



The comparative dynamics of bulk liquid flow and interpolymer diffusion during inkjet ink imbibition in porous coating structures

Taina Lamminmäki



#### **VTT SCIENCE 2**

# The comparative dynamics of bulk liquid flow and interpolymer diffusion during inkjet ink imbibition in porous coating structures

Taina Lamminmäki

Doctoral dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the School of Chemical technology for public examination and debate in Auditorium (Forest Products Building 2) at Aalto University School of Chemical Technology (Espoo, Finland) on the 4th of May, 2012, at 12 noon.



ISBN 978-951-38-7455-1 (soft back ed.) ISSN 2242-119X (soft back ed.)

ISBN 978-951-38-7456-8 (URL: http://www.vtt.fi/publications/index.jsp) ISSN 2242-1203 (URL: http://www.vtt.fi/publications/index.jsp)

Copyright © VTT 2012

JULKAISIJA – UTGIVARE – PUBLISHER

VTT PL 1000 (Vuorimiehentie 5, Espoo) 02044 VTT Puh. 020 722 111, faksi 020 722 4374

VTT PB 1000 (Bergsmansvägen 5, Esbo) FI-2044 VTT Tfn. +358 20 722 111, telefax +358 20 722 4374

VTT Technical Research Centre of Finland P.O. Box 1000 (Vuorimiehentie 5, Espoo) FI-02044 VTT, Finland Tel. +358 20 722 111, fax + 358 20 722 4374

# The comparative dynamics of bulk liquid flow and interpolymer diffusion during inkjet ink imbibition in porous coating structures

[Liuoksen virtausdynamiikka ja polymeerien diffuusio mustesuihkuvärin asettumisessa huokoisiin päällysterakenteisiin]. **Taina Lamminmäki**. Espoo 2012. VTT Science 2. 187 p. + app. 89 p.

## Abstract

The focus of this thesis is to establish the timescale of interactions, physical and chemical, during dye-based inkjet ink imbibition into calcium carbonate (CaCO<sub>3</sub>) pigmented coatings. Comparison is made between conventional offset quality  $CaCO_3$  (GCC), and special inkjet qualities in the form of either modified (MCC) or precipitated (PCC) CaCO<sub>3</sub> combined with swelling diffusion driving or non-swelling diffusion-inert binder. The selection of pigment is based on the control of pore volume, pore size distribution and connectivity of the coating layer. Pigments containing nano-size pores (intra-particle) are primarily exemplified. The final coating layers display discrete pore size bimodality in relation to the intra-particle and inter-particle pores, respectively, Polyvinyl alcohol (PVOH) is used as the diffusion sensitive binder and styrene acrylate latex (SA) as the bulk diffusion-inert binder. By changing the coating layer structures and using the contrasting binders the roles of liquid diffusion, capillary pressure and permeation flow are clarified both in the short and long timescale imbibition. The wetting force within the finest coating layer capillaries drives the inkjet ink into the porous structure, whilst the viscous drag within the pore structure resists the movement. The nano-size capillaries initiate absorption of the ink vehicle, though typical impact pressure of an inkjet droplet is shown to provide forced wetting. During the subsequent flow, the hydrophilic binder swells, acting to close the smallest pores and reduce the remaining pore diameters. The total pore volume decrease competes with the initial capillarity, reducing absorption rate. The diffusion is shown to have a marked effect on the polar liquid absorption rate into the PVOH-containing coatings over different timescales. The swelling opens the polymer matrix so that the colorant of the ink fits into the binder structure and can either hydrogen bond or become mechanically trapped there on drying. The diffusion coefficient of water in PVOH and on SA latex films is shown to be very similar, despite the difference between bulk diffusion and surface diffusion, respectively. The colorant fixing is enhanced mainly by the ionic interactions between the colorant and coating surface adsorption sites. The anionic colorant fixes under chromatographic separation to the cationic components of the coating layer. There is seen to be an optimal absorption rate beyond which the colorant has insufficient time to translate under the Coulombic attraction potential toward the cationic adsorption sites or to respond to the binder interpolymer matrix diffusion potential. The final print density of a high-speed inkjet printed surface depends on the colorant location in the coating layer and the optical properties of the whole coated paper. Therefore the competing mechanisms of liquid flow, ab- and adsorption are seen as crucial to developing a high quality print. The intercolour bleeding is additionally dependent on the coating layer capability to absorb enough ink at adequate high absorption rate in competition with colorant spreading on the surface. Spreading can be further curtailed using a cationic surface treatment.

Keywords diffusion, absorption, permeability, porosity, ionic charge, coating binder, coating, inkjet printing

#### Liuoksen virtausdynamiikka ja polymeerien diffuusio mustesuihkuvärin asettumisessa huokoisiin päällysterakenteisiin

[The comparative dynamics of bulk liquid flow and interpolymer diffusion during inkjet ink imbibition in porous coating structures]. **Taina Lamminmäki**. Espoo 2012. VTT Science 2. 187 s. + liitt. 89 s.

# Tiivistelmä

Väitöskirjatyön tavoitteena on selvittää vuorovaikutusilmiöiden, sekä fysikaalisten että kemiallisten, aikaskaaloja liukoisen mustesuihku- eli inkjet-värin asettumisessa kalsiumkarbonaattipigmentti-päällysteissä (CaCO<sub>3</sub>). Vertailuja tehdään perinteisen offset- (GCC) ja inkjet-laadun CaCO3 välillä. Inkjet-puolella on tutkittu sekä modifioitua (MCC) että saostettua (PCC) CaCO<sub>3</sub>:a, ja sideaineina on käytetty turpoavaa diffuusioherkkää tai ei-turpoavaan diffuusio-inerttiä sideainetta. Pigmentit on valittu siten, että päällystekerroksen muuttujiksi on saatu sekä huokostilavuus, -kokojakauma että -rakenne. Tämä on toteutettu muutamissa päällysteissä siten, että päällysteessä on käytetty nanohuokosia sisältäviä pigmenttipartikkeleita. Tällöin lopullisissa päällysteissä esiintyy bimodaalinen huokoskokoiakauma, jossa on sekä partikkelien välisiä että sisäisiä huokosia. Diffuusioherkkänä sideaineena käytetään polyvinyylialkoholia (PVOH) ja diffuusio-inerttinä styreeni-akrylaattilateksia (SA). Päällystekerroksen rakenteen vaihtelulla ja erilaisten diffuusioherkkien sideaineiden käytöllä tutkitaan kapillaari- ja permeaatiovirtauksia sekä lyhyen että pitkän aikaskaalan nesteen imeytymisessä. Kostutusvoimat päällysteen pienissä kapillaareissa ajavat inkjet-väriä huokoisen rakenteen sisään, kun taas viskoottinen voima vastustaa liuoksen liikkumista. Inkjet-värin liuotinosan absorptio alkaa nanokoon kapillaareista, tosin inkjet-pisaran aiheuttamaa iskeytymispainetta ei pidä unohtaa tässä yhteydessä. Seuraavassa vaiheessa hydrofiilinen sideaine turpoaa, sulkee pienimmät huokoset ja pienentää jäljellä olevien huokosten halkaisijoita. Kokonaishuokostilavuuden pieneneminen kilpailee alkuperäisten kapillaariilmiöiden kanssa hidastaen absorptionopeutta. Työssä osoitetaan, että diffuusiolla on merkittävä vaikutus polaarisen liuoksen absorptionopeuksiin PVOH:ta sisältävissä päällysteisissä. Turpoaminen aukaisee polymeerimatriisia siten, että värin väriaineosa mahtuu sideainerakenteeseen ja voi joko sitoutua vetysidoksilla polymeeriin tai jäädä polymeerimatriisin sisään sen kuivuttua. PVOH- ja SA-lateksifilmin veden diffuusiokerroin on samaa suuruusluokkaa, tosin PVOH:n yhteydessä on kyse massadiffuusiosta ja SA-lateksilla pintadiffuusiosta. Väriaineen kiinnittymistä päällysteen pintaan voidaan parantaa ionisilla vuorovaikutuksilla. Anioninen väriaine sitoutuu kromatografisen erkanemisen aikana päällystekerroksen kationisiin komponentteihin. Tulokset osoittavat, että on löydettävissä optimaalinen värin absorptionopeus, jossa väriaineella on riittävästi aikaa sitoutua Coulombisilla attraktiovoimilla kationisiin ryhmiin tai siirtyä sisään sideainepolymeerin matriisiin diffuusiolla. Nopean tulostuksen inkjetin painojäljen densiteetti riippuu väriaineen sijainnista päällystekerroksessa sekä koko päällystetyn paperin optisista ominaisuuksista. Liuoksen virtauksen kanssa kilpailevat absorptio- ja adsorptioilmiöt ovat välttämättömiä, jotta saavutettaisiin hyvä painojäljen laatu. Värien välinen sekoittuminen (bleeding) riippuu siitä, miten paljon päällystekerros kykenee absorboimaan väriä ja miten nopeasti väri siirtyy pinnan sisään. Lisäämällä kationista pintakäsittelyainetta päällysteen pinnalle pystytään vähentämään värin leviämistä.

Avainsanat diffusion, absorption, permeability, porosity, ionic charge, coating binder, coating, inkjet printing

### Preface

This thesis work has been done in the School of Chemical Technology, Department of Forest Products Technology of Aalto University during the years 2007– 2011. Firstly, I would like to express my sincere gratitude to my supervisor, Professor Patrick Gane, Chair of Printing Technology, Aalto University, and Head of Research and Development, Omya Development AG, Oftringen, Switzerland, who gave me constant and invaluable guidance, and support throughout the work. I am most indebted to him for being always available and responding rapidly with his excellent comments to each of the research papers and the final thesis. Professor Gane also kindly arranged an opportunity for me to use the measuring devices of Omya Development AG and Aalto University for the purposes of this thesis.

The study commenced at Oy Keskuslaboratorio – Centrallaboratorium Ab (KCL) and continued and has been completed after the integration of KCL with VTT Technical Research Centre of Finland. This PhD work benefited from the positive attitude of these two organizations and the instructor of this work, Dr. John Kettle. I would like to express my greatest gratitude to him for being available whenever I needed support. He has always patiently guided me and helped me both in my research and with the English language.

I also wish to thank Dr. Cathy Ridgway, Omya Development AG (Oftringen), for her guidance in the use of mercury porosimetry and microbalance measurement techniques. I also wish to thank all of my co-authors involved in the publications of this thesis.

The data of this thesis work was collected from several projects at KCL and VTT. I would like to take this opportunity to thank my colleagues Anu Ilmonen, Eija Kenttä, Jukka Ketoja, Annaleena Kokko, Jorma Koskinen, Heikki Pajari, Pasi Puukko, Hille Rautkoski, Robert Roozeman, Yingfeng Shen, Asko Sneck and Oleg Timofeev for the many helpful discussions. I also would like to thank Seija Rinkinen and Sinikka Rosenlöf who were both involved in some aspects of the production and analysis of the coated papers.

Last, but definitely not least, I would like to express my deepest gratitude to my family, Seppo and Nina, and to all my friends who gave their support and encouragement during this work.

Espoo, 4.5.2012

Taina Lamminmäki

# List of publications

This doctoral thesis is based on seven publications. All publications have been published in peer reviewed journals named below. In all publications the author has been in charge of the experimental plan, and has made the analyses of results and first manuscript. Some of the measurements made on specialist equipment and related model calculations have been performed via the grateful assistance of specialists in the field. The focus of each paper and how they assist the study of inkjet ink imbibition in the coated paper structure is explained in the "Introduction" section to the thesis (Chapter 1).

- I Lamminmäki, T., Kettle, J. P., Puukko, P., Gane, P., Ridgway, C.: Inkjet print quality: the role of polyvinyl alcohol in speciality CaCO<sub>3</sub> coatings, Journal of Pulp and Paper Science 35(2009)3–4, 137–147.
- II Lamminmäki, T., Kettle, J., Puukko, P., Ketoja, J., Gane, P.: The role of binder type in determining inkjet print quality, Nordic Pulp and Paper Research Journal 25(2010)3, 380–390.
- III Lamminmäki, T., Kettle, J., Rautkoski, H., Kokko, A., Gane, P.: Limitations of current formulations when decreasing the coating layer thickness of papers for inkjet printing, Industrial and Engineering Chemistry Research 50(2011)12, 7251–7263.
- IV Lamminmäki, T. T., Kettle, J. P., Puukko, P. J. T., Gane, P. A. C.: Absorption capability and inkjet ink colorant penetration into binders commonly used in pigmented paper coatings, Industrial and Engineering Chemistry Research 50(2011)6, 3287–3294.
- V Lamminmäki, T. T., Kettle, J. P., Puukko, P. J. T., Gane, P. A. C.: The chromatographic separation of anionic dye in inkjet coating structures, Colloids and Surfaces A: Physicochemical and Engineering Aspects 377(2011)1–3, 304–311.
- VI Lamminmäki, T. T., Kettle, J. P., Puukko, P. J. T., Ridgway, C. J., Gane, P. A. C.: Short timescale inkjet ink component diffusion: an active part of the absorption mechanism into inkjet coatings, Journal of Colloid and Interface Science 365(2012)1, 222–235.

VII Lamminmäki, T. T., Kettle, J. P., Gane, P. A. C.: Absorption and adsorption of dye-based inkjet inks by coating layer components and the implications for print quality, Colloids and Surfaces A: Physicochemical and Engineering Aspects 380(2011)1–3, 79–88.

## Author's contributions

Author has taken part in the planning of experimental work, developed and refined especially the thin layer chromatography measurement, done part of the actual measurements, analysed the data and based on the results written the first versions of the manuscripts.

- Paper I The coating trial using the SAUKKO device was performed by Seija Rinkinen from OY Keskuslaboratorio – Centrallaboratorium AB (KCL). Anu Ilmonen (KCL) produced the layouts of the printing trial. The mercury porosimetry measurement was made by the guidance of Dr. Cathy Ridgway from Omya Development AG (OMYA).
- Paper II Seija Rinkinen (KCL) measured the capacitance-based absorption (Clara) analysis.
- Paper III Hille Rautkoski (VTT Technical Research Centre of Finland) was responsible for the curtain-coating trial at the Metso Paper, Inc. (Järvenpää), pilot coater, and Seija Rinkinen (VTT) made again the corresponding measurements on the Clara device.
- Paper IV The ToF-SIMS measurement was performed by Jyrki Juhanoja from Top Analytica.
- Paper V Cathy Ridgway (OMYA) measured the pore volume and pore size distribution by mercury porosimetry. Asko Sneck (VTT) arranged the camera system for the TLC measurement and made the gray level determination.
- Paper VI Philip Gerstner (Aalto University) and Kimmo Koivunen (Aalto University) advised how to produce coating tablets. Cathy Ridgway (OMYA) arranged the mercury porosimetry analysis and guided in the measurement of liquid wicking by microbalance. Oleg Timofeev from VTT assisted in the diffusion coefficient calculations.
- Paper VII Robert Rooseman (VTT) assisted in the interpretation of the UV-VIS results and Sinikka Rosenlöf (VTT) measured the Clara results.

#### Errata

- Paper II The base paper grammage was reported wrongly. The grammage was 67 gm<sup>-2</sup>, not 53 gm<sup>-2</sup>.
- Paper IV Figure 2 the legend "Cationized PVOH, no additive" should be "Carboxylated PVOH, no additive".

# Contents

Ab	strac	t		3
Tii	vistel	mä		5
Pre	eface			7
Lis	st of p	ublicat	ions	8
Au	thor's	s contri	butions	10
Lis	st of s	ymbols	3	15
1.	Intro	oductio	n	18
	1.1	Backg	Iround	18
	1.2	Objec	tives	20
	1.3	Hypot	heses and outline of the work	20
2.	Lite	rature r	eview	26
	2.1	Prope	rties of inkjet inks	26
		2.1.1	Water-based soluble inks (dye)	28
		2.1.2	Water-based pigment inks	31
		2.1.3	UV-curable inks	33
	2.2	The w	etting and imbibition of inkjet ink	34
		2.2.1	Wetting of a surface	35
		2.2.2	Liquid penetration into porous coating layers	37
		2.2.3	Transport by diffusion	41
		2.2.4	Separation	45
		2.2.5	Adsorption	46
		2.2.6	Colorant fixing	46
	2.3	Effect	of coating layer on inkjet ink imbibition	48
		2.3.1	Coating pigments	49
		2.3.2	Binders	52
		2.3.3	Additives	54
3.	Exp	erimen	tal	55
	3.1	Mater	ials	55
		3.1.1	Calcium carbonate inkjet coating pigments	55
		3.1.2	Swelling and non-swelling coating binders	57
		3.1.3	Adjusting the ionic charge by additives	58
		3.1.4	Inkjet inks and printing devices	58
		3.1.5	Substrate: pre-coated base paper	60
	3.2	Desig	ned coating structures and binder films, and their production	า62
	3.3	Analy	ical methods	66
		3.3.1	Porosity of coating structures	66
		3.3.2	Liquid penetration	67

		3.3.3 Absorption of liquid into binder films	.73
		3.3.4 Absorption/adsorption of liquid colorant by coating components	.74
		3.3.5 Use of more conventional paper testing methods	.76
		3.3.6 Print quality	.77
		3.3.7 Summary	.81
4.	The	structural effect of the coating layer on inkjet ink imbibition	.83
	4.1	Impact of coating pigment type and binder selection on the	
		structure formation of the coating layer	.83
	4.2	The effect of coating structure and binder selection on liquid	
		imbibition rate	.92
		4.2.1 Inkjet ink absorption into the top layer of coating	.92
		4.2.2 Gravimetric determination of liquid absorption into the	
		coating structure	.94
		4.2.3 Liquid and colorant movement – impact of charge on	
		chromatographic separation in the coating layer	.98
		4.2.4 Inkjet ink penetration in coated papers monitored by	
		electrical capacitance1	103
	4.3	The role of coating layer thickness in inkjet ink penetration	110
	4.4	Summary of the coating structure effect on ink imbibition1	115
5.	Мес	hanisms influencing liquid absorption in coating binders1	18
	5.1	Liquid absorption by binder films1	18
	5.2	Diffusion of liquid into coating binders1	23
		5.2.1 Diffusion coefficient1	123
		5.2.2 Colorant penetration1	128
	5.3	Water and colorant in the binder film structure1	33
	5.4	Diffusion in the coating layer during inkjet ink absorption1	34
	5.5	Binder swelling – impact on nano-size capillaries1	38
	5.6	Summary of diffusion mechanisms in coating binders1	140
6.	Inkje	et ink colorant fixing and transfer into the coating layer1	42
	6.1	Colorant fixing to the anionic or cationic coating layer	142
		6.1.1 Thin layer chromatography1	142
		6.1.2 Absorption and/or adsorption of coating components1	46
	6.2	Colorant transfer into the binder1	50
	6.3	Summary of colorant fixing and movement1	151
7.	Fact	ors influencing the print quality of dye-based ink prints1	52
	7.1	Coating layer structure1	152
	7.2	Binder amount and type1	55
	7.3	Coat weight1	61
	7.4	Cationic additive applied directly onto the top of coating surface1	63
	7.5	Summary of print quality formation1	68

8.	Conclusions				
	8.1	The effect of coating structure, binder properties and surface			
		adsorption on inkjet ink imbibition and colorant distribution	170		
		8.1.1 The interplay of capillarity and diffusion	170		
		8.1.2 Detailed role of binder	171		
		8.1.3 Adsorption and dye fixation	172		
	8.2	Print quality – factors relating to the identified interaction			
		mechanisms	173		
9.	Sug	gestions for future work	175		
Ref	References177				

#### Appendices

Papers I-VII

# List of symbols

Symbols

Symbol	Description	Number of publication	Unit
А	Area	II, III, VI	m²
a*	Colorimetric component in the CIELab orthogonal representation of colour space describing the position along the magenta/ red-green axis	VII	-
b*	Corresponding colorimetric compo- nent on the yellow-blue axis	VII	-
Во	Bond number, Eötvös number	-	-
с	Concentration	VI	e.g. (mol)m <sup>-3</sup>
С	Capacitance	11, 111	F
C*	Chroma	-	-
d	Thickness of paper	II, III	m
d	Diameter of capillary	VI	m
D	Diffusion coefficient	VI, VII	m <sup>2</sup> s <sup>-1</sup>
g	Gravitational acceleration, 9.81 ms <sup>-2</sup>	-	-
ΔE	Colour change measured with CIELab* values (CIE76)	VII	-
Н*	Hue	-	-
J	Diffusive flux	-	(mol)m <sup>-2</sup> s <sup>-1</sup> e.g.
k	Porous medium permeability	III	m²
kв	Boltzmann constant, 1.3806503 × $10^{-23}$	VII	JK <sup>-1</sup>
1	Length of capillary, characteristic length of fluid flow	III, ∨	m
L	Paper depth	III	m
L*	Luminance component in the CIELAB color space	VII	-
т	Mass	VI	kg
I	Liquid phase	V	-
М	Moisture content	VI	%
Ν	Number of consecutive layers	VI	-

р, <i>Р</i>	Pressure	III, VI	bar
q	Particle electrical charge	-	С
Q	Volumetric liquid flux	-	ms⁻¹
s	Solid phase	-	-
r	Internal radius of capillary	III, V, VII	m
R	Radius of ink droplet	-	m
t	Time	II, III, V, VI	S
Т	Temperature	VII	°C or K
u, v, w	Velocity (in three Cartesian directions)	-	ms⁻¹
V	Volume of capillary, fluid or droplet	III, V, VI	m <sup>3</sup>
v	Vapour phase	V	-
We	Weber number	-	-
x	Position of meniscus	VI	m

#### Greek letters

Symbol	Description	Number of publication	Unit
γ	Interfacial/Surface tension	V	Nm <sup>-1</sup>
3	Material dielectric permittivity	II, III	Fm⁻¹
<i>E</i> r	Dielectric constant (relative permittivity)	III	-
E	Amplitude of oscillation	-	m
η	Viscosity	III, V, VII	kgs <sup>-1</sup> m <sup>-1</sup> (Pas)
θ	Contact angle	V	o
λ	Distance between atoms	VI	m
ρ	Density	VI	kgm⁻³
σ	Binder film thickness	VI	m
Τ	Time	VI	S
ω	Frequency	III	s <sup>-1</sup>
μ	Dynamic viscosity	-	kgs <sup>-1</sup> m <sup>-1</sup> (Pas)
$\mu_{ m q}$	Electrical mobility of a charged particle	-	$m^2V^{-1}s^{-1}$

#### Abbreviations

Abbreviation	Description
cat.	cationic
CD	Cross-direction
Clara	Capacitance-based penetration measurement
DIGAT	Dynamic inkjet ink absorption time measurement
DSC	Differential scanning calorimeter (calorimetry)
GCC	Ground calcium carbonate
MAX	Maximum
MCC	Modified calcium carbonate
MIN	Minimum
PCC	Precipitated calcium carbonate
polyDADMAC	poly(diallyl dimethyl ammonium chloride)
pph	Parts per hundred
PVOH	Polyvinyl alcohol
SA (latex)	Styrene acrylic latex
SEM	Scanning electron microscopy
Si-oil	Silicon oil
ToF-SIMS	Time of flight secondary ion mass spectrometry
TLC	Thin layer chromatography
UV-VIS	Ultraviolet-visible spectroscopy
UV/NIR/VIS	Ultraviolet-near infrared-visible spectrometry
wt-%	Weight percent

### 1. Introduction

#### 1.1 Background

The popularity of using high-speed inkjet printing in the printing of products like books, labels, packages, direct mails, transactional mails (bills, statements, cheque books, credit cards and communications from the central government and local authorities), displays and security products, amongst others, has recently shown a large increase (Batz-Sohn *et al.* 2010, Smyth 2010). During the last twenty years, the inkjet printing method and application have developed both in terms of speed and print quality (Smyth 2010, Ward 2010, van Laethem 2003). Even though inkjet is still a minor printing method in terms of total volume in the printing world today, there are forecasts for its strong growth (Smyth 2010). Despite this, there is no commonly accepted or determined speed definition for a high-speed inkjet printing operation, but quite often speeds in excess of 10 m·min<sup>-1</sup> are typically quoted in the emerging digital printing world. The main drawbacks related to inkjet remain, to a large extent, the high cost of inks and substrates, in many cases inferior print quality compared to existing conventional printing methods, and the lack of good product ideas to utilize the full capabilities of variable data printing.

