DISTRIBUTION OF INK-JET INK COMPONENTS VIA TOF-SIMS AND OPTICAL IMAGE ANALYSIS

by

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ABSTRACT

In this work the methodology is developed to study spreading and penetration of a custom ink-jet ink formulation, containing hydrophobic cationic crystal violet dye, ethoxylated surfactant, and ink solvent marked by lithium salt. With a new technique utilizing Time-of-Flight Secondary Ion Mass Spectrometry imaging, the ink component distribution and its effect on print quality of uncoated and coated papers are evaluated. High spatially resolved images obtained by ToF-SIMS illustrate differentiation of individual ink components, with ink solvent spreading more than the dye in all paper samples. Uncoated papers show greater and more irregular spreading leading to poor edge definition and poor print quality. Large separation of the dye from the solvent in the vertical direction of multipurpose and photo glossy ink-jet paper suggests a step-wise progression of ink penetration: ink flows through a more porous structure in the x-direction before advancing to the next sublayer in the z-direction of paper.
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CHAPTER 1 – INTRODUCTION

It is predicted that in less than twenty years, digital printing will have 25% (second largest portion) of the printing market [1]. Conventional printing presses (e.g. offset, gravure) have reduced cost per copy with increased print run length [1]. This dependence of cost per copy on print run is due to operating costs – development of the plates, their removal from and mounting in the press for each job [2]. Digital printing, on the other hand, has a constant cost per copy, making it attractive to the low volume user [1]. It could be estimated that in gravure printing process, 100 000 copies must be printed before the cost per copy reaches that of digital printing [1].

Digital printing is apparent in small office and home office settings, as well as in low volume commercial settings [2]. Digital photography is a significant driving force in the growing trend of digital colour printing in homes [2]. In 2005, the Japanese camera industry reported shipment of 4 million conventional or traditional film cameras versus 60 million digital cameras [1]. Due to lower complexity (light and compact construction of printing heads), ink-jet printing, in particular, as a subset of digital printing, has potential for integration in-line with other printing methods or processes [2]. Thus, commercially, ink-jet printing has the advantage of possible customization and individualization of the prints.

Paper is the printer’s biggest single operating cost [1]. Ink is the second largest cost in printing; however its unit price is ten times that of the paper [2]. The fact that ink-jet printing is relatively recent and is rapidly growing [1], presents the papermakers and ink-suppliers with a moving target for quality ink-jet performance [3]. Thus, considering the
need to compete with conventional printing methods that have been around for several decades [2], the pressure for better quality and performance of both ink-jet paper and ink-jet ink is tremendous. Furthermore, improvements in digital media imaging will introduce additional pressure for further development in high quality printing that could reproduce the level of image resolution.

It is well known that the quality of the print is judged by its optical properties. These optical properties depend on the properties of the ink, the quality of the paper, and the characteristics of the printer and the printing method. For a given printing process, every combination of ink and substrate is unique due to unique ink-media interactions. In recent years, some research has been conducted with the objective of relating print properties of printed papers to ink components of the ink formulation (dye/pigment, solvent, and surfactant) [4,5,6,7,8,9]. The majority of these studies have examined sorption of individual ink components as separate processes through microscopic techniques [4-6]. Few studies characterized the spatial arrangement of all ink components simultaneously [7-9]. Even fewer studies have related this spatial arrangement of ink components qualitatively and/or quantitatively to print quality [7].

It is generally accepted that ideal print is one of high print density and uniform border resolution – directly determined by the optimum and balanced combination of spreading and penetration [1]. In particular, excessive spreading may cause loss of resolution, while excessive penetration may cause loss of print density [1]. In addition, high retention of the dye or separation of the dye from the ink solvent may also be an indication of print quality: as the dye is preferentially retained by the paper, ink solvent
freely penetrates through the paper and eventually evaporates. Thus, high separation or retention of the dye may improve image quality by reducing dye spreading and penetration.

A better understanding of spatial arrangement of ink components and their interactions with the substrate will enable both papermakers and ink suppliers to engineer optimum paper coating structure and ink formulation, respectively. It will allow a more fundamental and cost-effective approach to product design. Knowledge of the ink component distribution within or on top of the substrate will also provide solutions to challenging print quality problems, and will provide opportunities for papermakers to upgrade their offerings and their quality.

Although efforts have been dedicated to evaluate factors affecting print quality, the data obtained thus far is incomplete with regards to simultaneous ink component distribution. The cause of this incompleteness is attributed to limitations in the methodologies and the lack of well known ink composition that could be traced in printed paper samples. Without a well developed technique, interactions among the ink components, their interactions with the substrate, and their impact on print quality cannot be evaluated. In recent years, advances on ink and paper analysis using chemical spectroscopy methods have been made [7-10]. Use of chemical spectroscopy methods allows simultaneous study of all ink components. Among these techniques, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has the highest spatial resolution, providing means of analysis of the sample surface as well as its cross section. In addition, ToF-SIMS has excellent mass resolution providing not only elemental and chemical information, but
also molecular information required for the study of preferential absorption of ink-jet ink components.

There are two main objectives for this study. The first objective is to develop a custom ink-jet ink formulation of known composition and a methodology for the analysis of the distribution of these ink components in printed paper samples. High spatial resolution ToF-SIMS imaging is the selected analytical tool to identify individual ink components and their spatial distribution on printed samples. The custom ink formulation allows to mitigate one drawback of ToF-SIMS analysis – the overwhelming wealth of information it provides. Various fragments and peaks within ToF-SIMS spectra are identified and assigned to individual ink components through full knowledge of chemical composition of ink. The second objective is to apply the developed methodology to study distribution of ink components on coated and uncoated papers of different specialization and quality. The comparison of ink component distribution on different papers should improve our understanding on how distribution of ink components, specifically dye, solvent, and surfactant, affects the print quality, defined by print density and border resolution.

The experimental approach used in this thesis is summarized in Figure 1.1. In the development of the methodology, as stated previously, ink is formulated, samples are printed, and ToF-SIMS analysis is performed to identify individual ink components and their distribution. Once methodology is developed, custom ink formulation is used to print samples on five coated and uncoated papers. For the cross section analysis, samples are given a rigid support, by either embedding the samples or by sandwiching them between two plastics, and are microtomed using diamond trimming knife. To evaluate
print quality, image analysis is performed on both the surface of the samples and the cross sections of the samples. To evaluate distribution of ink components, ToF-SIMS analysis is performed. Both analyses, optical and ToF-SIMS imaging, are used to make conclusions on how distribution of ink components affects print quality.

Similarly, following the introduction, some background on printing process is reviewed in CHAPTER 2. CHAPTER 3 is a detailed investigation with regards to the development of the methodology to study distribution of ink components on the xy-plane of paper. Further development of the technique for the vertical plane of paper is reported in CHAPTER 4. In addition to applying ToF-SIMS imaging to study distribution of ink components on coated and uncoated papers, CHAPTER 4 also evaluates print quality of all papers and correlates it to the ink component distribution. Finally, major findings, their significance, and implications are summarized in CHAPTER 5. The organization of the thesis is such that each chapter, e.g. CHAPTER 3 and CHAPTER 4, can be
considered as a separate article/paper, and thus can be evaluated on its own individual basis.

References


CHAPTER 2 - BACKGROUND

2.1 Ink-jet Printing Process

Two methods of ink-jet printing exist: continuous and drop-on-demand ink-jet systems. In continuous ink-jet system, an electrical charge is selectively impressed on the drops of the continuous ink stream [1]. The charged drops, passing through electrical field, are deflected into a gutter for recirculation, and the uncharged drops are placed directly onto media to form an image [1]. In drop-on-demand ink-jet system, droplets are ejected only as needed, thus eliminating the complexity of drop charging and deflection hardware [1]. In addition, all generated drops are placed onto substrate [2], thus again eliminating the inherent unreliability of the ink recirculation system required for continuous ink-jet devices [1]. Resolution reached with drop-on-demand systems can exceed that of the continuous ink-jet systems by a factor of five [2]. The majority of use in ink-jet printing utilizes the drop-on-demand methods.

Drop-on-demand ink-jet printers classify into four categories using thermal, piezoelectric, electrostatic, or acoustic ink-jet principles [1]. While electrostatic and acoustic ink-jet methods are still in the developmental stages, thermal and piezoelectric methods represent the majority of the activity in drop-on-demand systems [1]. Drop-on-demand thermal ink-jet printer has a heating element that heats the ink periodically causing a phase change and an increase in volume [2]. This increase in volume in the vaporized state leads to some ink squeezing from the nozzle, producing a drop that travels to the substrate [2]. The thermal element cools before the cycle is repeated and another drop is produced [2]. Due to rapid thermal gradients within the thermal drop-on-demand printers, reliability of the ink’s performance may become an issue [1,3]. Since in
piezoelectric ink-jet system ink is not heated or cooled, this system has significant advantage over thermal ink-jet method [3]. In drop-on-demand piezoelectric system, an application of an electrical field causes deformation of the piezoelectric crystal against ink’s volume, as a result droplets of ink are ejected [1,3]. Printing process parameters such as ejection rate, applied voltage (to create an electrical field), and pressure waveform (generated by volume change of ink) must be optimized with this drop-on-demand method [1,4]. Performance and reliability of the printing process, controlling drop volume, velocity, and trajectory, directly affect the final quality of the printed image [1].

Dimatix Materials Printer (DMP-2800 - FUJIFILM Dimatix Inc., Santa Clara, CA) uses drop-on-demand piezoelectric inkjet technology specifically designed for research and development [4]. This printer has been successfully utilized in previous studies [5]. An advantage of Dimatix printer is that cartridges may be filled with inks designed in house [4]. In addition, drop characteristics can be optimized through a waveform editor and a drop-watch camera system allowing manipulation of the electronic pulses to the piezoelectric device [4]. Cartridges of the DMP system have a capacity of 1.5mL, utilizing 16 nozzles linearly spaced at 254µm [4]. Considering the trend towards smaller ink drop volume for higher resolution [1], DMP system comprises of nozzles of 21µm in diameter, producing a typical droplet of 10pL in volume [4].
2.2 Ink Requirements

2.2.1 Composition

Chemistry and composition of ink formulation dictates the drop ejection characteristics, the reliability of the printing, and consequently the quality of the printed image [1]. Water-based inks are common in home and small office ink-jet printers [1]. A typical water-based ink composition is summarized in Table 2.1. Both dye-based and pigment-based inks are common in ink-jet printing. Pigment-based inks are advantageous over dye-based inks in terms of colour durability when exposed to light and water/weather conditions [1]. The overall trend, however, is towards smaller drop volume for higher resolution and higher number of nozzles for increased print speed [1,2]. With this trend, pigment-based inks may have the intrinsic disadvantage when compared to dye-based inks, due to their pigment dispersion instability leading to clogging of the nozzles and thus unreliability of the printing ejection characteristics [1].

Table 2.1: Water-based Ink-jet Ink Composition [1,6]

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye or pigment</td>
<td>Provides colour</td>
<td>1.0 – 10.0</td>
</tr>
<tr>
<td>Solvent (water)</td>
<td>Acts as carrier medium</td>
<td>60.0 – 90.0</td>
</tr>
<tr>
<td>Co-solvent</td>
<td>Water soluble humectant – slows down evaporation rate within the printing system and prevents clogging of the nozzles, viscosity control</td>
<td>5.0 – 30.0</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Decreases surface energy of ink to achieve wettability</td>
<td>0.1 – 10.0</td>
</tr>
<tr>
<td>Biocide</td>
<td>Prevents biological growth</td>
<td>0.1 – 1.0</td>
</tr>
<tr>
<td>Other additives</td>
<td>pH buffer, chelating agent – solubilizes trace metals, dye/pigment solubilizer</td>
<td>&lt; 1.0</td>
</tr>
</tbody>
</table>
Ink dye or pigment acts as the colourant of the print. Spreading and penetration of the dye directly affects optical properties of the print. Excessive penetration causes reduced optical density, and excessive spreading results in feathering and loss of resolution of the print [7]. The dye or pigment used in the formulation must be compatible with both the receiving substrate and the solvent of the ink [2].

