STUDIES IN OFFSET INK SETTING

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Department of Chemical Engineering
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To Feelixi and Norsku

I am among those who think that science has great beauty.
A scientist in his laboratory is not only a technician:
he is also a child placed before natural phenomena
which impress him like a fairy tale.
- *Marie Curie* -

Preface

The work for this thesis was carried out during the years 2005-2011 at the Laboratory of Paper Coating and Converting, and the Center for Functional Materials under supervision of Professor Martti Toivakka. While a visiting scientist at Department of Chemical and Biological Engineering at the University of Maine during the period June 2007-July 2008, Professor Douglas Bousfield acted as a second supervisor.

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VII. Koivula, H., Kamal Alm, H. and Toivakka M., 2011. Temperature and Moisture Effects on Wetting of Calcite Surfaces by Offset Ink Constituents. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 390(1-3), pp. 105-111.

The author has the permission to use the papers.

Contributions

Paper I. The author was in charge of the planning, the execution of experiments and the analysis of the results and writing the first draft of the article. Douglas Bousfield (University of Maine, Orono, ME, USA) performed the computer modeling.

Paper II. The author was in charge of the planning, the execution of experiments and the analysis of the results and writing the article. John Tefft and Kelly Edwards (University of Maine, Orono, ME, USA) are acknowledged for the training and guiding the use of Confocal Scanning Laser Microscope.

Paper III. The author was in charge of the experimental plan, performing the printing of the samples for DOG tests, collecting and formulating the data obtained from other parties, analysis of the data and writing the first manuscript of the paper. Mikko Juuti (University of Joensuu, Joensuu, Finland) was in charge of using and advisory on the technical details of DOG. Jong Suk Sonn (University of Maine, Orono, ME, USA) was responsible for performing printing and measurements with Dynamic Gloss Meter. Douglas Bousfield was responsible for clarifying the technical details of their equipment. Janet Preston and John Parsons were in charge for producing the Polarized Light Reflectometer results and Nick Elton gave technical advisory regarding it.

Paper IV. The author was in charge of the sample preparation for FIB testing, FTIR experiments, analysis of the data and first draft of the paper. Experimental plan was formulated together with Janet Preston (IMERYS, St Austell, and UK). FIB tests were performed by Peter Heard (University of Bristol, UK).

Paper V. The author was in charge of sample preparation, performing all the experiments, analysis of the data and first draft of the manuscript. Martin McGarvey and Fiona Browne (CIBA, Paisley, UK) were guiding the model ink manufacturing. Mika Sundqvist (M-Real, Äänekoski, Finland) guided the rotational rub off measurements. Cathy Ridgway (Omya, Oftringen, Switzerland) guided the ISIT tack tests and rub off testing.

Paper VI. The author was in charge of the experimental setup, handling of the tablets prior experiments, performing the experiments, analysis of the data and first draft of the manuscript. Cathy Ridgway (Omya, Oftringen, Switzerland) prepared the wet pressed tablets. Jani Kniivilä modified the image analysis software Drop Snake Plug-in.

Paper VII. The author was in charge of the planning, conducting and analyzing contact angle experiments, and first draft of the paper.

Supporting publications

Koivula, H., Fardim, P., Toivakka, M., 2006. Characterization of Pigment Particle Surfaces by TOF-SIMS. In: TAPPI, *9th Advanced Coating Fundamentals Symposium*, Turku, Finland, February 8-10, 2006. Atlanta, GA: TAPPI Press.

Koivula, H., Juuti, M., Bousfield, D.W., Preston, J., Silvennoinen, R., Peiponen, K.-E., Toivakka, M., 2007. Comparison of Dynamic Print Gloss Measurement Techniques. In: TAPPI, *2007 TAPPI Coating and Graphics Arts Conference,* Miami, FL, USA, April 22-25, 2007. Atlanta, GA: TAPPI Press.

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Koivula, H., Gane, P.A.C., and Toivakka, M., 2008. Influence of Ink Components on Print Rub. In: TAPPI, *10th Advanced Coating Fundamentals Symposium*, Montreal, Canada, June 11-14, 2008. Atlanta, GA: TAPPI Press, pp.73-92.

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Niskanen, I., Räty, J., Peiponen, K.-E., Koivula, H., Toivakka, M., 2007. Assessment of The Complex Refractive Index of an Optically Very Dense Solid Layer: Case Study Offset Magenta Ink. *Chemical Physics Letters*, 442(4-6), pp.515-517.

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Juuti, M., Koivula, H., Toivakka, M., and Peiponen, K.-E., 2008. A Diffractive Glossmeter for Local Gloss Measurements of Papers and Prints. *TAPPI Journal.*, 7(4), pp.27-32.

Supporting Publications

Peiponen, K.-E., Kontturi, V., Niskanen, I., Juuti, M., Räty, J., Koivula, H., and Toivakka, M., 2008. On Estimation of Complex Refractive Index And Colour of Dry Black And Cyan Offset Inks by a Multi-Function Spectrophotometer, *Measurement Science and Technology*, 19(10), 115601.

Silvennoinen, R., Juuti, M., Koivula, H., Toivakka, M., Peiponen, K.-E., 2008. Diffractive Glossmeter For Measurement of Dynamic Gloss of Prints, *TAGA Journal*, 4, pp.59-71.

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Abstract

The offset printing process is complex and involves the meeting of two essentially complex materials, printing ink and paper, upon which the final product is formed. It can therefore be expected that a multitude of chemical and physical interactions and mechanisms take place at the ink-paper interface. Interactions between ink and paper are of interest to both the papermakers and ink producers, as they wish to achieve better quality in the final product.

The objective of this work is to clarify the combined influence of paper coating structure, printing ink and fountain solution on ink setting and the problems related to ink setting. A further aim is to identify the mechanisms that influence ink setting problems, and to be able to counteract them by changing properties of the coating layer or by changing the properties of the ink.

The work carried out for this thesis included use of many techniques ranging from standard paper and printability tests to advanced optical techniques for detection of ink filaments during ink levelling. Modern imaging methods were applied for assessment of ink filament remain sizes and distribution of ink components inside pigment coating layers. Gravimetric filtration method and assessment of print rub using Ink-Surface-Interaction-Tester (ISIT) were utilized to study the influence of ink properties on ink setting. The chemical interactions were observed with the help of modified thin layer chromatography and contact angle measurements using both conventional and high speed imaging.

The results of the papers in this thesis link the press operational parameters to filament sizes and show the influence of these parameters to filament size distribution. The relative importance between the press operation parameters was shown to vary. The size distribution of filaments is important in predicting the ink setting behaviour, which was highlighted by the dynamic gloss and ink setting studies. Prediction of ink setting behaviour was also further improved by use of separate permeability factors for different ink types in connection to filtration equations. The roles of ink components were studied in connection to ink absorption and mechanism of print rub. Total solids content and ratio of linseed oil to mineral oil were found to determine the degree of print rub on coated papers. Wax addition improved print rub resistance, but would not decrease print rub as much as lowering the total solids content in the ink. Linseed oil was shown to absorb into pigment coating pores by mechanism of adsorption to pore walls, which highlights the need for sufficient pore surface area for improved chromatographic separation of ink components.

These results should help press operators, suppliers of printing presses, papermakers and suppliers to papermakers, to better understand the material and operating conditions of the press as it relates to various print quality issues. Even though paper is in competition with electronic media, high quality printed products are still in demand. The results should provide useful information for this segment of the industry.

Svensk Sammanfattning

Tryckprodukten består av papper och färg. Vid tryckning kombineras dessa två principiellt komplexa material. Offset-tryckning är en något invecklad metod och inkluderar ytterligare variabler. Vi kan därför förvänta oss att ett stort antal kemiska och fysikaliska växelverkningar sker i gränsytan mellan tryckfärg och papper. Det är viktigt för papperstillverkare och färgproducenter att förstå dessa skeenden för att kunna uppnå ännu högre kvalitet hos de slutliga tryckprodukterna.

Målsättningen med detta arbete var att förtydliga de kombinerade effekterna av pigment-bestrykningsskikt, tryckfärg och fuktvatten på färgsättning och olika problem relaterade till färgsättning. Ett ytterligare mål var att identifiera mekanismer som har inverkan på färgsättningsproblem, och att kunna motverka dessa genom att förändra egenskaper, antingen hos bestrykningsskiktet eller hos tryckfärgen.

Arbetet i denna avhandling utfördes genom att använda ett flertal olika metoder, från rutinmässiga mätningar av pappers- och tryckningsegenskaper till avancerade optiska metoder för detektering av tryckfärgsfilament (filament uppkommer vid spjälking av tjock och viskös tryckfärg i trycknypet under påverkning av stora deformationskrafter) och rester av filament under färgsättning. Moderna avbildningsmetoder tillämpades vid analys av storleksfördelningen hos tryckfärgens filamentrester och fördelning av enskilda tryckfärgkomponenter inne i bestrykningsskiktet. Tryckproblem som kallas till print rub (smetning, nötningstyrka) definieras oftast som markeringar som sker på ett icke-tryckt papper till följd av kontakt med ett tryckt papper under inverkan av både tryck och skjuvning. Inverkan av tryckfärgsammansättning på färgsättning studerades med hjälp av en gravimetrisk filtreringsmetod och utvärdering av smetning utfördes med ISIT och spektral analys av överförd färgmängd. De kemiska växelverkningarna studerades med hjälp av modifierad tunnskiktskromatografi och kontaktvinkelmätningar, både med standard och med höghastighetskamera.

Resultaten i denna avhandling visar relationen mellan tryckpressens operationsvariabler och filamentstorleken. De visar också hur filamentens storleksfördelning ändras då operationsparametrarna ändras. Den relativa vikten av de olika variablerna, så som hastighet och ytråhet, varierade vid olika tryckningsomständigheter. Kännedom om storleksfördelningen hos filamenten är viktig, när man försöker förutsäga tryckfärgsättningen. Detta poängterades i resultaten av tidsberoende glansmätningar, och i resultaten av gravimetriska filteringsförsök. Samstämmigheten mellan de experimentella och de enligt filtreringsekvationen modellerade värdena att beskriva färgsättning förbättrades genom användning av skilda permeabilitetsfaktorer för de olika tryckfärgerna.

Tryckfärgkomponenternas bidrag till färgabsorptionen och smetning bestämdes. Den totala torrhalten och förhållandet mellan linolja och mineralolja var de viktigaste faktorerna som bestämde graden smetning (print rub) hos en viss kombination av bestruket papper och tryckfärg. Smetningsförmågan kunde minskas med tillskott av vax, men en minskning av den totala torrhalten var ett mer effektivt sätt att öka smetningsresistansen. Arbetet visade att absorption av linolja till pigmentbestrykningsskikt sker genom adsorption till porväggar i strukturen. Detta lyfter fram behovet av ett tillräckligt stort ytområde inne i porstrukturen, så att kromatografisk separation av oljekomponenterna kan ske utan hinder.

Dessa resultat kan vara till nytta för tryckerier, tryckmaskinsleverantörer, papperstillverkare och deras leverantörer så att de bättre kan förstå sammanhangen mellan material och operationsomständigheter när det gäller tryck-kvalitetsfrågor. Även om papper numera tävlar med elektronisk media, finns det fortfarande efterfrågan av tryckta produkter av hög kvalitet. Dessa resultat bidrar till ökandet av kunskapen inom detta industrisegment.

Keywords

Offset printing, pigment coating structure, ink setting, filamentation, dynamic print gloss Focused Ion Beam (FIB), Confocal Laser Scanning Microscopy (CLSM), Modified Thin Layer Chromatography, ink setting, coated paper, visualization, filtration, ink rheology, filtercake, emulsification, offset ink constituents, surface wetting, temperature, calcite, sodium polyacrylate, polarity, print rub, matte coated papers, ink components, tack, contact angle

Abbreviations

BCGCC	GCC with coarse particles and a broad particle size distribution
CLSM	Confocal Laser Scanning Microscope
DOE	Diffractive Optical Element
DOG	Diffractive Optical Element Based Glossmeter
ESEM	Environmental Scanning Electron Microscope
F1-F5	Ink Formulations 1-5
FG	Fast Setting, Glossy Coating
FIB	Focused Ion Beam
FM	Fast Setting, Matte Coating
FTIR	Fourier-Transform Infrared
GCC	Ground Calcium Carbonate
HS	Heatset Ink
HSE	Heatset Ink, Emulsified with Fountain Solution
ISIT	Ink Surface Interaction Tester
LED	Light Emitting Diode
LVB	Lower Viscosity Ink, Black
LVC	Lower Viscosity Ink, Cyan
MCC	Modified Calcium Carbonate, having a bimodal pore structure for rapid liquid uptake
NaPA	Sodium Salt of Polyacrylic Acid, Dispersant
NCGCC	GCC with coarse particles with a narrow particle size distribution
PE	Polyethylene
PSD	Particle Size Distribution
PTFE	Polytetrafluoroethylene
RH	Relative Humidity
SB	Styrenbutadien
SF	Sheet-fed Ink
SG	Slow Setting, Glossy Coating
SM	Slow Setting, Matte Coating
TB	Thicker Ink, Black
TC	Thicker Ink, cyan
TLC	Thin-Layer Chromatography
TLW	Thin-Layer Wicking

Abbreviations

UV	Ultra Violet (Radiation)
ÅAGWR	Åbo Akademi Gravimetric Water Retention Tester

Nomenclature

		Units
ϕ_f	The volume fraction of pigment in the filter cake	
ϕ	The volume fraction of pigment in the ink	
$K'm$	Darcy coefficient of the medium (the coating)	m^2
Kf	Darcy coefficient of the filter cake	m^2
ΔE	Total color difference in the CIE L*a*b* color space	
Δb^*	Color difference of the yellow to blue axis of CIE L*a*b* color space	
s%	Oil separation percentage	%
L_t	Total absorption length	mm
Li	Absorption length of the component i.	mm
G	Gloss	
I_{meas}	Intensity measured by the DOG	
I_{ref}	Intensity measured from a gloss reference	
w-%	weight percent	%
k*	Darcy permeability coefficient	m^2
n	Exponent for scaling the contact diameter log-log plots according to hydrodynamic or molecular kinetic model	
Tg	Glass transition temperature	
gel %	Degree of cross linking	

1. Introduction

In Finland, the history of printing dates back to 1642 when the first printing press was established in Turku, to provide means of publication for the newly founded first Åbo Akademi University (Clair, 1976). Offset lithography was invented by Johann Alois Senefelder in about 1800. In the early days most process stages were done by hand and the material of printing plate was stone. Offset printing of paper in its current form has been around since the early 1900s (Bruno, 1985). Offset lithography is a well established printing method and still the most important technology (Kipphan (Ed.), 2001). In 2009, the share of offset printing was 53% of the world's printing markets (Smyth, 2009). It continues to be the most economical way to produce high quality, medium length (10 000 to 100 000 copies) print runs. A continuous demand for improvements in the process has taken the form of increased productivity, higher operating speeds and value-adding in-line finishing stages. These increased speeds especially set new challenges for the ink makers to keep up, so that the inks will run well on the presses without technical problems (Leach and Pierce, 2004).

Pigment coating of paper is performed to enhance the physical properties of paper and printability. The coating generally makes paper whiter, brighter and more opaque. The coating color fills in the voids between the base paper fibers, creating a smooth surface. The gloss of the paper, and more importantly that of the print, is increased on coated grades. Application of coating color will also improve the surface strength. However, the mechanical strength of the paper will decrease when compared with an uncoated paper at the same basis weight. The obtainable paper properties will depend, besides on the base paper properties, on the coating color components, the coating method and the chosen finishing. Pigment coated papers are used to produce printed products such as magazines, catalogs, advertisements, and books. Additionally, pigment coated board is utilized in various packaging applications, making it another important product segment.

The role of interactions between the pigment coated paper and immiscible liquids: water and oil, is a key aspect of offset printing process. The splitting of emulsified ink layer in the printing nip creates filaments and filament remains on the surface of the print. The properties of the ink and the pigment coating layer along with the printing conditions influence the leveling and the size distribution of the filaments. The leveling then again is connected to ink setting and the final quality of the printed product. Many of the problems occurring in the process, whether they relate more to the paper or the ink, often originate from imbalance in spreading or absorption of offset ink components and water. Therefore, it is of essence to understand the interfacial and physical phenomena which drive the process of ink setting on the coated paper. Ink setting related problems are partially a consequence of distribution of ink components into the coating structure. Print rub, which is defined as the marking occurring on an unprinted sheet as a result from contact with a printed sheet under pressure and shear, is one example of such a problem. Print rub is a problem limiting the use of matt and silk coated papers.

The objective of this thesis was to clarify the role of the printing ink and ink components in respect to the filamentation and subsequent ink setting, with a special focus on the mechanism causing print rub.

2. Background

2.1 Offset Lithography

Offset printing is based on the lithographic principle. The ink is carried onto the image substrate by a completely smooth printing plate on which the printing and non-printing areas are chemically separated. The ink repellent, non-printing areas are hydrophilic and carry a film of dampening solution, also called fountain solution. Application of fountain solution is the first step of the offset process. In the next step, oil-based ink is transferred to the hydrophobic ink accepting image areas of the plate. The ink transfer on to the non-printing areas is limited, due to the film split, which takes place in the fountain solution layer having lower cohesion to that of the ink film. After the ink has been transferred to the plate, it is not directly transferred to the substrate, but offset to the printing substrate via a compressible rubber blanket cylinder. The ink and fountain solution transfer to the substrate is schematically described in Figure 1.

