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INK-PAPER INTERACTIONS AND EFFECT ON PRINT QUALITY IN INKJET PRINTING

Anna Lundberg

Supervisor: Dr. Jonas Örtegren, Mid Sweden University
Examiner: Prof. Hans-Erik Nilsson, Mid Sweden University
Assistant supervisor: Prof. Göran Ström, Innventia

Department of Information, Technology and Media.
Mid Sweden University, SE-851 70 Sundsvall, Sweden

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Anna Lundberg

Department of Information, Technology and Media.
Mid Sweden University, SE-851 70 Sundsvall
Sweden

Telephone: +46 (0)771-975 000

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ABSTRACT

This thesis concerns paper and ink interactions related to inkjet printing. The main purpose of this work was to gain a deeper understanding in which parameters control the flow of ink into papers and how the ink interacts with the paper surface. The overall objective was to find key parameters to optimize the print quality in inkjet printing.

Characterization of paper-surfaces in terms of porosity, surface roughness and surface energy was made. Objective and subjective measurements were used for print quality evaluation. Light microscopy imaging and SEM was used to see how ink interacts with the paper surface in a printed image. A high speed camera was used to study the absorption of picolitre sized inkjet droplets into fine papers.

An initial study on the effect of paper properties on print quality was made. Result indicated that there were small differences in print quality for pilot papers with different composition (in a specific parameter window) and the commercial paper COLORLOK® reproduced a noticeable high colour gamut compared to the other samples.

Research was made to see how surface fixation can affect the print quality for printouts made with pigmented ink. Surface fixation promotes retention of the pigmented colorant in the outermost surface layer of the paper and has been denoted "colorant fixation" in this thesis.

It was shown that applying colorant fixation onto a paper surface before printing can increase the detail reproduction in a printed image. Different concentrations of calcium chloride were applied onto the paper surface on full-scale produced non-commercial papers. Test printing was made with a SoHo (Small office/Home office) printer using pigmented ink and results showed that using calcium chloride as surface treatment can lead to aggregation of pigments at the surface resulting in a higher detail reproduction.

Fast absorption of the carrier liquid into the paper and fast fixation of colourants on the surface is important in inkjet printing to avoid colour to colour bleeding. These demands will be more pronounced when the printing speed increases.

It is important to understand which parameters affect the absorption process to be able to control the mechanisms and to optimize the print quality.

A study of absorption of picolitre size inkjet droplets into fine paper was made in this work. Theoretical equations describing fluid absorption into capillaries were tested and compared with experimental results. The result showed that the time dependence in the Lucas-Washburn (L-W) equation fits fairly well to data whereas the L-W equation overestimates the penetration depth.

The results are directly applicable to paper and printing industry and can be used as a base for future studies of absorption of picolitre sized droplets into porous materials and for studies of aggregation of colloidal particles on surfaces.

KEYWORDS: inkjet, print quality, printability, ink absorption, Lucas-Washburn equation, dyes, pigments, colourant

SAMMANDRAG

Den här avhandlingen handlar om papper och bläck interaktioner relaterat till inkjettryck. Syftet var att få en djupare förståelse av hur papprets egenskaper kan påverka och styra de mekanismer som sker vid inkjettryck samt att förstå hur detta kan relateras till tryckkvalitet.

Objektiva mätningar av tryckkvalitet har utförts tillsammans med subjektiva utvärderingar i perceptionsstudier. Ljusmikroskopi och SEM har använts för att se hur bläck interagerar med pappersytan. En höghastighetskamera har använts för att utföra studier av absorption av picoliterstora droppar i papper.

En inledande studie av hur tillsatser i papper påverkar tryckkvaliteten för inkjetutskrifter med SoHo skrivare (Small office/Home office printers) har utförts. Denna studie utfördes för att få en överblick över området. Resultat från denna studie visar på små skillnader i tryckkvalitet mellan olika pilotpapper samt att bland kommersiella prover gav det med COLORLOK® en avsevärd större färgrymd än de andra kommersiella obestrukna proverna.

Det är känt att ytfixering (fixering av färgämne till ytan) ger en högre tryckdensitetet för obestrukna papper. I detta arbete har studier gjorts för att se hur ytfixeringsmedel kan ge en förbättrad detaljåtergivning.

Forskning med kalciumklorid som ytfixeringsmedel har utförts genom att olika salt-koncentrationer lagts på fullskaligt tillverkade icke-kommersiella papper. Resultat visar att salt som ytfixeringsmedel kan leda till en aggregering av färgpigmenten på ytan som kan ge en förbättrad detaljåtergivning och en högre tryckdensitet.

Vid tryckning med höga hastigheter, s.k. höghastighetsinkjet ställs höga krav på att bärarvätskan snabbt skall absorberas in i papperet och att färgämnena skall stanna vid ytan. Det är viktigt att förstå vilka parametrar som påverkar absorptionsförloppet för att kunna kontrollera detta förlopp. I detta arbete har en studie av absorption av picoliterstora inkjetdroppar in i papper utförts.

Den teoretiska beskrivningen av absorption av vätska i kapillärer enligt Lucas–Washburn ekvationen har studerats och jämförts med experimentella data. Reultatet visar att tidsberoendet i L-W ekvationen stämmer väl överens med experimentella data, medan L-W ekvationen överskattar penetrationsdjupet vid absorption av picoliterstora bläck droppar i papper.

Resultaten från denna avhandling är direkt tillämpbar inom både pappersindustrin och vid utveckling av tryckmetoder och kan ligga till grund både för fortsatta studier av absorption av picoliterstora droppar i porösa material och för fortsatta studier av aggregering av kolloidala partiklar på yta.

AKNOWLEDGEMENTS

First of all, I want to thank **You** for reading my thesis! It makes it worth every minutes of writing.

This thesis is a result from work made within the **"Next generation substrates for inkjet printing"** project in which I have been working together with colleagues from the institute for surface chemistry (**YKI**), **EKA chemicals**, **Innventia**, **MoRe research**, **M-real**, **KODAK** and **DPC**. It has been three intensive years with many interesting challenges. I want to thank all representatives within the reference group for their engagement in the project.