The extent of ink spreading is ultimately limited by penetration, i.e. spreading will continue until all of the drop volume has penetrated through and until all of the fluid has been immobilized by the substrate [8]. A faster penetration is achieved by addition of surfactants that increase wettability between liquid ink and media substrate. Poor wettability (caused by absence of surfactants), on the other hand, may lead to ink-drop coalescence - formation of a large, freestanding pool of liquid - causing unintended variation in the optical dye density [8]. The addition of the surfactant may also aid spreading of the ink on the surface of the substrate, allowing greater access to the available pores of the medium, thus again improving the rate of penetration [8]. The function of the surfactant becomes even more important in multicolour printing, where the availability of ink droplets on the surface may cause unintentional intermixing of colours [7].

Water is the solvent in ink-jet inks and acts as the carrier of the dye/pigment. Humectants, with high boiling points, are used as co-solvents to slow down the evaporation rate of the ink [6]. Thus, humectants’ function is to ensure stable delivery of the ink, while preventing nozzle clogging within the ink-jet printing system [6].
2.2.2 Properties

The physicochemical properties of drop-on-demand ink-jet ink are summarized in Table 2.2. Both surface tension and viscosity greatly influence the droplet velocity, drop size, and droplet stability within the printing system [6]. In addition, physicochemical properties of ink influence ink-media interactions. Low surface tension of ink causes difficulties in well-defined drop size formation; however, inks of high surface tension do not wet the receiving substrate, thus limiting the extent of penetration and increasing drying time [6]. Printing head performance is matched to the viscosity of the ink [6]. With the use of water as the solvent, the viscosity of ink-jet inks is generally low. However, in order to control the drop migration, high viscosity is preferred [9].

Table 2.2: Physicochemical Properties of Drop-on-Demand Ink-Jet Inks [6]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface tension, mN/m</td>
<td>&gt; 35</td>
</tr>
<tr>
<td>Viscosity, cP</td>
<td>1 - 10</td>
</tr>
<tr>
<td>Drying time, s</td>
<td>&lt; 10</td>
</tr>
</tbody>
</table>

2.3 Paper Requirements

Every grade of paper (e.g. ink-jet, laser) has its own specifications in terms of its properties [7]. Since ink-jet inks typically contain 60-90wt% of water solvent [1], ink-jet inks represent extreme case of application of water to paper [10]. This places contradicting requirements on ink-jet paper. Papers must have high absorbency due to significant amount of water present in ink-jet inks [7]. However, too much absorbency may cause loss of print density and possible print through - visible image showing through on the reverse side of the print [7,11]. Papers having heavy surface sizing with
little absorbency, on the other hand, may produce images of low resolution due to defective lateral migration of ink [1,7]. Little absorbency becomes even more important in multicolour printing, where different liquid inks may mix and bleed into each other on the surface of paper [7]. State of the art technology for ink-jet paper incorporates both high water absorbent coating layer and heavily sized basesheet preventing water penetration and basesheet distortion [1,7]. Use of high surface area pigments, such as hydrophilic silicas, for the coating structure ensures acceptable drying time and high image quality [6]. Smooth, uniform, microporous substrate has the most potential of good quality print [2,7]. In addition, internal and surface sizing of paper play important role in ink-jet print quality [7,12]. Internal sizing significantly reduces penetration within the substrate [7], thus improving colour intensity on the surface of the paper [12]. Surface sizing further reduces lateral migration of ink across paper’s surface [7], thus improving resolution and sharpness of the print [12].

2.4 Ink-Paper Interactions

Upon impact with paper, a short time elapses before inertial forces of the drop dissipate [6]. Croucher and Hair referred to this short time as a wetting delay, during which the contact area of the drop with the surface of paper is determined [6]. Gane reported that at these shortest times finer pores fill first due to inertial retardation according to Equation 2.1, i.e. penetration depth is inversely proportional to the square root of pore radius of the substrate [13]. This inertial retardation at shortest times explains the fact that high pore volume matt coatings with large pore radii imbibe slower than microporous gloss coatings with small pore radii [13]. However, due to its short-lived nature with respect to the length of a theoretical capillary, the aspect of inertia is generally overlooked [13].
\[ z(t) = t \sqrt{\frac{2\gamma \cos(\theta)}{R\rho}} \]

- \( z \) = penetration depth; \( R \) = pore radius; \( t \) = time
- \( \gamma \) = liquid surface tension; \( \rho \) = liquid density
- \( \theta \) = contact angle between liquid and pore wall

**Equation 2.1:** Penetration Depth at Short Times [13]

At longer times, the transition from inertial retardation in large radii to viscous retardation in fine structures occurs [13]. At these longer times, the conventional relationship to describe penetration is the Lucas-Washburn relation (**Equation 2.2**), where depth penetration is proportional to the square root of pore radius of the receiving substrate [10,13].

\[ z(t) = \sqrt{\frac{R\gamma \cos(\theta)t}{2\mu}} \]

- \( z \) = penetration depth; \( R \) = pore radius; \( t \) = time
- \( \gamma \) = liquid surface tension; \( \mu \) = liquid viscosity
- \( \theta \) = contact angle between liquid and pore wall

**Equation 2.2:** Lucas-Washburn Relationship [10]

Desie and Van Roost established that dye based inks follow Davis-Hocking model based on this Lucas-Washburn equation [14]. In addition, Desie and Van Roost concluded that, for dye based inks, the parabolic penetration zone is entirely within the coating structure, in contrast with pigment based inks where the colourant remains on the top of the medium [14]. Both Aspler and Le confirmed Desie’s and Van Roost’s observations and stated that dye-based ink-jet inks penetrate either into the coating pigment on coated media or penetrate into the bulk of paper on uncoated media [1,10]. Le added that the spreading on uncoated paper tends to be along the paper fibers [1]. Though Aspler confirmed that the spreading on uncoated paper is well correlated with Lucas-Washburn theory [10], he stated that penetration depth can be overestimated using the Washburn
equation [7]. Some of this overestimation may result from the fact that contact angle is not constant and is experimentally questionable on rough and/or porous substrates [7,13]. In addition, the Washburn equation assumes collection of cylindrical pores, however, pores are a network of interconnecting and tortuous pores with variant geometries [7,13]. Aspler also noted that the pore structures in vertical (xz or yz) planes and the horizontal plane (xy) are very different [7,10]. Fluid flow in the xy direction encounters much more open pore structure with larger pore size and broader pore size distribution than the fluid flow in the vertical direction [15]. Traditional porosity measurements (e.g. mercury intrusion), however, are indicative of an average porosity of all directions [7,15]. Nonetheless, Aspler reported that the Washburn equation can rank samples in the proper order [7]. Daniel and Berg concluded that true deviations from Washburn-like behaviour are caused by initial wetting delays, and five parameters can fully describe and define simultaneous spreading and penetration uniquely: drop volume, pore size, paper thickness, porosity, and contact angle [8].

Interactions among the ink components directly dictate the consecutive interactions between these individual ink components and the substrate. However, few studies have actually investigated all ink components simultaneously. In addition, since ink colourant, dye or pigment, is what consumers evaluate visually in the final print [16], most of the research has been dedicated to these components. Furthermore, some studies use a general term “ink” to investigate ink-media interactions, when in reality the analysis involves only the dye/pigment colourant [7,10]. Desie and Van Roost [14] as well as Dalton et al. [17] investigated absorption of dye/pigment of ink-jet inks and offset inks, respectively, using optical image and chemical spectroscopy method analysis (e.g. ToF-
SIMS, XPS). Both of these studies produced concrete results confirming the interaction mechanisms of dye and pigment with the substrate. However, results relating to other ink components are mostly hypothetical due to limitations in the methodology. Nonetheless, such studies have been useful in the development of the methodology to evaluate the simultaneous distribution of all ink components. For example, Grim et al., using Laser Desorption Mass Spectrometry, elaborated on the study of dye absorption by identifying characteristic mass peak of a common crystal violet dye [18]. Grim et al. also identified peaks of the demethylated fragments of the crystal violet dye on paper [18]. Tag et al., on the other hand, investigated surfactant distribution in relation to offset printing using Time-of-Flight Secondary Ion Mass Spectrometry [19]. Tag et al. identified several peaks of ethoxylation stages of the ethoxylated surfactant [19]. Thus, the simultaneous study of both dye and surfactant, at least in theory, is possible.

Identifying the ingredients of an ink formulation on printed paper is not trivial. Instead the distribution of ink components can be established using labels or tracer compounds. For example, osmium tetroxide was used to trace the offset ink solvent using SEM imaging [17]. In ToF-SIMS, lithium chloride was used as the tracer of starch penetration relating to surface sizing process in uncoated fine paper [20]. Lipponen concluded that lithium chloride tracer migrated through the fiber network with the water in the solution, thus overestimating starch penetration [20].

Thus, the challenge for investigating ink components, as well as their interactions among themselves and with the substrate, is applying the right methodology for a given ink-jet ink formulation. The challenge may be reversed by choosing or formulating an ink-jet
ink such that for a given chemical spectroscopy method, components of ink can either be distinguished based on their molecular structure or be identified with the use of tracers.

2.5 Print Quality

In order for ink-jet printing to compete with other printing processes, two main performance factors are of essence: speed and quality [2]. Speed of printing is dependent on the resolution of printed image, where resolution is defined as number of distinguished pixels/dots printed per inch [2]. Higher resolutions require greater number of printed pixels, thus decreasing the speed of printing [2]. Higher resolution also signifies a better quality print [2]. Thus, generally, a good ink-jet print quality is represented by a sharp print and intense colour [7,12]. Level of colour density achieved with a given amount of ink is the most basic and the most important factor in print quality [2]. Intensity of colour is quantified by means of optical density measurement. Though density values depend on the densitometer used, all measurements are based on the same principle described by

\[ \text{Density} = D = \log_{10} \frac{I_o}{I} \]

Equation 2.3: Optical Density Calculation

where \( I_0 \) is the incoming light intensity and \( I \) is the reflected light intensity [2]. For example, if 100% of the incoming light is reflected density is 0; if 10% is reflected, density is 1; and if 1% is reflected, density is 2. Thus darker image absorbs more light, lowering the percentage of light that is reflected, and as a result density of the image is greater. Increased ink penetration reduces the darkness of the print and thus reduces print density [21]. Roughness of the paper also effects print density. Rough surfaces may
have discontinuous ink film due to uneven setting of the ink and perhaps even due to exposed unprinted fibers or pore walls [7]. This discontinuous ink film as a result will cause the light to be reflected off exposed surface of paper, producing a reduced print density [7]. General values of print density for different grades of paper are summarized in Table 2.3.

**Table 2.3: Density Units for Various Imaging Processes [2,7]**

<table>
<thead>
<tr>
<th>Process</th>
<th>Values/Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newsprint</td>
<td>0.85 – 1.00</td>
</tr>
<tr>
<td>Coated papers</td>
<td>1.20 – 1.50</td>
</tr>
<tr>
<td>Photograph on paper</td>
<td>1.50 – 2.00</td>
</tr>
</tbody>
</table>

Print raggedness is defined as irregularity of the dye position within the printed image. Edge raggedness is common on rough papers [2]. Sharpness of the print is of most significance in high quality printing. Sharpness is associated with the slope of the colour density at the edge of the inked region, with infinitely steep slope representing a sharp image [2]. Quantification of these print properties is made through image analysis, and thus greatly depends on the user and the methodology, i.e. no standardization of evaluating ink-jet print quality exist [2,12]. Hensema et al. evaluated lateral migration of ink using line width and the associated line edge roughness [12]. Line width in their study was reported as an absolute value in pixels [12], thus greatly depending on the imaging software used for the analysis. In addition, no comparison was made to the theoretical line width, and instead comparison was made only between samples [12]. Edge roughness in Hensema’s study was evaluated as the ratio of the actual length to the theoretical length of the boundary between inked and non-inked regions of a printed line.
lower ratio signified lower edge roughness [12]. Kowalczyk and Trksak used area of the printed image as an indication of the sharpness of the print, and perimeter or coastline of the image as an indication of uniformity or raggedness [22]. Lower area and perimeter signified a sharper and more uniform print [22]. Similar to Hensema’s study, comparison of area and perimeter values of different samples was made only between samples, rather to a standard value [22]. Even though both studies, Hensema and Kowalczyk and Trksak, used the Hewlett Packard’s Paper Acceptance Criteria for evaluating ink-jet print quality [12,22], no comparison between the two studies is possible due to lack of standardization. In addition, Kowalczyk and Trksak showed that absolute values for area and perimeter, as the tools for evaluating ink-jet print quality, vary for different printers even when the same paper is used [22]. Thus, again comparison between experiments is difficult. Barker et al. used dye border variability as an indication of edge raggedness [23]. This border variability was evaluated as the average magnitude of the differences between the actual dye position of a set of points along an edge and the best-fit line through those edge points [23]. In their study, Barker et al. stated that the measurements of border variability were inconclusive due to the need for higher spatial resolution [23].