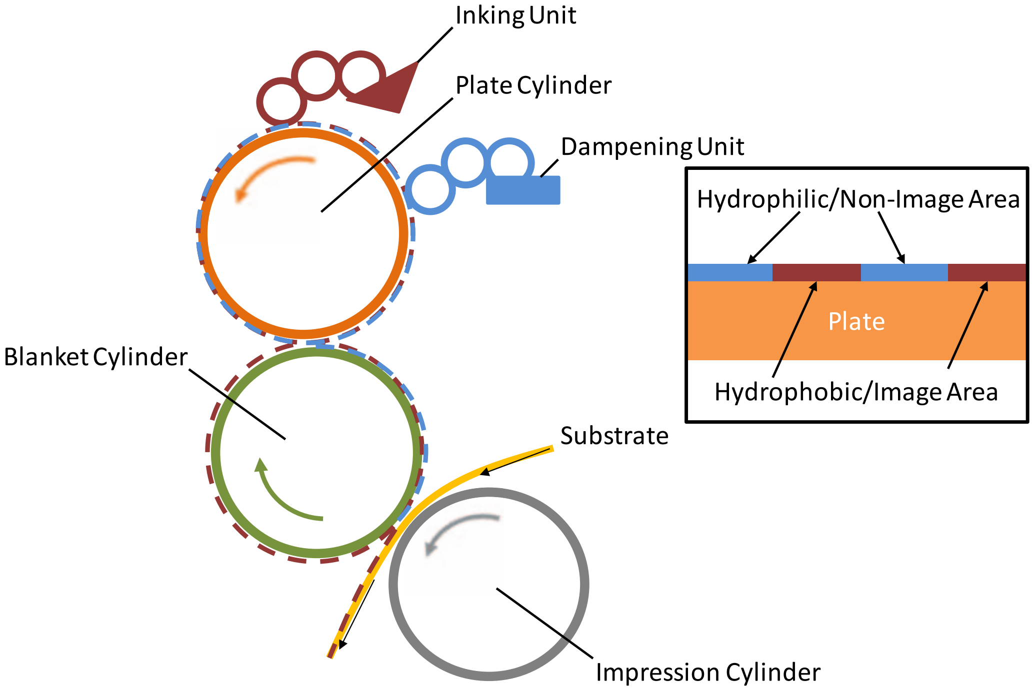


Figure 1. Schematic illustration of the key elements in offset printing. Figure redrawn from Kipphan (2001).

There are four types of offset printing methods: heatset web offset (HSWO), coldset web offset (CSWO), sheet-fed offset (SFO) and waterless (or dry) offset. The methods are differentiated by the target product ranges, but also by the feeding mechanism of the substrate, ink composition and ink drying mechanism. Waterless printing is a fairly novel method and it is not considered as a conventional offset method, since it lacks the use of fountain solution, and utilizes a silicon surface on non-printing areas and a photopolymer on image areas. After offset printing, finishing processes such as cutting, folding and binding of the product are regularly performed on the products.

In addition to paper, foil, film and thin metals can be used as substrates in offset printing, especially on sheet-fed presses (Adams and Dolin, 2002). On the web-fed presses the main substrate type is paper. Uncoated paper grades can be used, but coated paper makes out the most significant portion of offset printed products in form of magazines, brochures, and books.

2.1.1 Ink Transfer in the Printing Nip

Many of properties of a printed surface and printing related problems can be traced back to a specific position in the printing process. Here, the printing nip appears to often play a critical role. There the ink is transferred from the blanket cylinder to the paper and ink film is split. The nip phenomena consist of a region of shear in the beginning of the nip, followed by cavitation of the ink layer, filamentation and filament elongation before final splitting of the ink at the end of the nip region (Oittinen and Lindqvist, 1981; Oittinen and Saarelma, 1998). The pressure distribution in a printing nip along with the ink transfer and filamentation are illustrated in Figure 2.

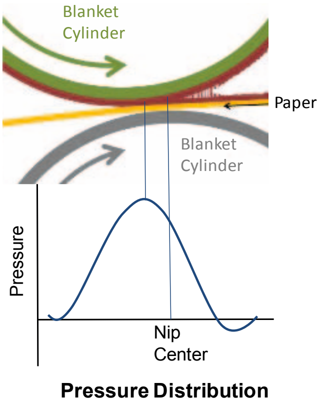


Figure 2. Illustration of ink layer passing through a printing nip and the filaments forming at the nip exit. The bottom part of the figure shows the corresponding pressure distribution in the printing nip.

Ink filaments are then a result of the ink splitting in the printing nip and the elongational forces acting in the ink. Fetsko and Zettlemoyer (1962) concluded that the most important ink factor for the gloss and uniformity of prints is the size of ink filaments during the ink splitting when ink is transferred from the printing cylinders to the paper. The filament remains on the paper surface are the starting point for ink leveling and setting, print gloss and the basis for the quality of the prints. The ink film splitting is influenced by the intrinsic properties of the ink, properties and geometry of the printing equipment and properties of the paper. Additionally, the fountain solution, which is emulsified into the ink, contributes to the ink splitting as it has lower cohesion than the ink.

2.1.2 Printability and Print Quality

Good optical properties are a necessity for both the coated paper and printed products. Key optical properties include opacity, brightness, translucency and gloss. Gloss is physically defined as the intensity ratio of specularly reflected light to the incident light. Gloss is strongly dependent on the surface roughness and the directionality of the reflected light (Leskelä, 1998; Pauler, 2002).

High print gloss, such as shown in Figure 3, is a major attribute for offset printing paper grades as it is visually associated with high print quality. Also, it focuses attention and increases the intensity of colors. The difference between the ink gloss and the paper gloss, often called delta gloss or print snap, is advantageous as it provides good contrast to the eye and assists reading.

The gloss of a printed product is the result of many factors, including the paper, coating layer and ink properties. It is generally known and accepted that coating layer properties such as surface roughness, porosity, pigment particle size and shape and their distributions have an influence on print gloss via changes of the coating structure (Desjumaux, *et al.*, 1998c; Donigian, *et al.*, 1997, 2004; Preston, *et al.*, 2002a; Ström, *et al.*, 2003b; Jeon and Bousfield, 2004). When the paper gloss increases, a high delta gloss is more difficult to obtain. The print gloss should always be evenly distributed in the print. Relating to the evenness of optical appearance, gloss and ink density mottle are other common print defects. Mottle can occur due to imbalance of fountain solution and ink absorption into the coating as stated earlier. A high correlation has been found also between print mottle and basepaper/board macro-roughness variations (Kuni, 2003).

Figure 3. A glossy multicolor print.

The fountain solution is one source of accumulation problems in offset printing. It is known that problems such as picking are a result of weakening of the coating layer, causing particles to detach from the coating, to transfer to the blanket and to cause defects in the print. Pigment type and pore structure features have been shown to determine the extent of fountain solution absorption and contribute to the loss of coating strength (Reinius, *et al.*, 2006; Preston, *et al.*, 2008b). Husband, *et al*. (2009) showed that adhesion between latex and mineral surfaces involves ionic bonding, and that converting those ionic bonds to covalent bonds increased the strength of the coating.

Matt papers are continuing to be popular in the printing industry, among designers, publishers and consumers, because their appearance is pleasing to the human eye and the matt surface provides good readability of printed text and high print snap. The advantages of matt papers include their ability to produce sharp half tones with high ink densities and high total contrast (Chamberlain, 1990). One of the challenges for matt coated papers is that they tend to have a lower resistance to print rub than glossy papers. The problem is often noted only after the printing has been completed, while the finishing operations such as cutting, folding and gathering take place (Kinnaird, 1990). Low rub resistance can be a major reason behind customer complaints and is also an end-cost consideration. There are several different terms that are used to describe the problem of low rub resistance. Terms such as marking, rub-off, print rub, print abrasion, smearing, ink scuff and carbonation are used. The definition of the term is very much dependent on both the mechanism proposed for the phenomenon (Gane, *et al.*, 2005) and the mutual agreement of those involved. All of the terms refer somehow to ink that has been transferred from the printed paper to the unprinted paper in operations after printing. A photo of such transferred ink on a blank piece of sheet is shown in Figure 4.

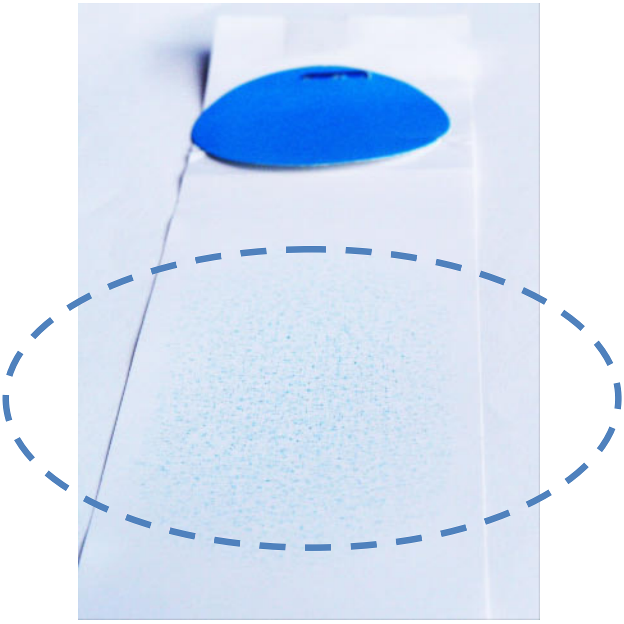


Figure 4. Photo of markings transferred from a print to an unprinted paper. The area with print rub is indicated by the dashed blue circle.

The problem of print rub is most intense in solid areas of print that are in contact with an unprinted page. The set off principle is defined as a transfer of ink from the print to the reverse of the adjacent sheet in the stack (Leach and Pierce, 2004). A definition is given by Gane, *et al.* (2006), who state that the difference between ink rub and set off is that in the case of rub, strain is applied to the set off principle. This idea was originally presented by Gumbel (1999). In order to overcome the markings and gloss variations that abrasion and shear cause to the print, various tools can be used. On the ink formulation side, use of wax additives can be helpful to minimize print rub. The printer can add another process step and apply a (UV-) varnish layer on top of the ink layer, thereby hardening the surface and protecting the ink layer (Rousu, *et al.*, 2006). However, this adds extra cost and it may be more economical only to varnish the cover pages.

2.2 Ink-Coating Interactions

This section discusses in more detail the properties of pigment coating layer and ink, which affect the ink setting in, or directly after, the printing nip.

2.2.1 Pigment Coating

Paper is coated to improve in particular the printability and also the optical properties of paper for added value. The coating consists of mineral pigments, binder, water and small amounts of additives such as rheology modifiers and optical brighteners. The resulting coating color is applied on paper as a wet suspension and is then dried. Application amounts of coating vary between 6 to 12 g/m^2 per side, and the high quality papers can have more than one layer of coating (Paltakari, Lehtinen and Imppola, 2009). Figure 5 shows a cross-section of mineral coating on top of the fiber network.

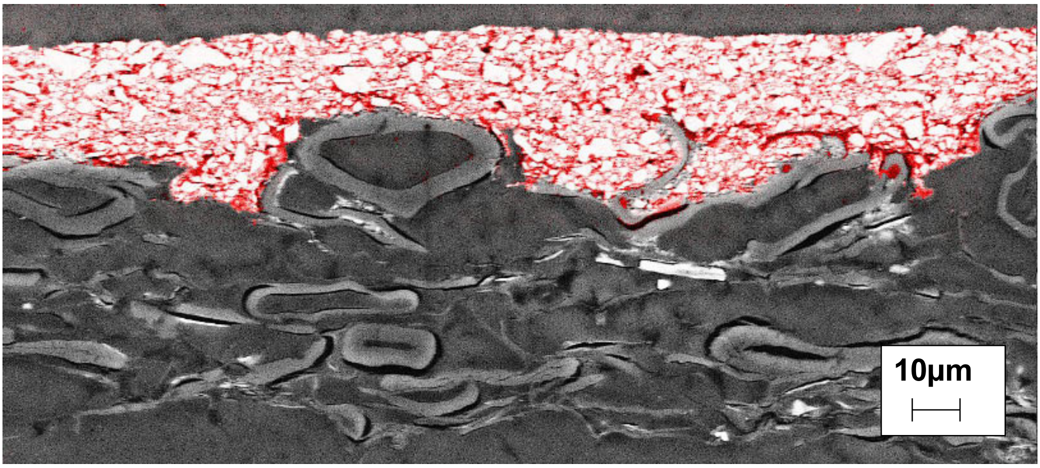


Figure 5. Cross-section of pigment coated paper showing the coating layer on top of fiber network. The coating layer is artificially colored to highlight it.

Pigment Coating Structure

The structure of a pigment coating develops during the water removal and coating consolidation as a result of pigment and binder particle interactions (Watanabe and Lepoutre, 1982; Engström, 1994; Grön, 1998; Sand, 2010). Essentially, the single pigment particles are responsible for the creation of the three dimensional porous structure of the coating layer. The properties of that structure are then responsible for providing the required light scattering properties, and necessary void volume for the ink absorption. The requirements set for the coating optical properties often conflict with the printability requirements with respect to the pore structure (Gane, *et al.*, 2005). Therefore, a coating color recipe is always a compromise, made in order to fulfill the varied requirements of the coated paper. The desired coating layer properties can be obtained by modifying the coating color composition: pigment blends and binder type. Coatings where ink sets fast typically have more small pores and the slow setting coatings have larger pores. Another important factor in addition to the porosity of the coating is also the permeability, i.e. the pore connectivity. The porous structure is often described by the particle size distribution and aspect ratio of the pigment. The void space of a coating is frequently measured with mercury porosimetry and described using pore size distributions.

The role of the coating pore structure to the ink setting has been studied by a number of groups over the last decades. The packing of pigment particles and resulting void features: absorptivity, porosity and pore volume, pore size distribution are important parameters for a coating interacting with a printing ink (Triantafillopoulos and Lee 1996; Preston, *et al.*, 1999; Xiang, *et al.*, 1998, 2002; Rousu, *et al.*,. 2000b, 2001, Dubé, *et al.*, 2008). Zang and Aspler (1995) studied the ink transfer and splitting mechanism in an offset printing nip and determined a relationship between the coating gloss and coating absorbency to print gloss. Fine pore sizes, usually created with fine pigment particle sizes cause the ink film to set rapidly and result in lower printed gloss (Donigian, *et al.*, 1997; Jeon and Bousfield, 2004). Preston (2001) and Preston, *et al.*, (2002a) point out that in order to gain access to the internal pores; an adequate surface pore density is required. The geometry of the pores contributes to create fast or slow ink setting structures (Ridgway, *et al.*, 2001). Ridgway and Gane (2002) showed that changing the pore connectivity, resulting from combination of the pore size and permeability can produce very different ink setting even though the total porosity does not change significantly.

The porous structure is also affected by post-treatment of the coating such as calendering. Calendering aligns particles and smoothens the top coating layer and increases the coating gloss. At the same time the coating structure is compressed whereby the pore sizes in the bulk coating structure decrease (Hiorns, *et al.*, 1998, Larsson, *et al.*, 2007). In calendaring, process optimization is beneficial so that optimal balance of ink setting properties and surface optical appearance can be obtained (Resch, *et al.*, 2010). Length scale of coating surface roughness is also an important factor for print gloss. Macro-scale roughness dominates the formation of gloss with high ink amounts on rough papers while micro scale roughness is important in areas with low ink coverage (Oittinen, 1983). For smooth papers, the coating pore structure and resulting ink setting rate are dominant in determining the printed gloss (Ström, *et al.*, 2003b).

Pigment Coating Chemistry

Latex binder in the coating color influences printed gloss by changing the pore structure, partially due to latex shrinkage during drying (Lee, 1982). During the structure change the pore size can be decreased and some pores may be blocked. It is well acknowledged that diffusion of ink oils into the latex takes place during ink setting. A significant amount of work has been done combining modeling and experimental work on the diffusion dynamics. (Desjumaux and Bousfield, 1998a; Xiang, *et al.*, 1998, 2000; Fouchet, *et al.*, 2004, 2006) and parameters such as polymer polarity, glass transition temperature (Tg) and degree of cross linking (gel %) were identified to strongly influence the absorption of oils into the latex. High interactivity latex at constant latex addition promotes faster setting of the ink than latex with low interactivity (Gane, 1994). Increased binder level (Triantafillopoulos and Lee, 1996), higher degree of crosslinking (Van Gilder and Purfeerst, 1994) and addition of acryclonitrile co-polymer to styrene-butadiene (Forbes and Ave'Lallemant, 1998) have been shown to slow down the ink setting. Increased butadiene content in styrene - butadiene polymers on the other hand increases oil-latex interactivity (Triantafillopoulos and Lee, 1996). The role of low solubility parameter in increasing oil interaction was highlighted in the work of Rousu, *et al.* (2001). In addition to solubility parameter influence, Rousu, *et al.* (2001) showed that low Tg and gel % increased interactivity of ink oils with latexes.

The surface chemistry of the coating pigments should also be considered. However, as coating pigments are typically handled and transported as slurry, the pigment surface is most often fully covered with a dispersing agent, which stabilizes the particles in the suspension. The polar and hygroscopic dispersant has been shown to interact with both moisture from the air and the fountain solution (Gane and Ridgway, 2009; Alm, *et al.*, 2010).

Ink-coating interactions impact directly the quality of the printed product. Mottle, uneven density and gloss variations of the print, is a fairly common print problem in offset. Several authors link the occurrence of mottle to uneven coating chemistry and to uneven absorption of the ink into the coating structure (Engström, 1994; Preston, *et al.*, 2006, 2008a; Tåg, *et al.*, 2008). Print rub is suggested to be caused by the residual solvent that is trapped in the print resulting in lack of chemical and mechanical resistance. (Cordery, 1990; Aurela and Räisänen, 1993). Guest (1990) pointed out that the latex level and Tg have a marked influence on occurrence of print rub.

2.2.2 Offset Lithographic Ink and Fountain Solution

It is quite apparent that the printing ink applied onto the coating has an influence on the interactions that occur with the coating layer. Therefore it is not enough just to study the properties of coating layer, but also to comprehend how the inks' inherent characteristics affect printability. This section discusses the main components of offset printing ink and their function.

Offset printing inks have a thick and pasty consistency. Figure 6 demonstrates the consistency by showing the ink varnish being moved from one container to another. The solvent/diluent in the ink is a mixture of oils and the whole ink is bound together and to the coating with a resin component. The resin- oil system is referred to as varnish or vehicle in the ink formulation. It is responsible for most of the physical properties of the ink and sets basis for the ink performance. For example, alkyd resin chemistry has been shown to influence ink pigment dispersion, fountain solution emulsification and ink setting (Wickman, 1998). The color is created by pigment particles which are fully dispersed into the varnish. Small amounts of additives are used for example to modify the consistency, prevent ink from drying too early or to provide slip for the print surface at finishing stages. Sheet-fed offset inks are dried by oxidation and polymerization and heatset offset mainly by evaporation of the solvent. This causes component ratios to vary during ink formulation, but the main components remain the same.