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I want to thank my assistant supervisor **Göran Ström** at Innventia, **Elisabeth Alfthan,** and my friend **Thomas Mejtoft** at Umeå University for support and valuable comments to the manuscripts.

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Last, but not least, I would like to thank all my friends, my family and especially **Jonny** who has always been there for me and who never stopped believing in me.

Thank you all!

TABLE OF CONTENTS

LIST OF PAPERS

This thesis is mainly based on the following papers, herein referred to by their Roman numerals. The papers are appended at the end of the thesis.

Paper I *On the Effect of Variations in Paper Composition on Inkjet Print Quality.*
Lundberg A, Örtegren J, Alfthan E.
In Proc. 25th international Non Impact Printing conference, Kentucky, Louisville, pp. 316-319, (2009)

Paper II *Improved Print quality by Surface fixation of Pigments*
Lundberg A, Wågberg K, Norberg O, Örtegren J.
In Proc. 26th international Non Impact Printing conference, Austin, Texas, pp. 251-255, (2010)

Paper III *Aggregation of Color pigments by Surface fixation treatment.*
Lundberg A, Örtegren J, Norberg O.
Manuscript submitted to Journal of Imaging Science and technology, (2011)

Paper IV *Micro scale droplet absorption into paper for inkjet printing.*
Lundberg A, Örtegren J, Alfthan E, Ström G,
Accepted for publication in Nordic Pulp and Paper Research Journal, (2010)

1. INTRODUCTION

Inkjet is a widely used printing technology, both for production interest and for home office printing. The print quality for inkjet is high and digital printing opens up possibilities for a new market with variable data printing, personalized printing and print on demand.

Until today the main challenge with digital printing has been the low speed, resulting in high costs for long production runs. The fast development of new techniques has lead to high speed printing techniques.

Inkjet printing is a non impact printing method where the droplets are ejected from a nozzle and projected onto a substrate without any contact between the print head and the substrate. The droplets are settled on the surface and depending on the characteristics of the ink and paper the drop starts to spread and partly penetrate the substrate.

The absorption of ink into the substrate controls the printability of the papers in terms of ink setting rate (wetting, capillary flow, separation of colourant from solvent, absorption, diffusion and fixation of colourants). The ink setting rate strongly depends on the characteristics of the ink and paper and on the printing method as well.

One of the challenges with high speed printing using inkjet technology is to find the right combination of substrate and ink. The need to understand which parameters control the ink setting rate increases when the printing speed increases.

The overall aim with this thesis was to gain a deeper knowledge in inkjet printing and an increased understanding in which parameters affect the dynamics and interactions between inkjet ink and papers.

The investigation addresses following work: An introduction to print quality studies on commercial papers and on uncoated pilot papers with different composition (Paper1). A print quality study on surface treated papers to see how colourant fixation can improve detail reproduction in a final image (Paper II) and a study of aggregation of pigments on salt treated surfaces related to detail reproduction (Paper III). A study of absorption of picolitre size inkjet droplet printed onto different paper samples (paper IV).

2. BACKGROUND

2.1. Inkjet technology

The two main technologies for inkjet are Drop On Demand (DOD) and continuous inkjet (CIJ). A map that illustrates an overview of Inkjet technology is depicted in **Figure** 1 [1]. A common method for CIJ is the piezoelectric technology.

In a continuous (piezo) inkjet print head a piezoelectric crystal divides an ink stream into droplets. The droplets pass a charge electrode that charges the droplets depending on the image. The CIJ process can be divided into two processes: Binary and multi deflection. In a binary deflection process, the droplets have two states of charge: uncharged for conveyance to the paper and charged for defection in an electrical field. In a multi deflection process the drops receive different charges so that they can be deflected in different directions on the substrate.

Drop On demand (DOD) processes generates a droplet only if the printed image requires a drop. Classification of drop on demand processes is made based upon the way the droplets are created. In thermal inkjet the ink is heated up until it vaporizes and ink is ejected from the nozzle as a result of the pressure from the vapor bubble in the chamber. In piezo inkjet systems a piezo electric material is vibrating depending on the applied voltage, resulting in variations in volume in the chamber that lead to ink drop from the nozzles. There are different types of electrostatic inkjet process variants [1]. Common for all processes is that an electrical field exists between the inkjet system and the surface to be printed. A drop is ejected from the nozzle when a control pulse (electrical signal or supply of heat) disturb the balancing forces in the system.

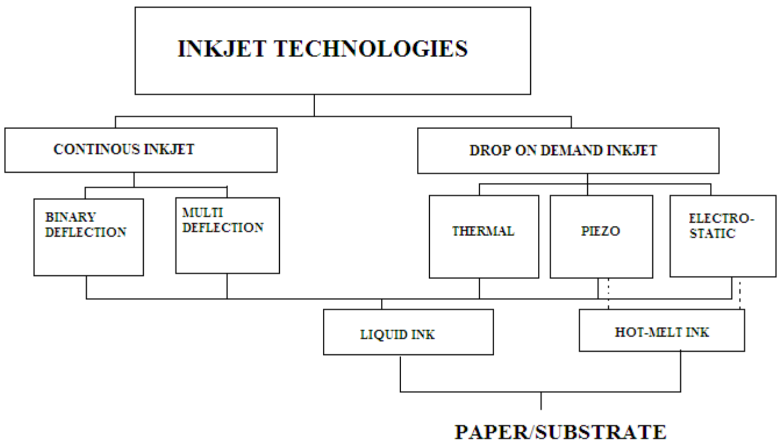

Figure 1. Overview of inkjet processes [1]. CIJ processes can be binary deflection or multi deflection. DOD can use thermal, piezo or electrostatic technology.

2.1.1. Historical overview

Inkjet printing is a non impact printing method where the final print is a result of deposition of inkjet droplets onto a substrate in a pre-defined pattern. The final print is strongly affected by both drop formation and interaction between ink and paper.

The initial studies of drop formation were made by Abbé Nollet in 1749. He demonstrated how a stream of liquid could be manipulated by static electricity [2-3].

The first inkjet-like recording device, a "Siphon recorder" was invented by Lord Kelvin in 1858. This device can be used for recordings of telegraph messages (**Figure** 2).