### 2.6 Chemical Spectroscopy Methods

Different state-of-the-art surface analysis techniques, such as Fourier Transform Infrared Spectroscopy (FTIR) mapping, Raman, X-ray Photoelectron Spectroscopy (XPS), and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) can be used to obtain distribution profiles of ink in paper. Spatial resolutions of different surface analysis techniques are summarized in Table 2.4.
Table 2.4: Spatial Selectivity of Several Surface Analysis Techniques

<table>
<thead>
<tr>
<th>Technique/Resolution</th>
<th>Lateral Resolution (µm)</th>
<th>Depth of Analysis (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOF-SIMS</td>
<td>0.100 [24]</td>
<td>0.005 [24]</td>
</tr>
<tr>
<td>Raman</td>
<td>1 [25]</td>
<td>2 [26]</td>
</tr>
<tr>
<td>XPS</td>
<td>10 [27]</td>
<td>0.010 [27]</td>
</tr>
<tr>
<td>FTIR</td>
<td>10 [28]</td>
<td>2 (ATR) [26]</td>
</tr>
</tbody>
</table>

The use of Fourier Transform Infrared spectroscopy (FTIR) to study distribution of ink-jet ink components is limited. Vikman and Vuorinen investigated light fastness of ink-jet prints on modified conventional coatings using experimental coatings and inks, and vibrational spectroscopic methods, such as FTIR – ATR [29]. The analysis of printed samples proved to be complex due to the fact that FTIR spectra contained several overlapping bands originating from both the coating components and the dye [29].

Lozo et al. tested applicability of Raman to investigate depth profiling of ink-jet prints on different grades of paper, ranging from tissue paper to photo paper [30]. Through oil immersion sampling method, Raman was found to be useful in the depth analysis of dye-based and pigment-based ink-jet inks throughout the vertical dimension of paper [30]. However, individual ink components could not be identified and instead the ink layer was classified into three categories: a homogeneous layer with high dye/pigment intensity, a non-homogeneous layer representing dye/pigment distribution or gradual dye/pigment-coating interface, and a deep or maximum dye/pigment penetration layer [30].

The use of X-ray Photoelectron Spectroscopy and Time-of-Flight Secondary Ion Mass Spectrometry on printed and unprinted samples has been extensive in recent years.
Fardim and Holmbom tested the applicability of ToF-SIMS and XPS to follow distribution of papermaking chemicals (e.g. fillers, pigment particles, optical brightener, latex, etc.) on coated and uncoated papers [27]. Fardim and Holmbom concluded that while XPS lacked lateral resolution, ToF-SIMS proved to be the most ideal of all chemical spectroscopy [27]. Aside from having the highest spatial resolution, ToF-SIMS also had excellent mass resolution providing not only elemental and chemical information (resembling XPS – X-ray Photoelectron Spectroscopy), but also molecular information for wide variety of materials [31]. Pachuta and Staral utilized ToF-SIMS to differentiate and qualitatively identify components of pen inks on standard white paper, e.g. mass peaks at 372amu and 358amu were assigned to crystal and methyl violet dyes [32]. Tag et al. employed ToF-SIMS to investigate distribution of ethoxylated surfactant in relation to offset printing, in the process identifying several peaks of ethoxylation stages of the surfactant [19]. Marking a component of interest with an easily identifiable peak within ToF-SIMS spectra is also common in the literature, e.g. Lipponen et al. used lithium chloride as the tracer of starch penetration in uncoated fine paper [20]. The significant amount of literature citing the use of ToF-SIMS for printed and unprinted samples of paper provides a strong and concrete background for further investigation of printed samples.

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CHAPTER 3 – DEVELOPMENT OF TOF-SIMS TECHNIQUE

3.1 Introduction

One of the driving forces of continuous growth in digital printing is the printing quality [1], which is directly defined by the optical properties of the final print. These optical properties are influenced by two mechanisms of ink-media interactions: spreading across or on the surface of the medium (xy-plane) and penetration or absorption into the underlying substrate (z-plane) [2-3]. A balanced combination of the two mechanisms produces a good quality print [3]. While ink colourant, dye or pigment, is what consumer evaluates visually as the final print, other components of ink (ink vehicle/solvent, co-solvent, surfactant, etc.) play a significant role in terms of how the final image is formed and how the ink, as a totality, is received by the medium [4]. Since ink-jet inks are complex solutions, i.e. not just simple solutions of dyes or suspension of pigment particles, penetration and spreading of ink are further complicated by possible preferential absorption of ink-jet ink components (e.g. preferential adsorption of dye on paper surface) [5].

Typical ink-jet ink consists of dye or pigment colorant, solvent, water soluble co-solvent (humectants, viscosity control), surfactant, as well as other potential additives such as biocide, pH buffer, solubilizer, and chelating agent [6]. Ink dye or pigment acts as the colourant of the print. Penetration of the dye directly affects print density; and spreading of the dye directly influences feathering and resolution of the print. The extent of spreading is ultimately limited by penetration, i.e. spreading will continue until all of the drop volume has penetrated through and immobilized by the substrate [3]. A faster penetration is achieved by addition of surfactants that increase wettability between liquid
ink and media substrate. Poor wettability (caused by absence of surfactants), on the other hand, may lead to ink-drop coalescence - formation of a large, freestanding pool of liquid - causing variation in optical dye density [3], poor resolution, and possible intermixing of colours in colour printing. Water is usually the solvent in ink-jet inks and acts as the carrier of dye/pigment. Since ink-jet inks typically contain 60-90wt% of water solvent [6], ink-jet inks represent extreme case of application of water to paper [5]. In addition to water solvent, humectants, with high boiling points, are used as co-solvents. Humectants’ function is to ensure stable delivery of the ink, while preventing nozzle clogging in ink-jet printing systems [7].

Interaction of printing inks with paper has been studied intensively in recent years. Desie and Van Roost [8] as well as Dalton et al. [9] investigated absorption of dye/pigment of ink-jet inks and offset inks, respectively, using optical image and chemical spectroscopy method analysis (e.g. ToF-SIMS, XPS). Grim et al. elaborated on the study of dye absorption by identifying characteristic mass peak of a common crystal violet dye, as well as peaks of its demethylated fragments on paper [10]. Daniel and Berg investigated spreading and penetration of surfactant-laden drops on thin commercial ink-jet photographic papers using high-speed video-based optical analysis [3]. Tag et al., on the other hand, employed ToF-SIMS to investigate distribution of ethoxylated surfactant in relation to offset printing, in the process identifying several peaks of ethoxylation stages of the surfactant [11]. Shibatani et al. utilized ToF-SIMS to investigate absorption of ink-jet ink co-solvent on commercially available resin coat-based and photo-grade glossy papers [7]. Gane investigated absorption of offset ink solvent, as well as segregation of miscible ink solvents/oils using optical and spectroscopic method analysis [12]. Marking
a component of interest with an easily identifiable peak within ToF-SIMS spectra is also common in the literature (e.g. Lipponen et al. used lithium chloride as the tracer of starch penetration in uncoated fine paper [13]). Sodhi et al. investigated distribution of ink and coating constituents of two different coating formulations [14]. However, the spreading of ink dye, solvent, and surfactant and more specifically their preferential absorption as well as their relation to one another has not been investigated in detail. Nonetheless, there is significant amount of literature citing the use of ToF-SIMS for printed samples of paper; this literature provides a strong and concrete background for further investigation. In this work, we build on the work by Sodhi et al. [14] by profiling the distribution of ink components using a custom ink-jet ink formulation of known composition on both coated and uncoated papers to study the effect of paper morphology on ink component distribution.

3.2 Experimental Procedures

3.2.1 Materials

The chemical composition of the ink formulation and the source of chemicals used in this study are summarized in Table 3.1. Crystal violet dye was introduced into solution as chlorine salt. An ethoxylated surfactant was used in the formulation, and ink vehicle/solvent was marked using 0.1wt% lithium chloride as tracer.

The two papers of fairly different properties were chosen as multipurpose paper (Domtar copy D82201 28397B) and high quality premium photo glossy ink-jet paper (EPSON America, Inc. S041667). Since both papers were purchased commercially, limited information about their properties was available. The multipurpose paper had a
grammage of 75g/m², brightness of 92, and whiteness of 145. Premium photo glossy inkjet paper was high gloss, instant-drying paper.

Table 3.1: Ink Formulation and Chemical Information

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical</th>
<th>Weight %</th>
<th>Source and Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant</td>
<td>Igepal CA-720</td>
<td>0.1-10.0</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Liquid Ink</td>
<td>Glycerol (Humectant/Co-Solvent)</td>
<td>5.0-30.0</td>
<td>Sigma Aldrich (≥ 99.5%)</td>
</tr>
<tr>
<td>Vehicle/Solvent</td>
<td>Water (Carrier)</td>
<td>60.0-90.0</td>
<td>DI water</td>
</tr>
<tr>
<td></td>
<td>Lithium Chloride (Tracer)</td>
<td>0.1-1.0</td>
<td>Sigma Aldrich (≥ 99.0%)</td>
</tr>
<tr>
<td>Dye</td>
<td>Crystal Violet</td>
<td>1.0-10.0</td>
<td>J.T. Baker (≥ 99%)</td>
</tr>
</tbody>
</table>

Surface Tension: 35mN/m; Viscosity: 1.5cP.

3.2.2 Sample Preparation and Measurement Methods

The two chosen papers were printed using formulated ink and a drop-on-demand Dimatix DMP-2800 Materials printer (FUJIFILM Dimatix Inc., Santa Clara, CA). Jetting conditions and parameters that had to be optimized within Dimatix Digital Printing software are summarized in Table 3.2 and were adapted from Di Risio and Yan [15] guidelines. The printed pattern was a series of 200µm lines 1cm apart.

Table 3.2: Jetting Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Nozzle voltage</th>
<th>Waveform</th>
<th>Pulse width</th>
<th>Meniscus vacuum</th>
<th>Firing frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimum</td>
<td>35 V</td>
<td>Single pulse; fall in two steps</td>
<td>10 – 15 µs</td>
<td>4.5 – 5 inches H₂O</td>
<td>15 kHz</td>
</tr>
</tbody>
</table>

For the analysis of the xy-plane, the printed samples were analyzed using ToF-SIMS without any further preparation. All spectra were collected with ION-TOF ToF-SIMS IV instrument (ION-TOF, Münster, Germany) located at Surface Interface Ontario in the
Department of Chemical Engineering and Applied Chemistry at the University of Toronto. A pulsed bismuth cluster liquid metal ion gun was used, with spectra obtained in both high-mass resolution and high spatial imaging modes [16]. The use of the polyatomic doubly-charged cluster ion, $\text{Bi}_3^{++}$, allowed greater yields in the analysis of molecular species with slightly more stable imaging resolution. Charge neutralization was achieved using electron flood-gun. All data was collected using static SIMS, i.e. the primary ion dose was low ($< 1 \times 10^{13}$ ions/cm$^2$), ensuring impact to less than 1% of the surface atoms or molecules, thus leaving bombarded surface virtually undamaged [14].

To show comparative spreading of ink components in relation to one another, images of selected masses of secondary ions were overlapped. The secondary ions images (or visual profiles) were also saved in numerical form, i.e. with intensity of all secondary ions recorded at each pixel of a selected field of view. Reconstructed distribution profiles of ink components, obtained from the numerical data, were then used to quantify preferential absorption of individual ink-jet ink components. This quantification was made by means of separation efficiency equation (modified from Gane [12]), where the difference between the total absorption length (in this study absorption length of ink vehicle) and the absorption length of the dye or surfactant was expressed as the percentage of the total absorption length. The variability in separation efficiency was measured as percent standard deviation of several selected areas of the print and their respective separation efficiencies.