Two ink drop formation techniques are used in high-speed inkjet printing: continuous jetting (CJ) and drop-on-demand (DOD) (Smyth 2010, Svanholm 2007). In both techniques, water-based soluble dyes, aqueous-based dispersed pigment inks, UV-curable inks and hot-melt inks are used. Additionally, in the case of CJ printing, solvent-based inks are also used.

Inkjet suitable papers are generally fine papers, though wood containing newsprint is becoming increasingly common as a substrate for inkjet compatibility. Amongst the woodfree fine grades, categories span surface sized papers, coated papers and photo-quality papers (layer-structure containing media) (Svanholm 2007, Glittenberg *et al.* 2003). The surface-sized grade is a fine paper where the surface has been treated most commonly with starch and/or polyvinyl alcohol (PVOH) (Svanholm 2007). The coated papers traditionally have silica pigments in the receiver and/or top coating layer, with their combination of high porosity micropores and high specific surface area, providing rapid ink drying and high pore volume (Chapman 1997). Different silica-based pigments have also been studied (Hladnik 2004), like precipitated, fumed, colloidal silica and silica gel. Surface modified calcium carbonate, surface modified clays, colloidal precipitated calcium carbonate, aluminosilicate and zeolite are seen as the most promising alternative pigments for silica (Klass 2007, Malla and Devisetti 2005, Vikman and Vuorinen 2004b, Cawthorne *et al.* 2003, Gane 2001). The most common binder used in inkjet coatings is polyvinyl alcohol (PVOH). This choice is due to the fact that it is one of the few binders providing sufficient surface strength for the adhesion of fine high specific surface area pigments. The binding strength of PVOH depends on the degree of polymerization. Modified PVOH has also been utilized: carboxylic, sulphonic-, acryl amide-, cationic- and silicone-modified PVOH (Hara 2006, Mowiol 2003). The use of various types of pigments in the inkjet area has enabled the use of some other binders, like polyvinyl pyrrolidone, polyacrylic acid, poly-acrylamide, methylcellulose, cellulose derivatives, gelatin, polyvinyl acetate latex, vinyl acetate ethylene and cationic starch (Nilsson and Fogden 2008, Hara 2006, Malla and Devisetti 2005, Yip *et al.* 2003, Glittenberg and Voigt 2001, Morea-Swift and Jones 2000, Khoultchaev and Graczyk 1999, Lavery and Provost 1997).

Anionic inks are widely used in inkjet applications (Glittenberg and Voigt 2001, Pond 2000). So, a cationic charge of the coating layer components is understood to accelerate the fixing of the colorant part of the ink to the top layer of the coating structure. The cationic charge of the coating layer is usually produced by adding a few percent of poly(diallyl dimethyl ammonium chloride) (polyDADMAC) into the coating colour (Svanholm 2007, Malla and Devisetti 2005, Vikman and Vuorinen 2004b, Morea-Swift and Jones 2000), but other chemical compounds have also been considered for use (von Raven et al. 1988). Further, the pH of the coating layer affects the ionic interactions (Kallio *et al.* 2006, Boisevert *et al.* 2003). Morea-Swift and Jones (Morea-Swift and Jones 2000) and Hamada and Bousfield (Hamada and Bousfield 2009) indicated that the dyes can also be coagulated on the surface, though this method is not widely used but rather applied to pigmented inks by flocculating physically using soluble divalent metal salt, e.g. calcium or magnesium chloride (Varnell 2001).

The interactions between the ink and the substrate depend highly on the ink type used. In the ink setting process, there are different ink-substrate interactions occurring, such as wetting, capillary flow, colorant and vehicle separation, adsorption, diffusion, ink colorant fixing, polymerization and drying (Kettle *et al.* 2010, Yip *et al.* 2003, von Bahr *et al.* 2000, Agbezuge and Gooray 1991). These interactions have a direct effect upon the print quality formation, for example the penetration depth of the colorant affects the print density and print-through, and the ink spreading on/in the paper surface affects the ink colour mixing tendency and bleeding properties. In the optimal ink imbibition condition, the colorant part of the ink adheres to the top layer of the coating, whilst the solvent part (ink vehicle) penetrates deeper into the structure before finally evaporating/drying out of the structure. Thus, during the ink setting there exist many concurrent phenomena both related to the ink colorant fixing and to the vehicle movement.

#### 1.2 Objectives

The first objective of this thesis is to clarify the role of *diffusion*. This is studied in particular during dye-based ink imbibition into model coating structures and components. Due to its increasing popularity as a cost effective alternative to silica pigment, the model structures are based on calcium carbonate coating pigments. Diffusion occurs wherever an interface or concentration gradient is present. Such interfaces can be phase boundaries of the same material, or contacts between materials. Specific cases relevant to the passage of liquid through a porous structure are the liquid-vapour, liquid-solid and liquid-polymer interfaces. Whilst diffusion is generally considered as either a precursor to subsequent mass transport, for example wetting and capillarity, or a progressive surface adsorption process, the interaction of diffusing liquid molecules with polymers is generally overlooked in respect to it being a mechanism for local mass transport. The diffusion of significant volume in the coating structure is exemplified by the use of various polyvinyl alcohols as "diffusion driving" (water diffusive) binders. Contrast is then drawn by comparison to a styrene acrylic latex, chosen as a "less water diffusive" (almost non water-interacting) binder. The behaviours of the studied binders are connected to the different pore structures (porosity and permeability) of the coatings, the polarity of ink vehicle and the ionic charge of the coating, especially its top layer. The research problem is approached by studying the physical properties and ionic charge of the coating structures, and their effects on the inkjet ink penetration by using several absorption measuring methods: these specifically being a capacitance-based measurement (Clara), a microbalance and thin layer chromatography. The final high-speed inkjet print quality was then correlated with the analysed coating layer properties.

The second objective is to determine the relevant *timescales of the various interactions* active during the imbibition of inkjet ink, especially short timescale phenomena. This timescale span is important to define in order to identify the relevance of the various mechanisms in practice, and crucial in deciding the role of diffusion. During this evaluation, the effect of coating layer thickness on the ink penetration was also taken into account, once again determined by capacitance change and mass balance.

#### 1.3 Hypotheses and outline of the work

The main interest in this thesis is concentrated on the physical properties of the coating layer, their effect on network capillary absorption and surface adsorption phenomena, and the role of diffusion during inkjet ink imbibition. The method of study adopts measurements employing model coating layers with known compositions.

The chemical as well as physical properties like permeability, connectivity and porosity of the coating layer control the imbibition of high-speed inkjet ink and the final location of colorant in the coating layer. The structure of the coating layer dominates where and how quickly the inkjet ink penetrates into the layer. However, the coating structural parameters controlling absorption are very complex. For example, a high void volume, permeable structure enables sufficient penetration of inkjet ink into the structure and thus less inter colour bleeding problems, but at the same time the colorant can penetrate too deeply into the structure and the print density as a result decreases and the print-through problem can appear. Thus, besides the structural properties, the ionic interaction between coating components and the dye-based ink colorant is needed to control the final fixing of the colorant. The surface must have suitable chemical groups which locate in the top layer of the coating structure and the surface area concentration of these groups is crucial.

The role of binder and/or additives in the coating colour is two-fold: affecting the coating structure established by the coating pigment packing and providing a significant portion of the chemical properties of the coating layer in addition to those brought by the coating pigment surface and the polymer species associated with it. The binders also affect the capillary phenomenon and the colorant fixing. The effect of diffusion into the binder matrix, and thus the binder swelling, is generally assumed to have only a slight, or no, role to play at the shortest timescales. However, in this thesis it is proposed that this diffusion plays an important role in inkjet ink imbibition into inkjet coating structures on both the second timescale and even at the shortest microsecond timescale due to its combination with certain pigment structures. The diffusion of ink vehicle and colorant on/into the binder and additive polymer structures starts immediately from the ink droplet arriving at the coating surface and it affects the ink penetration speed in the coating layers. Quite often it is postulated that after about 10 seconds from the ink arrival on the surface, the ink vehicle diffuses into the hydrophilic binder network and the swelling tendency of binders becomes more important (Kumaki and Nii 2010, Hodge et al. 1996). However, this is countered by the fact that, in the case of hydrophilic binders and surface polymers, the swelling in the coating layer decreases the amount of the smallest pores and therefore the ink penetration slows down. In addition, the binder swelling reduces the connectivity of the coating layer. The main role of additives in inkjet coatings is to fix the colorant. However, cationic additives in the coating colours can also influence the formation of the coating layer structure.

The hypotheses to be considered are based on the phenomena described in Figure 1, and in particular the competing timescales occurring.



Figure 1. The presumed interaction phenomena in the inkjet ink setting process and their relevant onset timescales (Kettle *et al.* 2010).

*Hypothesis I* – inter molecular diffusion of the liquid phase of inkjet ink into polymers acts on a sufficiently fast timescale and in sufficient volume to compete with the permeation of ink through coating structures.

*Hypothesis II* – inter molecular diffusion of the liquid phase of inkjet ink into polymers, acting as a colorant carrier, is a competing mechanism to the surface adsorption of ink dye.

*Hypothesis III* – the verity of Hypotheses I and II can be used to design porous coating structures, based on discretely bimodal pore size distributions, using binder and surface charge distribution characteristics to provide rapid fixing of ink colorant optimally close to the coating surface.

In illustrating the timescale selection consideration is given to the positioning of the absorbent binder and surface charge in relation to the pore structure, i.e. when considering porous particulate coating pigments. Such pigments exhibit internal pores (intra-particle) and pores between the particles (inter-particle). The intra-particle pores are designed to be within the nanometre size range (< 100 nm), providing capillarity, whereas the inter-particle pores are larger and interconnected (showing high connectivity) to provide sufficient permeability to allow effective access to the nanopores. Such a structure has a discretely bimodal pore size distribution with its respective parts referring to these intra and inter-particle pore types (Ridgway and Gane 2005). Due to the capillary dynamic during coating drying, soluble binder is drawn into the intra-particle pores, and its distribution is preferentially within these high surface nanopores forming part of the discretely bimodal pore structure. Thus, it is exposed by way of its position to the short time-

scale established interface with the ink vehicle, and, if absorbent to that vehicle by interpolymer diffusion, will take part in, and compete with, the shortest timescale phenomena.

Table 1 shows the main points in respect to the properties of inks and coating layers that affect the inkjet ink imbibition. A deeper study of the variables in a wide range of dye-based ink compositions is considered out of the scope of this study, but the generalities of ink component behaviour nonetheless satisfy the needs of the investigation in hand. The hypotheses of this thesis are therefore able to be challenged based upon combining the experimental observations made and the mechanisms found in the literature regarding the coating component-ink interactions utilized in Figure 1 and Table 1.

Table 1. Suggested major ink and coating layer properties that affect	the interaction
phenomena in the high-speed inkjet ink (dye- and pigment-based) se	etting process.

Interaction phe- nomena during inkjet ink imbibition	Ink	Coating layer		
Wetting	Impact speed Surface tension Viscosity Density	Topography Surface energy		
Capillary flow	Surface tension Viscosity Density Surfactants Vapour diffusion Pre-wetting At high humidity pore condensation	Surface energy Polarity Average pore diameter and pore size distribution Configuration of pores Type of binder and additive		
Differential separa- tion of colorant and solvent	Surface tension Viscosity Colorant type Colorant charge Ink type	Surface energy Void volume Average pore diameter and tortuosity Chemical groups (charge)		
Adsorption	Surface tension Viscosity Differential surface energies Molecular weight <i>M</i> <sub>w</sub> Colorant charge Concentration gradient Solubility/precipitation Nearest neighbour repulsion	Surface area Void volume Average pore diameter and arrangement Surface chemistry Temperature Moisture content Ionic charge		
Diffusion	Surface tension Viscosity Molecular weight ( <i>M</i> <sub>w</sub> )/size of species Concentration differential	Surface energy Temperature Pore connectivity Tortuosity Binder swelling		
Drying (= evaporation)	Solvents of ink	Void volume Average pore diameter and pore size distribution Tortuosity Temperature Binder type Thermal conductivity		

The thesis summarizes the findings of seven papers: Paper I concentrates on the pigment particle size and structure and how these influence the forming of the coating layer structure. At the end of the paper, it is reported how the coated papers are printed with a high-speed inkjet press and the print quality is analyzed. In Paper II, different contents of swelling (polyvinyl alcohol, PVOH) and non-swelling (styrene acrylic latex, SA) binder with one modified calcium carbonate are used. The paper is concentrated on the penetration of dye-based ink through the coated papers containing the different binder types and content, and the timescales observed during the inkjet ink penetration. The third paper (Paper III) illustrates how the thickness of coating layers affects the ink penetration, and the coatings derived from inkjet and offset coated pigments are compared in respect to the observed penetration of aqueous-based dye. This is then linked to the final ink mixing on the printing press. The penetration mechanisms are further explored using coatings on plastic film. Paper IV reports work concentrated on the binders, after film-forming, to identify and quantify their interactive properties with the ink vehicle and dyestuff. The cationic and anionic dye-based ink absorption into the three different polyvinyl alcohols and the styrene acrylic latex are studied by combining with applied cationic and anionic additives. Paper V illustrates the effect of coating structure on the liquid and colorant movement when the controlled variables in coating layers are the ionic charge of dispersing agent and the swelling/nonswelling of binder. The same coating structures, as well as two others adopting structured pigments, together with PVOH or SA latex binder are used in Paper VI, where the effect of liquid polarity vs. coating layer structure and hydrophilicity is researched. The seventh paper (Paper VII) concentrates on the absorption and/or adsorption of the different coating components, the effect of cationic additive application onto the top of the coating layer and its influence on the print quality. Figure 2 shows the interest focus of each paper.



**Figure 2.** A structural illustration of the individual study focus interests, and in which papers they have been explored more closely. The paper, in which there has been concentration on a certain item, has been pointed out with the respective Roman numbers in brackets.

## 2. Literature review

In the inkjet ink setting process, we are confronted with different phenomena, like wetting, capillary flow, colorant and vehicle separation, adsorption, diffusion and ink colorant fixing, as the section 1.3 "Hypotheses and outline of the work" emphasized. Kettle *et al.* (Kettle *et al.* 2010) summarizes the knowledge of the inkjet ink droplet setting on the surfaces as well as its imbibition into the structure, and the contribution to that publication from the literature study for this thesis is summarised here. In this chapter, the study concentrates on the most common inkjet inks found in the area of high-speed inkjet printing and how the coating layer properties will affect the imbibition of this class of inks.

#### 2.1 Properties of inkjet inks

The most important components in inkjet inks are the colorant and solvent/diluent. The colorant's fixing and movement on the surface of print media during the ink setting process determines the final print quality formation. The diluent in the ink vehicle is a carrier of colorant and it affects above all the ink viscosity, the droplet formation properties and the final colorant setting. The most common diluents in inkjet inks are water and/or various solvents. Water is used in desktop printers for the home and office market. The ink contains usually many other compounds as additives, which act as surfactants, solubilizers, rheology modifiers, polymer resins, humectants, carriers etc. Table 2 illustrates the main purposes of the ink components and their typical amount found in inks.

The properties of ink affect strongly the ink setting process and the final drying. The most common ink types in inkjet printing are dye-based and pigment-based inks. A dye is a colorant that is completely dissolved in the carrier fluid, and a pigment consists of solid colorant particles in the carrier fluid. In addition, the inks can be classified as aqueous, solvent-based, oil-based, UV-curable and hot-melt/phase change inks (Svanholm 2007).

Ink component	Purpose	Amount in the ink, wt-%
Colorant	Gives the ink its primary function as light filter – absorbing light of a particular wavelength band	2–8
Carrier fluid	Dissolves or suspends the colorant	35–80
Surfactant	Lowers the surface tension of the ink to promote wetting	0.1–2.0
Humectant	Inhibits evaporation (miscible with the carrier fluid) and assists to prevent inkjet nozzle build-up	10–30
Penetrant	Promotes penetration of the ink into the paper structure for the purpose of accelerating drying	1–5
Dye solubilizer	Promotes dye solubility in the primary carrier fluid	2–5
Anticockle additives	Reduces the interaction with paper fibres, which otherwise leads to paper cockle and curl	20–50

Table 2. Main components of inkjet inks and their purposes (Pond 2000).

Agbezuge and Gooray (Agbezuge and Gooray 1991) showed that, after the waterbased ink droplet impact, there exists a wetting delay. They used commercial thermal inkjet print heads, where the ink droplet was produced by temperature change in the nozzle. As previously described, at droplet impact the most important variables are ink rheological properties, initial shape and volume, surface tension and viscosity. During the wetting delay, the droplet settles on the surface without much spreading or penetration. Equilibrium contact angle is established so that cohesive forces in the droplet overcome the adhesive forces between droplet and paper, then the paper starts to absorb the liquid volume. The effective driving parameters for absorption related to ink are surface tension, viscosity, contact angle, temperature, and volume, and, in the case of pigment inks, solids content. After this stage, there is droplet spreading and penetration, where liquid and vapour phase diffusion occur. The most important ink properties at this stage are spot shape, volume, viscosity and vapour pressure.

The differences in ink viscosity and surface tension can affect the ink setting process (Rousu *et al.* 2000, Desie *et al.* 2004a). Inkjet inks have very low viscosities, typically < 10 mPas (Girard *et al.* 2006). However, the meaning of viscosity or

its change during the inkjet ink setting process is unclear as it depends on composition as a function of time in the various separation steps.

The demands placed on inkjet inks are shortly described in Figure 3. There are many demands for inks in respect to the printing head and nozzle design as well as from the final print quality side.



Figure 3. General description of the demands on inkjet inks (Kang 1991).

#### 2.1.1 Water-based soluble inks (dye)

Water-based soluble inks consist of water as diluent and soluble compounds, dyes, as a colorant forming part. Nowadays, there exist different types of dyes on the market. The dyes in inkjet inks can be classified similarly to those found in the textile industry (Sundquist 1985). Water-based soluble dyes are used both in the home and office area, and in high-speed inkjet printing. The classification of color-

ants based on Colour Index International is introduced in Figure 4 and the chemical structure of dyes in Table 3.

1.	Nitroso dyes	10.	Acridine dyes	19.	AminoketonYe dyes
2.	Nitro dyes	11.	Quinoline dyes	20.	Hydroxyketone dyes
3.	Azo dyes	12.	Methionine and	21.	Anthraquinone dyes
4.	Azo based dyes		polymethionine dyes	22.	Indigoidic dyes
5.	Stilbene dyes	13.	Thiazol dyes	23.	Phthalocyanine dyes
6.	Carotene dyes	14.	Indamine and	24.	Organic natural dyes
7.	Diphenylmethane dyes		indoprienoi dyes	25.	Oxidized base dyes
8.	3 Triacrylmethane dyes	15.	Azine dyes	26.	Inorganic pigments
0	Vanthana dyaa	16.	Oxathiane dyes	_0.	inorganio pignionio
9.	Adminene uyes	17.	Thiazine dyes		
		18.	Sulphur dyes		

Figure 4. Classification of colorants based on Colour Index (Sundquist 1985, Colour Index 2011).

**Table 3.** The chemical structure of colorants of different classes (Sundquist 1985,Shore 2011). The chemical structure refers to Figure 4.

Colour class	Chemical structure
Acid dyes (anionic dyes)	1, 2, 3, 8, 9, 15, 21
Azo developer dyes	4
Alkaline colours (cationic dyes)	3, 7, 8, 9, 10, 12, 13, 16, 21
Direct dyes	3, 5, 13, 16, 23
Dispersion dyes	2, 3, 12, 21
Optical brighteners	5
Mordant	3, 21
Oxidation based dyes	25
Pigments	3, 6, 21, 22, 23, 26
Reaction dyes	3, 21, 23
Sulphur dyes	18
Vat dyes	21, 22
Food dyes	24, 21, 22

Typical dyes in inkjet inks are water soluble acid dyes, direct dyes, modified direct dyes, reactive dyes and poorly water soluble dispersion dyes (Lavery and Provost 1997).

Acid dyes are low molecular weight anionic dyes. The small molecular weight enables the easy movement of dyes deeper into the porous structure of the coating layer and/or fibre network. The molecular structure of acid dyes is azo, antraquinone and triacrylicmethane dyes, and they have one or several sulphonic acid groups. Figure 5 shows an example of acid dye. 1:1 and 1:2 metal complex dyes are also included in the acid dyes. These complexes have metal atoms in the molecular structure (trivalent Co and Cr, and divalent Ni and Cu). The fixing to the fibres/coating structure happens usually with ionic bonds, for example with the ammonium groups and the sulphonic groups of dyes. There can also be hydrogen bonds and van der Waals interactions (Sundquist 1985). In section 2.2.6 "Colorant fixing" the binding mechanisms are described more closely.

Direct dyes have higher molecular weight than acid dyes and therefore they are larger. They have planar aromatic structures. Direct dyes have also better affinity for cellulose fibres and good water-solubility. The brightness of these colorants is not as high as the brightness of acid dyes, but they have better water and light fastness properties (Lavery and Provost 1997). Figure 5 illustrates an example of direct dyes. The direct dyes fix to the fibres/coating structure with ionic and hydrogen bonds and van der Waals interactions. The majority of the direct dyes belong to the family of dis, tris and polyazo dyes (Sundquist 1985).

Modified direct dyes contain added chemical functional groups to improve the interactions between colorants and fibres. The first generation of dyes had sulphonic acid groups. In the second generation dyes, the sulphonic acid groups had become replaced with carboxylic acid groups. These dyes have good solubility in water under alkaline conditions, but they flocculate at lower pH, for example advantageously on the top of the paper surface. The third generation of modified direct dyes have functional groups in their chromophores. These functional groups can improve, for example, water fastness of the printed surface (Lavery and Provost 1997). In Figure 5, the modified direct dyes of all generations are introduced.

Reactive dyes are also water-soluble dyes. There exists a covalent bond between the dye and the fibre/coating structure, and therefore the dye has very good affinity to the surface. However, the colorant fixing usually requires a treatment at elevated temperature or pH, which is quite a demanding requirement for use in inkjet papers (Sundquist 1985, Lavery and Provost 1997).

Dispersion dyes are insoluble in water, but they are solvent-soluble. The dispersion dyes can be used in colloidal liquids such as latex particles, emulsions, microemulsions or surface active agents, forming aggregates (Kang 1991). They are used for hydrophobic substrates, such as polyester (Lavery and Provost 1997). The print quality has good water fastness but the dye can easily block the print engine nozzles.



Modified direct dyes

**Figure 5.** Examples of acid dyes, direct dyes and modified direct dyes (Lavery and Provost 1997).

#### 2.1.2 Water-based pigment inks

Water-based pigment inks have a diluent part and a colorant part, as in the case of the water-based soluble inks. The colorant part in this case is insoluble pigment. The pigment colorants are a combination of about a thousand molecules, and they are much larger than their dye counterparts, usually less than 100 nm (Bermel and Bugner 1999). The pigment colorants have a platy like structure which have a bound-form remaining as an insoluble crystal structure. The colorant molecule itself has usually similar structure, such as in the case of soluble monomolecular dyes. These pigment inks are used in the dispersion form. The pigments are bound to the paper surface with binders.

The larger size of colour pigments gives a better light fastness of the printed surface (Vikman and Vuorinen 2004b). The rub resistance of the pigment-based inks has been problematic. By a careful binder selection for the inks, the rub-off problem can be reduced. On the other hand, the colorant pigments can form a

rough printed surface (Desie *et al.* 2004a) which causes a non-uniformity in light reflection. Moreover, the colour gamut can be smaller than that of the dyes. However, the cyan, magenta and yellow inks containing small pigment particles (under 50 nm) have significantly greater colour gamut than inks with larger pigment size (Bermel and Bugner 1999).