Figure 6. Thick and pasty offset ink varnish.

The two oils that have been the focus of this work are typical offset solvents. High boiling petroleum distillates are often referred to as mineral oils. There are three common boiling point ranges for such oils: 240-270°C, 260-290°C and 280-320°C. Another variable in the mineral oils is the level of aromatic content of the oil. The choices of boiling point range and aromatic content depend on the drying method and influence the stability of the ink on the press. The other type of ink oil used is the vegetable oils or alkyds. Linseed oil is the most common vegetable oil. It is extracted from flax seeds, and consists mainly of fatty acids and (tri)glycerides (Swern, 1979). Linseed oil is considered to be a strong drying oil, as it has high content of linolenic acid with three double bonds in the structure, which crosslink during drying. Other vegetable oils such as soy oil, tall ester and rapeseed ester are also used in printing ink formulation, but they are not considered in the frame of this work.

High molecular weight resin is one of the backbones of varnish system and is responsible for many physical properties of the ink such as solvent release and structure: tack and viscosity, pigment wetting and print gloss. Some typical resins are rosin-modified phenolics and hydrocarbon resins, also maleics and rosin esters may be used. Compatibility of the hard resin with the oils is essential for a successful ink formulation.

The offset ink is printed as a very thin layer (0.5-1.5 μm). Therefore, the ink pigment must have good color strength. Pigment tends to be the most expensive component in the ink, so its amount in the ink is minimized. Typically the pigment content of an offset ink is 10-30%. Offset pigments are either organic or of synthetic origin (Todd, 1994; Leach and Pierce, 2004).

As stated earlier, various additives can be included in the ink formulation to improve specific properties. Catalytic driers, for example cobalt and rheology modifiers such as organic aluminum compounds are frequently used. Ström, *et al.* (2003a), for example, showed that the polymerization rate of ink vehicles is highly dependent on the drier content and antioxidants. Waxes used as additives are of special interest in this work, since they are commonly used to reduce the surface friction at finishing stages to avoid the print rub problem. Waxes are added to the ink formulation as pastes or micronized powders during ink manufacture. The level of wax addition is typically around 1-2%. The fountain solution could be considered as part of the ink, as it is essential for the lithographic principle. Some of the fountain solution goes through the process as free liquid, while some 30% of it will emulsify into the ink. It is worth noting that incorporation of water or fountain solution into the inks does change the properties of the ink (Bassemir, 1981; Xiang and Bousfield, 1999; Fröberg, *et al.*, 2000).

2.3 Ink Setting and Oil Absorption into the Coating Structure

Absorption of fluids into coated paper is important for the end use application in printing processes; absorption of ink oils determines ink setting rates that link back to print quality issues and production limits. This section will shortly review current knowledge about filament formation and ink setting directly after printing. As shown for example by Ström, *et al.* (2003a), typical polymerization reactions in sheet-fed offset ink formulations are measured in hours and days rather than minutes. On the other hand in heatset process the ink is dried practically within seconds after printing. The drying processes are beyond the scope of this thesis, which concentrates in the phenomena taking place in the close vicinity of the printing nip.

2.3.1 Theories

Filament formation is very closely related to the development of print gloss in offset printing. Print gloss will also start to develop already in the printing nip when the two materials meet, as the ink gloss is typically higher than the gloss of a coated paper. After printing, the filaments level out and the degree of leveling before setting is related to the absorption capability of the coating layer and to the initial filament size. There is an initial rapid increase in gloss, which can be hypothesized to be caused by leveling of the ink filaments. At long times after printing, the gloss approaches a value that is related both to the paper gloss and the ink-setting speed. In most cases high paper gloss leads to high print gloss as stated by Ström, *et al.* (2003b) with some exceptions relating to filaments "freezing" due to too fast solvent absorption (Donigian, *et al.*, 1997; Jeon and Bousfield, 2004). For matte papers, the coating layer surface roughness can start protruding through the ink film as the ink sets and lead to reduction of the gloss value. These stages have been visually described in Figure 7.

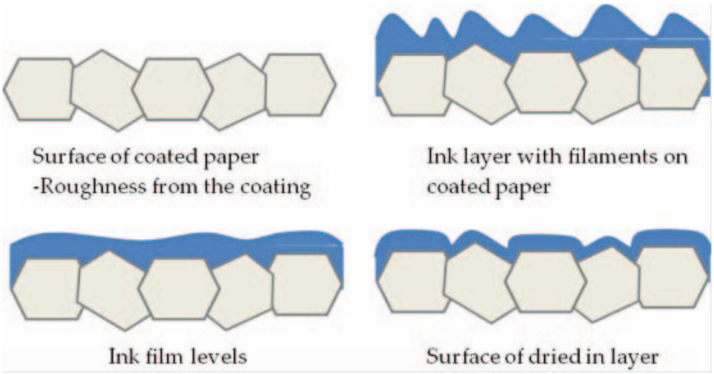


Figure 7. A Schematic illustration of coated paper surface and the stages of ink filament leveling on a rough surface.

The direct observation of filaments, even on a laboratory scale, is challenging because of the fine length scale and the high speeds. Attempts to observe filaments using high speed cameras or video have been reported in the literature (De Grace, *et al.*, 1993). At low speeds, filament length at rupture varied with ink formulation. Also increasing the shear viscosity of the ink increased the filament length. Bery and Loel (1992) studied the cavitation of ink film in the printing nip and correlated the asymmetrical splitting patterns with the residual splitting pattern on the blanket. Also acoustics have been successfully used to monitor and analyze differences in ink film cavitation and splitting within and around the printing nip (Voltaire, 2006; Voltaire, *et al.*, 2006).

The influence of ink rheology in relation to filament formation in the printing nip and the subsequent leveling of ink have been pointed out in several publications (Oittinen and Lindqvist, 1981; Lyne, 1990; Ercan and Bousfield, 2000; Désjumaux, *et al.*, 1998b). The gloss of a printed paper is highly influenced by the ink and ink leveling characteristics (Desjumaux, *et al.*, 1998b). Fine scale defects in ink layer level rapidly and large scale defects level slower (Glatter and Bousfield, 1997). High printing speed and high ink film thickness produce a variety sizes of defects in printing which level quickly initially but the leveling will slow down at longer times. Preston, *et al.* (2003) showed that in addition to ink film leveling the resin depletion impacts the printed gloss. Donigian, *et al.* (2004) reported on samples where gloss tack relationships were untypical. They concluded that the higher gloss of fast setting papers with small pore sizes was due to inks ability to keep on leveling even after the tack had decreased. Ström and Karathanasis (2007) estimated the effect of roughness caused by filament remains to be about 6 gloss units for a print on fast setting coating. Rousu, *et al.* (2003) studied offset ink constituents and showed a relationship between the absorption chromatographic fractionation of the inks and the resulting distribution of offset ink components to print gloss and print density.

Recently attention has been given to the operational parameters and ink parameters (Ercan, 2001). Kawashima and Bousfield (2009a, b) reported the influence of print speed and different blanket textures on print gloss development: blankets with a high roughness decrease the print gloss at high speeds. Khan (2010) studied the behavior of fountain solution exiting rolling nip geometry and found pressure induced cavitations at the nip to cause rupture of the fountain film and turn it into droplets.

A few different hypotheses have been proposed to describe the absorption of oils from the ink into the coating layer. The filtercake theory by Xiang and Bousfield (2001) suggests that there is a filtercake of ink pigment particles and hard resin building up at the interface between the ink and coating. Gradual solidification of the ink as suggested by Gane, *et al.* (2003a, b) states that ink oils absorb to the coating structure gradually solidifying and drying the ink, without any clear layering of components. The multiphase theory suggested by Donigian (2006) describes ink oil absorption under hypothesis that there exists at least two or more phases in the ink. The mobile phase releases oil rapidly, while the concentrated phase is prone to sequester oil. The oil loss depends on the capillary forces induced by the coating layer pores and on the diffusion rate of oil into the mobile phase from the concentrated phase. Figure 8 shows a schematic illustration for ink oil absorption according to these three mechanisms.

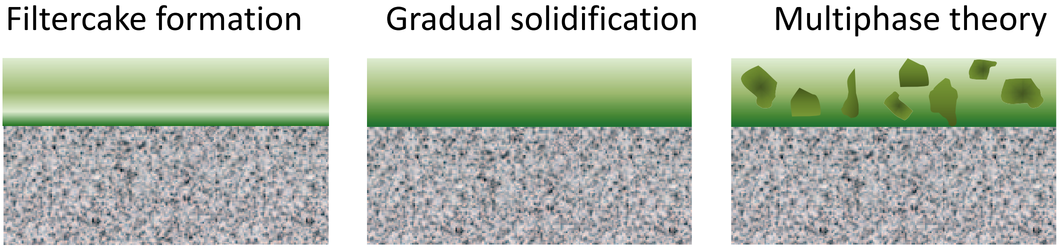


Figure 8. Simplified illustrations of the ink setting theories. The pictures illustrate a layer of ink on a pigment coating layer.

Rousu (2002) has previously extensively studied influence of ink constituents on differential absorption and separation of the components on coated papers. Rousu, *et al.* (2000b, 2001) systematically studied ink absorption on coatings with model inks and well-defined coatings with different physical structure and chemistry, showing that ink oils separate during absorption and that both chemical and physical properties of the ink and coating contribute to this separation. Fluid phase absorption into the coating structure is determined by capillary wetting and flow of ink oils into the coating structure, which in turn is controlled by viscosity-surface tension ratio of the penetrating fluid. Changes in coating chemistry significantly affect the ink oil penetration into the coating structure. Diffusion of oils into a latex binder polymer network is slower than the capillary-driven absorption, and is determined by the latex-ink oil interactions. Latex properties, such as latex type, Tg, and gel-% influence the oil uptake in addition to the main defining property of oil solubility parameter (Rousu, *et al.,* 2000a, 2002). Rousu, *et al.* (2003) pointed out that the absorption and distribution of offset ink constituents has an influence on the resulting print quality in terms of gloss and density of the prints. In their work they also note that the implications of the ink oil distribution within the coating structure are relevant in the finishing, especially in respect to print rub, after offset printing operations such as varnishing and folding.

While the oils penetrate into the coating structure, they follow preferred pathways in the coating (Schoelkopf, *et al.*, 2003a, b). Also the fountain solution along with the oils absorbs into the coating. The remaining ink components: pigment and resin, remain on top of the coating layer (Hattula and Oittinen, 1982; Ström, *et al.,* 2000). It has been shown that pigment particles may even protrude through the resin when oils are withdrawing fast from the ink and the ink loading is low (Preston, *et al.*, 2002b).

3. Materials and Methods

The materials and methods outlined in this chapter represent the key methodology of the work performed for this thesis. A multitude of routine measurements were also performed, but since these are well described in the literature and in the papers, the details of those will not be mentioned here.

3.1 Dynamic Gloss Measurement

3.1.1 Diffractive Optical Element based Glossmeter

The diffractive optical element based glossmeter (DOG) has been developed by Silvennoinen, *et al.* (1999). The instrument has been used in quality inspection of planar, concave and convex metal surfaces (Myller, *et al.,* 2006) and quality inspection of color laser prints (Palviainen, 2002). Juuti, *et al.* (2007) applied DOG for detection of local specular gloss and surface roughness from black prints. Peiponen, *et al.* (2006 a, b) used DOG for assessment of local surface quality of paper and additionally introduced statistical parameters for gloss evaluation. A schematic diagram of the DOG is shown in Figure 9.

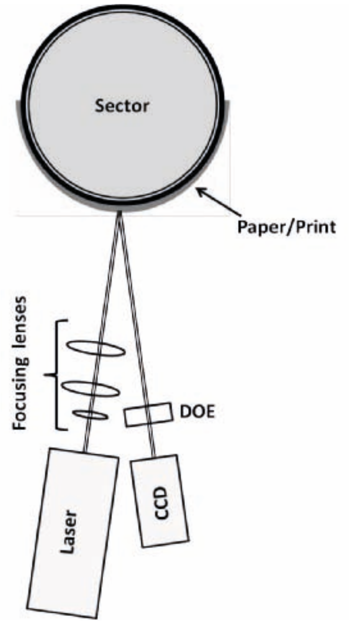


Figure 9. A schematic illustration of DOG setup for dynamic gloss measurement.

The light source in DOG is a low-power semiconductor laser with a wavelength of 635 nm. The expanded laser beam is focused onto an area of about 20 mm^2 of the printed paper sample. If desired, it is possible to employ even a tighter focusing of the incoming laser beam down to 50 µm diameter. The light scattered from the ink is incident on a Diffractive Optical Element (DOE) which is a computer generated hologram. The hologram reconstructs the intensity information from a speckle pattern. Note, that there is no objective lens in the charge-coupled device camera; the diffracted pattern is directly incident on its chip. The receptor aperture angle of the DOG is 0.4°. The image information is captured and recorded into the memory of a computer, which is also used for data analysis. The gloss G, detected by the DOG, is defined as the ratio $G=100*I_{meas}/ I_{ref}$, where I_{meas} is the intensity measured by the DOG and I_{ref} is the intensity measured from a gloss reference. The reference surface used was a gloss standard (Working Standard, Zehntner Testing Instruments, Switzerland). A good correlation between values measured with DOG and with standard gloss measuring devices has been reported for high gloss objects in Myller (2004). When measuring the dynamic print gloss, the paper sample was mounted onto a moving sector of a laboratory printer (Universal Testprinter, Testprint BV, The Netherlands) and printed with a layer of ink. After printing the sample stopped about 10 cm after the nip. The computer was set to collect data simultaneously with the start of each test. The gloss was followed from this moment onwards as a function of time every 0.1 seconds for ca. 5 minutes. Those data points which were measured before the sector has stopped were excluded and the first point after this was defined as start of the measurement.

3.1.2 Dynamic Gloss Meter

The dynamic gloss meter has been presented and used for studying paper-ink interactions by a group of scientists from the University of Maine (Glatter and Bousfield 1997; Desjumaux, *et al.*, 1998c; Xiang, *et al.*, 1998; Jeon and Bousfield, 2004). The method is based on laser and detector that are mounted directly adjacent to a laboratory printer (Model MPT800, Kumagai Riki Kogyo Co. Ltd., Tokyo, Japan) as is schematically shown in Figure 10. The laser has a light source with a wavelength of 675 nm and both the laser and the detector are mounted at an angle of 75° from the vertical. The light from the laser is reflected from a mirror to the sample and then back to a 0.23 cm × 0.23 cm light detector. A lens in front of the detector collects the light reflected from the printed ink film. Gloss is detected as a voltage signal and stored on a computer. The experiment was started by mounting a paper sample on a moving plate and printing it with a layer of ink. Simultaneously with the start of each test the computer was set to collect the gloss data. The sample was stopped within 0.1s after the printing nip and the gloss was followed from this moment onwards as a function of time every 0.1 seconds for ca. 2.5 minutes. The data was examined to determine the first deviation from the steady state value that was measured before the sample enters the gloss detection area. This time was recorded as time equal to zero.

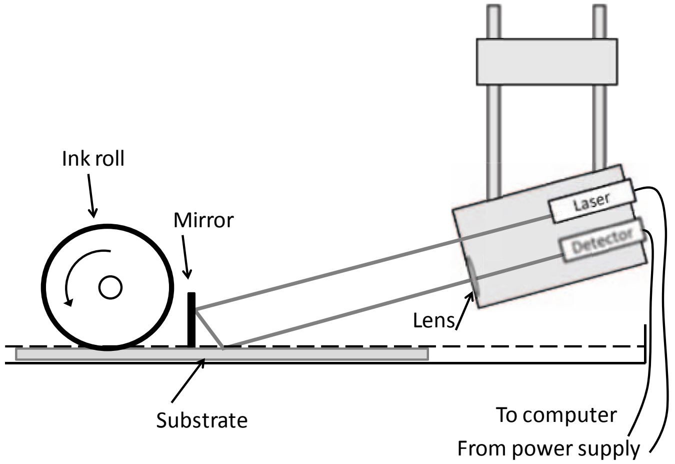


Figure 10. A schematic illustration of dynamic gloss meter setup.

3.1.3 Reflectometer

The polarized light reflectometer is a commercial instrument (The Surfoptic Imaging Reflectometer System (SIRS 75), Dayta Systems Ltd, Bristol, UK), which has been used to investigate paper surfaces and ink-paper interactions (Elton, *et al.*, 2006a, b). A schematic diagram of the instrument is shown in Figure 11. Lasers at wavelengths 635 nm and 670 nm are used as light sources. They are arranged to produce coincident and collimated beams at a fixed angle of incidence of 75° to the specimen normal. The collimated laser light is polarized and the state of the polarized light can be varied from p to s (p = plane polarized perpendicular with respect to the surface; s = plane polarized parallel with respect to the surface) using a variable retarder. A reference beam is used for compensation of the fluctuations in source intensity in all intensity measurements. The light is collected over approximately ±10° about the specular angle by a system of lenses and beam splitters, which maintains the angular distribution of the light. A complementary metal oxide semiconductor is used to measure the angular intensity distribution of the forward scattered light. In addition, photodiode detectors at two fixed acceptance angles (nominally 2° and 20°) are used to measure intensity. An additional photodiode detector, normal to the surface of the specimen, is used to measure diffusely scattered light. It is also used to correct the forward scattered intensities for the contribution of diffuse scatter. The detected gloss is reported as percentage compared to a black gloss standard with a refractive index of 1.54 at 652 nm. The Imaging Reflectometer can also be used in a mapping mode, which allows maps of up to 100 mm × 100 mm to be obtained of the surface. The laser spot in the mapping mode is oval in shape (a circle projected at 75° onto the paper surface). The spot has a width of 0.125 mm and length of 0.25 mm. The mapping mode is particularly useful when studying point to point variations in gloss which may lead to print mottle (Preston, *et al.*, 2006, 2008a). Other measurement modes are also available and descriptions of them can be found in Elton, *et al.* (2006a, b) and in Preston, *et al.* (2006).