In order to evaluate distribution profiles on different papers, profiles were also normalized: with distance expressed as a fraction of theoretical width of the printed line.
(as specified within Dimatix ink-jet printer software) and with intensity expressed as a fraction of maximum intensity of each component.

3.3 Results and Discussion

3.3.1 ToF-SIMS Peak Identification of Ink Components

The dye (of MW = 407.98) was introduced as a chlorine salt. Thus, the peak at mass 372amu in the positive SIMS spectra (Figure 3.1A) corresponds to aromatic cationic portion of the dye with Cl⁻ ion dissolved in the solution. The peaks at 356amu and 340amu are assigned to the demethylated fragments of crystal violet dye [10].

As discussed earlier, to follow the distribution of ink vehicle or solvent, lithium was chosen as the tracer of ink vehicle. Dissolved lithium chloride in the ink formulation was expected to be absorbed by paper along with water ink solvent. As in previous studies [13], distribution of lithium was followed with ToF-SIMS imaging using its both isotopes, at 6amu and 7amu (Figure 3.1B).

Distribution of surfactant was followed by the addition of several peaks at higher masses of 581amu, 625amu, 669amu, 713amu, and 757amu (Figure 3.1C). These peaks correspond to fragments of surfactant molecule with numerous ethoxylate groups (\(-\text{CH}_2\text{CH}_2\text{O}^-\) 44 amu) removed from the structure [11]. For premium photo glossy ink-jet paper the fragmentation of the surfactant was more extensive than that of the Domtar multipurpose paper, as was seen by numerous or greater amount of peaks for glossy paper in positive SIMS spectra.
Figure 3.1: Positive SIMS Spectra Emphasizing Fragments of: (A) Crystal Violet Dye; (B) Lithium Chloride Tracer of Ink Solvent; and (C) Ethoxylated Surfactant

3.3.2 ToF-SIMS Image Analysis

ToF-SIMS images of individual components and their overlaps for multipurpose and photo glossy ink-jet papers are shown in Figure 3.2 and Figure 3.3, respectively. It is clear from comparison of Figure 3.2 and Figure 3.3 that the two papers produce a line of
very different print quality. Print quality on the photo glossy ink-jet paper is very uniform and sharp, unlike that of the multipurpose paper. However, overlays of ink vehicle and dye on both papers show that ink vehicle, marked by lithium ion, spreads further across the paper than the dye colorant. In addition, the surfactant does not spread more than the dye, as seen by there being no separation between the dye and the surfactant for both papers.

Surface topography of the two papers can be seen from the total ion SIMS images in Figure 3.2 and Figure 3.3. The lack of coating on multipurpose paper is clearly visible by the random arrangement of fibers, while for photo glossy ink-jet paper the coating conceals the fiber structure. The dye on multipurpose paper may be preferentially adsorbed and absorbed by paper fibers – the dye spreads and penetrates through the fibers or along the fiber surface. This preferential adsorption by fibers is consistent with the electrostatic attraction of cationic crystal violet dye to negatively charged fibers. Thus, for uncoated multipurpose paper a reduced sharpness of the print may be as a result of preferential distribution of the dye along unpredictable fiber configuration of paper.

It is clear that ToF-SIMS is not only capable of distinguishing different components of ink, but it can also detect relative distribution or preferential absorption of individual ink components.
**Figure 3.2:** Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Domtar Multipurpose Paper

**Figure 3.3:** Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Premium Photo Glossy Ink-jet Paper
3.3.3 Preferential Absorption/Distribution Profiles of Ink Components

Distribution profiles for multipurpose paper and photo glossy ink-jet paper are shown in Figure 3.4 and Figure 3.5, respectively. Profiles of both papers show that the spreading of the dye is greater than the theoretical line width as defined within Dimatix printing system. However, components of ink spread further across on multipurpose paper than they do on glossy paper, as also shown in Figure 3.4 and Figure 3.5. Lower extent of spreading indicates a higher quality print of photo glossy ink-jet paper. These profiles also confirm that the ink vehicle spreads further than the dye, with greater separation between ink vehicle and the dye on multipurpose paper than that on glossy ink-jet paper. As a result, the separation efficiency of the dye from ink vehicle is greater on multipurpose paper (25%) than the separation efficiency of the dye from ink vehicle on photo glossy ink-jet paper (20%). Both papers show no significant separation between the dye and the surfactant of ink. The hydrophobic groups of the dye may interact with hydrophobic groups of the surfactant, leading to possible formation of micelles. In addition, similar to the dye, the non-ionic surfactant may be adsorbed preferentially by the paper. This preferential adsorption of the surfactant may be such that the substrate-ink interface is amphipathic, i.e. exposing the hydrophilic moiety of the surfactant molecule to the liquid [3], thus improving the penetration rate and print quality. These reasons may contribute to insignificant separation between the dye and the surfactant.

Sharpness of the printed image is a function of the uniformity of ink spreading on the surface of paper. Images obtained using ToF-SIMS clearly show that photo glossy ink-jet paper (with lower separation efficiency) produces a sharper and higher quality print compared to multipurpose paper. The higher quality print is associated with lower
variability in the separation of ink components. On photo glossy ink-jet paper, Figure 3.3, the separation of ink dye from ink solvent is relatively the same in all areas of print with percent deviation of only 5%; however, on multipurpose paper, Figure 3.2, the separation of the dye from ink vehicle varies in different areas of the print with percent deviation or variability of 25%. This finding suggests that lower variability in separation of ink components produces higher quality print.

The different distribution profiles for multipurpose paper and photo glossy ink-jet paper may be a result of paper surface chemistry, topography, and pore structure. In fact, smoother distribution profiles of photo glossy ink-jet paper are an indication of smoother surface of glossy paper. In addition, photo glossy ink-jet paper has a fine surface pore structure and a greater surface area as a result of fine coating pigment particles fabricating the smooth glossy surface of this type paper. This greater surface area may be causing greater absorption and penetration into underlying substrate, thus limiting the extent of spreading of dye and solvent, as indicated by lower fraction of theoretical spreading for glossy paper than that of the multipurpose paper. Since coating structure is relatively uniform, the variability in preferential absorption of ink components is lower for glossy ink-jet paper than that of multipurpose paper. The random formation of fibers of multipurpose paper, as well as preferential adsorption of the dye on or along fiber surfaces, causes greater variability in preferential absorption of ink components.
Figure 3.4: Distribution Profiles Obtained from Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Domtar Multipurpose Paper
Figure 3.5: Distribution Profiles Obtained from Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Premium Photo Glossy Ink-jet Paper

3.4 Conclusions

Ink-jet ink components were successfully identified and tracked in terms of their distribution. The preferential absorption of ink components was studied with the use of ToF-SIMS imaging. For the selected papers, it was found that ink vehicle/solvent spread more than the dye; while surfactant spread along with the dye. In both paper samples, the
measured spreading was greater than theoretical spreading value, with multipurpose paper having greater amount of spreading than photo glossy ink-jet paper. The preferential absorption was quantified in terms of separation efficiency with separation efficiency of multipurpose paper (25%) greater than separation efficiency of photo glossy ink-jet paper (20%). Separation efficiency could not be correlated with print quality, however, variability in separation efficiency, as a result of paper surface morphology, was correlated to print quality. Greater variability in preferential absorption resulted in lower quality print – multipurpose paper, having variability in separation efficiency of 25%, produced a lower image quality print than photo glossy ink-jet paper, having variability in preferential absorption of only 5%.

References


CHAPTER 4 – DISTRIBUTION OF INK COMPONENTS

4.1 Introduction/Background and Review

One of the driving forces of continuous growth in digital printing is the printing quality [1], which is directly defined by the optical properties of the final print (e.g. feathering [2], resolution [3], print sharpness [2,4,5], optical print density [2,3,4,5,6]). For example, feathering is defined by defective lateral migration of ink on the surface of paper [7], i.e. feathering is directly related to edge raggedness of the print [1]. A print with high raggedness results in loss of resolution as determined by the number of distinguished pixels/dots printed per inch [1]. Sharpness is associated with a sharp drop of the optical density at the edge of the printed image, with infinitely steep drop or slope representing a sharp image [1]. Print density is defined by degree of darkness of the printed image [8] and is the most basic and the most important factor in print quality [1]. These optical properties are influenced by mechanisms of interactions between ink components and the media [9]. In particular, spreading across or on the surface of the medium (xy-plane) and penetration or absorption into the underlying substrate (z-plane) are two important mechanisms governing the distribution of ink components [10,11]. A balanced combination of the two mechanisms produces a good quality print [10]. Too much penetration causes print through – a visible image on the reverse side of the print – and as a result loss of print density on the printed image [10]. Too much spreading causes feathering of the print as well as possible intermixing of different liquid inks in multi-colour printing [10]. Excessive spreading as a result produces a print of lower resolution due to reduced sharpness of the print.
Interactions of printing inks with paper have been studied intensively in recent years. Desie and Van Roost investigated the dynamics of droplet impingement, spreading, absorption, penetration, and evaporation for different ink-jet ink classes using cinematographic and high speed video techniques [12]. In their study, they have established that dye based inks follow Davis-Hocking model based on Lucas-Washburn equation (Equation 2.2), where depth penetration is proportional to the square root of pore radius of the receiving substrate [12]. In addition, Desie and Van Roost concluded that, for dye based inks, the parabolic penetration zone is entirely within the coating structure, in contrast with pigment based inks where the colourant remains on the top of the medium [12]. Both Aspler and Le confirmed Desie’s and Van Roost’s observations and state that dye-based ink-jet inks penetrate either into the coating pigment on coated media or penetrate into the bulk of paper on uncoated media [3,13]. Thus, optical print density can be significantly reduced by excessive dye penetration [14]. Aspler also confirmed that the spreading on uncoated paper is well correlated with Lucas-Washburn theory [13]. Le added that the spreading on uncoated paper tends to be along the paper fibers [3]. Aspler also noted that due to very different pore structure in different planes, fluid flow in the xy plane, i.e. spreading, is greater than the fluid flow in the xz or yz planes, i.e. penetration [13]. Surface chemistry of papers is a significant factor in sorption of water-based inks on coated and surface sized mediums [13]. For monochrome printing, use of hydrophobic sizing reduces both spreading and penetration resulting in good quality prints [10,13]. Unlike coated and surface treated substrates, the more dominant factor in ink sorption on uncoated papers is the surface smoothness and the pore structure of the substrate [13]. In fact, non-uniformity of ink component distribution on uncoated paper was reported to match to random fiber configuration in
CHAPTER 3. Both internal and surface sizing are needed to achieve a balance between penetration and spreading [10].

Gane investigated absorption of ink solvent, as well as segregation of miscible ink solvents/oils within the coating structure using optical image analysis and Fourier Transform Infrared spectroscopy (FTIR) [15]. Gane concluded that at the shortest times, finer pores fill first due to inertial retardation (Equation 2.1), i.e. penetration depth is inversely proportional to the square root of pore radius of the substrate [15]. This behaviour at shortest times is the opposite of Washburn equation, where penetration is proportional, rather than inversely proportional, to square root of pore radius. This inertial retardation at shortest times can be considered as a wetting delay cited by Croucher and Hair [16]. At longer times, however, Washburn-like relations may apply as the transition from inertial retardation in large radii to viscous retardation in fine structures occurs [15]. As a result, Gane reports that high pore volume matt coatings with large pore radii imbibe slower than microporous gloss coatings with small pore radii [15]. Thus, high surface area coating pigment with high capillarity particularly in fine pores may ensure rapid absorption during short times [15], and as a result may produce improved print quality [16].

Daniel and Berg investigated spreading and penetration of surfactant-laden drops on thin commercial ink-jet photographic papers using high-speed video-based optical analysis [11]. Daniel and Berg concluded that true deviations from Washburn-like behaviour are caused by initial wetting delays, and five parameters can fully describe and define simultaneous spreading and penetration uniquely: drop volume, pore size, paper
thickness, porosity, and contact angle [11]. Daniel and Berg also added that ultimate extent of spreading is bounded by the competition between spreading and penetration [11].