Red pigments can be, for example, azo pigments or 2,9-dimethylquinacridone pigments. The yellow colours are produced with benzimidazolone or pyridone (Bauer *et al.* 1998). The most common black pigment in inkjet inks is carbon black. The stability of carbon black requires polymeric surfactants which can be problematic in the inkjet nozzle.

All the abovementioned colorants are organic compounds. Inorganic compounds are rarely used, but may include, for example, titanium dioxide.

Desie *et al.* (Desie *et al.* 2004a) showed that the phenomena of the wetting of pigment inks and dye-based inks are very similar, when the droplet volume was 70 pl. However, the absorption behaviour of the inks is different. The pigments of pigment-based ink were shown to form aggregates on the coating layer, and the droplets do not mix together at any stage, even in the situation where the impact delay between the droplets was only 100 ms. They noticed that the pigment ink's dot diameter remains much more constant over time during the wicking process than that of dye-based inks, and, therefore, at the beginning of the pigment cake formation, the Darcy model explains better the ink absorption process (in section 2.2.2 "Liquid penetration into porous coating layers"), in which the controlling permeability is that of the concentrating ink pigment layer. Finally, the pigment particles, with the polymer blend, form a filter cake, and a barrier layer develops, thereby limiting the penetration of carrier liquid into the coating structure. Then the diffusion phenomenon becomes more dominating, and Fick's law describes this latter situation better.

The drying time of aqueous-based inks (70 pl droplet volume) can be longer with pigment inks than dye-based inks on a porous substrate (Desie *et al.* 2004b). The filter cake formation limits water movement into the substrate. The filter cake formation was also detected with solvent-based pigment inks on a microporous receiver in the study of Desie *et al.* (Desie *et al.* 2004b). The composition of the solvent-based inks affects the drying time and it can cause even faster ink penetration than that of the aqueous-based inks. They used "piezo pigment eco-solvent ink" (from Mutoh) that had quite similar viscosity to "piezo dye ink" (water-based). However, the surface tension was somewhat lower, 30.4 mNm<sup>-1</sup> with the solvent-based pigment inks had a very long drying time. By increasing the substrate temperature, the drying time could be shortened. The reason behind this is that the diffusion into the vinyl, as used in the substrate, increases (Desie *et al.* 2004b).

#### 2.1.3 UV-curable inks

UV inkjet inks are inks that cure under the influence of ultraviolet light. UV-curable inks consist of monomer, oligomer, photoinitiators, colorant pigment and additives. UV-curable inkjet ink is a rapidly developing technology, and these inks can also be used in the area of high-speed inkjet printing.

UV inkjet inks can be classified into two different types of formulation, depending on the mechanism of photoinitiation, free radical or cationic curing mechanisms. In the conventional free radical curing, the photoinitiators absorb UV-light and form free radicals to initiate the polymerization of monomers and oligomers. This happens immediately under the influence of UV-light, and the result is that the solvent does not penetrate into the substrate (Svanholm 2007). The reaction happens only if the photoinitiators are matched to the spectral output of the lamp. The cationic photo-induced polymerization is a ring opening polymerization process of epoxies or oxetanes initiated by protonic or Lewis acids. Cationic polymerization is a "living" process. The UV exposure starts the cationic polymerization process and it stops once all of the components have been consumed. This process can last up to 24 h (Biry and Dietliker 2006). The roles played by the ink components are:

- The monomers in the UV-curable inks are typically low-viscosity acrylates, like acryl esters, that function as diluents, cross-linkers and performanceproperty enhancers. They affect the viscosity of the ink, enhance cure speed and improve adhesion to the printed surface. The molecular weight of monomers is lower than oligomers. The viscosity of monomers varies from 5 mPas to 25 000 mPas (Klang and Balcerski 2002).
- Oligomers can have acrylated urethanes, epoxies, polyesters and acrylics. Their amount in the ink is quite low, and they mainly influence the film forming properties and pigment dispersion. Their molecular weight is 1 000–30 000 (Biry and Dietliker 2006). Oligomers determine the physical property formation of the printed surface.
- The UV-curing free radical-generating photoinitiator is selected based on the desired cure speed and the pigments used. The most common photoinitiators are mono- and di-functional monomers. They can be, for example, benzophenone, benzyl dimethyl ketal and 2-hydroxy-2-methyl-1phenyl-1-propanone (Klang and Balcerski 2002).
- The pigments produce the colours, and additives affect the ink flow, levelling, wetting, cure speed and adhesion (Klang and Balcerski 2002).

100 % of UV-curable inkjet inks are today working in drop-on-demand print heads. However, conventional UV inks have too high viscosity for the typical inkjet, and so this has been specifically adjusted. The viscosity requirement for workable UV inkjet inks is commonly about 10 mPas (Klang and Balcerski 2002). This is achieved by using lower functionality acrylates than in conventional UV inks. The increase of jetting temperature aids also to lower the viscosity of the inks. The photoinitiators, nonetheless, are similar to those used in conventional UV inks.

In the case of UV-curable inks (40 pl droplet volume), there exists only spreading on the substrate and very little absorption or capillary wicking (Desie *et al.* 2004b). The spreading continues until the equilibrium stage of the droplet has been reached or the UV-curing process has stopped the spreading. Desie *et al.* (Desie *et al.* 2004b) divided the UV ink setting process into three phases. In the beginning there is initial inertial spreading, after that the rearrangement of the droplet geometry, and then the capillary (surface wetting) spreading. The most important property in capillary spreading is the surface tension of ink and the surface energy of substrate. If the ink has much lower surface tension than the surface energy of the substrate, spontaneous spreading continues in a regime of perfect wetting (Desie *et al.* 2004b). If the difference between ink and substrate is small, then the spreading occurs until the equilibrium contact angle has been reached (Desie *et al.* 2004b).

#### 2.2 The wetting and imbibition of inkjet ink

In both the dye-based as well as pigment-based inkjet ink technologies the uptake of liquid (imbibition) is required to provide drying of the print and runnability in the press and post-press handling. The target is to attain sufficient ink vehicle penetration into the substrate with the colorant remaining in the top layer of the substrate to provide good image quality and high print density. If the colorant is transported too deeply into the structure, the print density will decrease and the print-through increase. However, a complete holdout of colorant on the outer surface of the substrate provides no physical or chemically bonded protection for the print, such that the print has poor rub-resistance. To achieve an optimal ink transfer process it is necessary to understand the control parameters involved in the many different interaction phenomena. At any given moment in the imbibition process there are usually one or two dominating phenomena, while the others at that instant have a less important role, manifesting their importance on a prior or subsequent timescale. Kettle et al. (Kettle et al. 2010) summarized different ink-substrate interactions such as wetting, capillary flow, colorant and solvent separation, adsorption, diffusion, ink colorant fixing, polymerization (if colorant requires this) and drying.

At the first stage, the inkjet ink droplet arrives onto the paper surface and wets it. The inertia of the droplet affects the ink movement at the substrate surface, initiating forced wetting and top surface pore structure penetration (von Bahr *et al.* 2000, Schoelkopf *et al.* 2000, Agbezuge and Gooray 1991). The droplet settles into the roughness volume of the surface and begins to spread in the *xy*-plane on the surface depending on the surface tension of ink and the surface energy of the structure surface (Desie and Van Roost 2006, Girard *et al.* 2006, von Bahr *et al.* 2000, Agbezuge and Gooray 1991). At the same time the capillary flow into the pore network structure begins, and it competes with the spreading action. The capillary force becomes a dominating phenomenon after the droplet arrives at the surface, and it forces the ink vehicle and mobile components into the structure.
Capillary penetration starts typically after about 0.1 ms from the droplet arriving (Schoelkopf et al. 2000, Ridgway and Gane 2002). The chemical properties of the paper surface and inkjet ink strongly affect the capillary flow, and the surfactants in the ink and the coating layer surfaces play an important role here, on the one hand ensuring wetting, but on the other hand frequently exerting a delay whilst the surfactant orients to favour the contact with the polar ink vehicle (water) (Desie and van Roost 2006, Pan and Yang 1996). After a further millisecond, the separation of the ink colorant and vehicle starts and the capillary penetration continues strongly. The most important ink properties at this stage are thought to be the viscosity and surface tension (von Bahr et al. 2000). The porosity of the substrate has an effect on the separation of ink vehicle from the colorant, in that the surface area exposed within the pore structure defines the adsorption capacity for colorant at a given interaction potential (Desie et al. 2004a, Desie and van Roost 2006, von Bahr et al. 2000). After about one second from the droplet arriving, the significance of adsorption onto the coating structure internal surface increases. In parallel, diffusion needs to be considered, which is often thought classically to be only a slow phenomenon. However, in the case of contact with high surface area species, the length of diffusion reduces to the nanoscale, and, over such short distances, molecular motion is rapid. It is this often neglected feature of the imbibition process that is one of the main focus points of this thesis. Finally, the ink dries, a process that can last hours, depending on ink type.

There are also many varieties of inkjet inks, which display other or additional ink setting mechanisms, for example UV-curable inks, that adopt a UV-initiated polymerization mechanism to dry. Unlike nanoscale diffusion, polymerization in practice is a slow phenomenon, and the final drying can take the order of a hundred seconds to complete, although initial polymerization of the upper ink layer may begin within milliseconds. Incomplete polymerization during the initial exposure to UV light relates to the poor short wavelength penetration properties of UV light and the construction of printers in which a dual exposure is often employed.

#### 2.2.1 Wetting of a surface

When the inkjet ink droplet arrives onto the paper surface the primary spreading of the droplet takes place under the influence of the inertia and surface forces. The dynamic spreading of the droplet is usually simulated by studying the contact angle of the moving wetting line, the dynamic contact angle,  $\theta_d$ . In the ideal case of liquid wetting, there is a balance of surface tension forces according to the Young-Dupré equation (equation (1)), in which the equilibrium contact angle ( $\theta_{eq}$ ) has a connection to the three interphase surface tensions (Young 1805, von Bahr *et al.* 2000, Girard *et al.* 2006)

$$\gamma_{\rm ls} + \gamma_{\rm lv} \cos\theta_{\rm eq} = \gamma_{\rm sv} \tag{1}$$

where  $\gamma_{sv}$  is the surface tension between the solid surface and vapour interface,  $\gamma_{ls}$  is the surface tension between the solid surface and liquid interface,  $\gamma_{lv}$  is the surface tension between the liquid and vapour interface (Figure 6).



Figure 6. A schematic figure of the ink droplet on the coated paper surface.

When the inkjet droplet arrives at the paper surface, it fills the roughness volume of the surface and begins to spread in the *xy*-planar direction on the surface (von Bahr *et al.* 2003, Desie and van Roost 2006, Girard *et al.* 2006). In the contact angle measurement of coated paper, the roughness of the surface, applied surface modifiers, such as dispersants and tensides, coating pigment crystallite orientation, and adsorbed components from the atmosphere and surroundings all can have an effect on the contact angle identification (Gane *et al.* 1999).

The gravimetric forces can also be involved in the motion of the droplet, for example, in cases where centrifugal forces or large volumes of liquid are involved or when accelerating the droplet before impact. Bond number or Eötvös number (Bo) is a dimensionless number expressing the connection between gravitational acceleration, g, and surface tension forces.

$$Bo = \frac{\rho g r^2}{\gamma_{1v}} \tag{2}$$

where  $\rho$  is the density of fluid and *r* the droplet radius. A high Bond number indicates that the surface tension between the liquid phase, I, and the vapour phase, V, has quite a small effect on the system compared to the gravitational interaction. A low Bond number (typically less than one) indicates that surface tension dominates the process.

In the case of a droplet striking the paper surface and being driven into spreading, the Weber number (We) is frequently relevant

$$We = \frac{\rho v^2 l}{\gamma_{\rm lv}} \tag{3}$$

where *l* is the characteristic length of the fluid flow, and v the velocity of the droplet. The Weber number is also a dimensionless number describing the fluid kinetic energy flow in respect to its surface tension forces.

Von Bahr *et al.* (von Bahr *et al.* 2003) assumed that the kinetic force caused by the droplet hitting the paper surface transforms into surface kinetic energy. It relates to the formation of the liquid-vapour interface (<sub>IV</sub>) and partly becomes dissipated due to viscous forces. The droplet oscillates for a while, and after that it settles down on the surface reaching the equilibrium stage and the contact angle,  $\theta_{eq}$ . The contact angle,  $\theta$ , of the sessile droplet with volume, *V*, follows equation (4)

$$\theta = \theta_{eq} + \epsilon \exp\left(-\frac{\eta t}{\rho V^{2/3}}\right) \cos\left[\left(\left(\frac{\gamma_{lv}}{\rho V}\right) - \left(\frac{\eta^2}{\rho^2 V^{4/3}}\right)\right)^{1/2} t\right]$$
(4)

where  $\epsilon$  is the amplitude of oscillation,  $\eta$  dynamic viscosity of liquid,  $\rho$  density of liquid,  $\eta_v$  surface tension of liquid and *t* time as oscillations damp down.

Equation (4) shows that the viscosity of the ink affects the oscillation, and as the viscosity increases the quicker the droplet settles. The other interesting thing is that the amplitude of oscillations is proportional to the square root of surface tension and decreases with time. Von Bahr *et al.* (von Bahr *et al.* 2003) showed that there is a critical droplet size, *d*, below which there occurs no oscillation, which might have a meaningful effect in the case of a small inkjet droplet

$$d \approx \left(\frac{\eta^2}{\rho \gamma_{\rm lv}}\right) \tag{5}$$

If the values of aqueous-based inkjet ink ( $\eta = 2^*10^{-3}$  Pas,  $\rho = 1.05^*10^3$  kgm<sup>-3</sup> and  $\gamma_{V} = 35^*10^{-3}$  Nm<sup>-1</sup>) are taken into account in equation (5), the calculated diameter of the droplet is 110 nm. In inkjet printers, the smallest volume of droplets is today near 2 pl (picolitres) and this corresponds to a droplet diameter of 16 µm. Therefore, it can be concluded that the oscillation has a meaningful influence during the initial droplet contact process.

Von Bahr *et al.* (von Bahr *et al.* 2003) concluded that a droplet oscillation period lasts about 8 ms. In their study, the droplet volume was large,  $1-5 \mu$ l. However, they measured that the damping occurs much faster than predicted by equation (3). They explained this difference by damping factors such as the contact line friction, internal vortices, and the viscous dissipation in air.

#### 2.2.2 Liquid penetration into porous coating layers

The dynamic spreading and absorption of the inkjet ink droplets on the porous structure has theoretically been approached by using a hydrodynamic model (Alleborn and Raszillier 2004, Desie *et al.* 2004a, Josserand and Zaleski 2003, Gane

2001, von Bahr *et al.* 2000) or a molecular kinetic model (Marmur 2003, von Bahr *et al.* 2000, Hayes and Ralston 1994) as well as their combinations (Schoelkopf *et al.* 2002, Sorbie *et al.* 1995). The hydrodynamic model assumes that the loss of energy during the droplet imbibition is based on the viscous drag within the spreading droplet, whereas in the molecular kinetic model the energy lost derives from the intermolecular interactions between the solid phase and the liquid phase. There are also studies (Desie and van Roost 2006, Tiberg *et al.* 2000), where the effect of diffusion has been combined with these models.

The hydrodynamic model is based on the Navier-Stokes equation (6), where the droplet of the inkjet ink is assumed to be an incompressible Newtonian fluid that has dynamic viscosity,  $\mu$ , and density,  $\rho$ , (Josserand and Zaleski 2003, Alleborn and Raszillier 2004). The equation describing liquid motion assumes that the fluid stress is the sum of terms relating to the pressure and viscosity controlled diffusivity,  $-\nabla p + \mu \nabla^2 \vec{u}$ , and these are combined to act according to Newton's second law,  $\rho \left( \frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u} \right)$ , considering any other externally acting force,

such as gravity.

$$\rho\left(\frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u}\right) = -\nabla p + \mu \nabla^2 \vec{u} + \rho \vec{g}$$
(6)

where,  $\vec{u} = (u, v, w)$  is the three-dimensional flow velocity vector, *t* is the time, *p* is the pressure and  $\vec{g} = (0, 0, -g)$  the vector of gravitational acceleration if the mass of fluid is big enough to warrant considering its action.

Following the wetting of the surface and the start of capillary pressure the droplet imbibition proceeds. The balance between the wetting force of capillaries and the viscous drag determines the rate of progress. As the viscous drag increases in proportion to the length over which the liquid flows within the structure, and to the inverse of the fourth power of the typical equivalent capillary size (Poiseuille effect, equation (7)), there comes a point when the drag equals the wetting force. The Hagen-Poiseuille equation (called also Poiseuille equation) can be derived from the Navier-Stokes equation (6) in cylindrical symmetry, making the assumption that the liquid undergoes steady laminar flow. The Poiseuille equation thus describes the liquid flow rate in a long capillary (longer than its diameter) under the application of pressure,

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{\pi r^4}{8\eta l} \Delta p \tag{7}$$

where dV/dt describes the volume flow rate across a given area of the sample of liquid that has shear viscosity  $\eta$  (defined at the respective shear rate) through the effective capillary pipe of radius *r* and length *l*, representing this area, under the driving pressure difference  $\Delta p$ .

The permeability of a porous structure is linked to the Poiseuille description of flow through a pipe, where the porous structure is described as having an equivalent hydraulic radius as if it were a simple pipe. The term permeability applies to a saturated structure, in which the liquid is forced through the porous medium under a pressure gradient,  $\nabla p$ . It can be described by Darcy's law (Darcy 1856, Yip *et al.* 2003, Alleborn and Raszillier 2004), which can also be derived from the Navier-Stokes equation for constant flow rate ( $\nabla \vec{u} = 0$ ).

$$\vec{u} = -\frac{k}{\eta} \left( \nabla p - \rho \vec{g} \right) \tag{8}$$

If we ignore the action of gravity within a microscopic structure, this reduces to

$$\frac{\mathrm{d}(V/A)}{\mathrm{d}t} = \frac{k\Delta p}{\eta l} \tag{9}$$

where A describes the area of cross-section of the porous sample perpendicular to the linear flow direction. The term k is the permeability of the porous medium with units of length-squared. In inkjet ink setting, 1/k describes the resistance to flow experienced when the wetting front lies deep within the coating structure or when the inertia of the droplet causes penetration into the top layer of the coating.

The Young-Laplace equation (equation (10)) (Young 1805, Ridgway *et al.* 2001, Schoelkopf *et al.* 2000) describes the wetting force,  $\pi r^2 p_c$ , of a liquid that has contact to the walls of a capillary

$$p_{\rm c} = \frac{-2\gamma_{\rm lv}\cos\theta_{\rm eq}}{r} \tag{10}$$

where  $p_c$  is the Laplace capillary pressure, *r* the internal capillary radius,  $\gamma_v$  the interfacial tension at the liquid-vapour interface, and  $\theta_{eq}$  is the equilibrium contact angle (Figure 6).

During inkjet ink imbibition, the liquid phase is transported dynamically in the capillaries, and the position of the liquid meniscus advances with time. At equilibrium flow, the moving position of the wetting meniscus, x(t), in the capillaries can be described by the Lucas-Washburn equation (equation (11)) in which the Young's pressure is balanced with the Hagen-Poisueille flow resistance (Washburn 1921, Desie *et al.* 2004a and 2004b, Marmur 2003, Gane 2001, Ridgway *et al.* 2001, Lundberg *et al.* 2011).

$$x(t) = \left[\frac{r\gamma_{\rm lv}\cos\theta}{2\eta}\right]^{1/2}\sqrt{t}$$
(11)

where  $\theta$  is the dynamic contact angle and x(t) is the horizontal distance of penetrated liquid in the capillary during the time *t*. The Lucas-Washburn equation (11) applies only after equilibrium is reached between the wetting force and the viscous permeability drag. It suggests that the rate of liquid flow at a given time, *t*, in the capillary should be greater when the structure has larger effective radius. Practical studies, for example in the offset printing area (Rousu *et al.* 2000), have shown, however, that smaller radius capillaries will initiate faster absorption and thus will initially fill faster than larger capillaries, which disagrees with the equation of Lucas-Washburn. There are differences between fine and large pores, and there are effects occurring on the short timescale on the pore surfaces and within the pore network that Lucas-Washburn does not capture (Schoelkopf *et al.* 2002, Ridgway *et al.* 2002, Sorbie *et al.* 1995). The flow entry effects into capillaries have been studied in respect to the energy loss equation of Szekely (Sorbie *et al.* 1995). Bosanquet (Bosanquet 1923) considers the relative timescales of inertial wetting and viscous forces during the fluid entry into a cylindrical capillary from a reservoir or supersource of fluid,

$$\frac{\mathrm{d}}{\mathrm{d}t} \left( \pi r^2 \rho x \frac{\mathrm{d}x}{\mathrm{d}t} \right) + 8\pi \eta x \frac{\mathrm{d}x}{\mathrm{d}t} = p_{\mathrm{e}} \pi r^2 + 2\pi r \gamma_{\mathrm{lv}} \cos\theta \tag{12}$$

where  $p_e$  is an external pressure, if applied, at the entrance of the capillary tube. The first term of the equation is the inertial drag, expressed as the rate of change of momentum, and the second is the frictional resistance derived from Poiseuille flow and dependent on the velocity of the meniscus front. Schoelkopf *et al.* (Schoelkopf *et al.* 2000) showed a solution of this equation for short timescale where the external pressure  $p_e$  is set to zero:

$$x = t \sqrt{\frac{2\gamma_{\rm lv}\cos\theta}{r\rho}} \tag{13}$$

When inertia dominates before viscous flow is fully established, i.e. for absorption into pores close to t = 0, equation (13) shows that the finest pores absorb preferentially further and faster. Ridgway *et al.* (Ridgway *et al.* 2002) developed the Bosanquet result by taking account of the shape of meniscus and the recirculation regions behind the edges of the meniscus, applying the dynamic via an algorithm to a wetting front encountering the individual components of a pore network structure. If a network of such fine pores is considered, remembering that fine pores are typically equally as short as their diameter, i.e. too short to establish viscous drag, it can be visualised to show a preferred pathway effectively by-passing the larger pores, or at least limiting the access to them. This has been described by Ridgway *et al.* (Ridgway *et al.* 2001) where they have used the Pore-Cor<sup>1</sup> visualisation. In this pathway, the absorption rate is high and so the passage into the porous medium is defined by the combination of pore sizes within the inertial wetting

<sup>&</sup>lt;sup>1</sup> Por-Core is a software network model developed by the Fluid and Environmental Modelling Group, University of Plymouth, PL4 8AA, UK.

regime (nanopores) and the connecting high volume structure consisting of larger pores which fill more slowly and develop the least permeation resistance. Thus, in relation to inkjet ink imbibition defined by pore structure, the short timescale phenomena in the nano-size capillaries are important in respect to rapid ink vehicle absorption.

#### 2.2.3 Transport by diffusion

The diffusional phenomena, which may occur over the short timescale, are the main interest of this doctoral study. Probably, the most important forms of diffusion taking place during inkjet ink imbibition by the coating structure are (Figure 7) (Radhakrishnan *et al.* 2000, Shaw 1996, Liang *et al.* 1990):

- Bulk diffusion, which means general volumetric motion of the liquid or gas within the coating/deposited layer
- Surface diffusion, where the motion of atoms, molecules and clusters of atoms or molecules follows the surfaces of the solid material
- Knudsen diffusion, when the diffusivity is additionally determined by the size of capillaries instead of by the thermodynamic state of solvents or solutes alone (capillaries with small sizes or very low pressure)
- Osmosis, defined as the spontaneous net movement of water across a semi-permeable membrane from a region of low solute concentration to a region with a high solute concentration, down a water concentration gradient, or, as usually described, up a solute concentration gradient. It is a physical process in which a solvent moves, without input of energy.



**Figure 7.** Diffusion types in inkjet ink transportation: d is pore diameter and  $\lambda$  distance between atoms, molecules, or atomic/molecular clusters. Based on Paper VI (Figure 1).