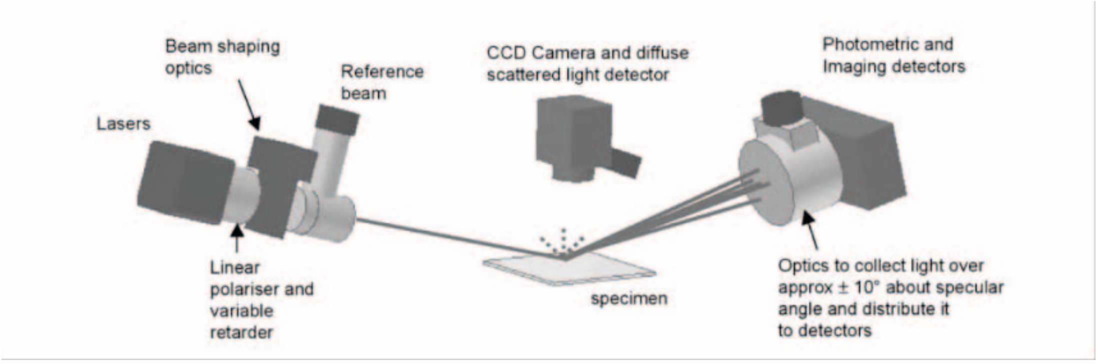


Figure 11. A schematic illustration of dynamic gloss meter setup.

When measuring the dynamic print gloss with the reflectometer the paper samples were first printed using a laboratory printer (IGT, IGT Testing Systems, The Netherlands) and then transferred to the reflectometer for measurement. The delay between printing and gloss measurement was approximately 10-15 seconds. The reflectometer results were time-shifted to make it possible to compare the three instruments. All the times quoted in the results section are relative to the time of printing. The measurement was carried out for 30 minutes and data points were collected every 0.8 seconds.

3.2 Gravimetric Measurement of Ink Filtration

Åbo Akademi Gravimetric Water Retention tester (ÅAGWR) (Kaltec Scientific, Inc., Novi, MI, USA) was used for the ink filtration experiment. This method, first described by Gros, *et al.* (2002), provides a way to characterize and understand the setting rate of a particulate ink. The filtration pressure was 103 kPa, and the filter used was an Isopore membrane filter with a pore size of 1.2 µm (Millipore, Billerica, MA, USA). Filtration times were varied between 2 min and 20 min. Figure 12 shows a schematic illustration of the setup. Ink was placed in the chamber on top of the membrane filter and multiple sheets of a porous paper, which absorb the ink oils. The reference paper was chosen because of its known small and narrow pore size, having pore sizes in the 30-nm range and 1-µm range, promoting fast absorption of ink oils. Several papers were added to have a sufficiently large absorption capacity. Offset inks have a thick and pasty consistency. Therefore, the inks needed to be diluted to be filtered. Mineral oil was chosen as a diluent, because it is a common component of offset inks and has one of the lowest viscosities among the ink components. Dilution ratio of ink to mineral oil was 50% : 50% by weight. The amount ink that was filtered was measured gravimetrically by weighing the papers before and after filtration.

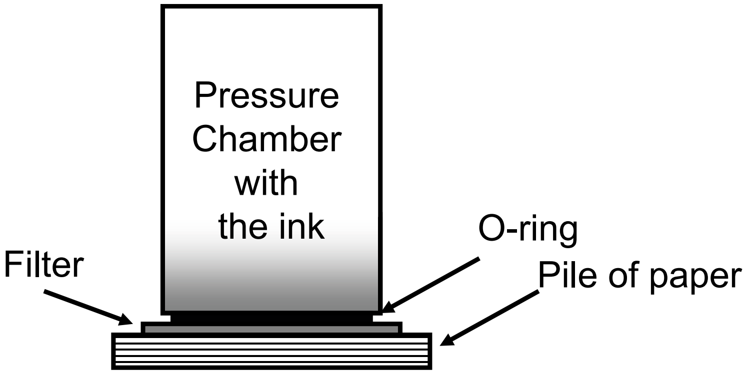


Figure 12. Illustration of the modified Åbo Akademi Gravimetric Water Retention Tester setup for the ink filtration experiment.

According to Gros, *et al.* (2002) the filtration resistance coefficient that is obtained does not depend on the dilution level.

3.3 Microscopy Methods

3.3.1 Focused Ion Beam

An FEI FIB201 gallium focused ion beam instrument was used for sectioning and high resolution imaging of printed samples. The instrument is capable of producing a gallium ion beam of between 7 nm (at 1 pA beam current) and 300 nm (at 12 nA) in diameter at 30 keV energy. A platinum organometallic gas injector allows ion beam assisted deposition of platinum over selected areas of the sample. This was used prior to the sectioning in order to protect the top surface of the sample during ion milling. For sample sectioning, a large ion current was used initially to remove a staircase-shaped trench. A finer beam of lower current was then used to 'polish' the larger vertical face of the trench by scanning the beam in a line and moving it progressively up to remove further material. The sample was then tilted to 45° and the polished face was imaged using the same ion beam, generally at a much lower beam current to achieve high resolution. The Figure 13 shows the geometry of the FIB 'trench'. The images of the samples are taken from the rear wall of this trench, viewed from above at an angle of 45°.

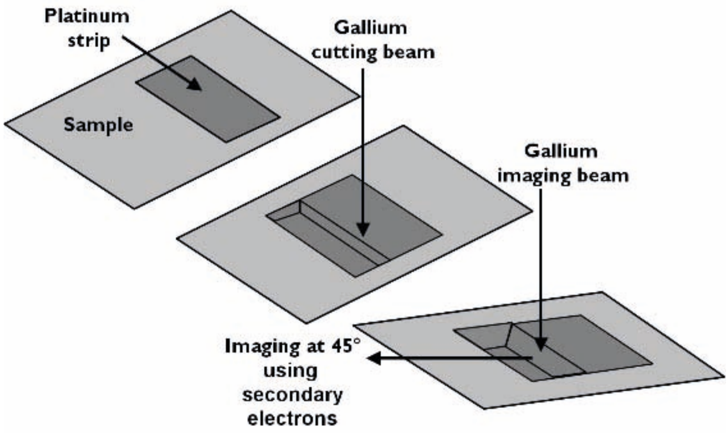


Figure 13. FIB methodology for sectioning and imaging printed paper samples.

The samples were cut and polished and then imaged without coating of the polished cut face with a platinum film. It has been found that 'organic rich' components such as the ink absorb the gallium, rendering them more conductive, so they are easily imaged in this technique. However, the coating layer does not absorb the beam to any great extent and the particles are not imaged without a conductive coating. Hence the ink layer can be seen, while the pores and the particles in the coating layer are not visible (Heard, *et al.*, 2004). The latex binder can only be seen if it forms a continuous pathway, i.e. if it is present at high enough concentrations. The latex binder would also be imaged in this case as part of the ink within the coating layer, as the filling fluid would provide the conducting pathway. The images were captured using the ion-induced secondary electrons whose energy distribution peaks at a few electron volts. If the potential of the sample rises by a few volts, then this signal is severely curtailed and the image will appear dark. For the potential of the sample to rise by a few volts as a result of a 4-10 pA ion current impinging upon it, the resistance of the sample to ground must be >1010 Ω. It appeared that this was the case for the coating material, while for the ink the resistance was less than this, and its appearance was light. After this image was collected, the cut section was coated with a layer of platinum, which allowed visualization of the particles as well as the ink layer. An example of sectioned printed paper is given in Figure 14.

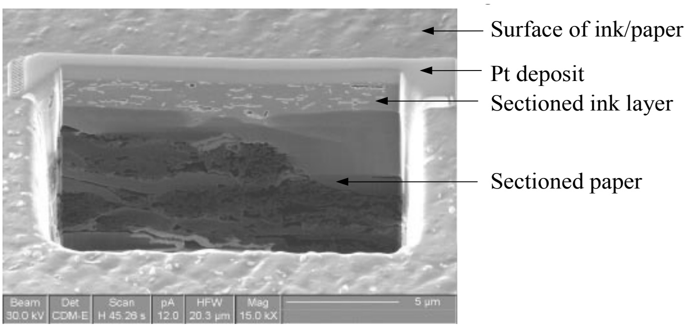


Figure 14. An example of a printed paper sectioned and imaged with focused ion beam.

3.3.2 Confocal Laser Scanning Microscopy (CLSM)

Measurements in paper V were performed on a Leica TCS SP2 confocal microscope (Leica Microsystems, Wetzlar, Germany) to obtain images and quantify surface roughness characteristics. A dry lens x20 (HC PL APO 20.0x0.70 UV (Leica Microsystems, Wetzlar, Germany)) was used for imaging. Excitation wavelength of 514 nm from an Argon laser (Power 50 mW) was used for observation by CLSM. The detected wavelengths ranged from 535 nm to 635 nm for the excitation wavelength of 514 nm (Rhodamine B). A dichronic beam splitter DD 458/514 separating the fluorescent wavelength from the excitation wavelength was used. A pinhole diameter was set to Airy 1, corresponding to 73 nm. Pixel count for each frame was set to 1024x1024. Imaging mode xyz, taking a series of images of the xy-plane at defined z-positions, was used. The corresponding physical size of the sample areas was 750 µm x 750 µm and step size in z-direction was set to 1 µm. Figure 15 shows an example 3D image obtained with CLSM with the typical dimensions for an imaged sample. The axes in xy-plane are unmodified and correspond to sizes described above. However, the z-axis in this image has been expanded by a factor of 5 in order to highlight the surface characteristics.

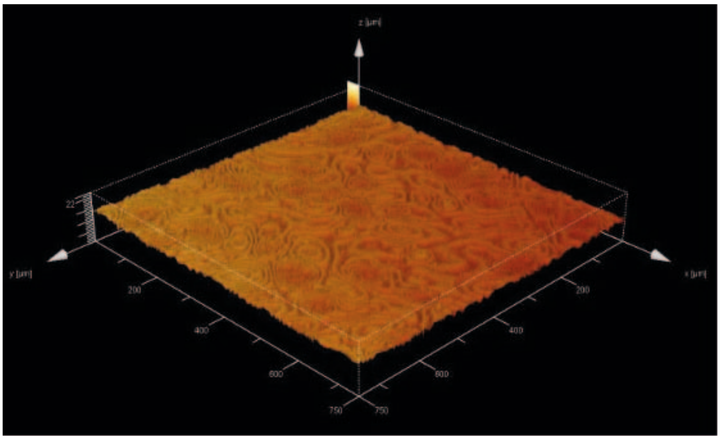


Figure 15. 3D CLSM image of printed surface with scaling for x-, y- and z- axis.

3.4 Modified Thin Layer Wicking and Thin Layer Chromatography

Modified thin layer wicking (TLW) and thin layer chromatography (TLC) were initially used to study ink oil absorption kinetics and chromatographic separation of ink oils by Rousu, *et al.* (2000b, 2002). Thin layer coating structures with constant application thickness were prepared on glass plates using a motorized laboratory drawdown coater (K control coater, R K Print-Coat Instruments Ltd., UK) with a wire application rod. Both the modified TLC in paper II and TLW of paper IV were performed as first described by Rousu (2000b, 2002).

A Fourier-transform-infrared-spectroscopy (Perkin Elmer Spectrum 1000) with diamond crystal-microscopy unit at wave numbers 550-4000 cm^{-1} was used to follow the chemical changes on modified TLC plates used in paper II. The plates were probed from bottom to top in approximately 1mm steps in order to determine how the absorptive chemistry influences the absorption path of the oils. Diamond microscopy was utilized instead of Germanium microscopy described by Rousu (2002). Otherwise the microscopy setup was similar, allowing spectra to be obtained directly from the plate surfaces without any special sample preparation. As many of the ink components had very uniform chemistries, spectra were collected from individual components on modified TLC plates and from the varnish samples, demonstrating the separation of the oils. The separation of oils is described qualitatively as percentage value (Rousu, 2000b, 2002). This value, s%, stands for the separation efficiency of the oils independently of the total absorption:

$$s\% = 100 \cdot \left(\frac{L_t - L_i}{L_t} \right) \qquad (1)$$

where s% is the separation percentage, L_t is the total absorption length and L_i is the absorption length of the component i.

For the TLW experiments (Paper VI), the determination of oil absorption kinetics was performed by visually following the proceeding translucency caused by the absorbing oils of as function of time. A scale with markings every 1 mm was drawn to the side of the coated plates to assist detection. A light source was used to assist the observation of translucency.

3.5 Model Ink Formulation

Model heatset inks were manufactured from a selection of raw materials. The model inks used here have their basis in the model inks used by Rousu, *et al.* (2000a, b and 2001). The hard resin, ester solvent and the oils were combined to make offset varnish, in which the hard resin was dissolved. The varnish components and their amounts (w-%) are described in Table I. The varnish was finally combined with the ink pigment, oils and waxes to make the final inks. These formulations are given in Table II.

Table I. Varnish recipe. The quantity of components is given in w-%.

Varnish	
Hard Resin	42
Ester solvent	6.25
Mineral oil	45.5
Linseed Oil	6.25
Dry Solids Content (%)	42
Ratio Linseed oil/ Mineral oil	0.14

Table II. Ink formulations. The quantity of components is given in w-%.

Ink Formulations	**1**	**2**	**3**	**4**	**5**
Pigment	10	15	20	15	15
Varnish	80	80	80	80	80
Mineral Oil	10	5	0	1	3.6
PE Wax (35% in Linseed Oil)				4	
PTFE Wax					1.4
Dry Solids Content (%)	43.6	48.6	53.6	50	50
Ratio Linseed oil/ Mineral oil	0.11	0.12	0.14	0.19	0.13
Ratio Resin/ Pigment	3.36	2.24	1.68	2.24	2.24

The average particle size of wax used in the formulations is 4 μm for the PTFE wax and 30 μm for the PE wax. A further 0.25 g of ester solvent (TE 9102) was added to 4.75 g of the ink, in order to make it printable (less tacky). Inks and ester were hand mixed and let stand overnight, and then printed.

Extending the work of Rousu, *et al.* (2000a, b and 2001) these model inks were primarily designed to vary in their pigment content. The use of waxes at the same pigment amount (15 w-%) was the secondary variable. Simultaneously, these formulations enabled the investigation of different oil contents. Table III shows the ink dry solids contents and the ratio between linseed oil and mineral oil for the ink formulations.

Table III. Oil ratios, resin to pigment ratios and solids contents for varnish and ink formulations.

	Varnish	**Ink Formulations**				
		1	**2**	**3**	**4**	**5**
Dry Solids Content (%)	42	43.6	48.6	53.6	50	50
Linseed oil (total, w-%)	45.5	55.5	50.5	45.5	46.5	49.1
Mineral oil (total, w-%)	6.25	6.25	6.25	6.25	8.85	6.25
Ratio Linseed oil/ Mineral oil	0.14	0.11	0.12	0.14	0.19	0.13
Ratio Resin/ Pigment	-	3.36	2.24	1.68	2.24	2.24

3.6 Analysis of Print Rub

The print rub measurements were carried out for fully dried prints. Firstly, the prints were oven dried directly after printing. The delay between printing and rub testing was about 2 weeks. This makes sure that the printed samples are not rubbing due to incomplete drying or lack of solvent removal capability.

The main method used for inducing rub in the laboratory printed samples was a modified Ink-Surface-Interaction-Tester (ISIT) test. The design adds a metal roller and a braking system to a regular ISIT. The setup and test procedure are described in detail by Gane, *et al.* (2005, 2006). An unprinted sample attached to the braking roll makes contact with the printed sample, 5, 15 or 50 times. After inducing rub, the counter paper is analyzed with a spectrophotometer for its remittance spectrum. A high remittance difference value indicates high print rub and is considered as an unwanted behavior. Examples of the ISIT induced print rub are shown in Figure 16.

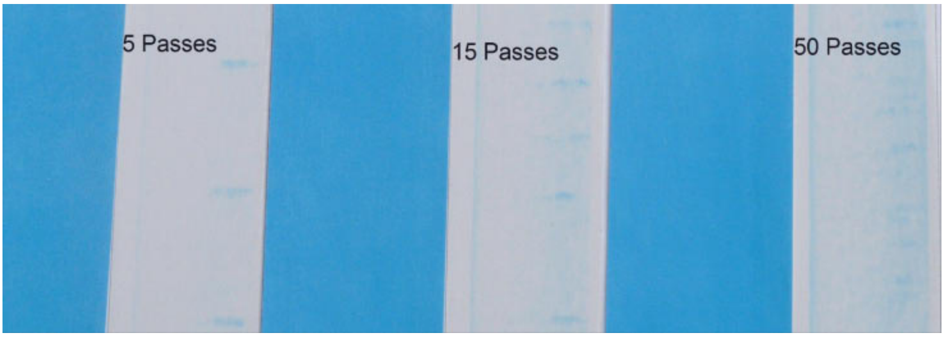


Figure 16. Example series of print rub induced with ISIT with 5, 15 and 50 passes through the nip.

The second instrument for inducing rub was the Prüfbau Quartant. A discrepancy between ISIT and Quartant is that the latter imparts also a partial circular motion during rubbing. It does lack the strain component of the ISIT rub test and does therefore characterize mainly the abrasion resistance of a printed ink layer. In this method a printed sample is rubbed against an unprinted paper in a back and forth motion for 20 times. After inducing rub marking, the counter paper and its ink traces are analyzed by spectrophotometer for their L*a*b* values and by calculating the color difference, ΔE.

3.7 Contact Angle and Droplet Absorption Tests

Contact angle measurements (Paper VII) were carried out using KSV Cam 200 (Attension/ Biolin Scientific AB, Finland). Initial stages of droplet spreading in Paper VI were studied using a high speed camera (Citius C100 Centurio, Citius Imaging Ltd., Finland). KSV Cam 200 was utilized for producing the droplets and as a source for monochromatic backlighting. Independent high intensity LED lights were used for additional lighting, mainly to enhance contrast between the substrate and the liquid droplet. This imaging setup is schematically shown in Figure 17. The LED lights were positioned in an angle of between 25-30° perpendicularly to the tablet surface, and in a slight (10-15°) forward angle in respect to the sample stand. The high speed camera was positioned on the same plane as the droplet base at a grazing angle of 3°, 11 cm from the droplet centroid. The image sequences for each droplet have 2 second duration with a frame rate of 1000 images/s. Table IV provides details of the high speed camera lens setup and imaging settings.

