used in this research is shown in Figure 26. Results of the above mentioned experimental runs for the low volatility neat solution (30% ethanol: 70% ethylene glycol) are shown in Figures 26, 27 and 28. Results for the high volatility neat solution (15% ethanol: 85% ethylene glycol) are shown in Figures 29, 30 and 31.

![Figure 25: Split Stream Bubbler Assembly.](image-url)
In Figures 27 and 28, we observe that the neat solution loses ethanol at both low and high atomization flow rates when the incoming nitrogen gas blend is only 20% wet. As the %wet component of the incoming nitrogen gas is increased up to approximately 50%, the amount of ethanol lost decreases. As we move beyond 50% wet nitrogen, over-compensation of ethanol begins. The RMS values of the ethanol
wt.% for all experimental runs at both atomization flow rates were calculated. The differences between the RMS value and the initial ethanol wt.% at time = 0 min (to determine the amount of change in ethanol content in the neat solution over the experimental run) were plotted against the %wet nitrogen gas proportions (Figure 29). The results obtained are summarized in Table 11.

![Figure 28: RMS – Ethanol Wt.% (Time =0) Versus %Wet Nitrogen Gas for the 30% Ethanol 70% Ethylene Glycol Co-Solvent Mixture](image)

From Figure 29, we can determine the optimal %wet nitrogen gas for atomizing the low volatility neat solution at 600 and 1000 ccm while maintaining ethanol equilibrium over the entire run time. Figures 30 and 31 represent the change in ethanol wt.% while being atomized at 600 and 1000 ccm respectively using predefined wet: dry bubbler combinations for the high volatility neat solution.
Figure 29: Weight Percent of Ethanol Versus Time Plot for Atomization of 85% Ethanol 15% Ethylene Glycol Co-Solvent Mixture Atomized at 600 ccm

Figure 30: Weight Percent of Ethanol Versus Time Plot for Atomization of 85% Ethanol 15% Ethylene Glycol Co-Solvent Mixture Atomized at 1000 ccm

Once again the RMS – ethanol wt.% (at time =0) versus %wet nitrogen gas were plotted, and the optimal values of %wet nitrogen gas for atomizing the high volatility neat solution at 600 and 1000 ccm while maintaining ethanol equilibrium in the atomization cup were determined (Figure 32). Results obtained from Figures 29 and 32 are summarized in Table 11.
Figure 31: RMS – Ethanol Wt.% (Time =0) Versus % Wet Nitrogen Gas for the 85% Ethanol 15% Ethylene Glycol Co-Solvent Mixture

Table 11: Optimal wet: dry nitrogen gas ratios for atomizing the neat solutions.

<table>
<thead>
<tr>
<th>Sr.no</th>
<th>Neat solution formulation</th>
<th>Atomization flow rate</th>
<th>Wet: Dry nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70% EG: 30% Ethanol</td>
<td>600</td>
<td>40: 60</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td></td>
<td>50: 50</td>
</tr>
<tr>
<td>3</td>
<td>15% EG: 85% Ethanol</td>
<td>600</td>
<td>85: 15</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td></td>
<td>90: 10</td>
</tr>
</tbody>
</table>

4.5 Validation with Copper Nano-Inks
The optimal wet: dry nitrogen gas values obtained from the neat solutions were then tested on copper nano inks prepared by Intrinsiq Materials Inc. Two nano inks were formulated with high and low volatility co-solvent mixing ratios and 14% of copper nano particles. The ink formulations are summarized in Table 12. The inks were atomized under the same conditions as the neat solutions for a period of four hours.

Aerosol Jet printing process parameters used for atomizing these copper inks are as follows:

- Atomization flow rate = 600 and 1000 ccm
- Delta P = 25 ccm constant
- Sheath gas flow rate = 50 ccm
- Inflight tube heater temperature = 40 °C
Platen temperature = 40°C

Ink samples were withdrawn at 30 minute intervals from the atomization cup, and the solid loading fraction (SLF) was used as the response variable. SLF was measured on the Q 2050 thermogravimetric analysis (TGA) system.

**Thermo Galvanometric Analysis:** Thirty micro liters of sample was loaded onto a platinum pan, and the ink was then heated in a sealed furnace at a steady rate of 20 deg C / min up to 800 deg C. The material was then maintained in isothermal conditions for 3 minutes before cool down. The change in weight versus temperature was plotted, and the final weight after complete solvent evaporation was recorded. Table 13 provides a summary of the SLF values obtained for both the low and high volatility nano-inks when atomized at the optimum conditions obtained from the neat solution experiments.