In this work, a linear relation between the absorbed liquid amount and the square root of time is detected with the results of the microbalance wicking measurement and the capacitance-based device (in Chapter 4). This indicates that the liquid after the first milliseconds proceeds either by equilibrated balance between wetting force and permeation resistance, i.e. a form of the Lucas-Washburn equation, and/or by diffusion, i.e. according to a Fick's Law diffusion response. Fick's first law describes the steady state of diffusion, where the concentration of diffusion volume does not change during time, equation (14). Fick's second law (equation (15) takes account of the concentration within the diffusion volume changing over time.

$$J = -D\frac{\partial c(x,t)}{\partial x} \tag{14}$$

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}$$
(15)

where *J* is the diffusion flux, c(x,t) is the concentration of liquid at position *x* and time *t*. *D* is the diffusion coefficient.

The formal solution to the diffusion equation (15) takes the form of the complementary error function,

$$c(x,t) = c(0,0)erfc\left(\frac{x(t)}{2\sqrt{Dt}}\right)$$
(16)

Usually, the first two terms of the corresponding Taylor series expansion are used.

$$c(x,t) = c(0,0) \left[ 1 - 2 \left( \frac{x(t)}{2\sqrt{Dt\pi}} \right) \right]$$
(17)

A satisfactory working equation for practical purposes, and used in this work to describe mass transport, can be derived dimensionally. The denominator  $x^2$  in equation (15) is proportional to the time *t*, and hence *x* is proportional to  $\sqrt{t}$ . The distance has a correlation to the volume of liquid being transported in the system and thus represents the mass of liquid uptake. Therefore the equation (12) can be written as

$$\frac{m(t)}{t} = D \frac{A \cdot c(x,t)}{x}$$
(18)

where m(t)/t is mass flow rate during the time *t* and *A* area of cross-section where the liquid is taken up by diffusion.

The timescale of diffusion has been studied by several researchers (Desie and van Roost 2006, Alleborn and Raszillier 2007, von Bahr *et al.* 1999). Desie and van Roost (Desie and van Roost 2006), who studied inkjet ink imbibition phenom-

ena by using aqueous dye-based and pigment-based inks, showed that diffusion is the main liquid absorption driving phenomenon into polymeric blend materials in contrast to capillary absorption into microporous coating. The timescales of long range diffusion and evaporation are much closer together than the timescales of capillary wicking and subsequent evaporation of ink water. They concluded that the diffusion phenomenon for bulk transport appears seconds after the liquid arriving on the surface. Instead of concentration in equation (17), they considered volume V(t) of liquid in a droplet in the form of a truncated sphere, radius R, sitting on the porous surface, and expressed the depletion of the droplet by bulk diffusion into the structure as

$$V(t) = V(0) - 2\pi R^2 \sqrt{\frac{Dt}{\pi}}$$
(19)

where V(0) is the volume of ink on the top of surface at the start of the inkjet ink imbibition process, R is the radius of the droplet in the form of a truncated sphere on top of the receiver, and D is the diffusion coefficient of the ink.

Von Bahr *et al.* (von Bahr *et al.* 1999) support the separate behaviour of capillary flow and bulk diffusion by dividing the liquid spreading onto a porous structure into a non-diffusive and a diffusive regime, but in their case they consider the diffusion of the surfactant present in solution rather than that of the solvent molecules. In the non-diffusive regime, the liquid spreading is described as very quick, and inertia, gravity and capillarity are the main controlling factors. In the second regime, the spreading is slower than in the first regime, and it is controlled by diffusion of surfactant molecules to the expanding liquid-vapour interface. However, von Bahr *et al.* (von Bahr *et al.* 2000, von Bahr *et al.* 2004) showed that when the front area of a surfactant containing liquid goes through the capillary network of sized paper, some of the surfactants transfer to the capillary walls. At the same time, more surfactants concentrate at the liquid surface and orientate by diffusion. They finally came to the conclusion that the surfactant diffusion has to work on a shorter timescale than seconds.

Alleborn and Raszillier (Alleborn and Raszillier 2004) connected the action of diffusion to a wetting front model with the concentration changes of the liquid front considered within the paper structure. As the solvent (water) moves forwards in the paper, the diffusion affects the behaviour of the paper fibres. The hygroscopic nature of a porous paper structure ensures that many mechanisms of moisture transport operate simultaneously (Massoquete *et al.* 2005, Radhakrishnan *et al.* 2000, Liang *et al.* 1990, Nguyen and Durso 1983). Moisture enters paper by vapour-phase diffusion through the interfibre void space, Knudsen diffusion in pores, surface diffusion over fibres, bulk-solid diffusion within fibres, and capillary transport (Liang *et al.* 1990). The first two mechanisms take place in the gas-phase and the other in the condensed state of the liquid. Liang *et al.* (Liang *et al.* 1990) saw that moisture transport is dominated by gas-phase transport through the interfibre voids or pores. The vapour-phase diffusion is reported to dominate in the paperboard at relative humidities below 60 %. At high moisture content, the

condensed phase or bound water movement appears to dominate. According to Ahlen (Ahlen 1970), the transport of water in the condensed or bound state was important even for relative humidity levels as low as 30–40 %. Similar diffusion behaviour was considered also to be relevant in the case of coating layers (Salminen 1988).

To consider more closely the diffusion rate over short distances through a spatially limiting polymer network, as is the case when considering water transport into, say, a swellable binder matrix, we need to consider the rate of movement of molecules as a function of the random thermodynamic energy and the resistance of movement in a viscous medium. The velocity of molecules thus depends on the temperature, the viscosity of fluid and the size of particle (molecule) according to the Stokes-Einstein relation (Reynolds and Goodwin 1984, Mehaffey and Cukier 1977), which for spherical particles passing through liquid at low Reynolds number is expressed as

$$D = \frac{k_{\rm B}T}{6\pi\eta r} \tag{20}$$

and for an electrically charged particle, such as the inkjet ink colorant molecule,

$$D = \frac{\mu_{\rm q} k_{\rm B} T}{q} \tag{21}$$

where *D* is the translational diffusion coefficient,  $k_{\rm B}$  Boltzmann's constant, *T* absolute temperature,  $\eta$  viscosity and *r* radius of spherical particle, or equivalent hydrodynamic radius for non-spherical particles. The term  $\mu_{\rm q}$  is the electrical mobility of the charged particle and *q* the electrostatic charge.

Acceleration of flow by heating has been used in some high-speed inkjet printing nozzle applications. For example in the nozzles of Versamark<sup>®</sup> VX5000e the ink is heated to a temperature of 40 °C. The effect of the temperature on dyebased inkjet ink penetration into porous coatings was studied with the capacitance-based device in section 7.4 "Cationic additive applied directly onto the top of coating surface". The advantageous use of the electrical properties of inkjet inks, other than just the ionic interaction properties, has also been considered in some applications, such as the printing of electronics (Haverinen *et al.* 2009, Walther *et al.* 2009). Additionally, preheating the ink and/or substrate will increase the rate of diffusion of ink components.

It is very probable that the concentration of the components of ink varies during the ink setting process. This is a dynamic process occurring until the solvent has evaporated out of the printed surface and the other components of ink vehicle as well as ink colorant have become bound or settled into the structure. The concentration changes cause variation of osmotic pressure as a result of the distribution of concentration gradients within the structure, and especially when components become trapped within absorbing polymer networks, and this reflects in the resultant ink movement tendency. There can even appear transportation of components in the reverse direction from the interim ink component location. The diffusion phenomenon appears even in the final stages of inkjet ink drying, where the concentration differences of ink components, caused by ink vehicle evaporation, generate the concentration gradient for diffusional movement. However, there are other dominant boundary condition phenomena to consider in the ink drying process coming from the process variable side, like the image size, desired print density, ink and paper type, sheet temperature and initial moisture content of paper (Agbezuge and Gooray 1991). In this work, the main interest is concentrated on the diffusional phenomena at the local position scale during inkjet ink imbibition, not during the final drying process.

#### 2.2.4 Separation

In the inkjet ink setting process, it is desirable that the colorant part of ink fixes into the top layer of substrate and the ink vehicle part penetrates deeper into the structure. This takes the form of chromatographic separation in the case of dye-based inks (Donigian *et al.* 1998, Rousu *et al.* 2000). In pigment-based inkjet inks, the separation takes place between colorant pigments and vehicle, where the ink pigments form a filter cake or agglomerate on the top of the substrate (Donigian *et al.* 1998, Vikman and Vuorinen 2004b, Svanholm 2007). In the ink separation, the controlling ink properties are thought to be the viscosity and surface energy (von Bahr *et al.* 2000). The surface properties of the substrate also affect the ink vehicle-colorant separation and movement (Desie and van Roost 2006, von Bahr *et al.* 2003).

In the area of offset printing, Rousu et al. (Rousu et al. 2000 and 2005) showed that the ink colorant pigment and diluent oil separated at the coating surface. Furthermore, it was shown that the oils, diluent (mineral oil) and solvent (vegetable oil) underwent chromatographic separation. The separation was controlled by specific surface area of pigment, degree of polarity and binder chemistry. The adsorption/desorption on the surfaces of pigments, therefore, leads to the chromatographic separation of ink diluent(s)/solvent(s) and colorant(s). The degree of separation depends on the surface area of pigments, if the comparison is made amongst chemically and morphologically similar pigments. However, it is the true surface chemistry of the pigments that is important, and this is defined more by the dispersant and/or surface adsorbed species and polymer(s) than the underlying pigment itself, unless the pigment is used in an undispersed or polymer-free environment. The morphology influences the hydrodynamic flow behaviour due to the changes in pore size, porosity and tortuosity. The addition of binder into the coating colour creates further surfaces, where the ink solvent as well as ink colorant can diffuse and/or adsorb, and in the case of swelling binder interpolymer matrix diffusion also takes place.

#### 2.2.5 Adsorption

During inkjet imbibition, the ink colorant and some other molecules of the ink can adsorb on the surface of the solid phases depending on surface charge or polymer structure, forming a molecular or atomic layer, or in some cases a multilayer structure. In the adsorption to a true solid, the liquid or solute does not go into the adsorbent, but it diffuses or migrates along the surface, in this case the pore walls, until a sorption site is found. The ink vehicle, however, wets and film forms along the pore walls, but it does not adsorb directly, other than by surface dissolution, to the chemical groups of pore wall material in competition with ink colorant, though it may adsorb at other sites than the colorant. Adsorption is usually described through isotherms, which connect the adsorbate amount on the adsorbent with its partial pressure or concentration.

The chemical properties of coating structure affect the movement of liquid and water vapour on the surface. As the inkjet ink vehicle (mainly water) transfers in the porous structure, it influences the surface chemistry. As the water content increases in the paper structure, the polarity increases and this is reflected in the adhesion of polar components of ink, affecting such print properties as mottling and rub/abrasion resistance of the printed surfaces (Gane and Ridgway 2008).

#### 2.2.6 Colorant fixing

The colorant adsorption can result in the forming of chemical bonds between the ink colorant and the different coating components. Lavery and Provost (Lavery and Provost 1997) named the possible bonds between the ink colorant and substrate in the order of decreasing strength of interaction: covalent bonding, Coulombic or ionic bonding,  $\pi$ - $\pi$  interactions, hydrogen bonding, hydrophobic interactions, dipole-dipole interactions, and van der Waals forces. However, in this section they have been introduced in the order of the most probable binding force in the fixing action of aqueous-based dye inks.

<u>lonic interactions</u> (ionic interactions, Coulombic bonds) exist, when the anionic ink contains water soluble groups, like SO<sub>3</sub><sup>2-</sup>, COO<sup>-</sup>, PO<sub>3</sub><sup>3-</sup>, which can interact with cationic groups on the surface, for example Ti<sup>4+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, and NR<sub>4</sub><sup>+</sup>. The interaction is strong and it has an effect over a long range. The ionic bonds immobilize effectively the colorant molecules of dye giving good print quality (Lavery and Provost 1997). This interaction manifests itself via a force action at a distance via soluble ions, such that water/moisture or a polar solvent must be present. Adsorption on the surface by ionic bonds, however, provides a permanent fixation, and an improved water fastness of dye-based inks on the coated paper surface (Vikman 2003).

The dominating fixing interaction in the case of uncoated paper grades is the <u>hydrogen bonding</u> (hydrogen attached to an end group bonds via covalent bonding to an electronegative atom). Groups like -OH and -COOH can easily support hydrogen bonding. Hydrogen bonding is a quite weak interaction and greatly influenced by the geometrical orientation of the components. However, if the molecule is large, there may be a large number of hydrogen bonding sites, and this increases the strength of the colorant bonding. There may moreover be interactions between the –OH groups of the cellulose and the  $\pi$ -cloud (electrons) of the aromatic groups of colorant.

<u>Van der Waals interactions</u> are amongst the stronger binding forces, but only occur when the interacting groups are very near each other. Van der Waals interactions act between all kinds of molecules. In the beginning of the ink setting process, there is a weak repulsion force between anionic dyes and the cellulosic substrate if uncoated. However, as the water of the ink absorbs, the colorant and paper interface becomes nearer and the opportunity for van der Waals attractive forces increases (Lavery and Provost 1997).

<u>Dipole-dipole interactions</u> are relatively weak and they are depending on the polarity of the interaction groups (Lavery and Provost 1997). Dipole-dipole interactions are forces that occur between two molecules with permanent dipoles. The molecules are two point dipoles which have opposite equal finite charges. The opposite charges of molecules attract each other forming dipole-dipole interaction.

 $\pi$ - $\pi$  interactions are important when considering bonding between the colorant molecules themselves, and they can lead to dye aggregation or crystallization. Quite strong  $\pi$ - $\pi$  interactions occur when the paper substrate contains aromatic groups. For example, the chromophores of phthalocyanines react like this (Lavery and Provost 1997).

In the case of reactive colorants, <u>covalent bonding</u> occurs (the strongest interaction), for example with cotton fibres. The electrophilic reactive group of ink reacts with a primary hydroxyl group. The reaction demands the action of temperature or pH. The final print has good fastness properties (Lavery and Provost 1997).

<u>Hydrophobic interactions</u> occur for solvent-based inks, which have hydrophobic groups such as alkyl chains. These interact with similarly hydrophobic groups on the paper. The hydrophobic interactions consist of a combination of hydrogen bonding and van der Waals interactions (Lavery and Provost 1997). The work by Wallqvist *et al.* (Wallqvist *et al.* 2006) has shown that the hydrophobic force develops itself between hydrophobic surfaces in water first only at short range as the surfaces approach each other, but then extends to long range as the surfaces are forced to retreat, suggesting that cavitation is the means by which the hydrophobic force can be expressed at long range. This force is expected to be highly sensitive to the location of chemical groups and the structure of the surface.

Surface wetting and the capillary imbibition driving force are intermolecular phenomena, and are mainly active via van der Waals, Coulombic and Lewis acidbase interactions (Gane *et al.* 1999). Van der Waals interactions form on the surface when there is unevenly distributed charge. Coulombic forces occur between charged surfaces and ions. When the surface has sites of specific electron donoracceptor interactions between uncharged surfaces and molecules there occur Lewis acid-base interactions.

Hydrogen bonds and van der Waals forces can also support the fixing of colorant to coated papers and films. However, in the fixing process the electrostatic interactions (ionic or Coulombic forces) are dominant (Lavery and Provost 1997, Pond 2000, Kallio et al. 2006, Vikman and Vuorinen 2004a) and the inks fix to the coating layer mainly through ionic forces (Lavery and Provost 1997, Pond 2000). The coating layer is more highly charged than the underlying fibrous, frequently surface sized, layer, resulting in attraction between the anionic colorant and the inorganic pigment, even in lightly coated papers. This interaction, of course, depends on the charge of the dispersing forces used to disperse the coating pigment in relation to the ionic charge of the dye. The inkjet coating structure has usually a cationic charge, which has been produced by applying a cationic additive. The cationic charge attracts the anionic dye, and this interaction increases the binding energies for the dyes. Vikman (Vikman 2003) showed that on anionic PVOH (fully hydrolysed, amount 5 and 10 pph) coatings the dye colorant is attached to the binder with hydrogen bonds, whereas on cationic PVOH coatings it attaches via ionic bonds. Donigian et al. (Donigian et al. 1998) hypothesized that the most important chemical groups of colorant from the binding point of view are carboxylic and sulphonic acid groups. By adjusting the pH of inkjet inks, the groups can become ionized (Donigian et al. 1998).

Besides the colorant ionic charge, the ink can contain other components that affect the final colorant fixing. There can be dispersant molecules, which have a portion that anchors them to the colorant surface, and a soluble polymer chain, which is not in contact with the colorant (Oka and Kimura 1995). It is via these chains that the colorant molecule fixes onto the coating layer. Such water-soluble polymers are, for example, polyethylene oxide, polyvinyl alcohol and polyvinyl pyrrolidone (Pond 2000). On the other hand, there is a possibility that the colorant remains physically at the paper structure (Morea-Swift and Jones 2000), for example within the roughness profile of the paper surface.

In the case of aqueous-based pigment inkjet inks, the colorant pigment forms a filter cake on the paper surface. The filter cake formation is also possible in the case of dyes. The dye can precipitate out of solution. One example of this being used is the designed evaporation of an amine to change the pH from basic to acidic when the ink reaches the paper surface (Pond 2000), and another for pigmented inks is the use of divalent cation, such as  $Ca^{2+}$  to act as a flocculant (Varnell 2001).

#### 2.3 Effect of coating layer on inkjet ink imbibition

As described above, the coating layer materials as well as the forming structures play a very important role during the inkjet ink imbibition and in defining the final colorant bonding to the structure (Desie *et al.* 2004b, Agbezuge and Gooray 1991). The ionic charge of coating components affects the colorant molecules fixing in the case of water-based inks, and the ink sorption volume and rate is determined by the coating structure and wettability. The fixing and absorption properties influence further the final print quality formation. A proper colorant fixation produces high optical print density, bright colour tones, low print-through, high

sharpness, low bleeding and high rub resistance and water fastness (Vikman and Vuorinen 2004a, Morea-Swift and Jones 2000, Donigian *et al.* 1998).

The topography of the surface affects, in addition, the droplet impact (Heilmann and Lindqvist 2000). For example, it affects the apparent wetting delay. The material properties like contact angle, sizing, coating, capillary structure, temperature and relative moisture content are important in respect to local surface and pore interior topography during ink imbibition. The spreading and penetration are affected by the coated paper porosity, permeability, thickness, sizing, fibre type, moisture content, temperature and capillary structure (Agbezuge and Gooray 1991). The construction of the printer and/or the printing machine variables also affect the final droplet setting, and also play an interactive role with respect to surface properties. However, machine variables are a further field of study and remain beyond the scope of this literature survey.

#### 2.3.1 Coating pigments

The sorption rate of liquids into the coating structure depends on the chemical properties of the surfaces encountered by the ink, and the pore network structure. Ridgway and Gane (Ridgway and Gane 2006) showed that the fine pores display a somewhat different effective surface chemistry to water than to non-polar alkanes. Fine pores are apparently more apolar than the large pores in that water suffers a delay in pore entry. They assumed that this is an effect caused by the swelling of polar, hydrophilic polyacrylates blocking the uptake of polar liquid into the finer pores, such that they appear apolar in respect to apparent wetting energy. By the choice of pigment particle size distribution and shape the coating layer structure can be manipulated. Gane and Ridgway (Gane and Ridgway 2008) showed that the broad particle size distribution of standard ground calcium carbonate produces slower initial adsorption of moisture than the more specialised narrow size distribution ground calcium carbonate pigments. The standard CaCO<sub>3</sub> provided a less permeable coating layer structure than the more specialised narrow size distribution CaCO<sub>3</sub>. They concluded that the nodes or throats in the porous coating structure, defining connectivity, determine the equilibrium saturated sorption of water vapour. Schoelkopf et al. (Schoelkopf et al. 2000) showed the opposite results when considering the liquid bulk uptake by capillarity. This is one example of the complexity of the interactions between polar liquids and the coating layer components depending on the sorption mechanism taking place.

Traditionally, a good inkjet print quality is produced by silica pigment coatings, which have high porosity, consisting of both micropores in the pigment particles as well as inter-particle pores, and high surface area, providing rapid ink sorption and dye-based ink colorant fixation. In the case of pigment-based ink, the binder of the ink fixes the colorant pigment to the top of the coating layer and the ink vehicle penetrates into the coating structure. The colorant pigment effectively forms a filtercake on the top of the coating. This filtercake effect may be enhanced by flocculating the ink pigment. This practice is common-place on uncoated papers

(ColorLok<sup>®</sup> (Koenig *et al.* 2007)) and is increasingly being considered for the new generation of coated papers to enhance print density (Romano *et al.* 2011). However, the expensive silica pigments are being progressively replaced with other less expensive pigments, like surface modified calcium carbonate, surface modified clays, colloidal aggregated precipitated calcium carbonate, aluminosilicate and zeolite (Klass 2007, Malla and Devisetti 2005, Gane 2001, Vikman and Vuorinen 2004b). Nonetheless, the basic properties have remained similar – high porosity and high surface area – although their relative distributions throughout the coating structure can differ. The following discussion goes on to illustrate the progression of studies from the behaviour of traditional silica-based formulations to those resulting from the more recent introduction of speciality calcium carbonate.

Morea-Swift and Jones (Morea-Swift and Jones 2000) studied different particle size synthetic silicas. The silicas produced a coating layer that allows fast ink drying, i.e. fast droplet sorption into the coating structure. They noticed that larger particle size silica produces a coating layer with higher print density. The silica coating with small particle size produces the sharpest text edges, but the bleeding is problematic. They concluded that the silica with small particle size and high pore volume guarantees the best performance for text reproduction on coated papers. For photographic papers and advertising wide web media, the silicas with large particle size and high pore volume are to be considered optimal. The pigmentbased inks form a pigment-rich layer, a filter cake, on the silica coating surface, whereas dye-based inks penetrate into the pores of silica pigment (Svanholm 2007). The larger particle size silica produces higher adhesion of pigment-based ink at a given certain pigment/binder ratio than smaller silica pigments (Adair 1998). At the same pigment/binder ratio of the coating colour, the smaller size pigments have more binder-free pigment-pigment contacts where the ink colorant pigment cannot bind.

Many studies (Shaw-Klein *et al.* 2007, Vikman and Vuorinen 2004a, Lee *et al.* 2002) have noticed that silica coatings can exhibit cracks. The cracks can be the results of shrinkage occurring from low solids content coating colours and the use of soluble binders that fail to resist shrinkage (Laudone *et al.* 2003). The smaller the particle size of silica, the greater is the surface tension force in the drying process and this can form cracks in the coating layer causing the gloss decrease of the surface (Lee *et al.* 2002).

Donigian *et al.* (Donigian *et al.* 1998) showed how dye-based ink fixes by different mechanisms to the silica and a comparative precipitated calcium carbonate (PCC) coating. In the case of silica coatings the high pore volume traps the whole ink, both ink colorant and vehicle. The silica provides a large specific surface area on which the ink colorant can bind as the evaporable part of the ink vehicle evaporates. The silica produces a higher affinity for the vehicle than PCC pigment. The PCC coating anchors the dye on the pigment surface while the vehicle penetrates deeper into the coating or base paper (Donigian *et al.* 1998, Glittenberg and Voigt 2001). PCC, however, has higher affinity for the dye components than silica. The colorant was shown in this case to bond mainly by hydrogen bonding to the chemical groups of the coating layer. One interesting result in their study is that the

yellow dye ink released more energy than would be predicted by the hydrogen bonds. This indicates that, in the case of this specific yellow colorant, some other or additional mechanism is involved in the bonding.

McFadden and Donigian (McFadden and Donigian 1999) showed that the brightness, and especially light scattering properties of the coating layer, has strong influence on the forming print density. They showed that inkjet coated papers often have lower opacity than the comparable offset or rotogravure coated papers, and this is actually beneficial for inkjet colour intensity. As the light scattering coefficient of the paper increased it is shown by these workers that the print density of the printed surfaces decreased (desktop printer using dye-based inks). High light scattering reduces print density contrast as the scattered white light raises the background spectral noise level.