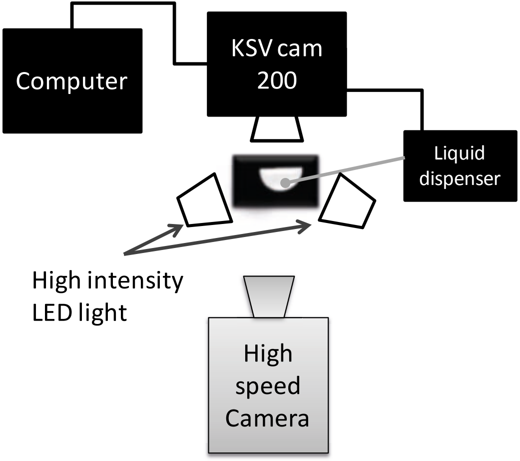


Figure 17. The setup for imaging the droplet spreading.

Table IV. High speed camera settings and lens combination for filming the liquid droplets.

C100 Centurio		Citius Imaging Ltd., Kisko		Finland
Image Resolution (pixels)	Frame rate (1/s)	Aperture	ISO setting	
832 x 620	1 000	2.8	350	
Lens Set up				
Sigma 105mm F2.8 EX DG Macro		Sigma Corporation, Kanagawa		Japan
Kenko 36mm DG extension tube for N-AF		Kenko Co., Ltd., Tokyo		Japan
5X DHG Macro Achromat 5 dptr 55mm		Marumi Optical Co., Ltd.		Japan

Image analysis was performed on the image sequences to obtain contact angles (left/right), volume, and contact diameter of a droplet as a function of time. A modified version of the ImageJ DropSnake plug-in was used in the analysis (Stalder, *et al.*, 2006).

4. Summary of Results

While multiple methods and sample sets were used in the published papers, the results section is structured following the order of events in an offset process. The results are summarized from the papers dividing them into two main sections. The first section will discuss the events in and directly after the printing nip, i.e. the filament formation and the consequent ink setting. The second section discusses the movement and location of the printing liquids after the printing and somewhat longer time scales are taken into account in this section. The final drying of the ink film, oxidation process in sheet fed or the hot air drying of heatset, are excluded from the scope of this work.

4.1 Filament Formation and Ink Setting

4.1.1 Pigment Coating Structure's Role in Ink Setting

Filament formation and ink setting were studied using three different equipment for the dynamic gloss measurements. In this first part the main variables of the study were the coating structure and the optical appearance. Four coated papers with varying ink setting speeds and glosses were prepared; SM (slow setting, matte), SG (slow setting, glossy), FM (fast setting, matte) and FG (fast setting, glossy). A more detailed description of the properties of these papers can be found in Paper II. Measurements were made with each paper using 0.3 cm^3 ink amount. It is assumed that the transferred ink amount from a printing disc to paper is equal in all printing as the paper-ink combinations are the same, but some differences in transfer cannot be ruled out. For the Reflectometer, the first 10-15 seconds are not reported since this time period was consumed to transfer the samples from laboratory printer to the gloss measurement instrument.

All the dynamic gloss measurement devices detected well the changes of the coating pore structure on the ink setting speed, but especially the Dynamic Gloss Meter works well to distinguish them. All the print glosses of slow setting coatings rise to higher values than the print glosses of corresponding fast setting coatings. The Dynamic Gloss Meter shows that ink on a slow setting matte coating can reach even a slightly higher printed gloss than on a fast setting glossy coating. If the ink sets quickly, it is possible that the filaments do not have time to level out and some ink surface roughness remains and the final gloss is slightly lower. This result agrees with the findings of Desjumaux, *et al.* (1988), Donigian, *et al.* (2004) and Xiang, *et al*. (1998).

The contribution of pigment coating surface roughness to print gloss is also indicated by the results. The matte coatings have lower printed gloss than the corresponding glossy coatings.

For matte papers, the coating layer surface roughness can start protruding through the ink film as the ink sets and leads to reduction of the gloss value. Evidence of such behavior is found in Dynamic Gloss Meter results in Figure 18.

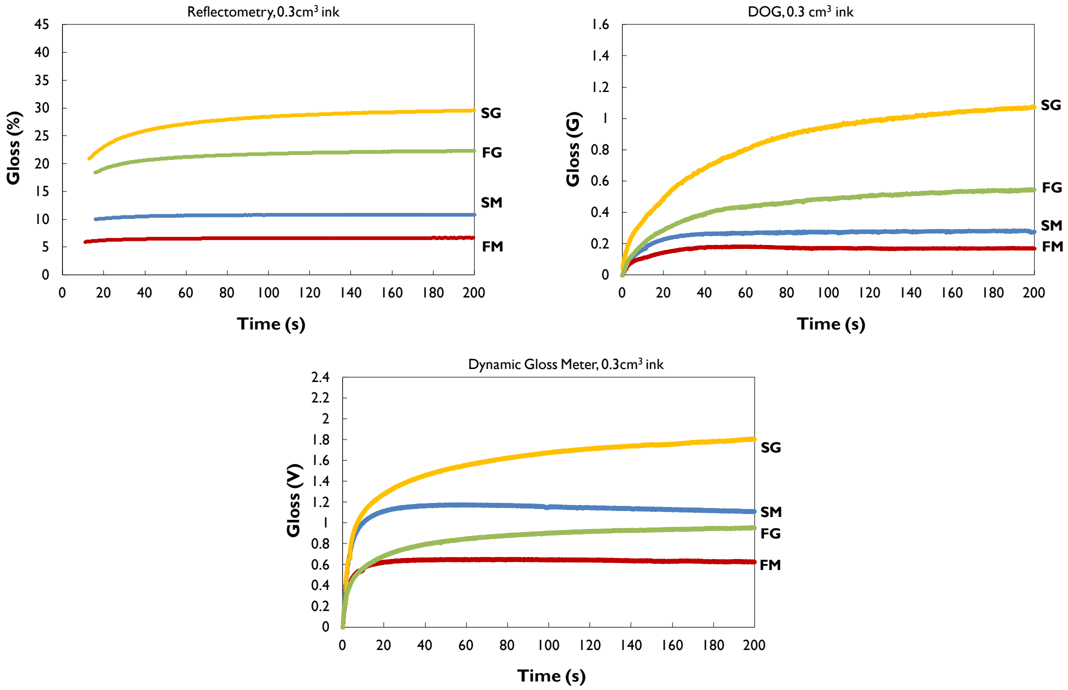


Figure 18. Comparison of dynamic gloss results obtained with the Reflectometer, DOG and Dynamic Gloss Meter. SG refers to slowly absorbing, gloss finished coating, SM to slowly absorbing, matte coating, FG to fast absorbing, glossy coating and FM to fast absorbing, matte coating.

Zang and Aspler (1995) have previously reported that based on the ink transfer parameters, printing smoothness (or roughness), induces differences mainly with low levels of ink, in which case the coating gloss largely determines the printed gloss. Jeon and Bousfield (2004) also reported on the strong influence of surface roughness on print gloss directly (within 2 seconds) after printing. In addition, Preston, *et al.* (1999) have reported on the ability of low levels of ink to cover the coating layers surface roughness, but pointed out that the inks leveling characteristics and other ink characteristics play a role as well.

One notable feature in Figure 18 is that the relative difference between gloss values of SG and FG papers for DOG was larger than that for the other two instruments. This is probably related to the measurement angles of the methods. Because the dynamic gloss meter and Reflectometer use a high angle (75º) and DOG uses a low angle (6.4º), the latter has more sensitivity at high gloss values. This sensitivity is based on the model of specular reflection (Silvennoinen, Peiponen and Myller, 2008).

4.1.2 Ink's Contribution to Ink Setting

Another use of gloss dynamics measurements is to study ink's contribution to setting. As previous research has shown, the ink properties and leveling characteristics influence the setting (Glatter and Bousfield, 1997; Desjumaux, *et al.*, 1998; Preston, *et al.*, 1999; Ercan and Bousfield, 2000). Prints were made by printing commercial inks (Premoterm 2000 and Premoterm 6000, Flint Ink, 0.3 cm^3 ink on distribution rolls, ca 2 g/m^2 ink layer) on the slowly absorbing, matte coated paper (used also in Papers II and V). Ink setting was followed by measuring the dynamic print gloss with DOG. Figure 19 shows the resulting comparison of the inks setting behavior. The thicker inks (TB and TC) obtain higher gloss and the lower viscosity inks (LVC and LWB) have very low gloss. When compared to Figure 18, in Section 4.1.1, the general gloss levels are lower, due to the rough matte surface of this paper. The results indicate that the gloss of the cyan inks is higher than that of the black inks. However, this should not be interpreted as a result of pigment color influencing the gloss. The varnish fully surrounds the pigment particles in the ink (Leach and Pierce, 2004). Therefore, the difference between cyan and black ink is more likely due to different varnishes in the respective inks.

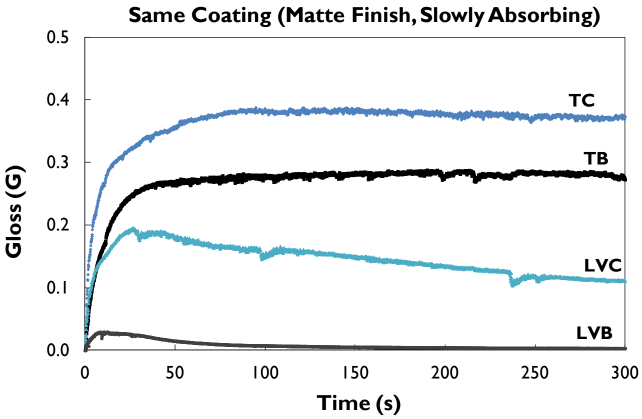
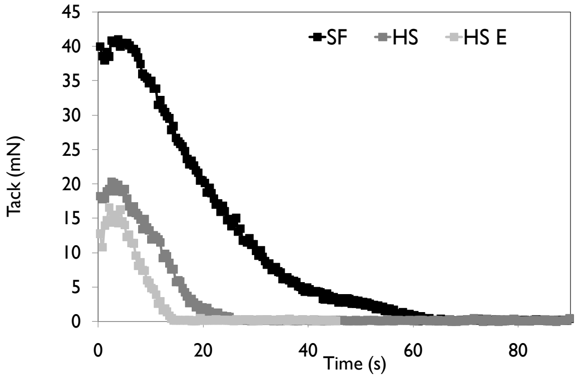


Figure 19. Setting comparison of four heatset inks on coated paper, measured with DOG. Abbreviations in the figure stand for the inks: TC is thicker, cyan ink; TB the thicker, black ink; LVC the lower viscosity, cyan ink and LVB the lower viscosity, black ink.

Both of the lower viscosity inks (LVC and LVB) show a quick initial increase in gloss, followed by a decrease of the gloss, a behavior similar to that seen in the Dynamic Gloss Meter results in Figure 18, in Section 4.1.1. The combination of LVB ink and matte coating is detrimental for print gloss. In this case, the gloss decrease is not necessarily related to the immobilization of the filaments, as the coating structure allows a relatively long ink setting time. The combination of thin layer of low viscosity ink and rough matte surface create conditions in which there is not enough fluid to fill up the surface roughness. Glatter and Bousfield (1997) suggest that in such conditions also the filament leveling rate may slow down, causing further lowering of print gloss.

However, using just viscosity to describe consistency is not sufficient when ink setting behavior is compared, as shown in Paper III. Lyne (1990) and Ercan and Bousfield (2000) have showed earlier that especially the elongational viscosity plays a role. Other ink parameters, such as the ink pigment and varnish distribution within the ink may additionally contribute to setting. The shear rate in the ink during ink setting is much lower than the high shear rate during ink transfer in the printing nip. At this lower shear rate the viscosity differences are small between the inks as shown in the table in Figure 20.



	Viscosity at 100 1/s (Pa*s)	K_f (m^2)
SF (50-50)	1.11	3E-20
HS (50-50)	0.22	5E-20
HSE (50-50)	0.2	5E-20
Oil	0.06	10

Figure 20. Tack decay curves for the inks SF (sheet fed), HS (heatset) and HSE (heatset, emulsified) with the data on ink viscosity and ink permeability constant K_f obtained from filtration experiments and calculations.

The heatset ink had a higher viscosity than the sheet fed ink. The emulsified ink set faster by a factor of about six compared to the sheet fed ink. If the setting rate of the sheet fed ink was only a function of viscosity, the setting rate should be about the same for all three inks. The time for the tack to decay between the sheet fed and heatset inks is around a factor of two or three. Permeability constant from filtration equation had a similar factor of difference as the time to reach minimum tack. Therefore, because of this factor, it would be expected that the sheet fed ink would set slower than the heatset ink.

The magnitude of the tack values ranked with the ink viscosity, but was not proportional to viscosity. Other factors, such as cavitation points within the emulsified ink must influence these results. Higher amount of mineral oil in heatset formulation than in sheet fed ink or addition of fountain solution (emulsified ink), seemed to decrease the internal cohesion of the ink layer. The setting rates, as determined by the time for the tack to fall, did not scale with low shear rate viscosity as expected. Instead, the filter cake permeability was found to predict a first order relationship between these inks.

4.1.3 Printing Parameters Influence on Filament Formation

The coating layer and ink contributions to ink setting were described in sections 4.1.1. and 4.1.2. The technical instruments used to measure print gloss dynamics and ink setting may also generate conditions that should be taken into account. The key technical differences between the three methods used in Paper II are compared in Table V. DOG has the advantages of not requiring the sample to be flat and that some vertical movement of the sample is allowed due to its low measuring angle (Myller, 2004; Myller, *et al.*, 2006). There are some technical differences between the instruments in the measurement units, in mapping and online capabilities. However, the influence of these differences for the results was found not to be significant and the most influential differences were the printing conditions.

TableV. Technical differences between the dynamic gloss measurement equipment. (Paper III).

	Meas. Angle (°)	Beam Shape	Meas. Unit	Printing Geometry	Online	Mapping of Static
Dynamic Gloss Meter	75	Elliptic	Volts *(V)*	flat/roll	Yes	No
Reflectometer	75	Elliptic	Percentage *(%)*	roll/roll	No	Yes
DOG	6.4	Circular	Gloss *(G)*	roll/roll	Yes	Yes

The ink amount used in printing is one of the parameters that plays a role in the development of print gloss and the filament formation. The influence of ink layer thickness on the size of the filaments was studied using CLSM in Paper I. It was shown that imaging of filament remains on a non absorbing plastic film was feasible and results in information about the variations in filament sizes caused by the printing parameters. As Figure 21 shows the increase of ink film thickness from 2 to 4 g/m^2 increases the size of filament remains. The filaments formed at 2 g/m^2 ink loading were smaller and more numerous compared to the 4 g/m^2 image. Leveling of larger filament remains will take a longer time. This will be reflected in the filament setting behavior and will contribute to decrease the print gloss. Preston, *et al.* (2003) and Kawashima and Bousfield (2007) show that on coated paper surfaces larger ink amounts produce lower gloss at fast print speeds. Ström, *et al.* (2007) also agree that roughness induced by the filaments depends on the ink film thickness.

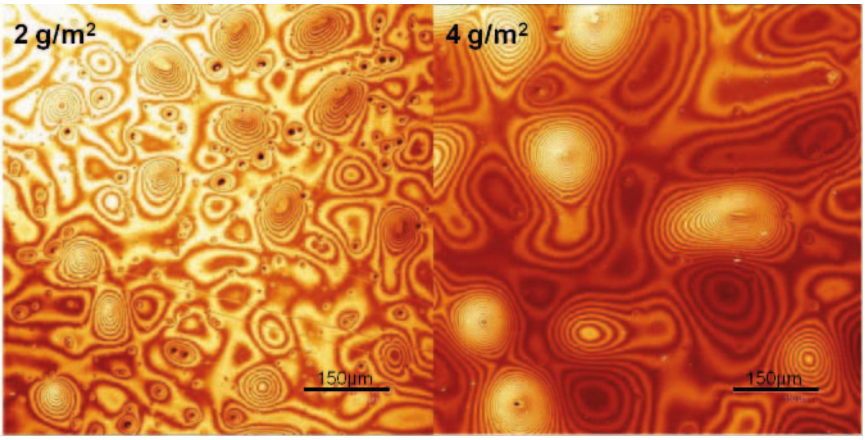


Figure 21. Effect of increased ink amount on filament remain size imaged with CLSM.

When the dynamic gloss instrumentation was compared in Paper II, results also revealed differences originating from the printing equipment. Printing geometry is mentioned as a variable in Table V. Results from DOG and Dynamic Gloss Meter are compared in Figure 22 as examples showing the influence of the nip geometry to the dynamic gloss results. DOG measurements used a roll-to-roll configuration and Dynamic Gloss Meter results were obtained on a roll-to-flat setup. The width of the printing disc was also a parameter that varied from some 2 cm up to 5 cm. At higher ink loadings, the gloss values decrease and relative ranking of the papers changed for DOG (and Reflectometer) from those presented in section 4.1.1. The relative difference between the coated papers marked FG (fast setting glossy) and SM (slow setting matte), becomes much smaller, when printed on a roll-to-roll configuration. However, another printing variable that changed in the dynamic gloss measurements was the printing disc surface texture. The printing in Dynamic Gloss Meter measurements was a smooth metal disc, while the other two methods used a rubber covered printing discs. The relative importance of these printing parameters in respect to each other was not studied further at this point of study. The results in Figure 22 imply though that these parameters can change the ink splitting patterns in the printing nip and therefore impact the ink filamentation and ink setting behavior.