A Siphon device produces a continuous stream of ink onto a moving substrate and a driving signal moves the Siphon back and forth to create a pattern on the substrate.

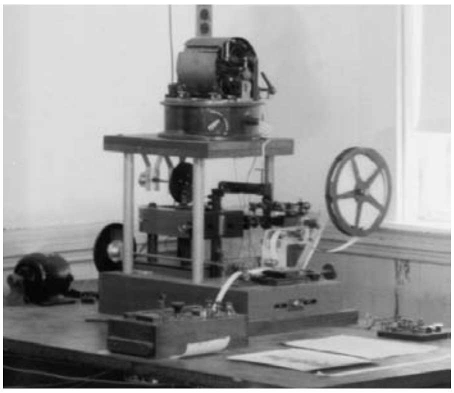

Figure 2. The siphon recorder invented by Lord Kelvin in 1858.

The foundation of modern inkjet technology is attributed to the Belgian physicist Joseph Plateau and the English physicist Lord Rayleigh.

In 1856 Plateau published "On the recent theories of the constitution of jet liquid issuing from circular orifices" [4] and ten years later he derived the relationship between a droplet size to jet diameter.

In 1878 Lord Rayleigh demonstrated how a stream of liquid could be divided into droplets [5]. This publication was the first in a series of publications that has come to be of great importance to modern inkjet technology.

The application of Lord Rayleigh´s research ended up in a"Rayleigh break-up device" and later on in a production of a "Mingograph", described in the US patent released in 1952 [6].

In the early 1960s, Dr. Sweet of Stanford University demonstrated that by applying a pressure wave pattern to an orifice, the ink stream could be broken into droplets of uniform size and spacing. The droplets could then be charged and deflected when passing through an electrical field to form an image on the substrate. The uncharged droplets were captured by a gutter and recirculated into the system. This version is known as continuous inkjet [7] with the "inkjet oscillograph" as first device.

Drop on demand (DOD) is another technique for inkjet printing where a drop is created only when an actual pulse is provided.

The first work in this direction was made in the late 1940s by Hansell of the Radio Corporation of America (RCA) [8]. This DOD technique uses a piezoelectric disc to cause a pressure wave that generates a spray of ink drops. This device was never commercialized [9].

The first DOD technique that really emerged was developed by the Casio, teletype and Paillard company in the 1960s; and is called the "electrostatic pull inkjet"[10]. The basics of this technique are conductive ink held in a nozzle by negative pressure. By application of a high voltage field the droplet could be pulled out. Depending on the deflection field the droplet could be located on the substrate.

Several companies developed printers with this technique but because of poor print quality, the electrostatic pull principle was abandoned (but research on this still exists).

Many of the DOD inkjet ideas systems available on the market today were invented and developed in the 1970s and 1980s and generally the basis of piezoelectric inkjet is attributed to three patents in the 1970s; one by Zoltan of the Clevite Company in 1972 [11], one by Stemme of the Chalmers institute of technology in 1973 [12] and one by Kyser and Sears of the Silonics Company in 1976 [13].

2.2. Inkjet ink

Digital printing using inkjet technology puts heavy demands on the physical properties of the ink.

When a droplet strikes a surface it starts to spread, partly penetrates the paper and evaporates **Figure** 3.

Surface tension and viscosity of the ink are important parameters affecting the drop formation and the spreading of the droplet on the surface [14].

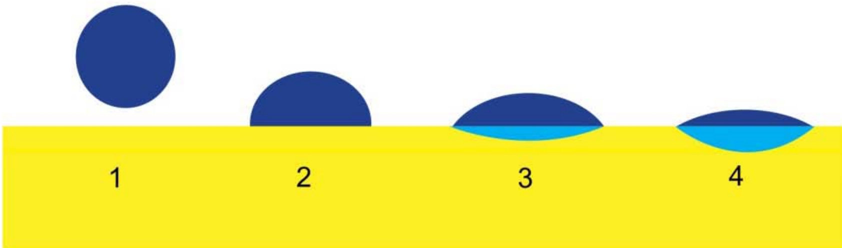

Figure 3. The printed dot is a result from spreading of the drop, evaporation and penetration of the ink into the substrate.

There are three main types of inkjet inks: aqueous, non-aqueous (oil/solvent) and phase- changing inks (hot melt/UV curable).

The main components of an aqueous/solvent based inkjet ink are carrier fluid (~35-80%), humectants (~10-30%), surfactants and additives (~2-5%) and colourants (~2-8%) [9].

The colourants in an inkjet ink can either be dyes fully dissolved in the solution or pigments dispersed in the solution.

Different printing techniques use different inks and the drying mechanisms differ between the types of ink [15]. Different ink types and drying mechanism for the type of ink are presented in Table 1.

Table 1. Different ink and drying mechanisms

Ink	Drying mechanism
Aqueous	Absorption/Penetration Evaporation
Oil	Absorption/penetration
Solvent	Evaporation
Hot melt	Solidification
UV curable	Polymerization

2.3. Inkjet paper

A paper for inkjet printing consists of chemical pulp (e.g. hardwood and softwood fibres with varying shares and beating), fillers (typically calcium carbonate from chalk or marble as Ground Calcium Carbonate (GCC) or Precipitated Calcium Carbonate (PCC), starch, internal sizing and surface size to control porosity and absorption, retention chemicals (to retain fillers, fines and other additives) and FWA (Fluorescent Whitening Agent) [16].

Paper properties are affected by both the composition of the paper and by the manufacturing process.

Some important properties for an inkjet paper are:

- Grammage
- Thickness
- Surface roughness
- Whiteness
- Opacity
- Strength, stiffness
- Porosity
- Sizing (water absorption)
- Stiffness

Each parameter is important for printability and runnability.

The main component of paper is fibres, usually from wood, cotton or grasses [16]. The wood used in paper pulp is divided into two categories: "Hardwoods" such as: oak, poplar, maple, birch, eucalyptus. (Short, soft, tubular and confer bulkiness and formation properties) and "Softwoods": pines, fur, spruce, etc. (long, soft, flat with considerable strength but with less bulking and formation tendencies). The fibres can be chemically or mechanically separated resulting in different properties in the final product.

Uncoated office papers are often used for inkjet printing of text or when the requirement of image quality is low.