Lee *et al.* (Lee *et al.* 2004) studied, in addition, the opportunity to reduce expensive and low solid content silica pigment by replacement with calcium carbonate pigments in higher gloss containing products. They studied the mixtures of fumed silica and precipitated calcium carbonate (PCC) or ultra fine ground calcium carbonate (UFGCC). The binder was partially hydrolysed polyvinyl alcohol. The coatings were applied as a single coat onto paper and subsequently calendered. Addition of carbonates increased the brightness of the coated papers. The addition of PCC increased gloss to the value of 60 % (TAPPI 75°) from 55 %, up to a PCC content of 30 % PCC. The packing of pigment particles explains the gloss improvement. In the case of UFGCC, gloss first decreased until a 30 % UFGCC pigment content, and after that it increased to the gloss level of 60 %. The use of CaCO<sub>3</sub> pigment, thus, has an effect on the gloss formation. The carbonate additions decreased somewhat the print densities of dye-based printed surfaces. The more permeable structure of CaCO<sub>3</sub> coatings, however, did not affect printed surface gloss.

Ridgway and Gane (Ridgway and Gane 2006) introduced a special modified calcium carbonate, which has small intra-particle pores. The pigment can absorb the diluent/solvent rapidly and it has high specific surface area. The final coating produced with this pigment has both nano- and micro-size pores. In their study, the pigment particle cakes produced from this pigment have ten times higher capability to take up fluid than normal offset quality ground calcium carbonate. The coating contains under 0.1  $\mu$ m pores that control the fluid capillary action and, on the other hand, there are larger interconnected pores controlling permeability.

One way to affect the paper structure is to calender the paper. Calendering the pigment coating layer increases the gloss and smoothness of the surface. This was exemplified in the case of fumed alumina and fumed silica by Lee *et al.* (Lee *et al.* 2005) (25 pph polyvinyl alcohol was used as binder). The 3 soft-nip calendering with 60 °C temperature and 123 kNm<sup>-1</sup> line load increased the gloss from 20 % up to 60 % (TAPPI 75° gloss). At the same time the Parker Print-Surf roughness decreased from 3 µm to 1.2 µm. A little higher relative gloss changes between unprinted and compact printed surfaces were detected with alumina than with silica coatings. For compact printed surfaces, the delta gloss changes were

the largest with alumina for both dye-based and pigment-based inks (Lee *et al.* 2002). The silica coatings maintained or even enhanced their coating gloss.

#### 2.3.2 Binders

The most commonly used binder in inkjet coatings is polyvinyl alcohol (PVOH) because of its capability to produce sufficient surface strength of the coating layer even for fine high specific surface area pigment coatings. The binding strength of PVOH depends on the degree of polymerization (Kumaki and Nii 2010). The higher the degree of polymerization the higher is the binding strength. The peel strength of PVOH coating is further shown to be greater with the higher degree of polymerization (Hara 2006). Modified PVOH has also been used: carboxylic-, sulphonic-, acryl amide-, cationic- and silicone-modified PVOH. The use of other types of coating pigments in the inkjet area has brought some other binders into use, like polyvinyl pyrrolidone, polyacrylic acid, polyacrylamide, methylcellulose, cellulose derivatives, gelatin, polyvinyl acetate latex, vinyl acetate ethylene, cationic starch (Malla and Devisetti 2005, Yip *et al.* 2003, Morea-Swift and Jones 2000, Glittenberg and Voigt 2001, Khoultchaev and Graczyk 1999, Lavery and Provost 1997).

Oka and Kimura (Oka and Kimura 1995) introduced four different mechanisms to describe how an acid red dye (anionic) solution can set on a PVOH containing silica coating layer (Figure 8). Their first assumption was that the PVOH covers the silica pigment. The colorant part can attach onto the PVOH layer (A), dissolve in PVOH (B), complex with adsorbed cationic polymer (dye-fixing agent) in PVOH (C), adsorb on the silica pigment (D) and/or adsorb on silica with cationic polymer (E). They finally concluded that most of the used dyes form a complex with dye-fixing agent, and this disperses in the PVOH layer – the mechanism (C) is, thus, the dominant phenomenon. The rest of the dye remains as a colorant layer on the PVOH surface (A).



**Figure 8.** The colorant setting states of anionic dye-based inkjet inks in a silica/ PVOH coating (Oka and Kimura 1995).

The diffusion phenomenon that has been described above, and its connection to swelling binder polymer networks, could be expected to decrease the diameter of pore capillaries. The hydrophilic binders, such as polyvinyl alcohol, have higher swelling tendency than, for example, latices in water. Adding PVOH in the coating slows down the movement of water in the case of dye-based inks (Donigian *et al.* 1998).

Svanholm (Svanholm 2007) studied PVOH containing silica pigment coatings on fine paper surfaces. He showed that the silica pigments with large pigment particles and large inter-particle pores require more binder than pigments with smaller particles and smaller pores to get the dye colorant remaining at the top of the coating. The PVOH can form a film-like structure in the top part of the coating, and the colorant can thus be made to remain there. The best colour gamut and the sharpest line edges of dye-based inks were achieved using a partially hydrolyzed and higher molecular weight PVOH.

The light fastness of inkjet printed PCC and kaolin coatings were studied by Vikman and Vuorinen (Vikman and Vuorinen 2004b). They used PVOH and cationic starch with cationic styrene acrylate latex as binder. With dye-based inks, the significance of structural properties of the coating layer in the light fastness decreased when the strength of the chemical paper-ink interaction increased. The dye-based ink benefits from a dense coating structure, whereas a coarse structure of the coating appears to be advantageous for the pigment-based inks.

Hailmann and Lindqvist (Heilmann and Lindqvist 2000) studied water-based inks in the area of continuous inkjet printing. A sized uncoated paper, a silica coated paper and one, surface swelling, superabsorber-based glossy paper were studied. They applied a single ink droplet on the surface and measured the droplet penetration into the substrate from the top side and in the cross direction. After the first 50 ms, the droplets reached the final dot size on the silica coated paper, while on the surface sized paper it took as long as 500 ms. The swelling binder/absorber containing coating had a shorter ink levelling time than the non-swelling coating. In the case of non-swelling coating, the final dot size was reached in 100 ms. Furthermore, small scale changes in the surface topography were seen to affect the size and shape of the forming dot, if the droplet is small. However, in the case of larger droplets, the topography has only a minimal effect on the shape of the final forming dot.

Rousu *et al.* (Rousu *et al.* 2005) indicated in offset coatings that the latex properties affect the ink setting. Low glass transition temperature and gel content of latex, together with oil-matched solubility index through monomer composition, increase fast ink setting. However, the latex particle size can affect the packing of the coating layer, and, through that, modifies the setting speed. Moreover, Rousu *et al.* (Rousu *et al.* 2000, Rousu *et al.* 2005) showed that the latex influences the oil separation of offset inks. Even a small amount of latex affected the separation process. The reason behind this can be found from the non-polar nature of the latex polymer. Latices to date are not usually used in inkjet coatings.

#### 2.3.3 Additives

Anionic inks are widely used in inkjet printing. From the point of view of colorant fixing, the coating layer should have opposite ionic charge to that of the ink colorant. The cationic charge is usually produced by adding a few percent of poly(diallyl dimethyl ammonium chloride) (poly-DADMAC) to the coating colour (Svanholm 2007, Malla and Devisetti 2005, Vikman and Vuorinen 2004b, Morea-Swift and Jones 2000).

Khoultchaev and Graczyk (Khoultchaev and Graczyk 1999) studied the effect of the charge density of ionic polymers in the coatings on the print quality of dye and pigment-based inkjet inks. They showed that a short dry time (time of ink set off onto an unprinted strip) does not always mean the best print quality. The quicker dry time surfaces can have cracks in the compact ink areas because the colour pigments separate too early out of the diluent/solvent and they flocculate with each other forming an uneven distribution of colorant on the coating surface. Moreover, they noticed that, on an anionic coated PET film, the pigment-based inks produced more cracks than on a cationic coated PET film. On the other hand, cationic coatings had lower print gloss than the anionic coatings. The increase of pH of coating slurry reduced the print gloss of both coatings.

One further opportunity to increase the bonding strength of ink colorant to the surface is to use cross-linkers or insolubilizers for coating formulations, like zirconium compounds (zirconium acetate, ammonium zirconium carbonate) (Hara 2006).

# 3. Experimental

### 3.1 Materials

#### 3.1.1 Calcium carbonate inkjet coating pigments

The most well-known pigment used traditionally in inkjet coatings is silica, which produces a print quality of high print density, low print-through, low bleeding and wide colour gamut. The capability of quick ink absorption combined with the high pore volume provides this high print quality. However, the price of silica pigments, their low solids content in suspension, as well as the demand of using more expensive high binding power additives makes silica today a less attractive coating pigment. Therefore, the emerging generation of more cost effective calcium carbonate (CaCO<sub>3</sub>) pigments was chosen for this study, having been developed to generate coating layers that can provide a good inkjet print quality. These calcium carbonate-based pigments are introduced in Table 4. The CaCO<sub>3</sub> pigment selection was based on the diversity in the mean particle diameter and the specific surface area of the pigments. The idea was to illustrate the effects of particle size and internal pore structure, including raw material sources from ground calcium carbonate (GCC), subsequently modified to generate high surface area and internal pores (MCC), and precipitated calcium carbonate (PCC). It should be noted that all of the pigments exhibit a cationic slurry property, being designed to bind anionic ink dye. The coating pigments were provided in the form of slurry by the pigment suppliers. In Papers V and VI, the "MCC large" pigment was used as a dry pigment that was dispersed in two ways, the first with anionic sodium polyacrylate, and the second using cationic poly(diallyl dimethyl ammonium chloride).

Table 4. The calcium carbonate pigments, their naming in this work and their
properties: in the last row it is indicated in which published paper(s) each pigment
has been used. The pigment sizes have been provided by the pigment suppliers.

Properties	Ground calcium carbonate – GCC	Modified calcium carbonate – "MCC large"	Modified calcium carbonate – "MCC small"	Precipitated calcium carbonate – "PCC large"	Precipitated calcium carbonate – "PCC small"
Weight median pigment particle diameter, $\mu m (d_{50\%})$	0.65 <sup>a)</sup>	1.60 <sup>a)</sup> 3.70 <sup>b</sup>	1.30 <sup>a)</sup> 2.50 <sup>b)</sup>	2.70 <sup>c)</sup>	Fine fraction 0.02–0.03 Ave. 0.25 <sup>d)</sup>
Specific surface area, m <sup>2</sup> g <sup>-1</sup> (BET, ISO 9277)	10.7	46.2	27.0	63.7	73.9
Zeta-potential, mV (AcoustoSizer II <sup>2</sup> )	-9	13	14	2	-1
Registered trade name	Hydrocarb 90 <sup>3</sup>	OMYAJET B6606 <sup>3</sup>	OMYAJET C3301 <sup>3</sup>	OMYAJET B5260 <sup>3</sup>	JetCoat 30 <sup>4</sup>
Structure of pigment	Rhombohedral	"Roses"	"Roses"	"Eggs"	Spherical
Illustrated structure of coating layer		Intra-particle pores	Intra-particle pores	Intra-particle pores	
Published paper(s) where the pigment has been used	I, III, VI	I, V, VI	I	I, II,VII	I, III, VI

a) Sedigraph 1500<sup>5</sup>, b) MasterSizer 2000<sup>6</sup>, c) HELOS<sup>7</sup> d) NanoSight<sup>8</sup> (results had two peaks: fine at 20–30 nm and average at 0.25 µm).

- <sup>3</sup> Registered trademark of Omya AG, Postfach 32, CH-4665 Oftringen, Switzerland.
- <sup>4</sup> Registered trademark of Minerals Technologies Europe N.V., Ikaros Business Park, Ikaroslaan 17, Box 27, B-1930 Zaventem, Belgium.
- <sup>5</sup> Registered trademark of Micromeritics Instrument Corporation, 4536 Communications Drive, Norcross, GA 30093, USA.
- <sup>6</sup> Registered trademark of Malvern, Enigma Business Park, Grovewood Road, Malvern, Worcestershire WR14 1XZ, United Kingdom.
- <sup>7</sup> Registered trademark of Sympatec GmbH, Am Pulverhaus 1, D-38678 Clausthal-Zellerfeld, Germany.
- <sup>8</sup> Registered trademark of NanoSight Ltd., Minton Park, London Road, Amesbury, Wiltshire SP4 7RT, UK.

<sup>&</sup>lt;sup>2</sup> AcoustoSizer II is a product name of Colloidal Dynamics/Agilent, Technologies (Finland Oy), Linnoitustie 2B, FI-02600, Espoo, Finland.

#### 3.1.2 Swelling and non-swelling coating binders

Polyvinyl alcohol (PVOH) is the most frequently used binder in the area of inkjet coating. It has high binding power and it has a hydrophilic nature. On contact with water, it swells. This swelling is caused by diffusion of water molecules into the polymer matrix. To compare the effects of a swelling versus a non-swelling binder, styrene acrylic synthetic emulsion polymerized latex (SA) was used in the study to complement the PVOH. The trade name of the SA latex was changed during the research due to a company takeover, but the material remained constant. The styrene acrylic latex type was selected because it is one of the least interactive latices when contacted by typical printing ink liquids, and can usually provide a more porous coating layer structure than styrene butadiene latex.

The PVOH binders had different degrees of hydrolysis. PVOH is produced by polymerization of vinyl acetate and the hydrolyzation is adjusted by saponification/hydrolysis of the hydrophobic acetate group (OCOCH<sub>3</sub>) with a hydrophilic hydroxyl group (OH) (Miller and Cook 1990). The final product contains vinyl alcohol and vinyl acetate units (Figure 9). The resulting polymer has both crystalline and amorphous regions in the structure, and the higher the degree of hydrolysis the more the polymer contains crystal regions within the polymer matrix (Kumaki and Nii 2010). In the case of the K-Polymer KL-318<sup>9</sup> PVOH polymer, a carboxylic monomer (COO<sup>N</sup>a<sup>+</sup>) has been added to the molecular chain. Table 5 shows the properties of the binders. The glass transition temperatures of the PVOH grades were not evaluated, but they usually lie between 40 °C and 80 °C (Mowiol 2003) depending on the origin, type and thermal history of polymer. PVOH does not have a defined particle size as it is applied as a soluble material, whereas latex has. The viscosity of SA latex was not measured.



Figure 9. Chemical structure of polyvinyl alcohol and the components of styrene acrylate latex.

<sup>&</sup>lt;sup>9</sup> Registered trademark of Kuraray Specialities Europe GmbH, Building D 581, D-65926, Frankfurt am Main, Germany.

Binder	Fully hydrolyzed PVOH (Mowiol 20-98 <sup>9</sup> )	Partially hydrolyzed PVOH (Mowiol 40-88 <sup>9</sup> )	Carboxylated PVOH (K-polymer KL-318 <sup>9</sup> )	Styrene acrylate latex (Latexia 212 = CSA 212 <sup>10</sup> )
Degree of hydrolysis, mol-%	98.4±0.4	87.7±1.0	87.5±2.5	
Density, gcm <sup>-3</sup>	0.4–0.6 *)	0.4–0.6 *)	0.4–0.6 *)	1.0
Glass transition temperature, °C	N/A	60–65 <sup>**)</sup> 30–35 <sup>***)</sup>	N/A	-20
Particle size, nm	-	-	-	180
Viscosity (4 % solution, 20 °C, DIN 53 015), mPas	20.0±1.5	40.0±2.0	25.0±5.0	N/A
Chemical nature	non-ionic	non-ionic	anionic	anionic

Table 5. The properties of studied binder polymers.

\*) Measured according to DIN 53 468 by Clariant International AG from the granulates. \*\*) bone dry, \*\*\*) ambient humidity.

#### 3.1.3 Adjusting the ionic charge by additives

The ionic charge of the pigments and binders was adjusted by adding either anionic sodium polyacrylate (Polysalz S<sup>10</sup>), having a molecular weight of 4 000 gmol<sup>-1</sup> or cationic poly(diallyl dimethyl ammonium chloride) (polyDADMAC, Cartafix VXU<sup>11</sup>, a molecular weiht 75 000 gmol<sup>-1</sup>). In the last *Paper (VII)*, a cationic additive was applied to the surface of the top-coating of a double-coated fine paper surface in order to clarify the role of ionic charge concentrated on the top part of the coated paper. In this study, cationic poly(diallyl dimethyl ammonium chloride) (poly-DADMAC, Cartafix VXU) was again used as the surface treatment additive.

#### 3.1.4 Inkjet inks and printing devices

High-speed inkjet printing was carried out on a Versamark<sup>®</sup> VX5000e<sup>12</sup>, which produces inkjet droplets by the continuous stream inkjet method. The printing

<sup>&</sup>lt;sup>10</sup> Registered trademark of BASF AG, Paper Chemicals, 67056 Ludwigshafen, Germany.

<sup>&</sup>lt;sup>11</sup> Registered trademark of Clariant International AG, Rothausstrasse 61, CH-4132 Muttenz 1, Switzerland.

<sup>&</sup>lt;sup>12</sup> Registered trademark of Eastman Kodak Company, 343 State Street, Rochester, NY 14650 USA.

press applied dye-base inks, and the main diluent/solvent was water. The surface tensions of the inks were observed to fall within the small range of 53-55 mNm<sup>-1</sup> (25 °C), depending on dye colour. At 40 °C, the surface tension was in the range of 48–52 mNm<sup>-1</sup>. Figure 10 shows the surface tension of black and cyan dye inks. The viscosity of cyan dye at 23 °C was 1.05 mPas, and at 40 °C 0.80 mPas, reflecting the expected thinning of ink as a function of temperature rise. Viscosity was measured with a Bohlin Rheometer<sup>13</sup>. In this measurement 10–12 cm<sup>3</sup> of ink are inserted into the space between two concentrically rotating cylinders. The torsion, caused by transmission of the movement of one cylinder relative to the other, through the liquid is then converted via the shear rate applied into a viscosity value. At the same temperatures, black dye had a viscosity of 1.25 mPas and 0.95 mPas, respectively. During printing, Versamark<sup>®</sup> VX5000e ink was automatically heated to 40 °C in the printing nozzles – a feature of the press to ensure consistency of ink flow.



**Figure 10.** The dynamic surface tension of the cyan and black inks of Versamark<sup>®</sup> VX5000e, measured with a Bubble Pressure Analyser KSV BPA800<sup>14</sup>, where the bubble life time is measured as a function of air flow. From this, the calculation of the dynamic surface tension is derived and indicates a possible dependence of the surface tension on the air flow speed.

In *Papers IV* and *VII*, laboratory formulated dye-based inks were used, in order to provide examples of inks containing either cationic or anionic cyan dye, respectively. The formula for the inks contained 4 (cationic) or 5 (anionic) wt-% colorant,

<sup>&</sup>lt;sup>13</sup> Malvern Instruments Ltd, Enigma Business Park, Grovewood Road, Malvern, Worcestershire WR14 1XZ, United Kingdom.

<sup>&</sup>lt;sup>14</sup> Registered trademark of KSV Instruments Ltd, Höyläämötie 11 B, FIN-00380 Helsinki, Finland.

5 wt-% polyethylene glycol (PEG 200), 5 wt-% diethene glycol, 0.3 wt-% Surfynol 465<sup>15</sup> and the remainder being water. The colorant was anionic (Basacid Blue 762<sup>10</sup>, Cu phthalocyanine) or cationic (Basonyl<sup>®</sup> Blau 636<sup>10</sup>, Victoria Blue FBO, Basic Blue 7, triarylmethane) (Figure 11). The colorant contained some impurities like sodium and sulphur. There was a slight difference between the surface tensions of the made-up inks: the anionic ink had a value of 49.5 mNm<sup>-1</sup> and the cationic 55.9 mNm<sup>-1</sup> (23 °C). This difference can have an effect on the colorant location due to the wetting characteristics in relation to the solid phase surface energy – binder in this particular case. By way of comparison, the surface tension of water at this temperature is 72 mNm<sup>-1</sup>. The observably different blue tone of anionic and cationic cyan colorant comes from the intrinsic properties of the dyes.

In *Paper VII*, the samples were printed with a desk-top printer, HP Deskjet  $3940^{16}$ . The idea was to clarify how the cationic treatment of the coating layer affects the print quality of dye-based inks. All the inks, except the black, were water-based dyes, the black in this case being pigmented. The surface tension of the cyan and magenta ink was  $25.0 \text{ mNm}^{-1}$ , yellow  $26.9 \text{ mNm}^{-1}$  and black  $50.5 \text{ mNm}^{-1}$ .





Basacid Blue 762, Cu phthalocyanine

Basic Blue 7, triarylmethane

**Figure 11.** The structure of Basacid Blue 762 and Basonyl<sup>®</sup> Blau 636 (Basic Blue 7) cyan colorant.

#### 3.1.5 Substrate: pre-coated base paper

Two base papers (fine paper grade) were used to provide the necessary substrate support for the subsequent various coatings under study. One was used either without pre-coat or had a pre-coat applied in the course of this study, while the other was supplied already pre-coated. The idea of choosing a pre-coated sheet was to prevent the top-coating penetrating into the paper fibre structure.

<sup>&</sup>lt;sup>15</sup> Registered trademark of Air Products PLC. Hersham Place Technology Park, Molesey Road, Hersham, Walton-on-Thames, Surrey KT12 4RZ, UK.

<sup>&</sup>lt;sup>16</sup> Registered trademark of Hewlett-Packard Company, 3000 Hanover Street, Palo Alto, CA, 94304-1185, USA.

The papers were, respectively:

- Commercial base sheet, as used for a coated fine paper, 67 gm<sup>-2</sup>. The precoating applied was a typical GCC-based offset coating formulation. This base paper was used in *Papers I, II* and *VII* either with two coating layers of the test inkjet coating formulation or with the separately applied pre-coat and the test formulation as top-coat.
- 2. Somewhat heavier weight commercially pre-coated fine paper having a grammage of 78 gm<sup>-2</sup> this was industrially pre-coated (coarse GCC-based offset), and was used in the curtain coating trial (*Paper III*).

In cases where the application of the experimental coatings failed to deliver sufficient coat weight in a single pass, a double top-coating procedure was adopted. Thus, the coating layers reported in *Paper I* were double top-coated by applying the same coating colour twice with a blade coater in order to achieve the target coat weight of 10 gm<sup>-2</sup>, which was not attainable with one pass. The first top-coating layer was allowed to dry and after that the second top-coating layer was applied.

In the trial reported in *Paper II*, the fine paper was first pre-coated with a coating layer of 7 gm<sup>-2</sup> using a film coater (1 000 m·min<sup>-1</sup>) on both sides of the base paper. The pre-coat had 100 pph of ground calcium carbonate (GCC) with a narrow particle size distribution, having 60 wt-% < 1  $\mu$ m (Covercarb 60<sup>3</sup>), together with 12 pph styrene-butadiene latex (SB latex, DL966<sup>17</sup>) and 0.6 pph carboxymethylcellulose (CMC, Finnfix 10<sup>18</sup>). The work in *Paper VII* utilized these same papers as in *Paper II*. Table 6 introduces the studied base papers and their pretreatments before the top-coating application.

<sup>&</sup>lt;sup>17</sup> Registered trademark of Dow Chemicals Company, Dow Europe GmbH, Bachtobelstrasse 3, 8810 Horgen, Switzerland.

<sup>&</sup>lt;sup>18</sup> Registered trademark of Noviant Oy, Kuhnamontie 2, M-realin tehdasalue, PL 500, 44101 Äänekoski, Finland.

	Base p	paper 1	Base paper 2		
	Commercial fine Commercial base paper base pa (67 gm <sup>-2</sup> ) <sup>-1</sup> (67 gm <sup>-2</sup>		Commercial pre- coated fine paper (78 gm <sup>-2</sup> )		
Pre-coating	No separate pre- coating (replaced by coating twice with same test colour)	100 pph GCC, 12 pph SB latex, 0.6 pph CMC	Industrially pre- coated (GCC-based offset coating)		
Application device of pre-coating	-	Pilot film coater	N/A		
Published paper(s) where the respec- tive substrate has been used	I	I, II, VII	111		

\*) Same fine base papers.