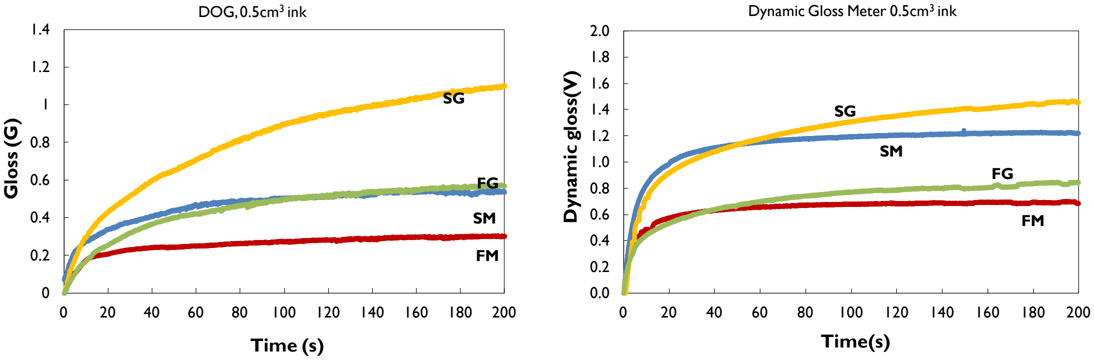


Figure 22. Variation in ranking of the dynamic gloss results likely to be caused by the nip geometry. DOG results are printed with a roll-to-roll configuration and Dynamic Gloss Meter uses roll-to-flat configuration.

The influence of printing disc surface texture on the filament formation was studied in more detail in the CLSM study in Paper I, both the experimentally and through computer modeling. Figure 23 shows an environmental scanning electron microscope (ESEM) image of the printing blanket used to print some of the samples in Paper I.

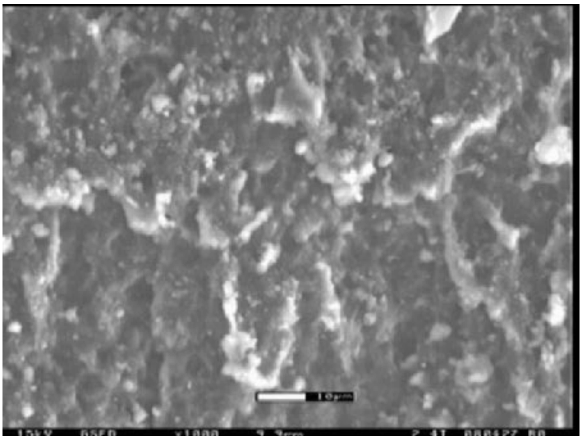


Figure 23. ESEM image of a printing blanket shows the surface porosity and unevenness. The white scale bar in the image is 10 μm (Paper I).

Using a blanket with surface texture instead of a smooth metal roll did increase the filament diameter slightly. The trend agrees with the work of Kawashima and Bousfield (2009a) even though the differences noted here were somewhat smaller.

The computer modeling showed that the surface roughness creates fine scale pressure variations. The wavelength of the texture had an optimum at 0.1 mm while the magnitude of the texture roughness was found to be the most important parameter. The pressure variation created by surface texture variations could lead, near the nip exit, to local high and low pressure regions, and may help organize cavitation. The results imply that the surface roughness can potentially generate a specific length scale for filaments.

The influence of printing speed was studied both experimentally and through computer modeling using a constant surface texture. An increase in printing speed decreased the print gloss at short times. The hypothesis put forward in the past work (Ercan, 1998) was that the increased printing speed increased the filament remain sizes. The confocal images in Figure 24 support this hypothesis. The mechanism that relates printing speed to filament size is still somewhat unclear. The top of filaments look flat with high speeds and were notably larger than with slow speeds. It is suggested here that with high speeds the filaments did not have time to elongate as much and hence the remaining filaments were thicker at the breaking point. This would cohere with the findings of Lyne (1990) and Ercan and Bousfield (2000) pointing out the role of elongational viscosity in offset ink applications.

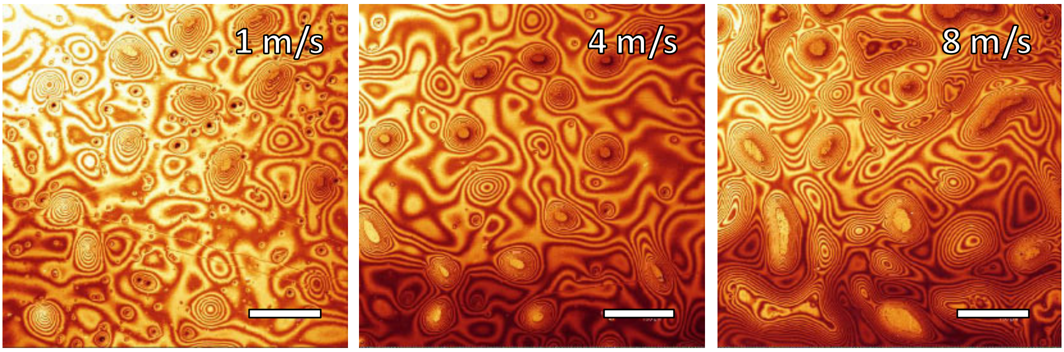


Figure 24. Influence of increased speed on filament shape. The white scale bar at the bottom is 150 μm.

The modeling results in Figure 25 indicate a sharper pressure pulse with increased speed at constant surface texture which would create smaller filament sizes. Interestingly, the influence of surface texture seems to fade at slower speeds.

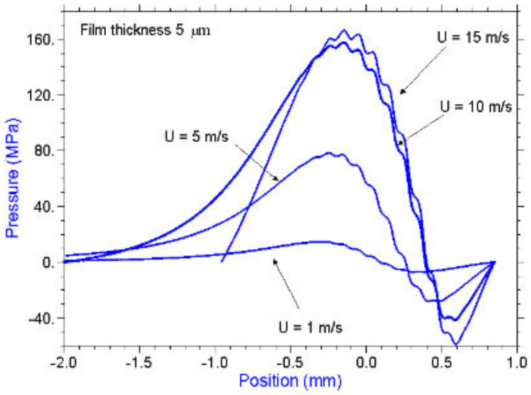


Figure 25. Modeling the pressure pulse in the printing nip at various speeds using a constant surface texture amplitude of 1 μm and wavelength of 0.1 mm. Higher speeds lead to a more rapid pressure rise and release.

This indicates that the influence of surface texture dominates over speed. This could be the explanation why the filament remain size increased instead of decreasing in the experiments at the highest speed. The smooth surface, which has no texture, dominates over the high speed.

These findings highlight the complexity of nip phenomena. In actual process several different variables act at the same time and their relative importance may differ depending on the predominant conditions.

4.1.4 Fountain Solution Contribution to Filament Formation

The fountain solution contribution to filament formation and filament size distribution was studied in Paper I. Fountain solution addition slightly decreased filament sizes, as can be observed from Table VI. However, this effect on the filament remain diameter can be considered minor. There was no marked difference between the filament sizes for alcohol free and alcohol containing fountain solutions observed in these laboratory scale tests. This could be partially explained by generally acknowledged difficulties in maintaining stable ink-water emulsions in laboratory conditions.

Table VI. Filament sizes obtained from image analysis.

			Filament remain diameter					
Ink-Fountain Solution Combinations	Ink Amount (g/m^2)	Printing Speed (m/s)	Average (µm)	Median (µm)	Min. (µm)	Max. (µm)	St.dev. (µm)	Nr of Droplets
Pure Ink	2	1	8.71	7.96	5.01	15.00	2.89	21
Ink with Alcohol Fount	2	1	5.85	5.60	3.13	10.83	2.01	31
Ink with Alcohol-free Fount	2	1	6.23	5.63	3.76	12.37	1.98	25
Ink with Alcohol Fount	4	1	7.15	7.29	3.44	12.50	2.37	21
Ink with Alcohol-free Fount	4	1	6.18	6.19	2.50	12.50	2.33	19

Even though the fountain solution did not have a significant impact on the filament remain sizes in this specific study, it does influence the ink-coating interactions in the printing nip. The location of the fountain solution may be determined by the film splitting phenomena: drops were stretched inside filaments at the nip exit and broke into finer drops. The location of the fountain droplets in the analyzed images were such that almost every filament had a trace of fountain solution either directly attached to the filament remains or very close to them. This indicated that the weaker cohesion of water/air during ink film splitting played a role in formation of filaments. These weaker spots were then more likely to act as initial points for cavitation and could play a part in determining the filament sizes.

4.1.5 New Possibilities in Filament Detection

When considering means to observe filaments as they level, it has been found during this study that the DOG may have potential to be used for such application. The beam diameter in the dynamic gloss measurements in Paper II was selected to be in millimeter scale as a larger spot averages out the signal from a given region. Smaller spot sizes introduce more noise and the standard deviations between samples can be large. This does suggest that there is more information available in the test method than is used currently. The noise from the use of a small beam could be connected to local differences in the filament patterns and their leveling. The relative location and amount of ink filaments changes from sample to sample. Then, as the beam size is decreased fewer filaments are detected by the equipment and the size and leveling characteristics of these few filaments will be reflected in the results. A modified DOG instrument has a possibility to vary the spot size from 5 mm to 50 µm. Based on the filament remain sizes reported in Paper I, the small beam size (around 50 µm to 100 µm) is therefore in the right length scale to detect a single filament or a small group of filaments while they level out.

The results in Figure 26 show that the small beam size measurement captured more variation as expected. The individual measurements show both rapid and slow changes in the gloss values. It is suggested based on the results in sections 4.1.3. and 4.1.4. that the local variation at this smallest beam size (50 µm) is (a group of) individual filaments leveling out under the detection beam.

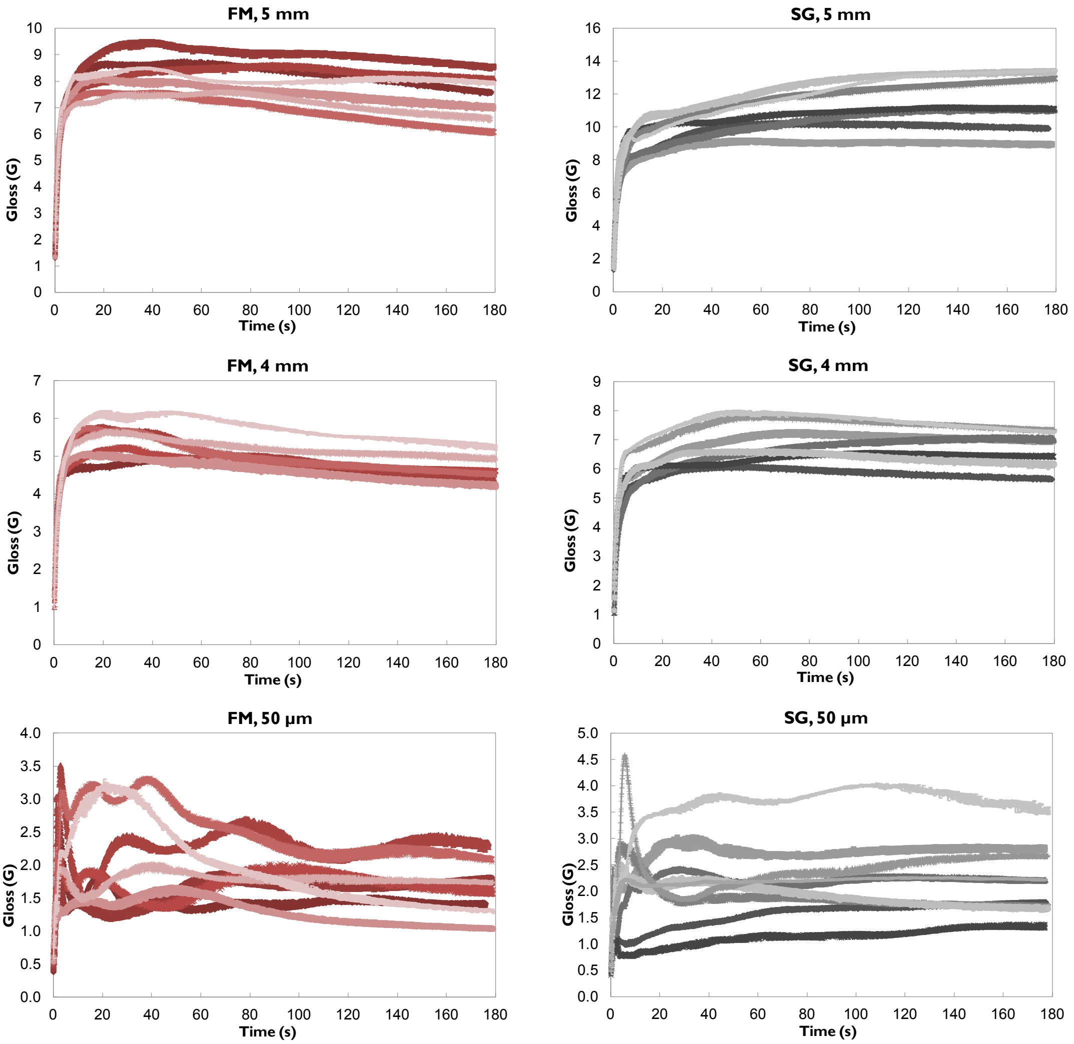


Figure 26. Various curve shapes were obtained for individual samples when measuring dynamic gloss the smallest beam size on FM and SG papers. The curve shapes are suggested to be related to leveling of ink filaments.

4.2 *Ink Component Distribution into the Pigment Coating Structures*

4.2.1 Ink Pigment and Varnish

Ink pigment and varnish are components that should stay on the surface of the coated paper. Pigment is needed to produce the colour with as little as possible penetration into the coating and varnish is largely responsible for the print gloss and binding of the pigment onto the surface of the coating layer (Leach and Pierce, 2004). The FIB may be a useful imaging tool for visualisation of penetration differences in practical problem cases with ink varnishes or pigments. The FIB imaging of the ink components (Paper IV) showed that the model ink mixture including varnish and pigment components did stay on top of the coating and only slight penetration was observed in Figure 27. Hattula and Oittinen, (1982) and Ström (2000) also reported on ink component penetration and their work agrees with the result of this visualisation. However, the penetration was significantly less than what was anticipated for the samples in this study. This is probably due to the fact that the model ink varnish only contained ~ 12% of the ester solvent and linseed oil, the larger proportion ~ 45% of the varnish was mineral oil which could not be seen in the images. A more detailed explanation on the reasons will be given in section 4.2.2.

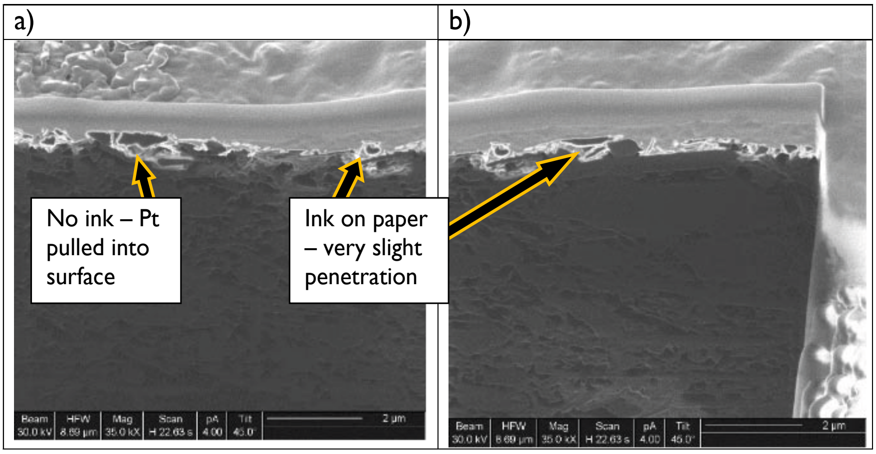


Figure 27. FIB images show only very minor penetration of the whole ink (including pigment) into the porous coating structure.

Marttila, *et al.* (2004) showed that as well as substrate properties, the ink formulation and especially the ink pigmentation level are key variables in offset printing. Therefore, it was of interest to study the effect of ink pigmentation level also in connection with the print rub. The results from Paper V with the model inks indicate that increased pigmentation level generated more rub on fast setting coating, Figure 28. This could be seen by comparing remittance spectra from formulations F1, F2 and F3 having pigment ratios of 10, 15 and 20 w-% respectively.

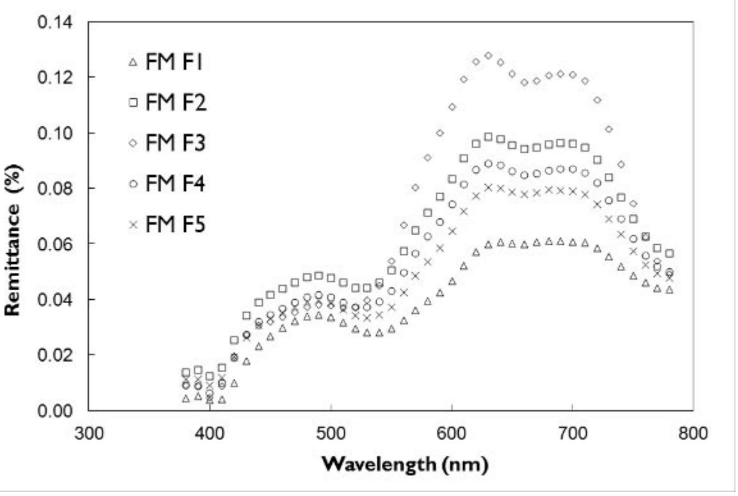


Figure 28. Remittance difference spectra of print rub model inks (formulations F1-F5) on fast setting matte paper.

When ink formulations were compared at same pigment ratio (15 w-%), with respect to the addition of wax (F2, F4 and F5), the results showed that the wax addition reduced the print rub problem. On the fast setting coating both the polyethylene (PE) and polytetrafluoroethylene (PTFE) wax decreased the degree of print rub. This agrees with the general understanding on ink formulation, as waxes are used to add slip and to improve the abrasion/rub resistance of inks (Cordery, 1990; Kipphan, 2001). It needs to be noted though, that neither one of these waxes had as low print rub as the ink with 10 w-% pigment. This ink had the lowest total solids content. This shows that an ink formulation can be to some degree modified with addition of waxes to be more resilient against print rub, but the total solids content of the ink plays a more decisive role.