Studies, described above, utilizing optical microscopic techniques are constructive and valuable aid in understanding ink sorption mechanisms. However, spreading and penetration of ink components, particularly dye/pigment [12-14], solvent [15], and surfactant [11], have been, thus far, considered as separate processes. The simultaneous spreading and penetration of all ink components is still insufficient and is required to understand the interactions among the ink components, their interactions with the substrate and their impact on print quality. Since ink-jet inks are complex solutions, i.e. not just simple solutions of dyes or suspension of pigment particles, penetration and spreading of ink components are further complicated by preferential absorption of these components (e.g. preferential adsorption of dye on paper surface) [13]. This was clearly demonstrated in CHAPTER 3, where the dye and the surfactant of the ink were preferentially retained by the paper. High retention of the dye or separation of the dye from the solvent, as represented in Figure 4.1, may be used as an indication of print quality: as the dye is preferentially retained by the paper, ink solvent is freely absorbed, penetrated, and evaporated. Low separation or retention of the dye, represented in Figure 4.2, may suggest that the dye is dragged further across and/or deeper into the paper along with ink solvent causing excessive spreading and excessive penetration. Thus, low separation or retention of the dye may cause degradation of image quality, increase in drying time, and loss or variation in print density as ink solvent evaporates upon ink drying.
In order to study spreading and penetration of all ink components simultaneously, chemical spectroscopy methods are required. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is one of the most advanced and versatile analytical techniques – Fardim and Holmbom [17] report it to be the most ideal of all chemical spectroscopy. ToF-SIMS has excellent mass resolution providing not only elemental and chemical information (resembling XPS – X-ray Photoelectron Spectroscopy), but also molecular information for wide variety of materials [18]. In addition to high mass resolution, ToF-SIMS also has the highest spatial resolution - 100nm [19] - when compared to XPS, confocal Raman, or Fourier Transform Infrared spectroscopy [17,20,21,22]. Thus, as was demonstrated in previous papers [18], as well as in
CHAPTER 3, ToF-SIMS provides chemical, molecular, and distributional information required for the study of preferential absorption of ink-jet ink components.

In ToF-SIMS, a pulsed primary ion bombards the surface of the sample, generating secondary ions, a portion of which is either positive or negative [18]. These secondary ions are analyzed in terms of their time-of-flight from the sample to the detector, with lighter masses reaching the detector first [18,23]. The resulting spectra consist of characteristic peaks and fragmentation patterns. Identification of these peaks and patterns is made from either comparison of model compounds or with the aid of library spectra [18]. In the case of this study, identification of ink-jet ink components was simplified with the use of a custom ink-jet ink formulation of known composition (CHAPTER 3).

During ToF-SIMS imaging, the mass spectrum is recorded at each pixel, producing images from all secondary ions [23]. SIMS imaging allows flexibility of selecting certain masses in order to obtain distributional information of ink components of the sample surface [23].

In recent years, advances in ink and paper analysis using chemical spectroscopy methods have been made. Dalton et al. investigated absorption of pigment-based offset ink using ToF-SIMS and XPS [6]. They concluded that both techniques, ToF-SIMS and XPS, are useful in the analysis of chemical composition through an offset ink film printed onto kaolin coated paper [6]. However, the applicability of these two techniques to ink-jet printing has not been noted. Lozo et al., on the other hand, tested applicability of several non-destructive microscopic and spectroscopic methods (Raman, CLSM, FTIR) to investigate depth profiling of ink-jet prints on different grades of paper, ranging from
tissue paper to photo paper [24]. Through oil immersion sampling method, both Raman and CLSM were found to be useful in the depth analysis of dye-based and pigment-based ink-jet inks throughout the vertical dimension of paper [24]. Three ink layer categories were identified: a homogeneous layer with high dye/pigment intensity, a non-homogeneous layer representing dye/pigment distribution or gradual dye/pigment-coating interface, and a deep or maximum dye/pigment penetration layer [24]. Dye-based inks were found to penetrate deeper than pigment-based inks [24]. Shibatani et al. appliedToF-SIMS to develop a new analytical method to investigate absorption of pigment-based ink-jet ink co-solvent on commercially available resin coat-based and photo-grade glossy papers [25]. The co-solvent, in this study, was marked by deuterated glycerin, and was distributed within the ink layer and at the boundary of ink-coating layer [25]. Tag et al., on the other hand, employed ToF-SIMS to investigate distribution of ethoxylated surfactant in relation to offset printing, in the process identifying several peaks of ethoxylation stages of the surfactant [26]. Sodhi et al. tested capability of ToF-SIMS in conjunction with PCA analysis to investigate distribution of ink constituents on two different coating formulations [18]. While peak assignments were based on reasonable expectations, Sodhi et al. reported that positive assignment of the various fragments to different ink components would require full knowledge of chemical formulation of ink [18]. Studies exploiting chemical spectroscopy methods clearly assess and demonstrate the control and capabilities of these spectroscopic techniques related to ink and paper analysis, however, greater knowledge on how these techniques can improve understanding of printing process and quality is still required. CHAPTER 3 examined and demonstrated capabilities of ToF-SIMS to study preferential absorption of ink-jet ink components of known composition on the xy-plane of coated and uncoated papers, thus
perhaps potentially relating ToF-SIMS techniques to print quality. In this work, we build on the work by Sodhi et al. [18] and on the work of CHAPTER 3 by investigating the distribution of ink components using ToF-SIMS analysis and using a custom ink-jet ink formulation of known composition to further study the mechanisms of spreading and penetration of ink components. Analysis of the vertical plane of the paper provides further understanding on penetration mechanism and its competing relationship with spreading on the surface of paper. The use of specialized ink-jet paper with other non-specialized uncoated papers enables the comparison and further understanding of ink component migration on commercial papers. In addition, the findings on sorption, penetration, and spreading of the ink components will be used to assess their impact on print quality.

4.2 Experimental Procedures

4.2.1 Materials

The chemical composition of the ink formulation and the source of chemicals used in this study are summarized in Table 4.1. Cationic crystal violet dye was introduced into solution as chlorine salt. This dye in the formulation was chosen for its hydrophobic nature [27], i.e. to ensure sufficient separation of the dye from the water solvent. The fact that crystal violet is a cationic dye [27] was also taken into consideration such that preferential adsorption by negatively charged fibers may be achievable. An ethoxylated surfactant, Igepal CA-720, was used in the formulation, and ink vehicle/solvent was marked using 0.1wt% lithium chloride as tracer.
Several papers were selected as summarized in Table 4.2. Since all papers were purchased commercially, limited information about their properties was available.

Table 4.1: Ink Formulation and Chemical Information

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical</th>
<th>Weight %</th>
<th>Source and Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant</td>
<td>Igepal CA-720</td>
<td>0.1-10.0</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Liquid Ink Vehicle/Solvent</td>
<td>Glycerol (Humectant/Co-Solvent)</td>
<td>5.0-30.0</td>
<td>Sigma Aldrich (≥ 99.5%)</td>
</tr>
<tr>
<td></td>
<td>Water (Carrier)</td>
<td>60.0-90.0</td>
<td>DI water</td>
</tr>
<tr>
<td></td>
<td>Lithium Chloride (Tracer)</td>
<td>0.1-1.0</td>
<td>Sigma Aldrich (≥ 99.0%)</td>
</tr>
<tr>
<td>Dye</td>
<td>Crystal Violet</td>
<td>1.0-10.0</td>
<td>J.T. Baker (≥ 99%)</td>
</tr>
</tbody>
</table>

Surface Tension: 35mN/m; Viscosity: 1.5cP.

Table 4.2: Selected Paper Information

<table>
<thead>
<tr>
<th>#</th>
<th>Paper Description</th>
<th>Comments/Properties</th>
<th>Brand Name and Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Xerox laser paper</td>
<td>- High Yield Laser paper</td>
<td>XEROX 3R11720</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Grammage: 67g/m² (18lb)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Brightness: 84</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Domtar multipurpose paper</td>
<td>- Grammage: 75g/m² (20lb)</td>
<td>Domtar copy D82201 28397B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Brightness: 92</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Whiteness: 145</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Staples standard ink-jet paper</td>
<td>- Grammage: 90g/m² (24lb)</td>
<td>STAPLES Business Depot Item 517386</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Brightness: 96</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Premium ink-jet paper (Presentation matte paper)</td>
<td>- Grammage: 165g/m² (44lb)</td>
<td>EPSON America, Inc. S041257</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Ultra smooth, non-glare, heavyweight paper</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Instant-drying paper</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Premium ink-jet paper (Photo glossy paper)</td>
<td>- Grammage: 252g/m² (68lb)</td>
<td>EPSON America, Inc. S041667</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- High gloss</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Instant-drying paper</td>
<td></td>
</tr>
</tbody>
</table>

* Note: Grammage is reported using both metric system convention as well as US basis weight system convention (converted to one another using standard conversions reported by Micro Format, Inc. [28]). Grammage reported in bold is one stated on commercial packaging.
4.2.2 Sample Preparation

The chosen papers were printed using formulated ink and drop-on-demand Dimatix DMP-2800 Materials printer (FUJIFILM Dimatix Inc., Santa Clara, CA). Jetting conditions and parameters that had to be optimized within Dimatix Digital Printing software were summarized previously in CHAPTER 3. The printed pattern was a series of 200µm lines 1cm apart, as well as 1cm blocks for measurement of print density.

The xy-plane of the printed samples was analyzed without any further sample preparation; however, for the analysis of the vertical direction of the paper, cross sections were prepared. To eliminate interactions between ink and the embedding liquid, instead of embedding samples in epoxy, samples were sandwiched between two plastics for rigid support. Detailed procedure for cross-sectioning is summarized in APPENDIX B. To minimize the area of cross-sectioning, the samples were given a pyramid shape using Leica EM TXP target sectioning system, located at Surface Interface Ontario. Samples were then microtomed with a diamond trimming knife (DiATOME UT726) using Leica EM UC 6 microtome, also located at Surface Interface Ontario laboratory. The experimental set-up for preparing a cross section is represented in Figure 4.3.

![Figure 4.3: Experimental Set-up for Cross-Sectioning using Microtome Techniques](image)
4.2.3 Optical Image Analysis

All images were obtained with Leica Optical DM LA Microscope and OpenLab 3.1.4 Improvision Software (Improvision Inc.) using a 10X objective lens. The field of view at this magnification is 0.870mm × 0.690mm, with recorded images of resolution 0.669µm/pixel. Since all paper samples have certain roughness associated with them, CombineZ5 Software [29] was used to attain images of increased depth of focus. For each sample, a focus series were collected with several images partially focused at different locations of the sample. Each focus series were then subsequently merged into one composite image using “Average and Filter” function of the CombineZ5 software package. Using Optimas 6.0 Software (Optimas Corporation), all images were converted to 8-bit gray scale, and were processed using the same thresholding to increase contrast between printed and unprinted regions of the samples. Optimas 6.0 Software was also used to determine width/area, perimeter, and penetration depth of the printed region of the samples. The average width of the line was calculated as measured area of the printed region divided by the length of the line (in this case 870µm for all samples). The average width of the line was used as an indication of print sharpness – the smaller the width, the sharper the image [2]. Perimeter was measured as the coastline of the printed line [2] and was utilized as an indication of both degree of spreading, i.e. line width, and degree of edge roughness, i.e. unevenness and raggedness of the print [2,5]. Average penetration depth was calculated as the measured area of the inked region divided by the longest axis of penetration. Print density was measured using X-Rite Spectrodensitometer 530. The same stack of paper sheets was used as backing in each of the measurements of print density. Color data in Spectrodensitometer was reported as
absolute colour measurement data (rather than colour difference, i.e. minus paper reference) [30].