To improve the print quality a coating layer consisting of binders, (starch and latex) and pigments (kaolin or calcium carbonate) can be added onto the paper surface [17].

When high quality papers are wanted, several coating layers can be added on top of the paper surface. An example of inkjet coated paper is depicted in **Figure** 4 (drawn after [17]).

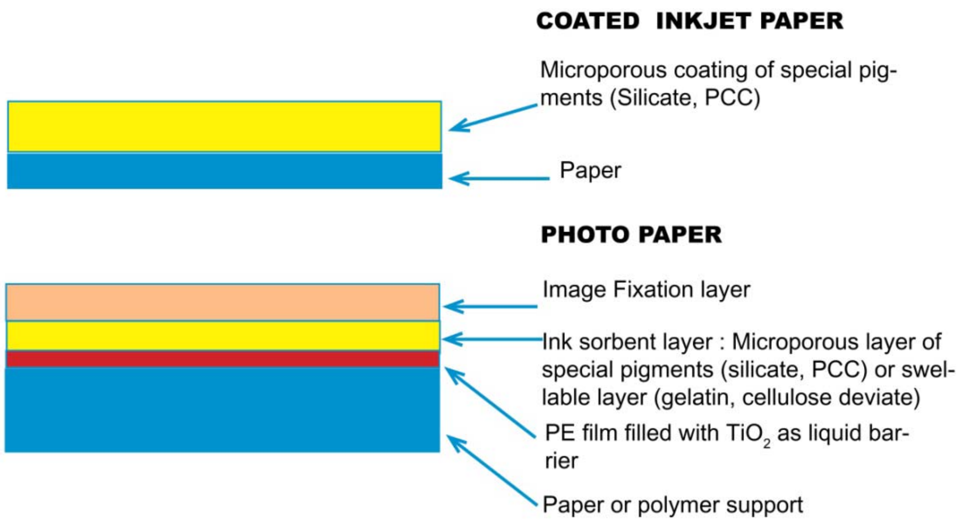

Figure 4. A high quality inkjet paper can have several layers of coating.

3. THEORY

3.1. Paper Optics

3.1.1. Light and colour

Light can be described both as a particle and as a wave; the wave-particle duality. When we talk about light we often refer to the electromagnetic spectrum that is visible to the human eye (380-770 nm), but it can also refer to other forms of electromagnetic radiation, such as infrared and ultraviolet light.

White light includes all wavelengths. An object that absorbs some part of the visual spectrum and reflects some appears coloured for a human eye.

The appearance of a coloured object mainly depends on the spectral power distribution of the reflected light and on the surface characteristics of the object, but also on surrounding colours, observing geometry and state of chromatic adaption [18].

An uncoated paper has a fairly rough surface whereas a coated paper for inkjet can have a matt or glossy surface. Depending on the smoothness of the surface, the incident light can be more or less specular reflected (glossy surface) or diffuse reflected [19].

Inside the paper bulk, the light can be reflected, refracted or diffracted to colour pigments, filler, fibres etc. **Figure** 5:1-3 illustrates reflection, refraction and diffraction

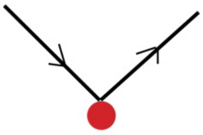

Figure 5:1. When light hits the surface or particles inside the bulk material it can be *reflected* in different directions.

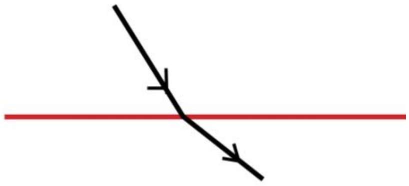

Figure 5:2. As light passes from one transparent medium to another it changes speed, and is *refracted*. How much depends on the refractive index of the mediums and the angle between the light ray and the line perpendicular (normal) to the surface separating the two media.

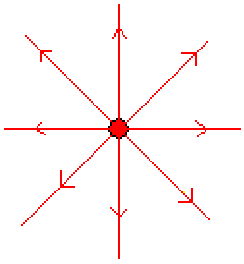

Figure 5:3. When a light wave interacts with a single particle that is as large as or smaller than the wavelength of light, the wave is *diffracted*. The particle scatters the incident beam uniformly in all directions.

Molecules can absorb and emit packets of electromagnetic radiation. Different molecules *absorb* radiation of different wavelengths due to the discrete energies dictated by the detailed atomic structure of the atoms; this is the mechanism of how colour is created for dye based ink.

3.1.2. CIE L*a*b*

In 1931 The Commission Internationale de l'Eclairage (CIE) introduced standard illuminates, the colour matching functions and the device independent tristimulus values. The aim of this was to get a uniform description of colours and light sources [20].

In1976 CIE introduced the CIELAB colour space. The CIELAB colour space takes the light source/object/human observer set of factors into account to the colour matching functions and to the tristimulus values.

The CIE L*a*b* forms a Cartesian, approximately perceptual uniform colour space, with the lightness coordinate L* (0 is black and 100 is white) and green-red coordinates a* (-a* = greenness and +a* = redness) and blue yellow b* (-b* = blueness and +b* = yellowness) [21]. **Figure** 6 illustrates the CIE L*a*b* colour space.

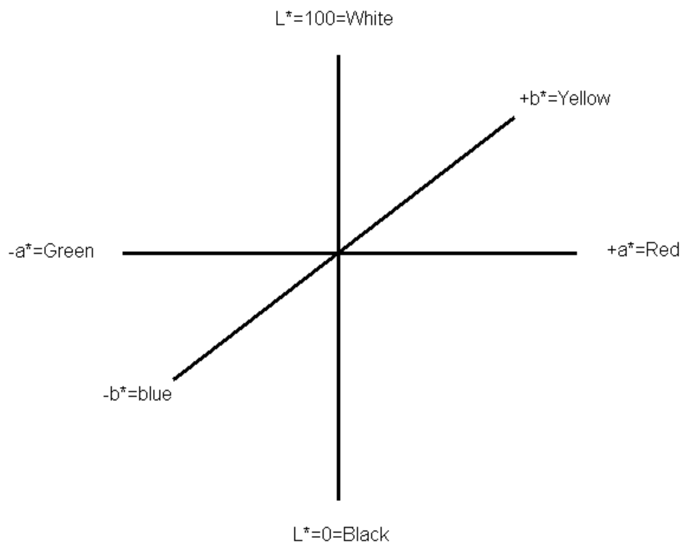

Figure 6. CIELAB is a pseudo-uniform colour space that is defined by L* a* and b*. L* represents the lightness, a* represents red to green axis and b* represents blue to yellow axis.