# 3.2 Designed coating structures and binder films, and their production

The work in this thesis concentrates on the effects of coating structures and their components, especially "high diffusion-driving", "less diffusing-driving" and virtually "non diffusion-driving" binders, in respect to their swelling behaviour in water, i.e. during dyebased inkjet ink imbibition. The coating colour binder component effects were studied either separately in 100 % binder only films, or in combination with the coating pigments and other chosen additives in the form of both coating structure filtercakes and tablets, and, finally, as applied in top-coating formulations onto the pre-coated fine paper structures. Additionally, thin layer chromatography (TLC) was made to identify the separation mechanisms of ink colorant and vehicle within the various structures and films, using the same coating formulations as thin layers on glass slides.

The coating trials were performed both on the laboratory and pilot-scale. In the laboratory a film applicator was used (draw down coater, *Papers III, IV, V* and *VII*) and a semi-pilot coater (SAUKKO, *Paper I*) (Pajari *et al.* 2007), and on the pilot-scale a larger pilot coater using a short dwell application blade (*Papers II* and *VII*) and a curtain slide applicator (*Paper III*), respectively. *Paper IV* has details of the binder films, in which the cationic (polyDADMAC) or anionic (polyacrylate) additive was included. In *Papers V* and *VI* coated TLC plates and tablets were produced, and these contained differently charged (cationic/anionic) dispersed pigments. There were also coating layers which had only 1 pph of binder (PVOH or SA latex), each present to provide a physical stabilising effect without dominating the interaction, and to study the primary occupied site of the binder resulting from the formation and drying of the coating layer. The idea contained in *Papers V* and *VI* is to study basic phenomena during liquid (polar and non-polar) absorption. *Paper* 

*VII* discusses results from coating cakes, which were re-ground/refined and the resulting powder exposed to the ink components analyzed by UV-VIS spectrometry.

Table 7 summarizes the coating colours and binder films that were studied. All of the carbonate pigments were sourced directly from pigment manufacturers, and most were in slurry form, and therefore the details of the dispersion agent and its amount are unknown. In the case of dry powder pigment(s), additional dispersant, when used, is described in the individual cases. The study samples of binder films, included films in which the cationic polyDADAMC (Cartafix VXU) or anionic sodium polyacrylate (Polysalz S) was added (1 or 4 pph) into the partially or fully hydrolyzed PVOH.

**Table 7.** The composition of studied coating colour structures, films and their ionic charge. Polyacrylate refers to anionic sodium polyacrylate. Each amount refers to the parts added per 100 parts of coating pigment.

	Pigmen	t	Bind	ler	Dispersing agent (used for pigment makedown)		Additive	lonic charge	Base paper
Туре	Amount (pph)	Form	Type (degree of hydrolysis)	Amount (pph)	Туре	Amount (pph)			
GCC	100	slurry	PVOH (partially)	7, 10, 15	N/A	N/A	-	Anionic	1
MCC large	100	slurry	PVOH (partially)	10	N/A	N/A	-	Cationic	1
MCC small	100	slurry	PVOH (partially)	10	N/A	N/A	-	Cationic	1
PCC large	100	slurry	PVOH (partially)	10	N/A	N/A	-	Cationic	1
PCC small	100	slurry	PVOH (partially)	7, 10, 15	N/A	N/A	-	Weakly anionic	1 <sup>+</sup> , 2 <sup>++</sup>
PCC large	100	slurry	PVOH (partially)	7, 12, 30	N/A	N/A	-	Cationic	1
PCC large	100	slurry	SA latex	7, 12, 30	N/A	N/A	-	Anionic	1
-	-	-	PVOH (partially)	100	-	-	-	Non- ionic	-
-	-	-	PVOH (partially)	100	-	-	Poly- DADAMC, 1 pph	Cationic	-
-	-	-	PVOH (partially)	100	-	-	Poly- DADMAC, 4 pph	Cationic	-
-	-	-	PVOH (partially)	100	-	-	Poly-acrylate, 1 pph	Anionic	-

		r							
-	-	-	PVOH (partially)	100	-	-	Poly-acrylate, 4 pph	Anionic	-
-	-	-	PVOH (fully)	100	-	-	-	Non- ionic	-
-	-	-	PVOH (fully)	100	-	-	Poly- DADAMC, 1 pph	Cationic	-
-	-	-	PVOH (fully)	100	-	-	Poly- DADMAC, 4 pph	Cationic	-
-	-	-	PVOH (fully)	100	-	-	Poly-acrylate, 1 pph	Anionic	-
-	-	-	PVOH (fully)	100	-	-	Poly-acrylate, 4 pph	Anionic	-
-	-	-	PVOH (carboxy- lated)	100	-	-	-	Anionic	-
-	-	-	SA latex	100	-	-	-	Anionic	-
MCC large	100	powder	-	-	Poly- acrylate	0.5	-	Anionic	-
MCC large	100	powder	-	-	Poly- DADMAC	0.5	-	Cationic	-
MCC large	100	powder	PVOH (partially)	1, 7	Poly- acrylate	0.5	-	Anionic	-
MCC large	100	powder	SA latex	1, 7	Poly- acrylate	0.5	-	Anionic	-
MCC large	100	powder	PVOH (partially)	1	Poly- DADMAC	0.5	-	Cationic	-
MCC large	100	powder	PVOH (partially)	1	Poly- acrylate	0.5	Poly- DADMAC, 3 pph	Cationic	-
GCC	100	powder	-	-	Poly- acrylate	0.5	-	Anionic	-
GCC	100	powder	PVOH (partially)	1	Poly- acrylate	0.5	-	Anionic	-
GCC	100	powder	SA latex	1	Poly- acrylate	0.5	-	Anionic	-
PCC small	100	slurry	-	-	N/A	N/A	-	Weakly anionic	-
PCC small	100	slurry	PVOH (partially)	1	N/A	N/A	-	Weakly anionic	-
PCC small	100	slurry	SA latex	1	N/A	N/A	-	Anionic	-

 $^{\rm +}$  in the case of 10 pph binder  $^{\rm ++}$  in the case of 7 and 15 pph binder.

The short dwell applications (blade) in the pilot trials in *Paper II* were performed at a coating speed of 700 m·min<sup>-1</sup>. The final top-coating layer consisted of 8 gm<sup>-2</sup>. The recipes and the properties of the coating colours for the respective top-coats are summarized in Table 8. The final moisture content of each coated paper was 5 %.

Component	Coating colour labelled according to the binder level, pph							
	7 pph PVOH (partially)	12 pph PVOH (partially)	30 pph PVOH (partially)	7 pph SA	12 pph SA	30 pph SA		
PCC large	100	100	100	100	100	100		
PVOH	7	12	30					
SA				7	12	30		
Polysalz S (sodium polyacrylate)				6	6	6		
Measurement								
Solids content, %	25.1	24.3	22.2	28.1	31.0	30.9		
Zeta-potential*, mV	2	2	3	-37	-33	-33		
рН	8.4	8.5	8.4	8.5	8.2	7.9		

Table 8. The top-coating colours in pilot trials.

\*AcoustoSizer II

The role of coating layer thickness on the pre-coated fine paper surface, Base paper 2, was examined using coatings generated with a curtain slide applicator. The speciality small size "PCC small" pigment containing coatings were produced and used for this study. The coating colours had 7 pph or 15 pph of polyvinyl alcohol (Mowiol 40-88) based on 100 pph of pigment. All colours had an additional 0.2 pph of surfactant, Lumiten DF<sup>10</sup>. Lumiten DF is the sodium salt of an ester of sulphosuccinic acid and an isotridecanol ethoxylate. The inclusion of surfactant acted to stabilise the curtain formation. The coating speed was varied from 1 000 m·min<sup>-1</sup> to 600 m·min<sup>-1</sup> depending on the applied coating colour weight. The highest speed was used when the coat weight was the lowest and vice versa. The final moisture content of the coated web was 5.1-5.4 wt-%. This means that the drying temperature had to be increased when the coat weight was high.

The inkjet ink penetration through the coating layers was also studied by applying the coating colour on polyethylene plastic film (Imperial NMO<sup>19</sup>). The coatings contained 100 pph of "PCC small" or GCC pigment and the binder was partially

<sup>&</sup>lt;sup>19</sup> Importer Kauppahuone Pesonen, Hermannin rantatie 12 A, PL 8, 00580 Helsinki, Finland.

hydrolyzed PVOH, which amount was 7 or 15 pph. An Erichsen<sup>20</sup> bench-top film coater (Model 288) was used, adopting wire wound spiral applicators (Spiral Film Applicator, Model  $358^{20}$ ), and the coating layers were dried at 105 °C during 5 min. The produced coating layer thicknesses varied from 2 µm to 35 µm.

## 3.3 Analytical methods

Several different testing methods were used. The coating layers were mainly characterized with interest focused on their porosity and pore size distribution, as well as the ionic charge. The liquid absorption speed from an applied ink layer into the coating structures was studied with a method in which the gloss change caused by drying inkjet ink on the surface was detected, DIGAT device (Lamminmäki and Puukko 2007). However, the main interest of this work was focused on the mass transport of the ink into the structures and was analyzed with a microbalance, a capacitance-based (Clara) device (Lamminmäki *et al.* 2010) and by thin layer chromatography. The uptake of ink into the binder films was studied with a microbalance, and the colorant distribution by Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and optical microscopy imaging of *z*-direction coating cross-sections. Ultraviolet-visible (UV-VIS) spectroscopy was used in the study of the ab/adsorption by the different coating components. The coated paper samples were printed and the print quality was evaluated using the methods reported in Table 11. Each method is now discussed separately in more detail.

#### 3.3.1 Porosity of coating structures

In *Papers I, III, V and VI*, the porosity of coating layer structures was characterized with several methods: a silicon oil absorption method, as well as water and hexadecane absorption in a microbalance measurement and mercury porosimetry determination. In silicon oil, water and hexadecane measurements the coating layer was immersed in each liquid and the weight change between the liquid saturated and air-filled sample prior to wetting was determined. Care was taken to allow escape of air from within the structure by maintaining a free surface not covered by liquid, relying on capillarity to fill the sample. In all cases, the studied material was a coating layer/structure without the paper, and they were produced with Teflon<sup>®21</sup> moulds or with a tablet former (Ridgway and Gane 2005). In the mercury porosimetry, the cumulative pore volume and pore size distribution was detected from the intrusion curve as a function of intrusion pressure, applying the

<sup>&</sup>lt;sup>20</sup> Registered trademark of Erichsen GmbH & Co., Am Iserbach 14, D-58675 Hemer, Germany.

<sup>&</sup>lt;sup>21</sup> Polytetrafluoroethylene, Du Pont.

corrections contained in the software package Pore-Comp<sup>22</sup> to account for penetrometer expansion, mercury compression and compression of the sample skeletal material according to Gane *et al.* (Gane *et al.* 1996). Both coated papers and coating cakes/tablets were measured. There were some small differences between the results of the absorption-based measurements and those from mercury porosimetry. The reasons behind this can be traced to one or more of the following: the external pressure that has been used in the intrusion measurements, the accuracy of pigment tablet size analyses in the case of determining the sample volume for liquid absorption, the presence of excess external silicon oil and irreproducibility when wiping off surface excess after the experiment, as well as the differences in the actual coating layer production (pressure in the tablet former and non-pressurized, shrinkage only, coating cake forming in the moulds).

#### 3.3.2 Liquid penetration

The absorption mass transport into the coating cake was analysed by using the microbalance (*Paper VI*) and the liquid movement through the pore networks of the pigment packing structures with the thin layer chromatography method (TLC, *Paper I* and *V*).

#### **Microbalance**

In the experimental recording of the uptake of liquid using the microbalance, the studied pigments were "MCC large", GCC and "PCC small" and binders were partially hydrolyzed PVOH and SA latex. The coating colours had 100 pph pigment and binder amount was 1 and 7 pph. The dispersing was made with Polysalz S or polyDADMAC (Cartafix VXU) to generate anionic and cationic coatings, respectively. The coating tablets were produced from coating colours by a wet filtration system (Ridgway et al. 2005 Gane et al. 1999) under an external pressure of 20 bar. The tablets were dried at 60 °C overnight. The PVOH uniformity within the tablets was studied with a Thermo Nicolet Nexus 870 FT-IR spectrometer<sup>23</sup> (IR spectra from KBr-tablets). The results show that the wire filter side (lower surface) of the tablet had a higher concentration of PVOH, explained as being a result of the soluble nature of the PVOH (Figure 12). (For this differential binder distribution determination, the PVOH content was 0.7 pph, whereas, in the microbalance study, the binder amount used was slightly higher, 1 pph.) Therefore, the final tablets fashioned for the microbalance absorption analysis were prepared so that both sides of the tablet (top and bottom side) were tested, each having the same

<sup>&</sup>lt;sup>22</sup> Pore-Cor and Pore-Comp are a software network model and sample compression correction software, respectively, developed by the Environmental and Fluid Modelling Group, University of Plymouth, UK.

<sup>&</sup>lt;sup>23</sup> Registered trademark of GMI, Inc. 6511 Bunker Lake Blvd., Ramsey, Minnesota, 55303 USA.

time in contact with the liquid, and an average formed. The filtrate that formed during the tablet making procedure was also analyzed with FT-IR spectrophotometry, and the result showed that it also contained traces of PVOH, confirming the soluble nature of the binder.



**Figure 12.** The IR spectra taken from the top and bottom surfaces of the tablet: GCC with 0.7 pph PVOH (partially hydrolysed). Notice the lower PVOH content of the colour in this measurement (= 0.7 pph) compared with the actual tablets made for the microbalance measurement (1 pph).) The lower surface was against the wire filter in the tablet former. The main peak of PVOH locates at the wavenumber 1 087 cm<sup>-1</sup>. Based on Paper VI (Figure 2).

In the microbalance measurement, the polarity of the liquid, and its effect on imbibition into pigment tablets, was studied using distilled water (100 % polar) and hexadecane (100 % apolar), respectively. The edges of the formed samples were polished and covered with octamethyl trisiloxane/toluene<sup>24</sup> so that the pores of edge areas did not affect the liquid uptake by exterior planar wetting. In the microbalance experiment, the amount of absorbed liquid was measured as a function of time after contact between the sample and the liquid supersource. The uptake of the liquid was measured gravimetrically via an automated microbalance computer interface (Gane *et al.* 1999, Ridgway and Gane 2002). The temperature of the surrounding air was 23.0±1.5 °C. The weight loss due to the water evaporation

<sup>&</sup>lt;sup>24</sup> Provided by Dow Corning GmbH, Postfach 13 03 32, 65201 Wiesbaden, Germany.

during the measurement was taken into account in the results. Hexadecane has a minimal evaporation over this time period.

#### Thin layer chromatography (TLC)

Both the eluent distance and the gray value change during time were detected in the TLC method. The coating pigment in question was "MCC large" and binders were partially hydrolyzed PVOH and SA latex. The coating layers had 100 pph of pigment and 1 pph binder. The dispersing of the pigment was made anionically by using sodium polyacrylate (Polysalz S) and cationically using polyDADMAC (Cartafix VXU). The coating colours were applied on glass plates with an Erichsen film applicator (Model 288). The applied coat weight was about 100 gm<sup>-2</sup>. The coating layers were dried at room temperature overnight. De-ionized water was the eluent in the TLC analysis and the adsorbate (substance adsorbed) was provided by a range of concentrations of anionic cyan colorant (Basacid Blue 762). During the TLC development, the term "eluent" in our case refers to the water phase (ink vehicle equivalent) of a solution of dye applied as a supersource reservoir, i.e. not the classical eluent travelling past a previously dried colorant, but a carrier. The distance of the eluent (water phase) movement over time was measured. Simultaneously, the gray level of surface reflectance was detected with a digital camera (Dolphin F145C<sup>25</sup>). The illumination of the surface was made on the same side as that viewed by the camera (Figure 13). The measurements were made at a temperature of 20.0±1.5 °C. The image analysis software Image-Pro 6.2<sup>26</sup> was used to parameterise the image. The detection area started about 0.5 mm above the advancing eluent front and the total detection area was 100 mm<sup>2</sup>. The gray level of the undeveloped plate was adjusted to a gray level of 150. The distance was expressed towards the base of the TLC plate passing from unsaturated to saturated sample.

<sup>&</sup>lt;sup>25</sup> Registered trademark of Allied Vision Technologies GmbH, Taschenweg 2a, D-07646 Stadtroda, Germany.

<sup>&</sup>lt;sup>26</sup> Registered trademark of Media Cybernetics, Inc., 4340 East-West Hwy, Suite 400, Bethesda, MD, 20814-4411 USA.



Figure 13. The TLC development system and the location of gray value measurement and the distance of eluent front.

#### Capacitance-based measurement

The capacitance-based Clara device (Lamminmäki et al. 2010) Figure 14, Papers II, III and VII) was used both in the analysis of coated films as well as coated papers. The Clara measures the capacitance change during the liquid penetration through the sample. The maximum value of capacitance is about 190 pF, and this value depends on the capacitance of the plastic film backing the sample. When the capacitance reaches the maximum value, it is interpreted that the ink has penetrated through the whole paper structure. Figure 15 shows some examples of the resulting curves when different external pressure was used. We can assume that in the case of no external pressure the absorption is driven by the capillary wetting force in coating pores fine enough to exert a Laplace pressure drop (Oliver 1982) and by any inter-polymer liquid diffusion. In larger pores the movement is followed by thin layer wall wetting and surface and/or bulk vapour diffusion. When external pressure is small compared to the capillary pressure in the fine pores liquid starts to be forced into the larger pores under Poiseuille flow whilst capillary pressure filling continues as above. As the pressure is raised higher than the capillary force, or when all the pores up to and including the wetting front are filled, then the action is by permeation flow according to Darcy's law in saturated structures. The bimodal behaviour of each curve illustrates the competition between the initial capillary wetting and the permeable flow characteristic once capillaries/pores behind the wetting front are filled.


Figure 14. The structure of the Clara device.



**Figure 15.** Result curves of Clara at five different external over-pressures: "PCC large" with 7 pph PVOH coated paper. The used liquid was cyan dye-based ink (used in Kodak Versamark<sup>®</sup> VX5000e). Based on Paper II (Figure 3).

The connection between the penetration depth and the capacitance value was evaluated by studying coating pigment cakes of GCC (lower porosity), "PCC small" (higher porosity) and "PCC small" with 7 pph SA latex (thickness 294– 540  $\mu$ m) into which different amounts of molten candle wax, containing a colorant for ease of observation, were allowed to absorb. The idea was that the wax fills partially the porosity of the coating structure and it simulates the liquid front at a certain depth within the sample. The capacitance of wax is on the same level as the relative highly porous inkjet PCC coatings, and clearly greater than air. The wax (partial insulator) in the coating structure does not interfere with skeletal connectivity, so the capacitance would be expected to rise. The capacitances (average from the results between 1 Hz and 1 000 Hz) and the wax imbibition distances (relative distance = wax distance divided with the sample thickness) were meas-

ured with another device than the Clara because the coating cakes were too small to be studied with the Clara. In this device, the detection area was 5 mm in diameter using a round detector. Figure 16 shows that, as the depth of wax increased, the higher were the capacitance values in the case of high porosity coating ("PCC small" and "PCC small" + 7 pph SA) layers. The reference value for the dielectric constant of plain candle wax was similar to, for example, polyethene and Teflon<sup>®</sup>, which have dielectric constants around 2.25 and 2.1, respectively. The action, therefore, is confirmed to be that of wax replacing air in the coating structure, and wax has a higher dielectric constant (~2) than air (~1).

The capacitance of air was lower  $(5.55 \cdot 10^{-14} \text{ F})$  than that of wax  $(1.04 \cdot 10^{-13} \text{ F})$ . In the case where air plays very little role in the coating layer capacitance, as in the GCC coating case (Figure 16), it would be expected that as a low porosity structure with high skeletal connectivity starts to fill with wax the result trends toward wax, i.e. wax replaces the particle contact with a lower dielectric constant. On the other hand, if air plays a large role in the coatings, which have little skeletal connectivity (as for inkjet porous coatings, for example, where the particles hardly touch each other and are not rich in dispersant), then the opposite will happen – the air which isolated the particles gets filled with wax of higher dielectric constant. This means that the use of wax is a way of determining the connectivity between particles made by conductive charged dispersant. This model experiment confirms that capacitance-based measurement can be used in the evaluation of liquid penetration depth.



**Figure 16.** A connection between relative distance and capacitance determined using molten candle wax, containing a colorant for ease of observation, imbibed into coating cake structures. Capacitance was measured with a Hewlett-Packard 4192A LF Impedance Analyzer with a 16451B Dielectric Test Fixture (Electrode-B). Based on Paper III (Figure 2).

If the finest pores are rendered inactive in respect to capillarity by the presence of swelling binder, the diffusion into the binder polymer network, represented in Figure 15, can be initiated at the shortest times once liquid contact is made, albeit that the volumes involved are at first small, corresponding to Hypothesis I.

From the capacitance result curves we can calculate the penetration depth and speed. Paper thickness,  $d_{paper}$ , in the *z*-direction can be divided into the dry,  $d_{dry}(t)$ , and wet,  $d_{wet}(t)$ , parts during the measurement. In the limiting case where dimensional changes on wetting are limited,  $d_{paper}$  remains constant.

$$d_{\text{paper}} = d_{\text{dry}}(t) + d_{\text{wet}}(t)$$
(22)

The total capacitance  $C_{tot}$  is the capacitive impedance series sum of the plastic capacitance,  $C_{pl}$ , coming from the plastic sheet under the sample, and the sample capacitance C(t):

$$1/C_{\rm tot} = 1/C(t) + 1/C_{\rm pl} \tag{23}$$

The total wetted paper has practically no impedance (pure conductor), and thus the capacitance of paper depends on the thickness of the dry paper.

$$C(t) = A\varepsilon/d_{dry}(t) \Longrightarrow d_{dry}(t) = A\varepsilon/C(t)$$
(24)

where A is the area and  $\varepsilon$  is the dielectric permittivity of the material.

The thickness of the wet part of the paper, which we estimate to be the penetration depth of the water front, can be calculated by combining equations 22, 23 and 24:

$$d_{\text{wet}}(t) = d_{\text{paper}} - A\varepsilon/C(t) = d_{\text{paper}} - A\varepsilon(1/C_{\text{tot}} - 1/C_{\text{pl}})$$
(25)

The liquid penetration distance is thus

$$d_{wet}(t) = d_{paper} \left[ 1 - \frac{\frac{1}{C_{tot}(t)} - \frac{1}{C_{tot}(t = \infty)}}{\frac{1}{C_{tot}(t = 0)} - \frac{1}{C_{tot}(t = \infty)}} \right]$$
(26)

In the capacitance-based measurement the over-pressure acts during the whole measuring time, which is a different situation than in the case of an inkjet ink droplet hitting the surface and then becoming imbibed. The other difference from reality is that the offered ink amount is greater than in the case of inkjet ink application.

#### 3.3.3 Absorption of liquid into binder films

The absorption capability of binder films was studied in *Paper IV*. The SA latex films were produced with a draw down coater (drying in an oven at 105 °C for 5 min time) and PVOH films with Teflon<sup>®</sup> moulds. The absorption of liquid dye

solution was detected gravimetrically, and the samples for cross-section analysis were prepared by embedding the film in an LR White resin<sup>27</sup> and placing them in a refrigerator to reduce smearing of the dye. The cross-sections were then imaged in a light microscope. The colorant separation from the ink vehicle was studied with Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) using a lithium tracer in the liquid water phase, and the water type, i.e. free or bound water in the binder film moisture content after absorption, determined with a differential scanning calorimeter (DSC) by observing the thermal energy of binding.