4.2.4 ToF-SIMS Analysis

All spectra were collected with ION-TOF ToF-SIMS IV instrument (ION-TOF, Münster, Germany) located at Surface Interface Ontario in the Department of Chemical Engineering and Applied Chemistry at the University of Toronto. A pulsed bismuth cluster liquid metal ion gun was used, with spectra obtained in both high-mass resolution and high spatial imaging modes [19]. Detailed information regarding both modes can be found in reference [19]. The use of the polyatomic doubly-charged cluster ion, Bi$_3$$^{++}$, allowed greater yields in the analysis of molecular species with slightly more stable imaging resolution. Charge neutralization was achieved using electron flood-gun. All data was collected using static SIMS, i.e. the primary ion dose was low (< $1\times10^{13}$ ions/cm$^2$), ensuring impact to less than 1% of the surface atoms or molecules, thus leaving bombarded surface virtually undamaged [19].

To show comparative spreading of ink components in relation to one another, images of selected masses of secondary ions were overlapped. The secondary ions images (or visual profiles) were also saved in numerical form, i.e. with intensity of all secondary ions recorded at each pixel of a selected field of view. Reconstructed distribution profiles of ink components, obtained from the numerical data, were then used to quantify preferential absorption of individual ink-jet ink components. This quantification was made by means of separation efficiency equation, modified from Gane [15], where the difference between the total absorption length (in this study absorption length of ink
vehicle) and the absorption length of the dye or surfactant was expressed as the percentage of the total absorption length. The differences in absorption lengths were taken at 50% maximum intensity of the ink component signal. Border variability of ink components was calculated as percent standard deviation of the average ink component border, as represented in Figure 4.4.

![Figure 4.4: Border Variability Definition](image)

In order to evaluate distribution profiles on different papers, profiles were also normalized: with distance expressed as a fraction of theoretical width of the printed line (as specified within Dimatix ink-jet printer software) for xy-plane, or as a fraction of the paper thickness (measured using Precision Micrometer) for xz-plane, and with intensity expressed as a fraction of maximum intensity of each component.

4.3 Results and Discussions
4.3.1 Optical Image Analysis
4.3.1.1 XY-Plane

Optical images for all selected papers, for one of the triplicates, are shown in Figure 4.5; and all the results are summarized in APPENDIX C. As seen from Figure 4.6, all papers spread beyond the theoretical width of the line as specified within the printing system. However, there seems to be no particular trend in the average width of the printed line as
the paper is more specialized towards ink-jet printing. Since no standardized procedure and values determining ink-jet print quality exist [4], comparison with previous work is difficult. For example, Kowalczyk and Trksak compared print quality of 27 commercial ink-jet papers [2]. Since commercial ink-jet printers were used, standardized values, i.e. ratios of actual to theoretical regions, of printed areas could not be reported in their study [2]. Due to the lack of this normalization, comparison between experiments greatly depends on the chosen methodology and image analysis software. For example, Hensema et al. measured width of the printed line in terms of number of pixels [5], which is greatly dependent on the image analysis software.

Both the degree of spreading and raggedness or evenness of the print (relating to feathering) were measured by the perimeter of the printed image [2,5], as outlined in red in Figure 4.5. It is clear from Figure 4.5 that as paper is more specialized towards ink-jet printing, the perimeter and thus the raggedness and spreading of the print decrease (Figure 4.7), improving the quality of the print. Nonetheless, the perimeter on all papers is greater than theoretical perimeter of 2.14mm ($2 \times 870\mu m + 2 \times 200\mu m = 2.14mm$), as represented in Figure 4.7. Ink-jet prints are known to have more ragged edges than those found in laser or offset printing [10], thus perimeter ratios (of actual perimeter to theoretical one) greater than unity are perhaps not surprising. Hensema et al. reported edge roughness or raggedness in terms of ratio of the actual length to the theoretical length of the border, i.e. coastline, between inked and non-inked regions ($L_{actual}/L_{th}$) [5]. Their highest reported ratio for edge roughness on multipurpose office paper was 2.33 [5]. In our study, multipurpose paper has average perimeter of 6.81mm and average width of 326µm, which translates to edge roughness ratio of 3.54. This higher value of
edge roughness ratio (3.54 versus 2.33) may be an indication that further optimization of ink formulation and printing process parameters is required. Nonetheless, photo glossy ink-jet paper has the lowest perimeter, closest to the theoretical value, while Xerox laser paper has the greatest perimeter, deviating the most from the theoretical value.

Ink-jet inks are mostly water, and thus represent extreme case of application of water to paper [3,13]. Thus, to minimize the extent of spreading, ink-jet papers should have high absorbency [10]. Since laser paper is not intended for ink-jet printing, it is not surprising that formulated ink-jet ink spreads the most on this paper, as indicated by the greatest perimeter of the printed line. Multipurpose paper is designed for every day use in the office, which includes both laser and ink-jet printing. Thus, it is expected that multipurpose paper would show lower extent of spreading than laser paper. This expected trend is indicated in Figure 4.7. The lower perimeter of multipurpose paper may perhaps be explained by increases in surface or internal sizing. In addition to surface and internal sizing, coated (standard, presentation matte, and photo glossy ink-jet) papers may have changes in surface chemistry and charge, changes in porosity, pore size and pore size distribution. Thus, with these possibly more optimized parameters intended for ink-jet printing a controlled spreading may be achievable. This expected trend of higher print quality with increased specialization towards ink-jet printing is clearly indicated by lower perimeters of coated papers in Figure 4.7.
Figure 4.5: Optical Images (870µm × 690µm each) of (A) Xerox Laser Paper, (B) Domtar Multipurpose Paper, (C) Staples Standard Ink-jet Paper, (D) Presentation Matte Ink-jet Paper, and (E) Photo Glossy Ink-jet Paper
The print density obtained for different grades of paper is shown in Figure 4.8. As the paper is more specialized towards ink-jet printing, print density of the image increases, as seen in Figure 4.8. Densities for uncoated papers (laser and multipurpose) fall into range between 1.00 and 1.20, which conform to the values reported by Kowalczyk and Trksak in their analysis of 26 uncoated quality papers [2]. Density values for coated (standard,
presentation matte, and photo glossy ink-jet) papers conform to the values reported by general standards [1,10], falling into a range between 1.20 and 1.50. Again, it is anticipated that the two highly coated mediums, presentation matte and photo glossy ink-jet papers, would show higher print density than the uncoated laser and multipurpose papers. The experimental results shown in Figure 4.8, match the anticipated trend of coated and uncoated papers. It is perhaps surprising that presentation matte ink-jet paper has slightly higher print density than that of the photo glossy ink-jet paper; however, the two densities are not statistically different.

One would expect that lower spreading, thus lower perimeter, would produce a more localized distribution of the dye, which should result in higher print density. This hypothesis is supported by the correlation presented in Figure 4.9. However, as indicated by low R\textsuperscript{2} value, changes in print density cannot be completely defined by the changes in perimeter. Since there is competition between the two mechanisms of ink sorption, print density would be dependent on both spreading, here indicated by
perimeter, and penetration, as seen in the next section. Thus, higher print density of the matte presentation paper may perhaps be explained by penetration data.

![Figure 4.9: Effect of Perimeter on Print Density](image)

4.3.1.2 XZ-Plane

Optical images of cross sections for all selected papers, for one of the triplicates, are shown in Figure 4.10; and all the results are summarized in APPENDIX C. It is seen from Figure 4.10 and Figure 4.11 that multipurpose paper has the highest penetration. The penetration zone for all ink-jet papers in Figure 4.10 is either entirely within the bulk of the paper or entirely within the coating layer for highly coated mediums. These observations match those made by Aspler and Le [3,13]. In addition, as seen from Figure 4.11 the penetration depths in coated (standard, presentation matte, and photo glossy ink-jet) papers are significantly lower than those in uncoated (laser and multipurpose) papers. As also seen from Figure 4.10, as the paper is more specialized towards ink-jet printing, the penetration zone becomes more defined and uniform – glossy ink-jet paper shows clear parabolic penetration zone that has been cited in literature [12].
Figure 4.10: Optical Images of Cross Sections (870µm × 270µm each) of (A) Xerox Laser Paper, (B) Domtar Multipurpose Paper, (C) Staples Standard Ink-jet Paper, (D) Presentation Matte Ink-jet Paper, and (E) Photo Glossy Ink-jet Paper
The relationship between spreading and penetration is shown in Figure 4.12. Uncoated laser and multipurpose papers have both higher spreading and higher penetration when compared to coated standard ink-jet, presentation matte ink-jet, and photo glossy ink-jet papers. Uncoated papers having pore structure on the larger scale than that of coated papers [15], generate higher spreading and penetration of the dye (Figure 4.12). This is supported by Washburn equation that predicts higher spreading and penetration with greater pore size. Thus, Washburn equation can be used to rank samples in the order of increased print quality, as was stated in previous work [10]. Within coated and uncoated papers, the same trend is observed in Figure 4.12: as penetration of the dye increases, spreading decreases. This behaviour was noted by Daniel and Berg, who state that the extent of spreading is bounded by the competition between spreading and penetration [11].
Both uncoated papers, laser and multipurpose, have high spreading and penetration and as a result have low print density, as seen in Figure 4.13. In addition to high penetration, laser paper has lower print density due to greater amount of spreading than that of the multipurpose paper, as shown in Figure 4.12. All three coated papers have higher print density values than those of uncoated papers (Figure 4.13). Though standard ink-jet paper has lower penetration than both matte and glossy ink-jet papers, print density of this paper is lower (Figure 4.13), perhaps due to higher perimeter and spreading of the printed line (Figure 4.12). In addition, both presentation matte and photo glossy ink-jet papers are highly coated mediums, with penetration zone entirely within the coating layer (Figure 4.10). This penetration mechanism in highly coated mediums may also contribute to higher print density values than that of the standard ink-jet paper. In Figure 4.13, higher penetration of the dye in photo glossy ink-jet paper may explain its slightly lower print density when compared to presentation matte ink-jet paper.

![Figure 4.12: Effect of Dye Penetration on Perimeter of the Inked Line](image)

Both uncoated papers, laser and multipurpose, have high spreading and penetration and as a result have low print density, as seen in Figure 4.13. In addition to high penetration, laser paper has lower print density due to greater amount of spreading than that of the multipurpose paper, as shown in Figure 4.12. All three coated papers have higher print density values than those of uncoated papers (Figure 4.13). Though standard ink-jet paper has lower penetration than both matte and glossy ink-jet papers, print density of this paper is lower (Figure 4.13), perhaps due to higher perimeter and spreading of the printed line (Figure 4.12). In addition, both presentation matte and photo glossy ink-jet papers are highly coated mediums, with penetration zone entirely within the coating layer (Figure 4.10). This penetration mechanism in highly coated mediums may also contribute to higher print density values than that of the standard ink-jet paper. In Figure 4.13, higher penetration of the dye in photo glossy ink-jet paper may explain its slightly lower print density when compared to presentation matte ink-jet paper.
Information regarding ink component peak identification within ToF-SIMS spectra can be found in CHAPTER 3 and is briefly summarized in Table 4.3. On matte paper, surfactant peaks could not be detected. Due to greater fragmentation of the paper itself, surfactant peaks on laser paper could not be distinguished from other peaks of significantly higher intensities. Thus, surfactant peaks could only be detected on multipurpose, standard ink-jet, and photo glossy ink-jet papers.

Table 4.3: Ink Component Peak Identification

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical (used for identification)</th>
<th>ToF-SIMS Peaks of Identification (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye</td>
<td>Crystal Violet</td>
<td>340, 356, 372 (16amu apart, representing demethylated fragments of the dye [27])</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Igepal CA-720</td>
<td>537, 581, 625, 669, 713, 757 (44amu apart, representing ethoxylation stages of the surfactant [26])</td>
</tr>
<tr>
<td>Solvent</td>
<td>Lithium Chloride (Tracer)</td>
<td>6, 7 (isotopes of lithium: $^6$Li – 7.5%, $^7$Li – 92.5%) [31]</td>
</tr>
</tbody>
</table>
4.3.2.1 XY-Plane

ToF-SIMS images of individual components and their overlaps for all papers are shown in Figure 4.14 to Figure 4.18. It is clear from comparison of Figure 4.14 to Figure 4.18 that all papers produce a line of very different print quality. Print quality of the coated, photo glossy ink-jet and presentation matte ink-jet, papers is very uniform and sharp, unlike those of the uncoated, laser and multipurpose, papers. However, overlays of ink vehicle and dye on all papers show that ink vehicle, marked by lithium ion, spreads further across the paper than the dye colorant. Surfactant on multipurpose and photo glossy papers does not spread more than the dye, as seen by there being no separation between the dye and the surfactant.