4.2.2 Oil Components of Printing Inks

It is well known that the oil components in the printing ink will enter the porous structure of the coating layer. It has been shown that chromatographic separation of oil components takes place during the process (Rousu, 2000b). In the heatset offset printing about 80-90% of the ink oil, typically mainly low boiling point mineral oil, will evaporate away from the coating structure and the remaining part will stay in the structure even after drying (Leach and Pierce, 2004). When printed on a coated paper and imaged with FIB (Paper IV), the ink oils are not visible on the surface of the coating layers. They have been removed from this surface layer into the coating by absorption. The mineral oil is sufficiently volatile, so that it can evaporate from the paper over time. Placing the sample in the vacuum chamber of the FIB instrument for imaging would have further helped the removal of the mineral oil, therefore preventing imaging of the mineral oil with FIB. The volatility of mineral oil under vacuum conditions was also confirmed by FTIR measurements (Paper IV). The evaporation of mineral oil further explains why the varnish penetration shown in section 4.2.1. was less than expected.

Linseed oil is a drying oil, which does not evaporate but rather absorbs into the coating structure. Linseed oil could be detected from the cross-sectional FIB image of the coating. Figure 29 shows a high magnification image where the coating pigments (the dark areas) are surrounded by the absorbed linseed oil indicated in the image (the bright areas). The use of platinum coating to improve the visibility of the coating particles decreased the contrast between the coating pigments and linseed oil. Therefore, if the interest is to locate the path of the linseed oil into the coating structure, the platinum coating of the sample is not recommended.

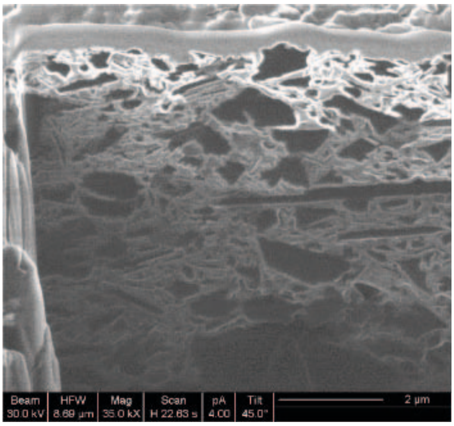


Figure 29. High magnification image of linseed oil in the coating pore structure.

The model ink formulations of Paper V behaved somewhat differently on slow setting coating, Figure 30, compared to the fast setting coatings shown earlier in section 4.2.1., Figure 28. The high total solids content was again creating more print rub. In addition to that, on the slow setting coating there was indication that the linseed oil to mineral oil ratio also played an important role. Formulations with high solids and higher amounts of linseed oil (F4, F2, F3) did not perform well on slow coatings in respect to print rub. F4 is the ink formulation which has most linseed oil, as the PE wax added to the ink formulation is itself dispersed in linseed oil. Low viscosity ink formulation F1 and ink formulation F5, which included PTFE wax and more mineral oil than formulation F4, performed best in print rub tests.

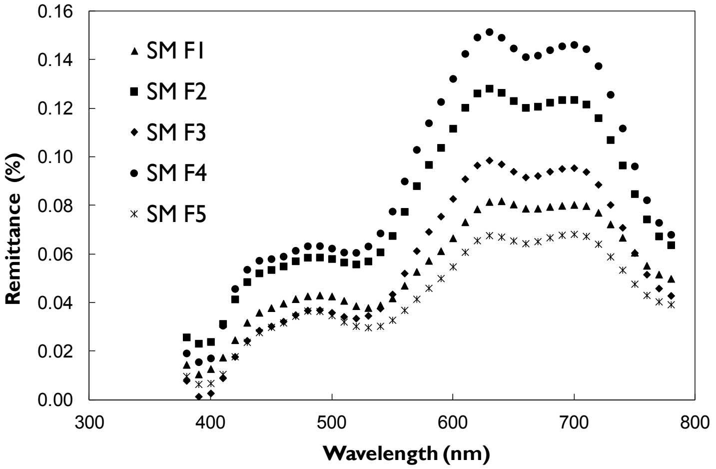


Figure 30. Print rub remittance difference spectra. The model inks (formulations indicated by F1-F5) were printed on and rubbed against a slow setting coating.

The need for sufficient chromatographic surface and capillarity to draw the linseed out of the ink, as suggested earlier by Rousu, *et al.* (2000a, 2000b and 2001), was evident from these results. The ink-paper combination of linseed oil containing ink on slow setting paper points this out, as coating pigment surface area exposed to the oils is reduced.

The work with the oil components was continued in Paper IV which studied the ink oil interactions with tablet samples wet-pressed from pigment having distinctive pore structures. The pigment tablets consisted of calcium carbonates (OMYA AG.; Hydrocarb ME): one of them had coarse particles and a broad particle size distribution (BCGCC), and a second one had coarse particles with a narrow particle size distribution (NCGCC). The weight fraction of particles <2 μm was 60% for the BCGCC and for the NCGCC 65% of particles were <1 μm. The third pigment was a modified calcium carbonate (MCC) creating a bimodal pore structure for rapid liquid uptake (Ridgway and Gane 2004; Ridgway, *et al.*, 2006a). Table VII shows the key structural parameters for the porous tablets used: total porosity, surface area and their relative capillarity indicated by the pore diameters.

Table VII. Porosity and permeability of the tablet structures (Paper VI).

Pigment tablet	Accessible porosity (%)	Total pore surface area (m²/g)	Pore diameter (µm)	*k* * (m²)
BCGCC	25.7	4.1	0.2054	$1.00 \cdot 10^{-18}$
NCGCC	27.4	6.2	0.1223	$5.77 \cdot 10^{-18}$
MCC	52.2	45.5	0.4097 and 0.0154	$1.45 \cdot 10^{-17}$

*Darcy permeability constant

It was found that the surface spreading of printing liquids on these tablets was dominant over absorption at short times. The contact angle droplet volume loss into the tablet structures was less than 5% at 2 s. Complete absorption occurred at much longer times than the observation time of the high-speed video measurements.

Contact angle measurements were performed by placing a droplet of each of two test liquids separately on top of the mineral pigment tablets, which were saturated with the third complementary liquid. Figure 31 shows example images taken at 0.5 s time for the combinations. A differentiation between the pigment structures was not possible to observe from the results. This leads to a conclusion that the main form of interaction is liquid-liquid interaction between the saturation liquid and the droplet liquid. The images also illustrate a phenomenon in offset printing: the faster spreading of the oils compared to the water.

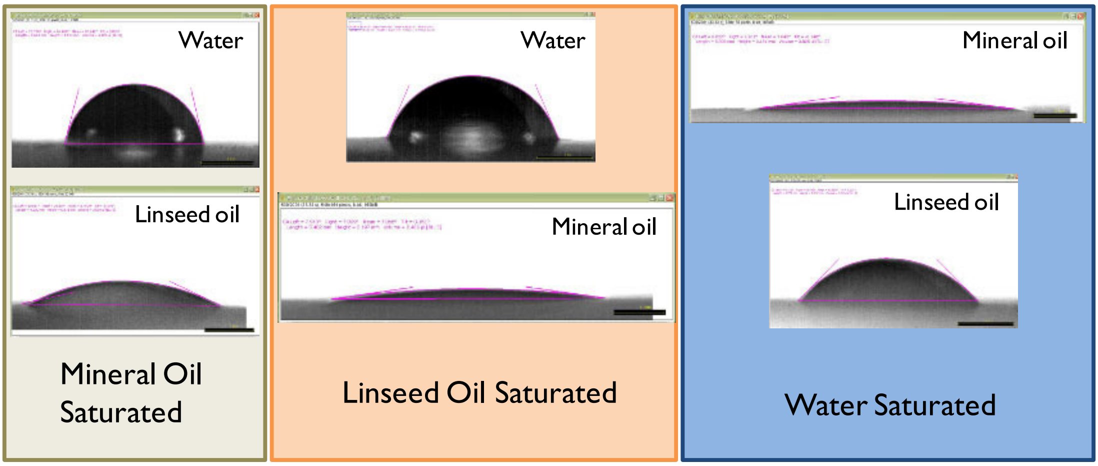


Figure 31. Snapshots at 0.5 s from the high speed videos (Paper VI). Printing liquids: linseed oil, mineral oil and water were imaged spreading on BCGCC tablet structures, saturated with a liquid complementary to the two measurement liquids.

Results of the thin layer wicking (TLW) experiments in Figure 32 were used to extend the analysis to thin coating structures. Only the oils were chosen as liquid in these experiments as testing with water suffer uncertainties due to evaporation at these long experiment times. The mineral oil absorbs furthest in all pigment layers. In thin structures the long timescale mineral oil absorption rate correlates, as expected, with the pore diameter and relative permeability of the structures. The linseed oil absorption, however, is retarded with respect to the mineral oil which agrees with findings of Rousu, *et al.* (2009a,b). In agreement also with another aspect of the findings by Rousu, *et al.* (2009a,b), the linseed oil absorption is promoted by an increased amount of small pores and increased pigment pore wall surface area. The polar compatibility between the pigment and linseed oil contributes to also to an adsorption-driven process in this case (Rousu, *et al.*, 2003).

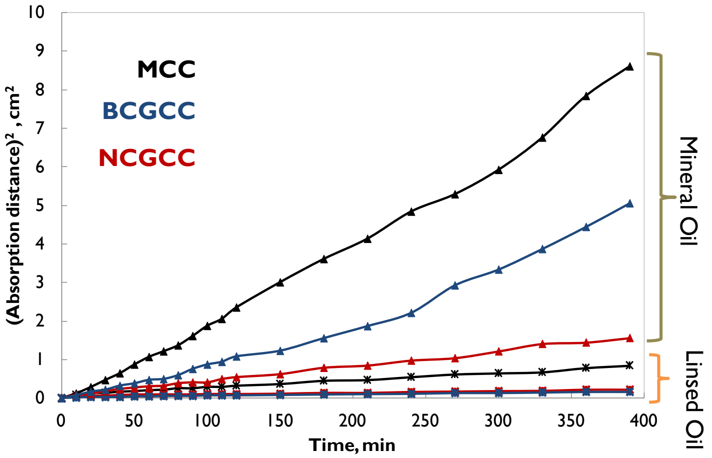


Figure 32. Absorption distances of mineral oil (MO, triangles) and linseed oil (LO, stars) into the thin coating structures on glass in TLW tests. MCC is indicated by black color, BCGCC by blue and NCGCC by red.

This result highlights again the contribution of viscosity to surface tension ratio for the absorption of printing liquids into pigment structures and the adsorption potential of the slightly polar linseed oil (Rousu, *et al.* 2000a, 2000b and 2001). The linseed oil absorption is promoted by increased amount of small pores and increased pigment wall surface area. The polar compatibility between the pigment and linseed oil contributes to this adsorption process as stated by Rousu, *et al.* (2003).

Based on the pore structure analysis and both the short and long term absorption results in Paper IV, it is suggested that at long times the relationship between pore size, permeability and surface area become important, especially for the linseed oil. Figure 33 shows that linseed oil differentiates the pore structures between the monomodal pore size distributions of the GCCs and the discretely bimodal MCC (Ridgway, *et al.* 2006b). Linseed has, at first sight, an unexpected gradient difference between the GCCs and the MCC in respect to the absorption response as a function of permeability, effectively eliminating the transition effect to reduced absorptivity seen for the GCCs as permeability increases, even in the case of NCGCC despite its also high permeability value. Linseed oil, thus, deconvolutes the effects of fine pores and large pores differently than water and mineral oil. If the MCC would only have the large pores, i.e. only consist of a highly permeable structure, the absorption rate of linseed oil too would be expected to decrease despite the increased permeability, since a structure with only large pores would lack the capillarity required for driving absorption. However, since the surface of the MCC particles has the in-built nanopores providing high capillarity and enhanced particle surface wetting, the MCC is following a continuous response in the permeability-rate trend, rather than the discontinuous one for the GCCs. The observed differences in absorption times between the liquids support the mechanism of chromatographic separation of ink oils suggested by Rousu, *et al.* (2000a, b, 2001). They observe that chromatographic separation of oils leads the ink oil mixture, mineral oil and linseed oil, to separate during absorption into the polar pigment structure so that the more polar linseed oil is retarded, while the apolar mineral oil absorbs faster. The degree of separation was found to be directly proportional to the pigment surface area.

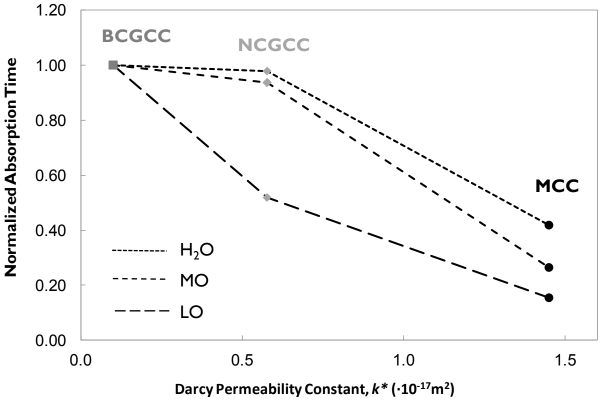


Figure 33. Absorption times of the liquids on pigment structures BCGCC, NCGCC and MCC normalized against the absorption times on BCGCC structure. The graph highlights the unique behavior of linseed oil on tablet structures when compared with the other liquids.

The results suggest that the linseed oil meniscus moves in the pores by adsorbing onto the pore walls. The slight polar component of the linseed oil is attracted to the polar surface of the pigment. The effective pore size of the GCCs is thus progressively decreased due to linseed adsorption onto the pore walls, which is unfavorable for rapid absorption if there is not sufficient permeability and surface area. When the area available for adsorption is increased, as in the case of the MCC pigment, in a part of the structure unassociated with the permeability, the high surface area aids the adsorption and the apparent permeation pore radius remains roughly constant through the absorption process. A low surface area pigment therefore results in decrease of the absorption rate, while for such a low surface area pigment structure there is an even greater saturation of surface area onto which the oil can adsorbs, and the connectivity-critical pores become blocked as the permeability is reduced due to the adsorbed layer. A high surface area coupled with high permeability allows free passage of such polar oil, without hindrance, as is shown schematically in Figure 34.

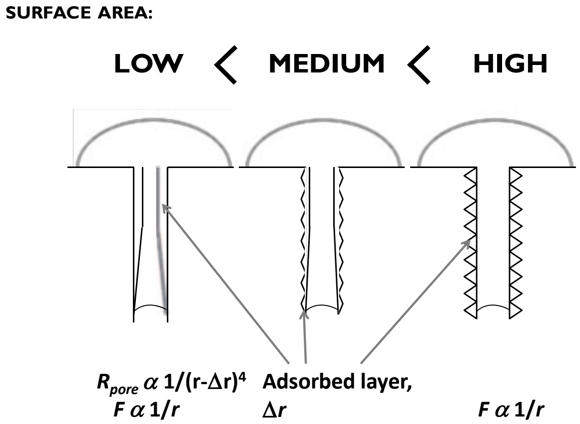


Figure 34. A schematic illustration of adsorption of linseed oil to the internal surface area of a pore when the pore has low, medium or high surface area.

A coating having only disconnected large pore sizes, but inadequate surface area and permeability, would in offset printing most likely suffer from problems arising from incomplete absorption/drying of the ink layer, such as manifested in print rub on matt or highly monosized porous structures (Gane, *et al.*, 2006).

4.2.3 Additives of Ink Formulations

Ink formulations use various additives to fine tune the ink properties. The key additives used in the model ink formulations (Papers IV and V) were the PE and PTFE waxes, and an ester solvent. The ester solvent is used in order to make the ink less tacky. As pointed out in sections 4.2.1 and 4.2.2. the main effects following from addition of waxes into the ink formulation was that they increased the total solids content of the ink and can change the linseed oil to mineral oil ratio. These parameters are tabulated in Table VIII. Some improvement in print rub resistance could be obtained by wax addition, but the increase of total solids and/or linseed oil to mineral oil ratio are more important. It was shown that the extent of print rub occurrence due to total solids content or oil ratio depends also on the relative ink setting speed of the coating.

Table VIII. Dry solid contents for the 15 w-% pigment containing ink formulations (Paper V) and respective ratios of linseed to mineral oil.

Ink Formulations	2	4	5
Dry Solids Content (%)	48.6	50	50
Linseed oil (total, w-%)	50.5	46.5	49.1
Mineral oil (total, w-%)	6.25	8.85	6.25
Ratio Linseed oil/ Mineral oil	0.12	0.19	0.13

The ink additives were printed and then imaged with FIB (Figure 35). The liquid fatty acid ester was seen to penetrate into the coating to a depth of 1-2 μm. The Minerpol PE wax (in linseed oil) penetrated deep into the coating structure. The contrast between the linseed oil dispersed wax particles and the coating pigment particles was very high. These kinds of images could be excellent visualization aid for fundamental studies of pigment layer microstructures.

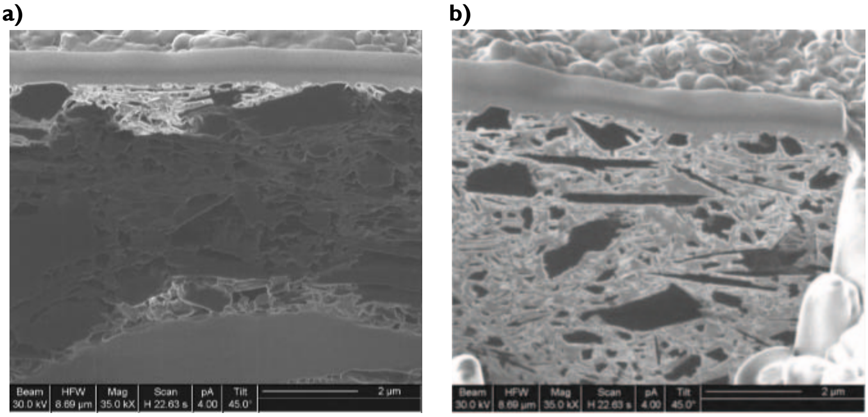


Figure 35. High magnification images of a) the ester solvent exhibiting slight penetration into the coating structure and b) the Minerpol wax in linseed oil with significant penetration. The Minerpol wax was clearly visible in the pores.