### 3.3.4 Absorption/adsorption of liquid colorant by coating components

The effect of coating components on the inkjet colorant absorption and/or adsorption was tested by using the measurement procedure that has been introduced in Figure 17. UV-VIS analysis has been used before in the inkjet ink adsorption study by Kallio et al. (Kallio et al. 2006), Shi et al. (Shi et al. 2004) and Hartus (Hartus 1998), but their sample preparation diverged from the method used here. Table 9 shows the coating colour formulations, and the layers of coatings produced from these formulations were formed in Teflon<sup>®</sup> moulds by letting the slurry dry at room temperature (23 °C). This meant that all components of the coating colours remained in the coating layer structure after drying. The dried coating layer was then ground with a homogenizer (three grinding balls with diameter 1 cm, at a rotation frequency of 30 s<sup>-1</sup>) for 2 min. By grinding the pigment coating structure systems, the extended pore network structure effect present in coating cakes or layers could be avoided, thus enabling the structure surface-related phenomena to be isolated. The grinding effect was assumed to be similar for each coating layer, and that the sample treatment was assumed to provide a sufficiently homogeneous distribution of structural components despite the potential for some soluble species migration during drying. During the grinding, some newly exposed surfaces of the pigment could appear that would otherwise be covered with binder. Additionally, new binder surfaces could also be exposed as the binder film breaks. However, these effects were assumed to be minimal as the energy delivered during grinding was relatively low. The ground powder was screened through a 300 µm slit screen, to ensure that the powders did not contain inhomogeneous lumps and that the particles of the resulting coating "mini-structures" were as monosize as possible.

<sup>&</sup>lt;sup>27</sup> Registered trademark of Electron Microscopy Sciences, 1560 Industry Road, Hatfiled, PA 19440, USA.

Coating structure system	Dispersing agent, amount added to define the charge of the surface	Binder, amount	Zeta- potential, mV
MCC large powder in water	-	-	21
Anionic MCC large	Sodium polyacrylate, 0.5 pph	-	-37
Anionic MCC large + 7 pph PVOH	Sodium polyacrylate, 0.5 pph	Sodium polyacrylate, PVOH, 0.5 pph 7 pph	
Anionic MCC large + 7 pph SA	Sodium polyacrylate, 0.5 pph	olyacrylate, SA latex, 5 pph 7 pph	
Cationic MCC large	polyDADMAC, 0.5 pph	-	24
Cationic MCC large + 7 pph PVOH	polyDADMAC, 0.5 pph	PVOH, 7 pph	11

**Table 9.** The studied "MCC large" coating structure systems. Zeta-potential was measured with an AcoustoSizer II.

In the UV-VIS analysis of the adsorption phenomenon anionic ink was used, which was formulated in the laboratory to be sure that it contained only one colorant. The ink contained 5 wt-% anionic colorant (Basacid Blue 762), 5 wt-% polyethylene glycol (PEG 200), 5 wt-% diethene glycol, 0.3 wt-% Surfynol 465 (surface active agent) and the rest being water. The surface tension of the ink was 49.5 mNm<sup>-1</sup> (measured at 23 °C using a Bubble Pressure Analyser KSV BPA800 tensiometer). The ink was diluted with water (7 cm<sup>3</sup> ink per dm<sup>3</sup> water, recalling that the original ink contained 5 wt-% dve colorant). 10 cm<sup>3</sup> diluted ink was mixed with 5 g of the produced coating structure system powder to form a suspension of the powder particles in the diluted ink. Mixing was continued for a series of selected times (5 min, 30 min, 2 h and 18 h). Then each mixture was centrifuged, and the remaining dye concentration in the filtrate was analyzed in the UV-VIS spectrophotometer. The experiments were carried out at room temperature (23±2 °C). The UV-VIS spectroscopy quantified the relation of the intensity of incident,  $h_0$ , and transmitted,  $l_1$ , radiation as a function of wavelength in the ultraviolet-visible spectral region. The absorbance result was detected at a wavelength of 610 nm, where the absorption maximum of cyan dye was located. The maximum absorbance (A =  $-\log(I/I_0)$ ) value of colorant at 610 nm was about 3.7. Repetitive trials showed that the values varied between ±0.2 from the average value.



Figure 17. The treatment of coating structure before UV-VIS analysis in the ad/absorption study.

### 3.3.5 Use of more conventional paper testing methods

More conventional paper testing methods (Table 10) of the coated papers were also applied: coat weight, thickness, air permeance, surface energy (contact angle of liquid) and scanning electronic microscopy (SEM). The liquid absorption speed into the surface was studied with a DIGAT device (Lamminmäki and Puukko 2007), which detects the time from the arrival of a sprayed liquid to the moment when the gloss of the liquid has disappeared. This is determined by measuring the voltage change in a glossmeter. The light source of DIGAT is a red laser (wavelength 633 nm) with light incidence and detection angle 20° from the horizontal plane. The used ink in the DIGAT measurement was cyan dye-based ink from Versamark® VX5000e, and the applied ink amount was 8 gm<sup>-2</sup>.

Property	Measurement	Description of method	Principle
Electrical charge of coating colour	Zeta-potential	Applying a high frequency electric field across the coating colour and measuring an ultra- sound signal generated by the motion of the charged particles in the alternating field.	Electro- acoustic technique
Pore volume	Si-oil porosity	Silicon oil absorption amount after one hour immersion time vs. the weight of sample before adsorption.	Gravimetric
Cumulative pore volume	Mercury porosimetry	The intrusion of mercury into the structure under the influence of low ( $0 < \Delta P < 140$ Pa) and high ( $140 < \Delta P < 440$ Pa) pressure (adopting the Pore-Comp correction)	Mercury intrusion
Pore size distribution	Mercury porosimetry	the differential mercury intrusion into the structure under the influence of low $(0 < \Delta P < 140 \text{ Pa})$ and high $(140 < \Delta P < 440 \text{ Pa})$ pressure (adopting the Pore-Comp correction)	
Permeance	Parker Print-Surf air permeance measurement using 20 kPa measuring pressure (permeation resistance of a material of undefined thick- ness)		Air leak

 Table 10. Methods used in the basic property characterization of coating layers.

### 3.3.6 Print quality

Printing was performed primarily with a high-speed inkjet printing press (Versamark<sup>®</sup> VX5000e), which adopted aqueous-based dyes. The printing speed was 50 m·min<sup>-1</sup> (*Paper III*) and 100 m·min<sup>-1</sup> (*Papers I, II, III*), and the drying drum and hot air dryer were set to a temperature of 70 °C (*Paper III*), 80 °C (*Paper I, II*) and 100 °C (*Paper I*). The ink amount was adjusted to match with the ink demand of a commercial coated fine paper which the printing press manufacturer recommended. After adjustment, each paper was printed with these commercial paper values so that the ink amount on the surface was maintained constant. Alternatively, in *Paper VII*, the printing was run on an HP Deskjet 3940 desk-top printer because the abovementioned inkjet printing press was no longer available. This printer used the drop-on-demand inkjet technique (piezo crystal). It also applied waterbased cyan, magenta and yellow dye colorants. There were slight differences between the surface tensions of the inks of this latter printer. The print quality was analyzed by means of print density, print-through, bleeding (line width, ragged-ness, edge width), mottling and water fastness tests, as Table 11 summarizes.

In the water fastness test, the colour change was measured with a spectrophotometer (GretagMacbeth SpectroEye<sup>28</sup>) by using the basic formula given in the standard SCAN-P 49:83:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{27}$$

where

$$\Delta L^* = L_{\text{after}}^* - L_{\text{before}}^* \tag{28}$$

$$\Delta a^* = a_{\text{after}}^* - a_{\text{before}}^* \tag{29}$$

$$\Delta b^* = b_{\text{after}}^* - b_{\text{before}}^* \tag{30}$$

The term L is a function of Y-value (luminous reflectance value), and a and b are calculated using the tristimulus values X, Y and Z. The subscript term "before" refers to the measured value before water treatment and "after" the result after a 5 min de-ionized water immersion treatment.

The print-through and show-through were measured by using a flatbed scanner (Epson Perfection V700 Photo<sup>29</sup>, resolution 300 dpi). The printed surface was observed from the reverse side of the printed paper (print-through) or through a further sheet of un-printed paper (same paper as the printed material, show-through). The detection area was 30 x 30 mm<sup>2</sup>. The image was analyzed with the MATLAB<sup>30</sup> based PTA<sup>31</sup> program. The colour difference on the printed surface was reported as Delta E94 ( $\Delta$ E94), which followed the CIE 1994 colour difference equation. Mäkinen *et al.* (Mäkinen *et al.* 2007) showed that CIE 1994 takes better account of the different colours of the printed surface than conventional CIELab\* described colour in terms of lightness, red-green and blue-yellow axes. In CIE 1994, the colour difference,  $\Delta$ E94, is defined using the changes in lightness ( $\Delta$ L\*), chroma ( $\Delta$ C\*) and hue ( $\Delta$ H\*):

<sup>&</sup>lt;sup>28</sup> Registered trademark of Gretag-Macbeth AG, Althardstrasse 70, CH-8105 Regensdorf, Switzerland.

<sup>&</sup>lt;sup>29</sup> Registered trademark of Espon Corporate, 3840 Kilroy Airport Way, Long Beach, CA 90806, USA.

<sup>&</sup>lt;sup>30</sup> Registered trademark of The MathWorks, Inc. 3 Apple Hill Drive, Natick, MA 01760-2098, USA.

<sup>&</sup>lt;sup>31</sup> Name of the computer program that has been written at the University of Joensuu, Tulliportinkatu 1, 80100 Joensuu, Finland.

$$\Delta E_{94} = \left[ \Delta L^{*2} + \left( \frac{\Delta C^{*}}{1 + 0.045 \,\overline{C}^{*}} \right)^{2} + \left( \frac{\Delta H^{*}}{1 + 0.051 \,\overline{C}^{*}} \right)^{2} \right]^{0.5}$$
(31)

Where

$$\overline{C}^* = \sqrt{C_1^* C_2^*} \tag{32}$$

$$\Delta C^* = C_2^* - C_1^* \tag{33}$$

$$C^* = \sqrt{a^{*2} + b^{*2}} \tag{34}$$

$$\Delta H^{*} = \sqrt{\Delta a^{*_{2}} + \Delta b^{*_{2}} - \Delta C^{*_{2}}}$$
(35)

and where subscript number 1 refers to an unprinted area and number 2 to the printed area.

The strike-through describes the ink penetration and show-through the opacity of the sheet. Together they define print-through (Larsson and Trollsås 1972). Thus, the print-through can be expressed as

In inkjet prints, the ink vehicle and colorant penetrates into the paper structure and the print becomes more visible from the reverse side as the penetrated colorant amount and depth increases. In the final printed product the role of ink vehicle in the print-through is probably lower than in offset printed products, because most of the ink vehicle will evaporate out of the structure whereas in offset the oil leads to persistent translucency.

The printed surface bleeding was evaluated in terms of edge width (Figure 18), line width and raggedness. In this evaluation, the printed line was scanned with the Epson Perfection V700 Photo scanner (resolution of 2 400 dpi). From the scanned image, the gray level profile of the printed line was measured with an image analysis program. Two definition points, A and B, were defined from the gray values. Point A was 15 % brighter than the darkest region and B 15 % darker than a background (in some cases the definition of A and B set to 10 % was also adopted). The zero value was defined as the black surface, and the white given a value of 254. Each unprinted paper was adjusted to the gray value 170. The line width is defined as a mean normal separation between the printed line and the background un-printed area outline, i.e. as an average distance between the 90 % reflectance and 10 % reflectance boundaries of the image. The raggedness of the line was defined by ISO-13660. This value is the standard deviation of the residuals





Edge of two different colours

Figure 18. The evaluation of edge width in the bleeding measurement.

The mixing of black and cyan ink at the high-speed inkjet press was also detected on-line with a camera system (*Paper III*), which was located 54.2 cm distance from the yellow nozzles (Figure 19). The target of this camera detection during the trial was to clarify the rate of bleeding. The on-line figures were detected with a digital camera (Dolphin F145C, i.e. the same camera that was used in the TLC detection).



**Figure 19.** The location of inkjet ink nozzles and the video camera at the Versamark VX5000e press trial. The meaning of the abbreviation letters above the inkjet print heads: C - cyan, M - magenta, K - black and Y - yellow. The distance from the yellow print head to the camera was 54.2 cm.

Property	Description of method
Print density	GretagMacbeth D196 spectrophotometer.
Print-through	The reverse side of printed area was scanned and analyzed with image analysis (MATLAB based PTA program). Result was Delta E94.
Show-through	The printed area was scanned through a contacting un-printed sheet of the same material and analyzed with image analysis (MATLAB based PTA program). Result was $\Delta E_{94}$ .
Mottling	Printed area was scanned (Epson Expression 1680 Pro, 300 dpi) and the scanned figure was manipulated mathematically with a wavelet transform (PapEye program <sup>32</sup> ) to evaluate the unevenness of printed (at least 20 mm <sup>2</sup> ) area. The resolution-dependent values of the mottling curve are used to determine the mottling index that corresponds to the visual impression of the human eye.
Bleeding (line width, edge width, raggedness)	Imaging the line and calculating from the gray value changes the edge width, the line distance of edge area and the total line width.
Water fastness	Putting the printed sample into de-ionized water for 5 min immersion, and measuring the print density and CIELab* values with a spectrophotometer (SpectroEye, enhanced polarization filter according to ISO/DIS 13655) before and after water treatment.
On-line ink mixing measurement	Detecting with video camera a black line printed on a prior applied cyan surface during the high-speed inkjet printing trial – without inter colour drying.

### 3.3.7 Summary

The main interest for the study of the coating layers was directed toward the absorption and adsorption properties in relation to inkjet ink vehicle and colorant. The thesis Hypotheses were individually challenged by considering the effects of pore structure on capillarity and permeability to decouple these from interpolymer liquid diffusion (binder swelling) and surface charge properties, affecting the ab- and adsorptive diffusion dynamic, respectively. Each physical property was studied using a variety of coating pigments with either anionic or cationic charge introduced on their surface, together with combinations of PVOH types or SA latex, identifying swelling properties and permeability constraints of the binders. Additionally, ink colorants with different charge were investigated to complement the coating charge experiments. Finally, coated papers were used to visualise the impact on print quality of the parameters investigated, and a specially prepared cationic surface treatment was evaluated as a fixing agent for anionic dye to cap-

<sup>&</sup>lt;sup>32</sup> Registered trademark of Tapio Technologies, Nuijalantie 13, FI-02630 Espoo, Finland.

ture the dye effectively at the coating surface. Table 12 summarizes the used sorption methods and in which paper each method has been used.

**Table 12.** Summary of methods used in the coating layer liquid sorption measurements and the colorant final location study.

Property	Measurement	Description of method	Principle	Paper(s)
Absorption rate and amount into the coating	Microbalance	Liquid transport into the porous structure on both the short and long timescales.	Gravimetric	VI
Absorption rate and adsorption of colorant in the coating	Thin layer chromategraphy (TLC)	TLC liquid rising distance and gray level change – videoing during water or inkjet colorant rising in coating layer – as a function of time.	Eluent dis- tance, gray level	V
Absorption rate and permeation through the coating	Clara	Liquid movement through the sample, measuring capacitance change over time.	Capacitance change	II, III, VII
Liquid thin film ab- sorption speed	DIGAT	Liquid penetration into the surface structure from given ink volume arriving at and disappearing into the structure.	Gloss change recorded as glossmeter voltage	I, II, III
Liquid uptake rate of binder films	Microbalance	Liquid/moisture uptake of binder films over time.	Gravimetric	IV
Water phase distribution	Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)	The distribution of chemical compounds in the cross-sectioned sample as a function of depth (lithium as a tracer for the vehicle imbibition path).	Detecting ions/electrons released from the surface	IV
Colorant location/ distribution	Cross-section optical microscopy imaging and image analysis	Printed sample, LR White resin embed- ding and placing into refrigerator, cutting with microtome, imaging in a light microscope.	Optical microscopy and imaging	I, II, III, IV
Water types	Differential scanning calo- rimeter (DSC)	The binder film analyzed in DSC at two moisture contents. Detection of differ- ence in the amount of heat required to increase the temperature of a binder sample.	Calorimeteric	IV
Colorant ab/adsorption into/onto the coating components	Ultraviolet-visible (UV-VIS) spectroscopy	Powder-form pigment system mixed with ink, centrifuged, filtrate (liquid phase) analysis by UV-VIS spectrometry.	Colorant absorbance of the liquid phase	VII

# 4. The structural effect of the coating layer on inkjet ink imbibition

The porosity and pore size distribution of the coating structure determine how much, in which direction and at what speed the coating layer absorbs the inkjet ink. By selecting correctly amongst the various speciality coating pigments one can control to a large extent the inkjet ink imbibition into the structure. On the other hand, the binder of the coating layer, which is often a high binding power capacity polymer, like polyvinyl alcohol (PVOH), influences the ink movement by changing both the coating structure and its pore network characteristics, and in the case of it being water soluble can interact dynamically during the penetration. The role of binder in combination with various pigments will be the main discussion point in this chapter, and a more detailed discussion of binder properties alone affecting liquid colorant interaction will be the topic of the next chapter.

# 4.1 Impact of coating pigment type and binder selection on the structure formation of the coating layer

The pigment selection is probably the most important parameter in the formation of the porosity and the pore network structure, including pore size distribution in the coating layer. There exist many types of structural pigments consisting of calcium carbonate as the main or starting material. The studied pigments of this thesis were introduced more closely in the section "3.1.1 Calcium carbonate inkjet coating pigments". The first one was standard ground calcium carbonate (GCC). Two further pigments were GCC subsequently modified to generate high surface area and internal pores (MCC), differing in respect to particle size ("MCC large" and "MCC small") and the last two precipitated calcium carbonate (PCC), differing similarly in respect to particle size. "MCC large", "MCC small" and "PCC large" with a discrete bimodal pore size distribution – described further below. The "PCC small" pigment had mainly nano-size particles with occasional agglomerates only.

### Coating tablets and cakes (coatings without the base paper)

The results of mercury porosimetry from three out of the five studied  $CaCO_3$  pigments have been introduced more closely in *Paper VI*. Figure 20 shows the pore volumes and pore size distributions of "MCC large", GCC and "PCC small" pigment tablets, which were produced with the tablet former (Ridgway and Gane 2005). All pigment slurries were made by using an anionic dispersing agent. The ground calcium carbonate produced the lowest specific pore volume, reflecting the high packing factor for the broad size distribution GCC. The finest pore diameters were reached with the "PCC small" pigment, which had the smallest particle size (20–30 nm), but nonetheless produced a higher pore volume than the GCC. The "MCC large" pigment, with its discrete bimodal pore size distribution, developed the greatest pore volume and displays a dual pore size distribution reflecting the structure of the coating layer having both 20–60 nm pores and larger pores in the region of 200–800 nm. The finer diameter peak of the "MCC large" coating structure describes the intra-particle pores, and the larger diameter peak the interparticle pores.



**Figure 20.** The specific pore volumes (A) and the pore size distributions (B) of "MCC large" GCC and "PCC small" coatings, measured from pigment tablets. Figure B is based on Paper VI (Figure 4).

The fractional pore volumes (%) of these same coating pigments and the pigments with PVOH or SA latex binder have been introduced in Figure 21. "MCC large" and "PCC small" pigments produced very similar pore volume within the coating tablets, whereas the ground calcium carbonate had clearly lower pore volume, as the prior mercury porosimetry results already showed. The addition of 7 pph PVOH binder into the "MCC large" pigment structure decreased the pore volume, whereas the addition of SA latex had very minimal effect comparing the pore volume of the pigment system alone without binder. The PVOH can transfer into the pigment intra-particle pores, as the results later will show, and therefore the pore volume is

diminished. The SA latex does not fit into the intra-particle pores (20–60 nm) because of the relatively large latex particle size of 180 nm, and therefore the porosity of the latex containing coating diverges from the porosity of the PVOH containing coating. In the case of GCC and "PCC small" pigment coatings, where the structure had a mainly monomodal pore size distribution, the addition of SA latex decreased the pore volume more than the addition of PVOH. In this case, the SA latex has filled the structure, whereas the PVOH has probably become transported more out of the tablet during the tablet forming process than during the forming of the "MCC large" pigment tablet.



**Figure 21.** The porosities of "MCC large", GCC and "PCC small" pigment structures with and without the selected binders. Measurements were made by using the absorption of silicon oil, water and hexadecane and the penetration of mercury under different applied pressures. Before the abbreviation of pigment type there is added the dispersing agent nature: "anionic" means that the pigment has been dispersed with anionic dispersing agent (sodium polyacrylate). Based on Paper VI (Figure 3).

The pore size distribution of coating tablets containing the chosen binders was also measured by mercury porosimetry. Figures 22A, 22B and 22C show the effect of 1 pph binder addition on the pore size distribution for each pigment. As the previous results of the coating pigments showed, the "MCC large" pigment produced a coating layer with a dual pore size distribution, and this structure characteristic could also be seen at a binder content of 1 pph. The addition of PVOH into the coating colour decreased the inter-particle pore diameter from 410 nm to 330 nm and the SA latex addition increased it to 790 nm. The result indicates that the PVOH fills some of the porous structure, whereas the latex produces some larger pores probably due to the repulsion of latex (anionic) and pigments (anionic, -37 mV) at the depletion flocculation stage (Ridgway *et al.* 2011). SA latex does

not fit into the intra-particle pores, and therefore the porosity of the coating layer diverges from the porosity of the PVOH containing coating. Thus, as the binder type is changed from PVOH to styrene acrylate latex (SA), the formed coating layer structure changes also.

The addition of 1 pph PVOH to the "MCC large" coating did not influence the size of intra-particle pores, but at 7 pph PVOH content there is already a decrease in the amount of the smallest pores, as will be illustrated later in Figure 27. 1 pph PVOH or 1 pph SA had a very minimal influence on the pore size distribution of ground calcium carbonate (Figure 22B). The 1 pph addition is such a low amount that it does not significantly show in respect to pore filling. The same could be seen in the structural results of adding small amounts of binder to the "PCC small" pigment (Figure 22C).



A - "MCC large" pigment





C - "PCC small" pigment

**Figure 22.** The pore size distributions of "MCC large", GCC and "PCC small" coatings. A – "MCC large" with different binders and binder amount (tablets), B – GCC with and without PVOH and SA latex (tablets) and C – "PCC small" with and without PVOH and SA latex (tablets). Based on Paper VI (Figure 4).

At this stage, the pigment selection was broadened so that there would be several pigments that have dual pore size coating structures. All five of the calcium carbonate pigments were studied with 10 pph PVOH binder, and "MCC large", "MCC small" and "PCC large" pigments produced both intra- and inter-particle pores in the coating layer. The coating cakes and their detailed analysis are introduced in Paper I. Figure 23 shows that the porosities of the studied calcium carbonate pigment coatings containing 10 pph of PVOH maintained the same ranking as in the case of non-binder containing coatings. The largest diameter pigments, "MCC large" and "PPC large", produced the highest porosities because there remains more open space between the large particles. However, the third dual-porosity pigment "MCC small" had a medium porosity (30 %) amongst these studied coating layers. The smaller diameter of the "MCC small" pigment provided a more densely packed coating structure. The lowest porosity was produced once again also in this series by the GCC pigment, having both smaller pigment size and broader particle size distribution than the larger sized speciality pigments. The finest pigment "PCC small" developed a medium porosity. However, all the porosity values are lower than in the case of 1 pph of PVOH in the previous series, indicating that a higher PVOH binder amount fills the porous coating structure.





The location of PVOH in the coating structure was studied more closely by detection in two different coating cake structures, derived from pigments having the same porosity without binder, namely "MCC small" and "PCC small". To enable this more detailed analysis, coating cakes of "MCC small" and "PCC small" with and without PVOH were produced, and portions used for mercury porosimetry. Figure 24 shows that the pigments without binder addition produced very similar specific pore volumes. It was noticed that 10 pph PVOH (partially hydrolyzed) added with the pigment decreased the pore volume in both cases, but that "MCC small" pigment showed a greater decrease than "PCC small". The "PCC small" coating structure had only nano-size pores in the 20–60 nm range (Figure 24B), whereas the "MCC small" coatings had both large and small size pores, indicating that the "MCC small" structures had both intra- and inter-particle pores. The PVOH addition decreased to some extent the volume associated with large size pores, but the peak of intra-particle pores in the "MCC small" pigment decreased most markedly, clearly indicating that PVOH had filled the intra-particle pores.