**Table 12: Copper Ink Formulations**

<table>
<thead>
<tr>
<th>Sr.No</th>
<th>% Copper</th>
<th>% Ethanol</th>
<th>% Ethylene Glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.6</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>13.6</td>
<td>80</td>
<td>20</td>
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</tbody>
</table>

**Table 13: SLF Results for Copper Inks When Atomized With Optimal Bubbler Settings.**

<table>
<thead>
<tr>
<th>Copper Ink Co-Solvent Compositions</th>
<th>20 ethanol: 80EG @ 600 ccm</th>
<th>20 ethanol: 80EG @ 1000 ccm</th>
<th>80 ethanol: 20EG @ 600 ccm</th>
<th>80 ethanol: 20EG @ 1000 ccm</th>
</tr>
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<tbody>
<tr>
<td>Time</td>
<td>% Solids</td>
<td>% Solids</td>
<td>% Solids</td>
<td>% Solids</td>
</tr>
<tr>
<td>Hours</td>
<td>13.58</td>
<td>13.63</td>
<td>14.76</td>
<td>14.7</td>
</tr>
<tr>
<td>0</td>
<td>12.66</td>
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<td>15.83</td>
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<td>12.55</td>
<td>12.86</td>
<td>15.74</td>
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<td>2</td>
<td>14.37</td>
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<td>16.21</td>
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<td>3</td>
<td>13.89</td>
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<td>AVG</td>
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<td>13.05</td>
<td>15.996</td>
<td>17.586</td>
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<tr>
<td>STDEV</td>
<td>0.787877</td>
<td>0.587665</td>
<td>0.968468</td>
<td>2.300354</td>
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</table>
From Table 13 and Figure 33, it is observed that the solid loading fraction of the copper nanoink remained approximately constant throughout the 4 hour experimental run for the low volatility inks for atomization at both 600 and 1000 ccm. For the high volatility inks, the solid loading fraction increased by 2.68% at 600 ccm atomization flow rate and by 6.44% at 1000 ccm atomization flow rate. In a high volatility ink, there seems to be difficulty in maintaining solvent equilibrium with in the atomization cup despite the high wet% of solvent add-back from the bubbler. Under these cases, it would therefore be recommended to run the system with just the bubbler (i.e. 100% bubbler gas, and no dry gas).
5. CONCLUSIONS AND FUTURE WORK

Most ink formulations used in Aerosol Jet printing use blends of low and high boiling point co-solvents. In some applications, slow drying inks that flow out and form a continuous coating are desired, whereas other applications call for fast drying inks used to print narrow lines and/or features with high aspect ratios. Depending upon the application, the concentration of high boiling point solvents may range from just a few percent up to nearly 100%. This study has demonstrated that Aerosol Jet printing with dry nitrogen gas leads to rapid loss of high boiling point solvents. As the ink dries out, the solid loading fraction of nano-particle suspensions increases, and the wetting and spreading behavior of the ink changes as well. Ultimately, inks with high concentrations of high boiling point solvents may become unprintable. A potential solution to this problem is to add solvent back into the atomizing cup through the use of a bubbler.

The solvent add-back method uses a bubbler to moisten the nitrogen gas before it enters the atomizing cup. This study has shown that the bubbler solvent add-back approach has the potential to overcome the loss of high boiling point solvents under certain conditions such as those shown in Figure 24 where the concentration of high boiling point solvents is high. It is, however, also possible to add back an excessive amount of solvent as shown in Figure 24 where the concentration of the high boiling point solvent is relatively low.

In studying Figures 23 and 24, one can envision that a blend of dry and moist nitrogen gas in the correct ratios will lead to continuous printing with a constant ethanol concentration. By using two mass flow controllers, we can independently control the relative proportions of wet and dry nitrogen gas being used. That being said, a split stream bubbler add-back system was used where one part of the stream was passed through the bubbler for moistening, and the other dry stream of nitrogen gas was then mixed with the wetted stream. This reduced the overall ethanol moisture content of the incoming nitrogen gas. By controlling the ratio of the wet and dry nitrogen gases, we were able to maintain much better ethanol concentration in the atomization cup over a three and a half hours of run time.

The optimal settings obtained from the neat solution runs were validated by using them to atomize copper nano-inks with same solvent compositions. The low volatility inks maintained relatively constant solid loading fractions over the four hour run cycle, while for the high volatility inks, the percent solids slightly increased with time – though not nearly at the rate observed without use of a bubbler. Hence with further investigation, ethanol equilibrium in the high volatility inks seems achievable.
Future Work:

1. **Co-Solvent Add-Back:**

In this study we have assumed that the rate of evaporation of slow drying solvent is minimal, and hence only the high vapor pressure solvent was used in the bubbler. Potential interaction effects between co-solvents from the bubbler has yet to be studied.

2. **Bubbler Temperature Regulation:**

The next logical step in refining the solvent add-back approach is to regulate the bubbler temperature. Since vapor pressure of a solvent is dependent on the process temperature, raising or lowering the bubbler temperature would influence the rate of solvent transfer from the bubbler to the atomization cup. Viewed a different way, it may be possible to increase or decrease solvent add-back via temperature control so that the use of a 2nd mass flow controller (for the dry nitrogen blended with moist nitrogen) is no longer necessary.

3. **Generalized Mathematical Model:**

This study was specifically focused on characterizing the solvent equilibrium of an ethylene glycol and ethanol co-solvent system. However, ink manufacturers use several types of solvents in varying proportions. Thus there is a need to develop a general purpose analytical model applicable to any solvent system to determine the optimal wet: dry nitrogen gas setting for the bubbler in order to maintain co-solvent equilibrium in the nano inks. This model will correlate the physical properties of the ink such as viscosity, surface tension and vapor pressures of the solvents used (which can be determined by in house testing) to the process parameters required for the printing application.
6. REFERENCES