The distance between two points in L*a*b* space is ΔE (Delta E). ΔE can be used to compare differences between two samples.

The Cartesian coordinates can be expressed in cylindrical coordinates, with the hue defined as the angle and the chroma as radius. CIE 1976 L*a*b chroma is defined as: $C^*_{ab}=(a^{*2}+b^{*2})^{1/2}$ and CIE 1976 hue angle: $h_{ab}=\arctan(a^*/ b^*)$

3.2. Wetting and spreading

When a droplet hits a surface, it can spread to increase the surface between the solid/liquid phase and the liquid/gas phase. The droplets can wet the surface depending on the physical properties of the liquid and of the substrate. Wetting means that the contact angle between the liquid and the substrate is very small so that the liquid spread over the entire surface [22].

During inkjet printing, a limited amount of liquid is deposited onto a paper surface. When the droplet hits the surface it starts to spread and wet the surface depending on the ink and paper properties.

3.2.1. Contact angle

Contact angle is a function of energy of adhesion (between molecules in the liquid and solid) and cohesive energy (between the molecules in the liquid. Strong adhesion and weak cohesion leads to a low surface tension and small contact angle, resulting in a high wetting.

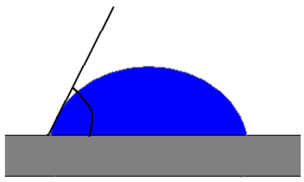

Figure 7. Contact angle is a measure of how the liquid wets the surface.

When a droplet hits a surface, the contact angle goes from larger values to smaller values until state of equilibrium has been reached. If the contact angle is higher than 90 degrees, no wetting of the surface will occur.

3.2.2. Surface energy/ Surface tension

Surface energy is defined as the free energy required creating a surface, i.e. the energy that must be added to increase the surface one area unit [23].

Surface tension can be described as the force per unit length that opposes the expansion of a surface, or as the energy per unit area. The two are equivalent, but in general, the term surface energy is applied to solids and the term surface tension is applied to liquids.

One method for calculating surface energy is to use static contact angle measurements together with Young's equation and the work of adhesion based on the Geometric Mean model.

Young's equation describes the relation between the surface energy and contact angle for a liquid on a solid surface (where the spreading pressure of the liquid's vapour on the solid is negligible), equation (1) [23].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cdot cos\theta \qquad (1)$$

γ_{SV} is the surface energy of the solid, γ_{LV} is the surface tension of the liquid, and γ_{SL} is the interfacial tension between solid and liquid. θ is the contact angle between the solid and the liquid.

The work of adhesion, W_a in general terms, the thermodynamic energy of interaction, is given by equation (2).

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} \qquad (2)$$

Combining eq. (1) and (2) yields

$$W_a = \gamma_{LV}(1 + cos\theta) \qquad (3)$$

The surface energy of a material can be divided into different parts, corresponding to various contributions from different interactions:

$$\gamma = \gamma^D + \gamma^P \qquad (4)$$

where γ^P corresponds to the polar component of the surface energy and γ^D corresponds to the non-polar (dispersive) component of the surface energy.

The work of adhesion based on the Geometric Mean model yields:

$$W_a = \gamma_{LV}(1 + cos\theta) = 2[(\gamma_L^D \cdot \gamma_S^D)^{1/2} + (\gamma_L^P \cdot \gamma_S^P)^{1/2}] \qquad (5)$$

Since the polar component of diiodmethane is zero, the dispersive energy of the solid can be determined by using data from measurements with diiodmethane, equation (3) and equation (5). The disperse energy of the solid can be expressed in terms of:

$$\gamma_S^D = \frac{1}{4}\gamma_{LV(diiod)}(1 + cos\theta_{diiod})^2 \qquad (6)$$

By using data from contact angle measurements with water and eq.5, the work of adhesion can be expressed as:

$$W_a = \gamma_{LV(water)}(1 + cos\theta_{water}) = 2[\left(\gamma^D_{V(water)} \cdot \gamma^D_S\right)^{1/2} + \left(\gamma^P_{V(water)} \cdot \gamma^P_S\right)^{1/2}] \quad (7)$$

Rearranging terms:

$$\gamma^P_S = \frac{\left(\frac{(\gamma_{LV(water)}(1 + cos\theta_{water}))}{2} - (\gamma^D_{L(water)} \cdot \gamma^D_S)^{1/2}\right)^2}{\gamma^P_{L(water)}} \quad (8)$$

By using equation (4), (6) and (8), the Surface energy for the substrate, φ_S can be expressed as:

$$\gamma_S = \frac{1}{4}(\gamma_{LV(diiod)}(1 + cos\theta_{diiod})^2 \frac{\left(\frac{(\gamma_{LV(water)}(1 + cos\theta_{water}))}{2} - (\gamma^D_{L(water)} \cdot \gamma^D_S)^{1/2}\right)^2}{\gamma^P_{L(water)}}$$

(9)

3.3. Absorption

Inkjet printing on paper can be described physically as a process of deposition of a finite amount of liquid into a porous structure and the print quality is directly associated to the imbibition process [24].

During the last few years, several studies have been made on droplet dynamics on porous substrate [25-37].

One theory describing fluid dynamics into capillaries is the Lucas-Washburn equation [38-39].

3.3.1. Lucas-Washburn equation

The first study on the movement of water and of aqueous solutions through paper and soils were made by the Bureau of Soils, U.S. department of Agriculture in 1905 [40]. Following equation was proposed.

$$Y^n = K \cdot t \quad (10)$$

where Y represents the distance through which the liquid has moved in the time t, and n and K are constants dependent on temperature and specific substrates.

In early 1900 Bell and Cameron analyzed the imbibition rate and found that the imbibition follows the square root of time [41]. Bell and Cameron made this study by using the Poiseuilles equation for laminar flow and equation (10)

$$Y^2 = K \cdot t \quad (11)$$

In 1918 Lucas [38] made studies to verify this square relation (eq. 11). Lucas made experiments with glass tubes and filter papers.