Surface topography of all papers can be seen from the total ion SIMS images in Figure 4.14 to Figure 4.18. The lack of coating on multipurpose paper is clearly visible by the random arrangement of fibers, while for photo glossy ink-jet and presentation matte ink-jet papers the coating conceals the fiber structure. Both laser and standard ink-jet papers have some, but not complete, concealment of fiber structure. These differences in topographies may have an impact on border definition (APPENDIX D). Some concealment of fiber structure in standard ink-jet paper greatly reduced variability in both dye and solvent borders when compared to both laser and multipurpose papers (Figure 4.19). Dye and solvent borders of presentation matte ink-jet paper are very similar to those of the standard ink-jet paper (Figure 4.19). Since matte coating pigment is coarser than the fine coating pigment of glossy paper, surface of the matte paper is more porous and perhaps has higher roughness, resulting in similar border variability as standard ink-
jet paper. Glossy paper has the least variability in the dye and solvent borders due to the very smooth microporous structure of the glossy paper itself.

**Figure 4.14:** Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Xerox Laser Paper

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- **no distinguishable surfactant peaks due to higher fragmentation of laser paper itself**
Figure 4.15: Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Domtar Multipurpose Paper

Figure 4.16: Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Staples Standard Ink-jet Paper
Figure 4.17: Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Presentation Matte Ink-jet Paper

Figure 4.18: Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Photo Glossy Ink-jet Paper

no surfactant peaks detected
Figure 4.19: Effect of Paper on Dye and Solvent Border Variability

There is a high correlation between dye border variability and perimeter of the inked line, shown by the correlation in Figure 4.20. Both variables are an indication of print quality.

Figure 4.20: Effect of Border Variability on Perimeter of the Inked Line

4.3.2.2 XZ-Plane

ToF-SIMS images of individual components and their overlaps for multipurpose paper and photo glossy ink-jet paper are shown in Figure 4.21 and Figure 4.23, respectively. It is seen from Figure 4.21 and Figure 4.23 that the dye penetration zone is entirely
within the bulk of the paper on multipurpose paper and is entirely within the coating layer
on glossy ink-jet paper, as was suggested by previous studies [3,12,13]. In addition, the
solvent penetration zone on glossy ink-jet paper is also entirely within the coating layer,
as seen in Figure 4.23. Aspler has suggested that state of the art technology for ink-jet
paper incorporates both high water absorbent coating layer and heavily sized basesheet
preventing water penetration and basesheet distortion [10]. Thus, the photo glossy ink-jet
paper may perhaps have high sizing of the basesheet, which prevents penetration of the
solvent into the bulk of the paper beyond the coating layer. Similar to the case of the xy-
plane, coated glossy paper has a very uniform penetration, while uncoated multipurpose
paper has variability in penetration depths (Figure 4.21 versus Figure 4.23).

While the dye penetrates between 20% and 40% of paper’s thickness, ink vehicle/solvent
penetrates throughout the paper’s thickness for multipurpose paper or throughout the
coating layer for glossy ink-jet paper. Thus, the separation of the dye from the solvent or
retention of the dye in z-direction is more prominent than the retention of the dye in the
x-direction (Figure 4.21 versus Figure 4.22 and Figure 4.23 versus Figure 4.24). This
may be an indication of the mechanism of the ink penetration. Aspler stated that the
spreading in the XY-plane may be greater than penetration in the xz or yz planes by the
order of magnitude [10,13]. Thus, perhaps, initially both dye and solvent spread across in
the x-direction with little separation or retention of the dye; however, at longer times as
penetration commences the solvent penetrates through, but the dye has already been
adsorbed and absorbed by the fibers or by the fine pigment of the coating layer. For
uncoated paper, the greater fluid flow in the xy-plane may also be explained by the
structure or formation of the paper as seen in Figure 4.25: the ink may travel in the more
open xy-plane either along the fibers or through the fibers, instead of through a more obstructed z-direction of paper.

Croucher and Hair also reported that, at the shortest time before the liquid penetration commences, there is a wetting delay defined by the dissipation of the inertial forces of the drop [16]. During this inertial retardation Gane reported that the penetration is inversely proportional to the pore radius, with finer pores filling first [15]. An example of this is evident in the outlined white area of the positive SIMS image of the dye on multipurpose paper (Figure 4.22), where some of the large pores remain unfilled by the dye. For uncoated multipurpose paper, finer pores created by the edges or by the overlap of fibers show higher intensity of the dye than the areas of larger pores (Figure 4.22). Similar observations were made by Roberts et al. in their visualization of fluid penetration into softwood kraft paper [32]. Coated glossy paper, on the other hand, having uniform distribution of finer pores, shows uniform distribution of the dye. Thus, at longer times when penetration into the substrate commences, the dye may have already been adsorbed either by fibers or by the fine pores created by the edges of fibers or by the fine pigment of the coating layer.
Figure 4.21: Positive SIMS Images of Z-Plane - Interface between Inked and Non-inked
Regions on Domtar Multipurpose Paper

Figure 4.22: Reproduced Positive SIMS Images of XY-Plane - Interface between Inked
and Non-inked Regions on Domtar Multipurpose Paper

Figure 4.23: Positive SIMS Images of Z-Plane - Interface between Inked and Non-inked
Regions on Photo Glossy Ink-jet Paper
4.3.3 Distribution of Ink Components

4.3.3.1 XY-Plane

Distribution profiles for all papers are shown in Figure 4.26 to Figure 4.30. Profiles of all papers show that the spreading of the dye is greater than the theoretical line width as defined within Dimatix printing system. However, components of ink spread further across on laser and matte ink-jet papers than they do on glossy ink-jet paper (with
multipurpose and standard ink-jet papers falling in between), as shown in Figure 4.26 to Figure 4.30. Lowest extent of spreading indicates highest quality print of photo glossy ink-jet paper. These profiles also confirm that the ink vehicle spreads further than the dye, with the greatest retention of the dye on standard ink-jet paper (20%), and zero retention of the dye on laser paper (Figure 4.31 and APPENDIX E). This zero retention of the dye may be explained by the non-specialized nature of laser paper towards ink-jet printing and its ink-jet ink formulation, i.e. instead of being retained, the dye is dissipated on the surface of laser paper along with the solvent.

Glossy and multipurpose papers show no significant separation between the dye and the surfactant of ink. The hydrophobic groups of the dye may interact with hydrophobic groups of the surfactant, leading to possible formation of micelles. In addition, similar to the dye, the non-ionic surfactant may be adsorbed preferentially by the paper. This preferential adsorption of the surfactant may be such that the substrate-ink interface is amphipathic, i.e. exposing the hydrophilic moiety of the surfactant molecule to the liquid [11], improving the penetration rate. These reasons may contribute to insignificant separation between the dye and the surfactant on glossy and multipurpose papers.
Figure 4.26: Normalized Distribution Profiles Obtained from Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Xerox Laser Paper
Figure 4.27: Normalized Distribution Profiles Obtained from Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Domtar Multipurpose Paper
Figure 4.28: Normalized Distribution Profiles Obtained from Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Staples Standard Ink-jet Paper
Figure 4.29: Normalized Distribution Profiles Obtained from Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Presentation Matte Ink-jet Paper
Figure 4.30: Normalized Distribution Profiles Obtained from Positive SIMS Images of XY-Plane - Interface between Inked and Non-inked Regions on Photo Glossy Ink-jet Paper
Effect of retention in the x-direction on print density (Figure 4.32) reveals that segregation of the dye from solvent or dye retention in the x-direction is not of significant nature. This is compatible with fast spreading in the x-direction versus slow penetration in z-direction [10,13].
According to Figure 4.33, lower dye retention seems to be associated with higher spreading expressed in terms of perimeter ratio. This effect has already been discussed for the case of laser paper.

![Figure 4.33: Effect of Retention of the Dye on Perimeter of the Inked Line](image)

### 4.3.3.2 XZ-Plane

Distribution profiles for multipurpose paper and glossy ink-jet paper are shown in Figure 4.34 and Figure 4.35. For multipurpose paper, the solvent, marked by lithium ion, penetrates throughout the bulk of the paper, while the dye penetrates 40% of the paper’s thickness (Figure 4.34). For glossy ink-jet paper, the solvent penetrates throughout the coating layer, while the dye penetrates only 10% of the paper’s thickness (Figure 4.35). The retention of the dye in this z-direction is 71% for multipurpose paper and 60% for glossy ink-jet paper. These retention values in z-direction are significantly higher than the retention values in the x-direction of 12% and 15% for multipurpose and photo glossy papers, respectively. These higher retention values could be due to the longer contact time between the ink components and the paper, resulting in more efficient segregation of
the ink components during penetration mechanism. This segregation in z-direction may be more important in determining and evaluating print quality than the separation obtained in the x-direction.

**Figure 4.34:** Distribution Profiles Obtained from Positive SIMS Images of Z-Plane - Interface between Inked and Non-inked Regions on Domtar Multipurpose Paper

**Figure 4.35:** Distribution Profiles Obtained from Positive SIMS Images of Z-Plane - Interface between Inked and Non-inked Regions on Photo Glossy Ink-jet Paper
4.4 Conclusions

The objective of this study was to profile distribution of ink components using ToF-SIMS imaging analysis and using a custom ink-jet ink formulation of known composition to further study the mechanisms of spreading and penetration of ink components. The impact of ink component distribution on coated and uncoated paper print quality was investigated. The print quality was measured in terms of print density and perimeter ratio. The two uncoated papers produced a lower print quality than the three coated ink-jet papers. In general, spreading was a key factor in determining print quality. Spreading and more importantly spreading non-uniformity was larger on uncoated papers, most likely due to their non-specialization towards ink-jet printing. Penetration was also an important factor, where lower penetration depths in coated papers produced higher print density values. Separation of the dye from the solvent in the x-direction showed little impact on print density. However, lower retention of the dye, as in the case of laser paper, resulted in larger dye spreading. On the other hand, retention of the dye in the z-direction was substantial (71%) for both multipurpose and photo glossy ink-jet papers. Overall, the data suggests that there is a fast initial spreading in the x-direction, with perhaps finer pores filling first, followed by slow penetration in the z-direction.

References


CHAPTER 5 – CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

A custom ink-jet ink formulation of known composition and a methodology for the analysis of the ink component distribution in printed paper samples were developed. ToF-SIMS imaging was the selected analytical tool to identify individual ink components and their spatial distribution on printed samples. Use of a custom ink formulation, containing a hydrophobic cationic dye, an ethoxylated surfactant, and a lithium chloride tracer, allowed identification of the characteristic peaks of each ink component. The developed methodology was then applied to study the distribution of ink components on coated and uncoated papers of different grades and quality. Thus, the results of this study are limited to surfactants with ethoxylated stages as well as to dyes of hydrophobic and cationic nature.

In the first part of this work, both specialized glossy ink-jet paper and multipurpose paper showed that ink vehicle/solvent spread more than the dye; while the nonionic ethoxylated surfactant spread along with the hydrophobic and cationic crystal violet dye. In both paper samples, the measured spreading was greater than theoretical spreading value, with multipurpose paper having greater amount of spreading than photo glossy ink-jet paper. These initial results showed great capability of ToF-SIMS imaging with regards to distribution of individual ink components, dye, solvent, and surfactant, on the xy-plane. The differences in ink component distribution between coated and uncoated papers provided grounds for further analysis of ink-jet ink components on various grades of paper. Simultaneous study of all ink-jet ink components, and their preferential
absorption, propelled further investigation of the mechanism of ink component spreading and penetration.