It has been shown that the ink additives can have quite a notable impact on the end result of printing, even when they are added to ink formulation in modest amounts. The ester solvent could potentially be used as visualization aid in fundamental studies of coating layer microstructures.

4.2.4 Coating Additives Interacting with Ink Components and Fountain Solution

In addition to structural properties of coatings, the ink oils and fountain solution also react to the surface chemical changes within these structures. One commonly occurring component changing the surface chemistry of a coating is the dispersant. Sodium salt of a polyacrylate (NaPA) is used often as dispersant in calcium carbonate coatings. The absorbed mass of the polyacrylate on coating pigment material has been shown to be 4 mg/m^2 (Longtin, *et al.,* 2011). In offset applications the liquid film layer thicknesses are very thin at a range of 1 µm. At these small thicknesses the interfacial interactions between the various components become very important.

In Paper VI the focus was to understand the effects of increased substrate temperature on wetting of calcite and NaPA coated calcite with offset printing liquids. The heat treatment had an indirect effect to the contact angles through surface bound moisture. Especially the linseed oil contact angles were reacting to changes in temperature and moisture content. The results of experiments where contact angles were measured on NaPA treated calcite crystals kept at room temperature in increased humidity conditions are seen in Figure 36. The instrument and image analysis resolution effects, together with the Wenzel roughness correction (Wenzel, 1936), limit the detection of contact angles below 25 degrees. The introduction of high humidity to the sodium polyacrylate swells the polyacrylate structure (Hansen, *et al.*, 2009, Ström, *et al.*, 1995). At 80% humidity a layer of water is most likely condensed on the surface of the polyacrylate as well.

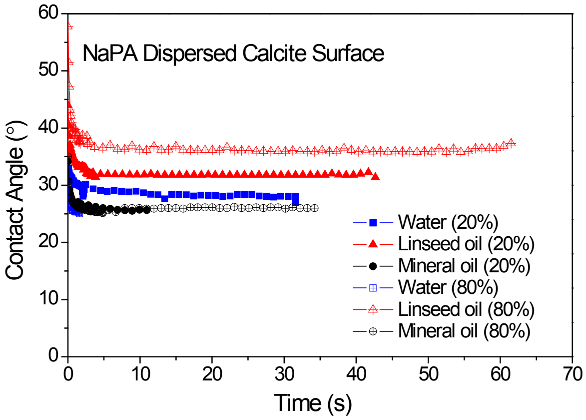


Figure 36. The printing liquid contact angles on NaPA coated surface at room temperature with controlled humidity of the surface. The humidity of the sample surface is the key factor in defining the interactions between the polymer and polar liquids.

The water drop will spread instantaneously on these water covered surfaces as is implied in Figure 36, even though the instrumentation limits the detection of low angles somewhat. Linseed oil was found to pick up changes of surface chemistry caused by applied heat in form of increased water mobility both in the pure calcite surfaces and on the NaPA coated calcite surfaces. Gane and Ridgway (2009) have looked at moisture pick-up via humidity exposure in tablets and showed that there exists a transition between surface sorbed saturation and effective liquid water condensation. They state that surface sorbed saturation and condensation are two different conditions. The mobility of water is reduced in the case of surface sorbed saturation when compared to condensed case. The linseed oil is not attracted to the mobile molecular water. It is stated in the Material Safety Data Sheet (MSDS) of the linseed oil (John L. Seaton &Co. Ltd, 2008) that it is not soluble with water. The main fatty acid component in linseed oil is the linolenic acid (Swern, 1979). The slight polarity of linseed oil originates from the polar groups in these fatty acids. However, when contact angle measurements with relevant liquids are performed on a linseed oil surface, as was done by Horn and Schulz (2002), it is exemplified that the polar component allows adsorption to occur on polar surfaces despite the lack of wettability by water. Hence, linseed oil will adsorb to polar surfaces, which are static and allow for reorientation of the oil. This confirms the hypothesis that the higher contact angles of linseed oil on calcite and sodium polyacrylate covered surfaces are in fact due to surface moisture and that the linseed oil is picking up this change.

In Paper VII in addition to solid calcite surfaces, porous pigment coating structures were used as substrates for contact angle type measurements with high speed imaging. Figure 37 shows images of water spreading on these porous structures. Due to the high surface tension of water it responded more strongly than the oils to the surface structural differences of the pigment tablets, i.e. to the surface porosity and to the size of the surface features. Any local change in curvature at the contact line, defined by the contact angle within the geometry of the surface feature, was more exaggerated in respect to wetting force for water compared to the cases for oils.

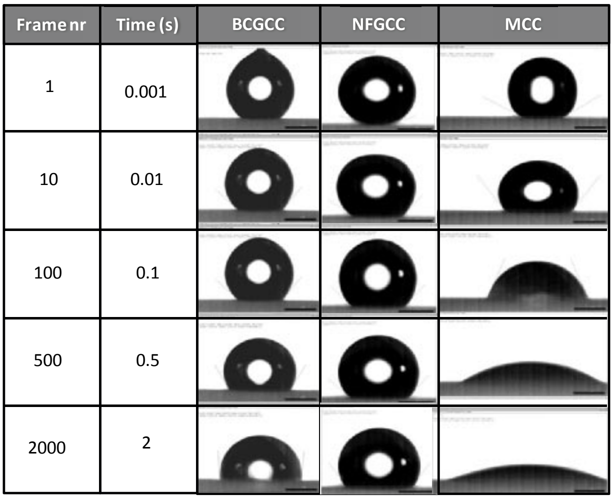


Figure 37. Representative sequences of five images of water droplet spreading on the three types of pigment tablets.

The surface features of BCGCC and NCGCC were larger compared to MCC. The spreading motion of water was slower on these pigments as the water front needs to overcome larger surface features and fill up larger surface pores in order to move forward. The correlation of surface pore sizes and spreading is supported by computer modeling of Lunkad, *et al.* (2010), who concluded that greater number of pores and increased pore density increase the spreading compared to a non-porous surface. This also agrees with the results of Alam, *et al.* (2007) on spreading of droplets on mono- and poly-disperse surface topographies. BCGCC had a tighter packing, smaller permeability (Section 4.2.2. Table VII) and was likely to have a larger amount of small pores at the surface. NCGCC, although it had a narrower pore size distribution, created mono-sized pores which slowed down the spreading of the water droplet in comparison to the other pigments. The NCGCC had a slightly higher permeability as the particle size distribution was narrower than that of BCGCC. The results indicated that on MCC tablets, the droplet front advanced rapidly by pinning to the nano-sized surface features of the pigment, as is suggested by Raiskinmäki, *et al.* (2000). However, as the MCC did not have a purely solid surface with a degree of roughness described by the Wentzel model (Wenzel, 1936), but a porous surface demonstrating sub-surface connectivity, the pinning was not the only mechanism taking place. Schoelkopf, *et al.* (2000a, b) used the Bosanquet equation to show that nanopores <100 nm will fill within nanoseconds at the surface. Therefore, in the case of the MCC, it is likely that the top surface of the structure became filled with the liquid almost instantaneously. Air in the pores was be displaced by water, which influenced the contact angle of the water. The drop would have seen this as a similar situation as if it would have been placed on a same liquid saturated structure. In addition to the size and number of pores, it is important the pores are connected, so that the fluids can freely move from one pore to another and there is sufficient volume available for absorption. The MCC is clearly showing highest permeability in Table VII (Section 4.2.2). This is caused by the bimodal pore structure of the packed MCC particles that produce larger inter-particle pores and thereby increased volume for absorption without losing the required capillarity that is provided by the intra-particle pores of MCC. Without this combined action, the absorption speed of the liquid would decline in the case of such large inter-particle pores due to the reduced capillarity despite the high permeability.

Contact angle results of the above porous tablets and solid calcite surfaces in Figure 38 were related to the hydrodynamic and the molecular kinetic theory of liquid spreading (Blake and Haynes; 1969, Voinov; 1976, Tanner; 1979, Ruijter, *et al.*; 2000, von Bahr, *et al.*; 2005, Drelich and Chibowska; 2005). This was done by plotting the contact diameter and the time in a log/log-graph and studying the respective slopes. The molecular kinetic model suggests that the wetting line moves as the individual liquid molecules interact with the solid at the three-phase zone. Hydrodynamic theory on the other hand suggests that the droplet spreading is controlled by an energy balance between the capillary driving force and the hydrodynamic resistance to spreading. It has also been suggested that these two theories would co-exist at different time scales (Ruijter, *et al.*, 2000). A power law type of behavior was seen for the contact diameter as function of time. The curves could be divided into two distinct regions, the first one being the inertial regime. In this regime the inertia of the falling droplet is considered to limit the spreading of it on the surface. The scaling factor of the contact diameter is $D \sim t^{1/2}$ for the inertial regime.

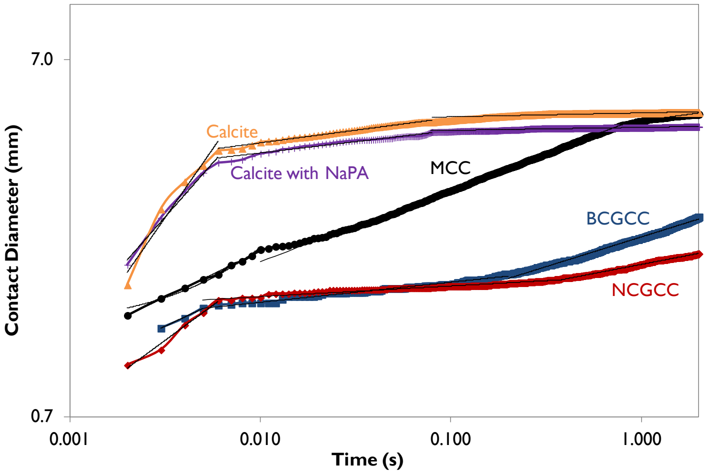


Figure 38. Contact diameters of water on the porous pigment tables (BCGCC [blue], NCGCC [red] and MCC [black]) and on solid calcite surfaces with and without sodium polyacrylate (NaPA) coating [marked with purple and orange, respectively].

Without NaPA on the calcite surface the slope *n* for the inertial regime equaled 0.71 and with added NaPA on the surface *n* = 0.61. It is plausible that the calcite and NaPA, as they interact quite strongly with water, would be a partial cause of larger exponent. A supporting conclusion of higher slope being due to the increased interactivity of water contacting a hydrophilic surface is found in the work of Drelich and Chiboswka (2005) and Wang, *et al.* (2009). The spreading after the inertial stage is often referred to as the capillary stage. Sodium polyacrylate is known to give an additional hydroscopic character to a surface. The later capillary stage of the curve showed that the water drop does not spread as far on the sodium polyacrylate covered calcite, indicating support to the retarding effect of the dispersant. The surface porosity certainly affected the results as well, and it was suggested to be the cause of the slightly smaller value than that originally proposed by Biance, *et al.* (2004). Furthermore, Figure 38 shows that the porous structure retarded the spreading of the droplet compared to spreading on a chemical-free solid surface. The amount of dispersant needed for dispersing is strongly dependent on the pigment particle size as it adsorbs to the pigment surface. Therefore, the finer the pigment, the larger the needed amount of dispersant is (Hansen, *et al.*, 2009). NCGCC and BCGCC surfaces were practically fully covered by polyacrylate, and as the dosage of dispersant is proportional to the surface area it means that the NCGCC structure has the largest amount of dispersant. As the dosage of dispersant used in MCC approximately equals that used in NCGCC, and while its surface area is much larger, it is apparent that the entire MCC surface was not covered with sodium polyacrylate. The relative order of the curves therefore suggests that the dispersant layer on the pigments retarded water at these short times, and the movement of the liquid front on the untreated pigment surface was faster due to lesser amount of interaction. This mechanism has been earlier proposed by Gane and Ridgway (2009) and Rigdway, *et al.* (2010, 2011).

Water and moisture in the offset process are in a key role. The surface interactions are important in offset printing where film thicknesses are low, of the order of 1 μm and less. Dispersant on top of the calcium carbonate is contributing to the interfacial processes taking place during ink setting and the chromatographic separation of ink oils. As the dispersant is hygroscopic and swellable, it acts to delay polar liquids, despite ensuring their wetting. Distribution of moisture within the coating structure may influence the distribution of ink oils and fountain solution. Mottle, which is unevenness of the print, is directly linked to uneven distribution of fountain solution or ink components in the coating structure. Additionally, the distribution of moisture in the structure may have an influence on the level of adhesion between the ink and coating and contribute to problems such as piling or decreased print rub resistance.

5. Concluding Remarks

The system of coating structure and ink that is printed on it is a combination of two complex materials. In the offset process a complicating factor is the presence of water, which is essential and needs to be balanced in respect to the ink feed for optimal performance. While many aspects of ink-paper interactions have been studied during the last decades from the paper coating view point, the ink and ink parameters have received less attention. Yet, understanding the ink's contribution is equally important.

The ink filamentation in the printing nip was studied through dynamic gloss measurements and the ink filament remains were imaged with CLSM. The ink film splitting in the printing nip is the origin of quality in prints. Fountain solution addition to printing ink contributes to film splitting by producing cavitation points in the nip, but the type of fountain solution (alcohol containing or alcohol-free) did not have a significant impact to filamentation in the laboratory scale experiments. The filaments formed in the nip were indirectly detected by dynamic gloss measurements. DOG was shown to be capable revealing additional information about levelling of (small groups of) single filaments through use of small beam size.

People generally report results from one gloss detecting instrument, but differences in instrumentation and printing method are rarely discussed. The instruments used to measure dynamic gloss: DOG, Dynamic Gloss Meter and Reflectometer were found to give similar results. The trends in the results for setting behaviour of the different coating and ink combinations were the same, although the absolute gloss values and the relative differences between the samples varied with both the instrumentation and the printing parameters. These printing parameters included differences in nip geometry, printing speed, printing roll geometry and surface texture. The experimental variations were found to have a significant impact on the results and should be carefully documented by authors. The printing parameters were also of interest when filament remains were imaged with CLSM. Fountain solution addition to the ink decreased the filaments size. Increased ink amount and increased speed, on the other hand, created larger filaments. It was found that the relative importance between the parameters may also change, as surface texture of the printing disc was seen to dominate over the influence of printing speed.

After the ink filaments have leveled out, the ink will set further. An improved prediction of ink setting behaviour was obtained when the permeability factor of the ink in the filtration equation was modified. The ink setting was also found not to be directly related to the ink viscosity, but the filtration equation implies a first order relationship of ink setting with the ink permeability factor.

Inside the coating the chromatographic separation of ink components will take place as the ink components enter further into the coating structure. FIB imaging was utilized to see the extent of penetration and absorption of individual ink components into the coating structures for the first time. It was shown in this study that imaging of offset ink components, other than the mineral oil; inside the coating structure is possible using Focused Ion Beam Technique. Especially the linseed oil incorporated wax showed excellent contrast between the coating structure and ink and can be further utilized for imaging coating microstructures.

The surface interactions of the oils and water with the pigment surfaces were studied at varying surface temperatures. The contribution of dispersant to these surface interactions was included. Mostly the temperature influenced the spreading by amplifying the influence of surface bound water both on the pure mineral surface and on the hydrophilic, hygroscopic sodium polyacrylate. Linseed oil was found to be sensitive for the polarity changes due to existence and migration of water, swelling and possible polymer re-alignments. These findings can be useful when finding solutions for sources of offset printing problems related to water and polar interaction, such as mottling, picking and print rub.

Further work relating to print problems especially print rub, was carried out using model inks, ink oil components and water, representing fountain solution. It was shown using a model ink with varying pigment concentration, and with or without wax addition, that the total solids content of an ink is more important than just the pigment content of the ink for generation of print rub problems. The waxes are important when trying to decrease print rub, but when added in combination with linseed oil, their positive influence does not extend as far what can be achieved by using an ink with lower total solids content. It was also demonstrated through experiments that the ratio of linseed to mineral oil contributes to print rub. The importance of surface interactions of linseed oil with the coating pigment was further verified by the high speed imaging and Thin Layer Wicking studies. These results showed that pigment coating structure having a combination of nanopores and larger pores with large surface area is beneficial for offset printing liquid absorption. They also support an earlier hypothesis that the linseed oil absorbs by a mechanism of adsorption to the pore walls. The coating structure can thereby enhance the chromatographic separation of printing inks. When ink oils adsorb effectively in the pores, they will be retained less in the ink layer and this will decrease the occurrence of print rub as was shown in Paper V. Quite often especially the matte coated papers suffer from print rub, because the optical and printability demands on the coating pore structure are conflicting to each other. These findings can be helpful in cases where certain ink-paper combinations are causing print rub. The results presented here give an option to redesign such papers to perform better. Of course, for the inks part, the ink type may be chosen or modified so, that it would have lower solids content, and lower ratio of linseed oil to mineral oil.

6. Outlook

This work has been done during a period of change in both the printing and paper industries. When the work was started there was still interest toward the traditional printing methods, as the extensive work done in the MolPrint project showed. The traditional printing methods will most likely shift their positions, as the newer digital media has taken a share of the communication markets. The paper-based products and prints will still remain in the use as they have benefits of being inexpensive, very tactile and environmentally sound choice due to recyclability. For example in advertising the use of mixed media, print and digital in combination, has shown very good results.

There is room for more scientific research in the area of printing and printing inks. Many industry methods are still based on relatively subjective interpretations such as feel and look, even though modernization has spread quite wide. There exists more instrumentation that could be implemented to measure the various properties. In the printing process the number of changing parameters is extremely high when all machinery, material and process variables are included. The materials are developed constantly, due to raw material, pricing and environmental reasons. This means that the printing industry, in future, will still have interesting and new challenges for researchers to solve.

Some new activities for a researcher have already been found in the field of printed functionalities. Functional device concepts produced by printing, such as paper-based diagnostics and electronics for low cost applications, have already been accomplished (Tobjörk, *et al.,* 2008, Bollström, *et al.,* 2011). Advances in such new fields require a multidisciplinary approach in combination with strong background and understanding of technologies of coating and printing.

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