Not aware of Lucas work, Washburn (1921) made similar research on horizontal and vertical capillaries [39].

The Lucas-Washburn equation describes penetration of liquids into cylindrical capillaries in the absence of a gravitational field.

Washburn applies Poiseuille's law for fluid motion in a circular tube according to eq. 12.

$$dV = \frac{\pi \cdot \sum P}{8\eta \cdot d(t)} (r^4 + 4\epsilon^3) dt \qquad (12)$$

dV describes the differential volume of the liquid that flows during the differential time, dt, η is the viscosity of the fluid, $\boldsymbol{\epsilon}$ is the coefficient of slip. ΣP is the total effective pressure acting to force the liquid into the capillary which is the sum of the participating pressures, such as the atmospheric pressure, the hydrostatic pressure and the equivalent pressure due to capillary force. r represents the radius of the capillary.

Under the assumption that the coefficient of slip is zero for wetting materials and for capillaries so small that the external pressure can be neglected, the penetration depth according to Lucas-Washburn, $d_{LW}(t)$, can be expressed as proportional to the square root of time.

$$d_{LW}(t) = k_{LW} \sqrt{t} = \sqrt{\frac{\gamma \cdot r \cdot cos\theta}{2\eta}} \sqrt{t} \qquad (13)$$

where γ represents the surface tension of the liquid and θ represents the contact angle.

4. METHODS AND MEASUREMENTS

4.1. Color meaurements

Spectral measurements made in this thesis were made by using a Gretag Macbeth spectrophotometer (**Figure** 8). The measurement geometry of this device is 45°/0° and it can be used with different physical filters, such as: D65 (approximated daylight), pol. (polarised) and without filter.

Colorimetry calculations can be made by using Spetrochart software with different Illuminants: D50, D65, A, C, D30… D300, F1…F12 and with 2° or 10° degrees of standard observer angles:

Figure 8. Gretac spectrophotometer measuring the spectral reflectance.

4.2. Line quality

Line quality is a measure of lateral spreading of ink onto the paper surface.
Scanner evaluation of printed lines can be made by using a flatbed scanner to scan the lines and evaluation can be made by using image analysis.

In this thesis MATLAB® was used to analyse the images. The scanned images were converted into grayscale values and the maximum and minimum reflectance was used to calculated raggedness, blurriness and line width in accordance to the ISO-13660 method.

A lower raggedness, less blurriness and smaller line width indicate lower spreading of the ink and greater sharpness in the image.

Raggedness

Raggedness is a measure of edge unevenness of the printed line. Calculations of raggedness were made by taking the contour of the printed line (extracted by using the threshold value T60, corresponding to 60% of the maximal intensity in the image).

The position of the ideal smooth line was calculated and the raggedness was defined as the standard deviation of the distance *d* from the contour to the smooth line. A description of raggedness is depicted in **Figure** 9.

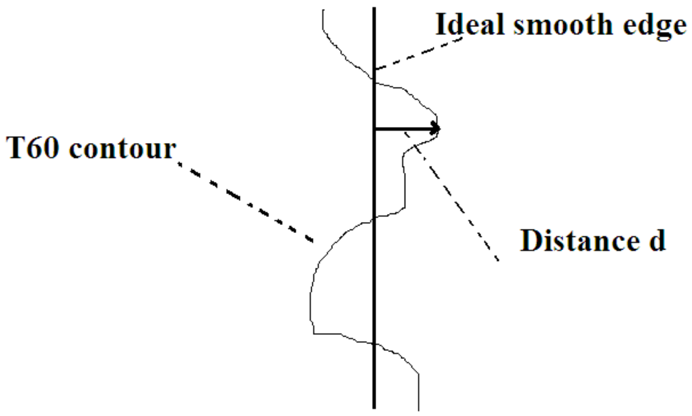

Figure 9. Raggedness is a measure of edge unevenness of the printed line. Definition of the raggedness is made by calculating the standard deviation between the edge contour and the ideal smooth line.

Line width

Evaluation of the line width was made by calculating the mean value of the width by using the threshold value 50% of the maximum intensity in the image. An illustration of the line width has been depicted in **Figure** 10

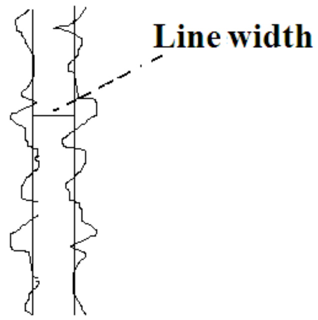

Figure 10. Illustration of line width.

Blurriness

Blurriness is another measure of edge unevenness of the printed line.

Calculations of blurriness were made by calculating the mean width of the edge zone defined as the part of the line with intensity in the range 1/3-2/3 of the maximum intensity range.

4.3. Perception study

Visual judgment of an image is an important tool in print quality evaluation [42]. There are various methods to perform perceptual studies, each one has its advantages and disadvantages.

Before making a visual judgment of an image it is important to plan the setup [42]. Selection of observers, samples: size and selection, and image content, number of samples, time for each sample viewing distance, illumination and surroundings and sample presentation are important parameters influencing the outcome of the study [42].

The perception study made in this thesis was used to assess small differences in detail reproduction between different samples in an image without being influenced too much of the differences in print density between the images. Because of the small differences in the images the 2-0 method was used.

Participants in the study were people working at paper mills and researchers within paper and printing. The observers in the test panel were selected because of their experience of paper and print, in order to be able to judge small differences in the images.

4.4. Surface characteristics

4.4.1. Surface tension and Contact angle measurements

Measurement of surface tension of the ink and contact angle measurements in this work were made with Fibrodat 1100 and the Pendant droplet method/sessile drop.

4.4.2. Porosity

The characterisation of porosity was made by using mercury porosity measurements and also the Bendtsen method using air leakage through the paper. Mercury porosimetry was measured in an Autopore IV 9500 from Micrometrics according to ISO/WD 1590-1.