In the second part of this work, the ink component distribution was studied using a greater variety of uncoated and coated papers. Print quality was evaluated in terms of print density and perimeter ratio. The two uncoated papers exhibited a lower print quality than the three coated ink-jet papers. While both spreading and penetration were found to be important, spreading was perhaps a more dominant factor in determining print quality. Non-specialized uncoated papers showed more spreading and more spreading non-uniformity due to non-optimized properties of the paper towards ink-jet printing. High retention values of the dye in the z-direction on multipurpose and glossy ink-jet papers suggested a greater importance to print quality than the values in the x-direction. Ink flows through a more porous structure in the x-direction and y-direction before advancing to the next sublayer in the vertical direction of paper. Thus, the use of ink formulation of known composition and the use of high spatially resolved ToF-SIMS images provided further understanding of ink spreading, penetration, and retention of ink components and their effect on print quality. Thus, the simultaneous spreading and penetration of all ink components has filled some of the gaps found in the literature, particularly those relating to the interactions among the ink components, their interactions with the substrate and their impact on print quality.

5.2 Limitations

Ink formulation was developed for the sole purpose of simplifying ToF-SIMS analysis. Properties such as viscosity and stability of the ink may be improved if the ink were to be
further optimized. Low viscosity of the ink may have contributed to significant amount of spreading. Also, due to inadequate stability of the ink, ink was re-formulated for each printing job. Though the same formulation was used for all samples, some error may have occurred. An ideal ink formulation may produce higher quality prints, which could potentially show more substantial differences between the chosen paper samples. However, the trends (e.g. coated papers better than uncoated papers) are expected to remain the same.

Sample preparation or cross sectioning of the printed samples for the ToF-SIMS analysis proved to be the limiting factor. The methodology of cross sectioning greatly affects the quality of the cross section and its subsequent analysis. It was found that embedding the samples in epoxy dissolved the dye, and thus removed it from the surface of the printed samples. In addition, the coating of the photo glossy ink-jet paper was also dissolving in epoxy. For these reasons and due to time constraints, ToF-SIMS images of the cross section were obtained only for the sample of multipurpose paper and photo glossy paper.

Since paper samples were obtained commercially, limited information of their physical and chemical properties is known. Knowledge of paper properties such as porosity, contact angle, pore size and pore size distribution can compel further understanding of ink-paper interactions. For coated papers, details of coating composition may also improve our understanding of ink-coating-paper interactions.
5.3 Recommendations

It is expected that penetration mechanism in coated mediums is different from uncoated mediums. Uncoated papers have larger porosity and broader pore size distribution than coated papers with fine pores and narrow pore size distribution. Thus, further analysis of ToF-SIMS cross sections of various paper grades is required for improved understanding of penetration mechanism. The use of “in-house” formulation with well defined coating formulation and properties can produce a more systematic analysis of the mechanism of ink penetration.
APPENDIX A – TOF-SIMS EXPERIMENTAL SET-UP

All spectra were collected with ION-TOF ToF-SIMS IV instrument (ION-TOF, Münster, Germany) located at Surface Interface Ontario in the Department of Chemical Engineering and Applied Chemistry at the University of Toronto. Use of static SIMS allowed yields of both elemental and molecular information of the surface chemistry [1]. Molecular distribution of the surface chemistry was essential to identify ink components of aromatic or ethoxylated nature used in this study. Thus, instead of using depth profiling, i.e. dynamic SIMS, to analyze vertical direction of paper cross section blocks were prepared as discussed in the next section. In addition, spectra were obtained in both high mass and spatial resolution modes. The former allowed mass identification, while high spatial imaging mode allowed distribution - thus "depth" profiles in z-direction of paper to be obtained on the cross section block as opposed to more "conventional" profiling which would destroy molecular information and also take a long time.

A pulsed bismuth cluster liquid metal ion gun was used to collect all spectra. The use of the polyatomic doubly-charged cluster ion, Bi$_3^{++}$, allowed greater yields in the analysis of molecular species with slightly more stable imaging resolution. Figure A.1 clearly shows higher intensity values obtained with Bi$_3^{++}$ primary ion gun at higher masses. Higher masses were essential to identify ink-jet ink components, in particular crystal violet dye of 408amu and ethoxylated Igepal CA-720 surfactant of 735amu. Charge neutralization was achieved using electron flood-gun.
Figure A.1: Positive SIMS Spectra (700-800amu) Obtained with (A) Bi$^+$ Primary Ion Gun, (B) Bi$_3^{++}$ Primary Ion Gun, (C) Bi$_5^+$ Primary Ion Gun or (D) with C$_{60}^+$

As mentioned before, all spectra were obtained in both high mass resolution and high spatial imaging modes, but not at the same time [1]. Detailed information regarding both modes can be found in reference [1]. ToF-SIMS high mass or spectral resolution mode of data collection is limited to about 2-5µm of spatial resolution; while high spatial imaging mode ensured 250nm of spatial resolution but at a cost to the mass resolution [1]. Since there is a compromise between good mass resolution and good spatial resolution, both modes were used to obtain the spectra. In particular, high mass
resolution ensured that peaks of interest are well-separated with no interferences. Thus, high spatial resolution was used to obtain a more detailed distribution of individual ink components, whose peaks had no interferences as ensured with the use of high mass or spectral resolution mode.

References

APPENDIX B – SAMPLE PREPARATION

For the preparation of cross sections, printed samples were given a rigid support, by either embedding the sample or by sandwiching it between two plastics. ToF-SIMS images at high spatial resolution for embedded sample and sandwiched sample are presented in Figure B.1 and Figure B.2, respectively. It is clear from the comparison of Figure B.1 and Figure B.2 that the embedded sample shows more details of the paper structure, perhaps due to higher quality of the cross section surface. However, Figure B.1 also shows that epoxy resin has penetrated through the paper and distorted the penetration profile of the dye. The dye of the embedded sample dissolves in the embedding medium, while the dye of the sandwiched sample is undisturbed and thus can be analyzed. Thus, cross sections prepared using a sandwiching technique were analyzed, while cross sections prepared using embedding technique were discarded.

Figure B.1: Positive SIMS Images of Z-Plane – Interface between Inked and Non-inked Regions on Domtar Multipurpose Paper using Embedding Technique

Figure B.2: Positive SIMS Images of Z-Plane – Interface between Inked and Non-inked Regions on Domtar Multipurpose Paper using Sandwiching Technique
Detailed procedure for preparing cross sections using sandwiching technique is summarized in Table B.1.

Table B.1: Detailed Procedure for Preparing Cross Sections

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Long pieces of polystyrene material, of 5mm width and 2cm length, were prepared from Petri dish using a razor knife.</td>
<td><img src="image1" alt="Image" /></td>
</tr>
<tr>
<td>2</td>
<td>Printed paper was sandwiched between two plastics prepared in step 1. For securing the two plastics and the printed paper in place, tape is placed around the sandwiched sample.</td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>3</td>
<td>The sandwiched sample is placed into a vice A that fits microtome and TXP target sectioning system. The TXP target sectioning system is then used to create a pyramid shape to minimize the area for cross sectioning.</td>
<td><img src="image3" alt="Image" /></td>
</tr>
<tr>
<td>4</td>
<td>To minimize the space between the plastic and printed paper sample a vice B that fits ToF-SIMS is also used. Using TXP, a clean cross section surface is prepared as close as possible to the vice.</td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td>5</td>
<td>The clean cross section prepared with TXP is then microtomed. The vice A is removed and the bottom of the sample is cut off to the height of the vice B. The sample is now placed into ToF-SIMS stage and analyzed.</td>
<td><img src="image5" alt="Image" /></td>
</tr>
</tbody>
</table>

All samples were microtomed with a diamond trimming knife (DiATOME UT726) using Leica EM UC 6 microtome. The clearance angle of the knife was 6°. The speed of the cut was 30mm/s and thickness of each slice was 800nm.
APPENDIX C – OPTICAL IMAGE ANALYSIS

C.1 XY-Plane

Optical image analysis performed with Optimas 6.0 Software and X-Rite Spectrodensitometer is summarized in Table C.1.

Table C.1: Optical Image Analysis Summary (XY-Plane)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Paper Description</th>
<th>Average Width (microns)</th>
<th>Perimeter/Theoretical Perimeter</th>
<th>Print Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td>Xerox laser</td>
<td>367</td>
<td>3.79</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>Domtar multipurpose</td>
<td>319</td>
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<td>1.21</td>
</tr>
<tr>
<td></td>
<td>Staples standard ink-jet</td>
<td>364</td>
<td>2.96</td>
<td>1.30</td>
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<td></td>
<td>Presentation matte ink-jet</td>
<td>382</td>
<td>2.45</td>
<td>1.59</td>
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<td></td>
<td>Photo glossy ink-jet</td>
<td>270</td>
<td>1.45</td>
<td>1.49</td>
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<td>Experiment 2</td>
<td>Xerox laser</td>
<td>357</td>
<td>3.33</td>
<td>1.05</td>
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<tr>
<td></td>
<td>Domtar multipurpose</td>
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<td>3.38</td>
<td>1.18</td>
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<td>Staples standard ink-jet</td>
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<td>Photo glossy ink-jet</td>
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<td>Presentation matte ink-jet</td>
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<td>Photo glossy ink-jet</td>
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<td>Average</td>
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<td>Domtar multipurpose</td>
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<td>1.18</td>
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<td>Photo glossy ink-jet</td>
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<td>1.57</td>
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<td>Standard Deviation</td>
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<td></td>
<td>Photo glossy ink-jet</td>
<td>19</td>
<td>0.12</td>
<td>0.04</td>
</tr>
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</table>

* Note: Theoretical width of the line is 200µm as defined and specified within Dimatix Printer Software.
C.2 XZ-Plane

Optical image analysis performed with Optimas 6.0 Software is summarized in Table C.2.

Table C.2: Optical Image Analysis Summary (XZ-Plane)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Paper Description</th>
<th>Average Penetration Depth (microns)</th>
<th>Percentage of Paper Thickness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment 1</td>
<td>Xerox laser</td>
<td>27.00</td>
<td>24.06</td>
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<td></td>
<td>Domtar multipurpose</td>
<td>35.81</td>
<td>37.77</td>
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<tr>
<td></td>
<td>Staples standard ink-jet</td>
<td>17.30</td>
<td>15.60</td>
</tr>
<tr>
<td></td>
<td>Presentation matte ink-jet</td>
<td>17.00</td>
<td>7.90</td>
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<td></td>
<td>Photo glossy ink-jet</td>
<td>19.71</td>
<td>7.58</td>
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<tr>
<td>Experiment 2</td>
<td>Xerox laser</td>
<td>20.00</td>
<td>17.82</td>
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<td>Domtar multipurpose</td>
<td>27.00</td>
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<td>Staples standard ink-jet</td>
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<td>Presentation matte ink-jet</td>
<td>18.00</td>
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<tr>
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<td>Photo glossy ink-jet</td>
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<td>8.46</td>
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<tr>
<td>Experiment 3</td>
<td>Xerox laser</td>
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<td>Domtar multipurpose</td>
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<td>7.28</td>
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<td>1.94</td>
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<td>0.54</td>
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<tr>
<td></td>
<td>Photo glossy ink-jet</td>
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<td>0.61</td>
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</table>

* Note: Thickness of paper was measured using Precision Micrometer.
APPENDIX D – TOF-SIMS IMAGE ANALYSIS

Border variability values of all samples, determined using ToF-SIMS image analysis, are summarized in Error! Reference source not found..

Table D.1: ToF-SIMS Image Analysis Summary (XZ-Plane)

<table>
<thead>
<tr>
<th>Paper Description</th>
<th>Dye Border Variability (%)</th>
<th>Solvent Border Variability (%)</th>
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<tbody>
<tr>
<td><strong>Experiment 1</strong></td>
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<tr>
<td><strong>Experiment 2</strong></td>
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<td>12.54</td>
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</table>

* Note: Border variability was calculated using methodology represented in Figure 4.4.
APPENDIX E – DISTRIBUTION OF INK COMPONENTS ANALYSIS

Retention values of all samples are summarized in Table E.1.

Table E.1: Retention Values in x-direction

<table>
<thead>
<tr>
<th></th>
<th>Paper Description</th>
<th>Retention of the Dye in the x-direction (%)</th>
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<tbody>
<tr>
<td><strong>Experiment 1</strong></td>
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* Note: Retention values were calculated as summarized in Section 4.2.4 ToF-SIMS Analysis and as represented in Figure 4.1.