4.4.3. Surface roughness

Surface roughness were characterised with the Bendtsen method using air leakage at the paper surface (with a glass plate on the back side of the paper sample).

4.4.4. Absorption of picolitre size droplets into papers

A high speed camera was used to capture film sequences of a droplet printed onto a paper. A Matlab routine was used for image analysis. The method is described in detail in paper IV.

5. SUMMARY OF THE PAPERS

The papers included in this thesis focus on dynamics and interactions between inkjet inks and fine paper related to print quality.

Paper I addresses the effect of different variations in paper composition on printouts made with SoHo printers and can be seen as an overview/ introduction to this work. Paper II-III describes the effect of using salt for surface treatment on fine paper before printouts made with pigmented ink. Paper II shows the effect on detail reproduction whereas paper III examines the pigment aggregation on a salt treated surface.

An experimental study of fluid dynamics of an inkjet droplet has been made in Paper IV. Different paper properties such as surface roughness, porosity and apparent surface energy have been measured and related to the absorption process. The Lucas-Washburn equation has been tested and fitted to experimental data.

5.1. Paper I

In this paper, the effect of different paper composition on inkjet print quality in desktop printers has been studied. The background to this work was to improve the physical paper-properties such as cockle and waviness without reducing the print quality. Here the aim was to investigate how different paper composition in terms of level of filler, internal sizing, level of beating, levels of hardwood fibres and type of pulp affects the print quality for printouts made with SoHo (Small office/Home office) printers.

Nine pilot papers produced in a small paper machine (lab-scale) with different level of filler, internal sizing, hardwood content and levels of beating were used and compared with eight commercial papers. The commercial papers were two different high-speed inkjet papers, two different inkjet coated papers, and copypaper with and without COLORLOK®.

Printouts were made in two different SoHo printers: one printer using pigmented, water-based ink and one printer using dyes in water-based ink. The print quality measurements were line quality measurements and colour gamut measurements.

The result showed that paper composition variations (in a specific window) in hardwood content, filler content and type of pulp did not affect the line quality or colour gamut in an important way. It was found that an increased amount of filler slightly decreases the colour gamut volume and low beating of the fibres worsened the line quality.

Among the commercial paper, it was observed that COLORLOK® gave a high colour gamut for pigmented ink and a low colour gamut for dye-based ink. Most of the high speed inkjet papers exhibited a larger colour gamut than the pilot papers and the standard copy paper in the case of pigmented inks.

5.2. Paper II

The purpose of this work was to determine the influence of different levels of colourant fixation of a paper in a final printout. The colourant fixation used in this study was calcium chloride solution added in the surface sizing and the printouts were made in a desktop printer using pigmented, water based ink.

Both commercial papers with and without colourant fixation and trial papers were used. The trial papers were uncoated, surface sized papers produced in the same production run in a full scale paper machine. The only parameter that was varied among the trial papers was the level of salt.

Print quality evaluation was made objectively by measuring edge sharpness CIE L*a*b chroma and dot gain. Subjective measurements were made in perceptual studies.

It is known that an increased level of colour fixation affects the print density. To separate the results on detail reproduction from the variations in print density two additional samples were therefore added to this study. One sample was created to resemble a printout with the same print density as the sample with a low level of colourant fixation, printed out on a paper with a high level of fixation. The other sample was made by adding a Gaussian blur filter, to create a blurred image printed out on a paper with a high level of fixation, i.e. high print density.

The perceptual study was made in three different laboratories with controlled illumination and the judgment was made in a pair-wise comparison.

This study showed that the detail reproduction in a printed image is an interplay between the print density and the edge sharpness originating from the surface spreading of the droplet.

The results showed that an increased level of colourant fixation slightly reduces the droplet spreading resulting in a higher detail reproduction. An increased level of colourant fixation also increases the print density resulting in a higher detail reproduction.

5.3. Paper III

In this paper, print quality in terms of detail reproduction and chroma for papers with and without colourant fixation has been related to surface properties for paper such as surface roughness, porosity and hydrophobicity.

The main purpose of this study was to investigate if high levels of salt can lead to aggregation of pigments on the paper surface before printing making the pigments stay closer to the surface. The papers and printer used in this work was the same as used in paper II.

SEM analyses have been used to study the printed surface and a light microscope was used to study cross section images of the ink penetration into paper.

Results show that salt as colourant fixation fixates the pigments close to the surface resulting in better detail reproduction chroma and higher print density. It also affects the ink stability making the pigments aggregate on the surface. The aggregation of pigments might explain the smaller droplet spreading on the paper surface resulting in a better detail reproduction.

5.4. Paper IV

This paper describes absorption of inkjet droplets into different paper qualities. The aim was to study the fluid dynamics during the absorption process and compare theoretical models to experimental data and relate the result to paper properties.

Papers used in this work were selected papers among the pilot papers and commercial papers used in paper I.

Inkjet droplets of dyes were printed out from a KODAK Versamark D5240 print head and images were captured by using a high speed camera and 2000 fps. Paper properties such as surface roughness, porosity and apparent surface energy were measured and related to the result from the absorption study.

The results showed that a paper containing internal sizing had a lower apparent surface energy, resulting in a smaller droplet spreading radius. The rate of absorption of ink into an internal sized paper was slower compared to an unsized paper. Evaporation played an important role in the absorption process for internally sized papers.

The Lucas-Washburn equation for describing the penetration depth was tested and compared to experimental data. It was found that the time dependence in the Lucas-Washburn (L-W) equation was in the accordance with experimental data whereas the L-W equation overestimated the penetration depth and the absorption speed.

6. CONTRIBUTION TO THE THESIS

This thesis contributes to the inkjet printing area and the main part of the results is directly related to the printing and paper production area. The study of dynamics in terms of liquid penetration and flow into paper as porous substrates is directly related to the high-speed printing area.

The overall contribution is to gain an increased knowledge in the field to be able to produce high quality ink receptive substrates.

In this section the contribution to the thesis and the novelty of the listed papers is described together with the contribution of the author of the thesis to each paper.

6.1. Paper I

This paper shows that variations in paper composition (in a certain window) for uncoated pilot papers did not have a major impact on the print quality for printouts made with SoHo printers. This leaves the opportunity to continue to vary the surface treatment to improve the print quality for inkjet printing with SoHo printers.

The paper samples used are the result from cooperation between the authors and the project partners with the aim of producing papers with good runnability and print quality.

This paper is the result of cooperation with Dr. Jonas Örtegren and Elisabeth Alfthan. The contribution of the author of this thesis was part of the experimental planning and main part of printing, measuring and analysis of color gamut and line quality and presentation of the material and writing.

6.2. Paper II

This paper shows that the print quality for uncoated copy papers can be improved by adding colourant fixation to a paper without changing the paper composition.

The final result from this work showed that the detail reproduction in a final printout is an interplay between print density and surface spreading of the droplet.

This paper is the result of cooperation with Dr. Ole Norberg, Kristina Wågberg and Dr. Jonas Örtegren. The contribution of the author of this thesis was part of the experimental planning and main part of printing, measuring and analysis of CIE L*a*b* chroma and line quality, measuring and analysis of dot gain and analysis of data from the perception study and presentation of the material and writing.

6.3. Paper III

This paper points out one of the effects of surface mechanism on print quality, namely aggregation of ink pigments on the paper surface.

Printouts made with water-based ink have been studied on papers with different concentrations of salt as colourant fixation.

The final results show that the ink stability can be affected by adding calcium chloride as colour fixation making the pigments start to aggregate on top of the surface.

The results also show that the aggregation of ink pigments improves the detail reproduction and increases the CIE L*a*b* chroma.

This paper is the result of cooperation with Dr. Ole Norberg and Dr. Jonas Örtegren. The contribution of the author of this thesis was part of the experimental planning and main part of printing, measuring and analysis of print quality, analysis of SEM imaging and presentation of the material and writing.

6.4. Paper IV

This paper describes the fluid dynamics of dye based ink into paper. The results show how surface energy, surface roughness and porosity affect the absorption rate, and droplet spreading of inkjet droplets on paper. It is also shown that the Lucas-Washburn equation can be used in some extent to describe the absorption process during printing.

This paper is the result of cooperation between Dr. Jonas Örtegren, Prof. Göran Ström and Elisabeth Alfthan. The contribution of the author of this thesis was part of the experimental planning and main part of printing, developing and testing software for analyzing the droplet absorption as a function of time, adapt L-W parameters from measurement and analysis of how well they fits to the experimental results and presentation of the material and writing.

7. DISCUSSION AND FUTURE WORK

The main advantages with digital printing are the possibilities to variable printing and profitability in short runs. The challenge with inkjet printing is to find an ink receptive substrate that rapidly absorbs the carrier liquid and fixates the colourant to the surface.

This work investigates the interaction between inkjet paper and ink. The aim was to get an increased understanding in what mechanisms affect the print quality.

Digital printing in SoHo printers uses extremely small droplets (~1-4 pl.). Printouts made with SoHo printers in Paper I did not show significantly large differences in print quality for papers with different composition. However a low degree of beating worsened the line quality. The results can be discussed in terms of small spreading of the small droplets on the surface. For these small droplets sizes, the surface spreading is low; independent of paper surface characteristics and in the production process of pilot papers, the process differs from a full scale production paper machine in terms of production speed resulting in more porous paper. This might explain the small differences in print quality between the pilot papers.

In paper I it was also shown that among the commercial papers, the copy paper COLORLOK® reproduced a high colour gamut volume compared to the other commercial uncoated papers for printout made with pigmented inks, (not with dyes). In the patent literature, the COLORLOK® has been describes as a method to improve the print quality by adding metallic salt on the surface treatment before printing to affect the ink stability for printouts made with pigmented ink.

Pigmented ink often contains anionic dispersants to stabilize the ink and to avoid undesirable aggregation of particles. By adding metallic salt to the paper surface it might be possible to change the ink stability, by shielding the repulsive forces that stabilizes the ink. This can make the pigments to aggregate faster.

In Paper II-III research has been made with bivalent salt at different concentrations, to see how CMC can affect the print quality in terms of detail reproduction. The reference paper in paper II-III contains mono-valent salt. To be able to verify the DLVO theory, the CMC should be reached by added a high concentration of monovalent salt.

Suggestion for future work would be to study the print quality and aggregation of pigments by using mono, di-and trivalent salt and different types of model ink with known composition.

One important parameter during inkjet printing at high-speed is the absorption speed. Low absorption speed can lead to colour to colour bleeding and low sharpness. In this work (paper IV) it has been shown that hydrophobic character of the paper plays an important role for the absorption speed when printing is made with picolitre sized ink droplets. Adding internal sizing to the paper strongly reduces the absorption process compared to an unsized paper.

The L-W time dependent in the L-W equation was fairly well fitted to data, whereas the overall equation overestimates the results. The L-W equation was derived for an absorption process in an infinite cylindrical tube and this might not be the right model for describing absorption into paper as porous material. Paper can be described as an inhomogeneous porous network of fibers, filler etc. The L-W equation describing a fluid in a cylindrical tube fails in this case, due to the complexity in the paper fiber network.

To be able to separate the mechanisms, i.e. how the porosity affects the absorption, homogenous model substrate should be used.

8. CONCLUSIONS

This thesis sums up some of the mechanisms that can occur during inkjet printing and affect the print quality. The result is directly applicable to paper and print industry.

The result showed that there are small variations in print quality for printouts made with desktop printers on uncoated pilot papers with varying composition (in a specific parameter window). This leaves the opportunity to work with parameters to improve runnability without affecting the print quality in an important way.

The detail reproduction and the print density for printouts made with pigment containing inks can be improved by adding color fixation onto a paper before printing. Adding a solution with calcium chloride as colourant fixation can lead to aggregation of the pigments and reduce the ink penetration.

The detail reproduction in a printed image is an interplay between the print density and the edge definition originating from surface spreading of the droplets.

Internal sizing in the uncoated papers lowers the apparent surface energy, the droplet spreading and the rate of ink absorption. Evaporation played an important role in the absorption process in the case of internally sized, uncoated papers.

The Lucas-Washburn (L-W) equation overestimated the penetration depth and the speed at which the pores are filled, but it was found that the time dependence in the L-W equation was in accordance with experimental data for absorption of an inkjet droplet into a paper.

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