**Figure 24.** The effect of the addition of PVOH (10 pph, partially hydrolyzed PVOH) into the structure of "PCC small" and "MCC small" coatings. A – cumulative pore volume, B – the first derivative of the mercury intrusion curve indicating the pore size distribution. Based on Paper I (Figure 5).

### CaCO<sub>3</sub> coatings on fine paper surface

The same model coatings with 10 pph PVOH, as studied above, were applied on the commercial fine base paper surface, which did not have any pre-coating layer. All coating colours were applied twice so that the target of coating amount, 10 gm<sup>-2</sup>, could be achieved. Between each application time, the coating layer was dried. The coated paper production has been described in chapter 3 section 3.2 "Designed coating structures and binder films, and their production". Paper I contains the complete results from the testing of these coated papers. The cumulative pore volumes of the coated papers, determined by mercury porosimetry, are illustrated in Figure 25A. The results show that most of the coating colours had some partial penetration into the base paper structure, which can be seen as a higher level of the specific pore volume of the base paper than those of coated papers. The porosities of the coating layers were calculated from the coated paper results by taking into account the base paper effect and the amount of coating layer, following the method of Ridgway and Gane (Ridgway and Gane 2003). Figure 25B shows the cumulative pore volumes of the coating layers. The "PCC large" coating produced again the greatest pore volume, and it had more large size pores. The lowest porosities were seen for GCC and "MCC small" coatings. The porosity results of the "MCC small" coating diverged somewhat between the mercury porosimetry and the silicon oil based measurement. In the case of silicon oil, the results of the porosity of "MCC small" and "PCC small" coating cakes were close to each other, whereas, in the case of coated paper, they were clearly on different levels. One reason for this can be in the PVOH location. In the coating cake production, the whole coating colour is in the cake, i.e. it is a closed system, whereas in the case of coated paper some of the PVOH can also transfer into the base paper. Otherwise, it seems that the porosity results comparing coating cake and coated paper agree with each other very nicely.



**Figure 25.** The cumulative pore volume distribution as a function of pore size of the different calcium carbonate containing coatings containing 10 pph partially hydrolyzed PVOH, measured with mercury porosimetry. A – the results from double-coated papers, i.e. 2x experimental coating formulation, B – the results as the base paper values have been subtracted from the results using the method of Ridgway and Gane (Ridgway and Gane 2003). Based on Paper I (A – Figure 11 and B – Figure 3).

The pore size distributions of the studied  $CaCO_3$  pigment coatings, containing the 10 pph PVOH, as derived from the cumulative intrusion curves in Figure 25, are illustrated in Figure 26. The standard ground calcium carbonate (GCC) had mainly pores in the diameter range of 100–300 nm, with a decreasing amount of nanopores. The very small particle size inkjet coating pigment, "PCC small", produced also a coating structure that had mainly monosize pores and they located predominantly in the nano-size area, 20–60 nm. The "MCC large" and "PCC large" pigment coatings had dual-pore size distributions, meaning that there were nanoscale pores in the diameter region of 20–60 nm as well as large pores in the greater than 700 nm region. This bimodality once again describes the discrete pore structures, namely the intra-particle pore volume, representing those inside the particles themselves, and the inter-particle pore volume, representing those



between the particles. The "MCC small" pigment had some small size pores but the main pore volume is associated with pores located in the area of 200–600 nm.

**Figure 26.** The pore size distribution curves from the mercury porosimetry of the studied  $CaCO_3$  coated papers containing 10 pph PVOH (partially hydrolyzed). The base paper values have been subtracted from the results by using the same method as proposed by Ridgway and Gane (Ridgway and Gane 2003). A – nanosize pores, B – large size pores. Based on Paper I (Figure 12).

The effect of binder amount was studied further in Paper II, and the hydrophilic, soluble PVOH was compared to the styrene acrylate latex in the "PCC large" pigment model coatings. In the case of the latex, the polymer itself is hydrophobic, but the surface is partially carboxylated, and together with the stabilising surfactant used in emulsion polymerisation the surface is hydrophilic. Figure 27 shows the pore size distribution of the coatings. The top-coatings were applied on the GCC pre-coating that contained 12 pph SB latex and 0.6 pph CMC. The measurement was made with another mercury porosimetry device than the previous measurements. In these results, the y-axis has been shown as per cent and not specific volume. PVOH coatings displayed more of the smaller diameter pores than the SA latex containing coatings. This can also be seen in the cross-section micrographs (Figure 28) of coated paper structure where the SA latex containing coating has a more porous and thicker structure than the PVOH containing structure at the same coat weight. The particle size of SA latex was guite large compared to the pore size, 180 nm, which can keep the pigment particles apart from each other during the consolidation, whereas the soluble PVOH can fill the capillaries immediately under the influence of capillary forces. The increase of PVOH binder content thus decreased the pore diameters and the volumetric amount of small size pores because of the filling effect of binder polymer. At the binder content of 30 pph, the PVOH coating had fewer pores within the 35-85 nm diameter region than for the case of the SA containing coating. The PVOH has continued to fill the smallest pores. On the other hand, from the pore size intrusion results, the basic pigment dual-pore size distribution can still be seen to some extent.



**Figure 27.** The pore size distributions of "PCC large" coatings with 7, 12 and 30 pph PVOH and 7 and 30 pph SA latex measured from the application of the experimental coating on pre-coated paper (SB latex containing GCC coating). Based on Paper 1 (Figure 8) and Paper II (Figure 5).



**Figure 28.** Cross-section micrographs of coatings comparing the cases with 7 pph of PVOH and SA binder, respectively. The paper had a pre-coating of offset type coating colour (SB latex containing GCC coating). Printed with cyan dye from Versamark<sup>®</sup> VX5000e. Based on Paper II (Figure 15).

By using PVOH and styrene acrylate latex as contrasting binders, representing soluble versus particulate, different kinds of coating structures as well as potentially different interactions with water can be produced. These changes in the coating structures will affect the absorption properties of the layers, which were subsequently studied more closely by observing the inkjet ink absorption as a function of gloss change (DIGAT), gravimetric determination (microbalance) and electrical capacitance (Clara), as well as the colorant chromatographic separation (thin layer

chromatography, TLC). By using these methods, the absorption rate and the pore volume uptake differences can be detected, and furthermore the role of interpolymer diffusion during inkjet ink imbibition into the coating structures can be evaluated (Hypothesis I) along with surface adsorption behaviour.

# 4.2 The effect of coating structure and binder selection on liquid imbibition rate

### 4.2.1 Inkjet ink absorption into the top layer of coating

The coating layer structure as analyzed above affects the ink absorption rate into the coated paper structures, and this has been studied in Papers I and II. The wet ink causes an increase of gloss on the paper surface, and the gloss decreases during the time it takes the ink to penetrate into the structure. The gloss change as a function of time was detected with the DIGAT device, which has been described in section 3.3.5 "Use of more conventional paper testing methods". The GCC coating had the longest absorption time (Figure 29A) because of it both having the lowest porosity and a monomodal pore size distribution limiting the permeability (Paper I). The more highly porous and permeable surfaces made from the speciality pigments absorbed the ink quicker. As the binder amount in the coating layer increased from 7 pph to 12 pph (Paper II) the absorption time became longer (Figure 29B). The high binder polymer amount decreases the porosity of the structure, and the PVOH can move into the intra-particle pores, as we have seen in the previous pore analysis studies. However, interestingly, the further increase of binder amount (30 pph) did not change the absorption time any more. In the case of PVOH containing coating, the inkjet ink diffusion into the binder polymer causes the swelling of polymer and this diffusion compensates for the structural impact on penetration rate, keeping the rate on the same level (600 ms) as it was in the 12 pph PVOH containing coating.

When the inkjet ink droplet arrives onto the coated paper surface, the ink should first penetrate quickly enough into the structure so that the mixing of the droplets is controlled. At this point, an optimal balance between spreading and absorption is obtained. The droplets always spread to some extent, but the mixing of different colour inks should not be so large that intercolour bleeding becomes a problem. As the results of Figure 29 show, the large or medium porosity coating structures generated here a quick absorption of inkjet ink into the coating layer just after the ink has arrived onto the coating surfaces. On the other hand, it is known that large porosity is not a sufficient criterion for fast absorption. These structures should additionally have more nano-size pores. It seems that when the inertia dominates, after the surface wetting, the finest pores will absorb liquid further into the structure and faster, if there is sufficient permeability to allow access to these pores. This is essential for quick inkjet absorption. The work of Bosanquet (Bosanquet 1923) and the further studies of Schoelkopf *et al.* (Schoelkopf *et al.* 2000) and Ridgway *et al.* (Ridgway *et al.* 2001) show that when the inertia dominates wet and the structure and faster al.

nates on the short timescale, when imbibing liquid encounters a sudden change in geometry or pore size within the network structure, the nano-size pores play a very important role in the liquid imbibition during the local short time absorption. The penetration distance of liquid by absorption into the small nano-size pores has proportionality to time, *t* (Bosanquet equation (12)), rather than the equilibrium flow associated with viscous drag, which is proportional to  $\sqrt{t}$  (Lucas-Washburn equation 11).







**Figure 29.** The absorption time of applied ink on the 10 pph PVOH (partially hydrolyzed) containing CaCO<sub>3</sub> pigments (A, Paper I, Figure 13) and "PCC large" coatings with different amounts of PVOH and SA latex (B, Paper II, Figure 6): measured with the DIGAT device using 8 gm<sup>-2</sup> Versamark<sup>®</sup> cyan dye-based ink. (C) – the air permeance of "PCC large" pigment with the different binder content of PVOH or SA latex (Paper II, Figure 4).

### 4.2.2 Gravimetric determination of liquid absorption into the coating structure

In the hypotheses of this thesis it was presented that the inter-molecular diffusion of the vehicle of inkjet ink into the polymer binder matrix acts on a sufficiently fast timescale and in sufficient volume to compete with the permeation of ink through coating structures. The first approach to study the role of diffusion was to measure the polar (water) and non-polar (hexadecane) absorption rate into the coating tablets with a microbalance measurement (Paper VI), which was described in section 3.3.2. The studied "MCC large", GCC and "PCC small" structures contained (a) different dispersing agent (cationic or anionic) and (b) different binder type (PVOH or SA latex) and binder amount. Figure 30 illustrates one example of the result curves. At first, all result curves had a higher absorption rate and after about 2 s the rate decreased. The resultant curves of all the studied coating tablets are shown in Figure 31. Both parts of the curves, expressed as volume uptake per unit area, had a linear relation to the square root of time,  $\sqrt{t}$ , and therefore the absorption rate study was divided into short and long timescale absorption. The slope of the curves describes the effective absorption rate. Figure 32 shows the absorption rate results of the short and long timescale of studied coating tablets, and the discussion below has been divided into two parts: short and long timescale absorption.



**Figure 30.** The gravimetric result curves of water and hexadecane imbibing into the anionic "MCC large" coating structure with 1 pph PVOH: A – the results of the measuring time up to 1 500 s. B – the results of the first 4 s<sup>0.5</sup>. Based on Paper VI (Figure 5).







**Figure 32.** Absorption rate of modified, ground and precipitated calcium carbonate pigment coatings. The short (A) and long (B) timescale  $d(V(t)/A)/dt^{0.5}$  data are derived from the gradients of the absorption curves. Based on Paper VI (Figure 7).

### Short timescale absorption

The short timescale absorption rate in Figure 32A (*Paper VI*), the first few seconds time from liquid arriving onto the coating layer, shows that non-polar liquid (hexa-decane) absorbs more quickly into the coating layers than the polar liquid (water). The liquid is driven primarily by the capillary flow of the porous coating structure, and one competing phenomenon, amongst others, is diffusion (Ridgway *et al.* 2011).

The dispersing agent is a hydrophilic polymer that allows water molecules to diffuse into the inter-polymer space, causing swelling of the polymer at the entry to the finest pores, and this at first slows down the liquid water uptake. However, hexadecane does not diffuse into the polymer and therefore the capillary flow dominates in this non-polar liquid transfer. In addition, the results show that the coating structure with both intra- and inter-particle pores ("MCC large") transports the hexadecane most effectively. Similar pore size structure coatings were found by Ridgway and Gane (Ridgway and Gane 2005) to be favourable for inkjet inks. Firstly, the small capillaries transfer liquid quickly into the structure and from there and behind the wetting front it moves further into the larger pores. This has a connection to Hypothesis III, where it is presumed that the bimodal pore size distributions provides an optimal pathway for quick absorption of inkjet inks.

If the water absorption rate into the dispersed pigments (without binder) is studied, the "MCC large" and GCC pigment coatings had very similar rate, whereas "PCC small" coating absorbs the polar liquid fastest. One possible explanation for this higher absorption rate can be in respect to the surface agents of the pigment dispersion. The GCC and the "MCC large" pigments were dispersed by using an anionic polyacrylate dispersant, which remains on the pigment surface. The water diffuses into this polyacrylate polymer network, swells it and renders it fully hydrophilic, and this needs time. In the case of "PCC small", it requires additional polyacrylate to render it more strongly anionic in dispersion. This indicates that the "PCC small" has a higher polyacrylate demand to render it more strongly anionic in dispersion. Thus, the "PCC small", effectively underdispersed in respect to a given polyacrylate dose, reverses the absorption preference from hexadecane to water at the shortest timescales.

The addition of 1 pph of PVOH or SA latex binder in the pigment tablets provided still faster hexadecane absorption rates at the short timescale for "MCC large" pigment coatings than for GCC and "PCC small" coatings. The importance of both intra- and inter-particle pores in the non-polar liquid transfer is again reflected here. Both binders absorb only a minimal amount of non-polar liquids (Figure 46 in chapter 5 section 5.1 "Liquid absorption by binder films"). This means that swelling of the polymer in the presence of hexadecane is minimal, and therefore the smallest pores in the coating remain open during the hexadecane absorption and the diameters of pores are unchanged. Thus, during the non-polar liquid imbibition, the capillary flow dominates.

If the water absorption into the PVOH and SA latex containing "MCC large" and "PCC small" pigment coatings are studied, it is seen that the SA containing coating had lower absorption rate results than in the PVOH containing coatings. The PVOH containing "MCC large" coating had more small-diameter pores than the SA coating, as Figure 22A shows, and the swelling of hydrophilic PVOH binder changes the amount of small pores dynamically during the water absorption. The PVOH absorbs polar liquid, like inkjet ink (Figure 46 in chapter 5 section 5.1 "Liquid absorption by binder films"). This polymer diffusion causes the PVOH to swell and therefore some of the nano-size pores will close and/or there will also be a diminishing volume/number of these pores already at the short timescale, supporting

the Hypothesis I. In the case of SA latex containing coatings, the latex polymer does not swell in the presence of water (as the chapter 5 "Mechanisms influencing liquid absorption in coating binders" later shows) and thus the capillary flow controls the water imbibition. The reason for slower absorption rates can be in the hydrophobic nature of SA latex polymer that prevents the penetration of polar water and thus a loss of effective absorptive volume. However, wetting will still occur, and this is probably related to the surfactant and/or carboxylation used to stabilize the latex. A similar binder behaviour difference between PVOH and SA containing coatings in respect to water uptake was noticed with the "PCC small" coatings.

### Long timescale absorption

In long time absorption (Figure 32B, *Paper VI*), the diffusion is still progressing, and, in parallel, the porosity of the structure (permeation flow) permits continued liquid imbibition by pore surface wetting and subsequent meniscus flow. The absorption rates of polar and non-polar liquids at the long timescale were slower than in the short timescale region. During the progressive absorption over time, the viscous drag increases in proportion to the length over which the liquid flows within the structure, as the Poiseuille equation indicates (equation (7)), and this slows down the absorption. The results show further that the water absorbs quicker than hexadecane. The polymer structures on the pigment surfaces have had time to reorient due to the water vapour front diffusion and this promotes polar liquid movement.

The "MCC large" coatings had again higher absorption rate values than either the GCC or the "PCC small" coatings. The coating with the dual-porosity structure is confirmed to be the most advantageous in respect of liquid absorption rate because it produces a coating structure with high permeability (Figure 20A) and it contains nano-size pores (Figure 20B) that drive the liquid front forward.

In the long absorption timescale, the SA latex containing "MCC large" coatings absorbed water faster than PVOH containing. In the short timescale absorption, the results were vice versa. In the over 2 s time absorption regime, the small diameter pores at the wetting front retain their action of providing the driving force, but the rate is determined by the permeation flow in the large pores, defining resistance to that driving force. The PVOH containing coating had smaller pore diameters (intra-particle pores) than the SA latex containing, as Figure 22A shows. These findings support the conclusions of Ridgway and Gane (Ridgway and Gane 2005).

## 4.2.3 Liquid and colorant movement – impact of charge on chromatographic separation in the coating layer

The second approach was to study how the liquid transfers through the different coating structures in thin layer chromatography (TLC, *Paper V*). The variables of coating colours were the ionic charge of dispersing agent (anionic/cationic), the

inter-polymer hydrophilicity of binder type (hydrophilic/hydrophobic) and the cationic additive application. "MCC large" pigment was selected because of its capability to produce a coating layer with the dual pore size structure and so producing a guaranteed fast absorption of inkjet ink, as the previous results in Figure 29A showed. The hydrophilic partially hydrolyzed PVOH and inter-polymer hydrophobic styrene acrylate latex were again selected for comparison, and the binder amount chosen to be sufficiently low that the chromatographic separation can be detected. The effect of the ionic charge of the coating layers was observed by using anionic (anionic sodium polyacrylate) or cationic (polyDADMAC) dispersing agent in the production of coating slurry. The pore volumes were measured from the coating tablets, and the results were very near each other, as Figure 33 shows. The SA latex containing coating had a little bit higher porosity than the other anionic coatings.



**Figure 33.** The pore volume of "MCC large" coatings (tablets) that were used in the thin layer chromatography research. Based on Paper V (Figure 4).

On contact with supersource soluble anionic colorant, the results show that there always exists a wetting front rising within the anionic coating structure in advance of the anionic colorant front (Figure 34) and behind this comes a colorant-rich ink layer and after that a less colorant containing ink eluent area. There is no obvious retardational adsorption mechanism on the basis of charge alone. The wetting water front height in this anionic case was about one millimetre ahead of the colorant front. The retarded colorant fronts were darker than the following (trailing) colours (Figure 35, anionic coatings). As the finest pores of the coating structure drive the wetting front forward, they seem to exclude the dye colorant. It seems that the surface area associated with the finest pores of these structures is either not available for adsorption of the dye molecules or a further rate determining step is involved. These results suggest that the <u>anionic repulsion</u> is the primary exclusion mechanism. This can be one force in the coating layer that might act against the diffusion.



**Figure 34.** The water front is seen to be ahead of the anionic colorant front in the anionic "MCC large" coating layers after 4 min: left 5.00 wt-% and right 0.54 wt-% anionic colorant in water. Based on Paper V (Figure 11).

The highest water rising distance and the highest penetration rate was observed for the binder-free coating structures (again considering the "MCC large" pigment structures). The coating with SA latex had a plateau height value roughly half that of the binder-free coating, and the lowest values were for PVOH containing coatings (Figures 35 and 36). Only 1 pph binder addition already caused such a significant difference to the liquid movement and final rise position. The SA latex containing coating had somewhat larger pore volume than the coating without binder and this can be one reason for a lower eluent rise. There were also less small capillaries that drive the eluent front forward, and the hydrophobic nature of SA latex can further reject the polar eluent, as will be described further below. The SA latex network does not support the diffusion of polar liquid into the polymer network whereas the polyvinyl alcohol binder can. In the case of PVOH containing coating, the polar eluent diffuses into the binder structure and the binder polymer matrix swells causing the closing of the smallest pores and the diminishing of remaining pore size. At the same time, the pore volume of the coating layer decreases and this slows down the eluent movement. Thus, the diffusion into the PVOH affects the permeability of the coating structure and so slows the permeation flow in the layer. The eluent colorant content did not change the behaviour, in that all the studied ink colorant amounts proceed to similar distance values upon each given coating TLC plate.

In the cationic coatings, the anionic colorant initially stayed at the bottom edge of the coating. After a development time of ten minutes, the fixed dye edge appeared to fill with colorant and part of the colorant volume started to rise little by little. Especially, this could be seen when there was the higher concentration (5.0 wt-%) of colorant in the water. The surface area associated with the cationised pores takes part in adsorption, and only when the surface area of pigment is saturated with colorant can the colorant move forward into the structure. The degrees of freedom of the normally random walk mechanism of diffusion is therefore limited by the local adsorption mechanism, which requires charge potential equilibration, and hence local concentration of anionic dye by diffusion of the colorant to the surface. Only then is random diffusion re-established until the next surface charge accumulation is encountered.

The importance of very small pores in inkjet ink imbibition can also be detected in the study of thin layer chromatography (Paper V). The surface coating structure first wets and the capillary flow drives the ink into the nano-size pores. The small size of a water molecule, 0.27-1.00 nm (depending on the amount of molecules in one cluster) (Topgaard and Söderman 2001), enables the capillary flow in the nano-size pores to occur, i.e. in the intra-particle pores of "MCC large" pigment (20-70 nm). The colorant-free wetting front connected with the higher colorant concentration just after the colorant front, as noted previously, suggests that the mechanism here is an anionic repulsion from the finest pores, allowing the water to imbibe into these pores, but not the dye. It can be concluded, therefore, that charge exclusion limits the passage, i.e. excludes the response to capillarity of the dye in the eluent into the pores. This sets up a diffusion gradient of colorant within the eluent when the charge of the surface is of the same sign as that of the colorant. As the amount of ink increases, the permeation flow in larger pores increases so that there are no more open pores in the coating. The size of a colorant molecule is about 1.3 nm (taking account of the length of different bonds in the Cu phthalocyanine colorant molecule and assuming the molecule is planar), which means that the colorant fits well into the 20-70 nm intra-particle pores. In the case of the cationic coating layer, the water front rises very similarly as in the anionic coating layers, and behind the capillary flow comes the filling of large pores (permeation flow), but now the anionic dye becomes fixed to the cationic surface in the bottom of the TLC plate.



Figure 35. The 5.0 wt-% anionic cyan colorant rising within different "MCC large" coating layers. Measured after 4 min time delay. Based on Paper V (Figure 6).

The structure of the coating laver and the selection of binder type affects how far the ink moves through (along in the case of TLC) the coating layer and how quickly. At first, the slope of the distance curves seems to be at its greatest, and it decreases as the development time increases. The TLC eluent moves further and with a faster rate in the anionic dispersed pigment layer than in 1 pph binder containing layers (Figure 36). After a distance of 30 mm there was no further change in the distance travelled in the anionic pigment layer, whereas in the PVOH containing coating the front of the eluent stopped after 7 mm, and in the SA coating after 17 mm. The balance between the wetting force (Young-Laplace equation) and the viscous drag determines the rate of progress. As the viscous drag increases in proportion to the length over which the liquid flows within the structure, and to the inverse fourth power of the typical equivalent capillary size (Poiseuille effect), there comes a point when the drag equals the wetting force. The SA coating had a higher pore volume indicating that it could both accommodate more liquid and, if permeable, transport it further than could the lower pore volume PVOH structure. The SA latex swells only a few percent under the influence of water (Lamminmäki et al. 2010). Thus, the capillary flow controls the water imbibition in SA latex containing coatings. The difference between the SA latex containing coating and dispersed pigment alone is additionally suggested to be caused by the possible difference in the hydrophilic/hydrophobic natures. The SA latex has a more hydrophobic nature indicating that the contact angle of polar liquid may effectively increase in contact with the polymer, or the timescale for the surfactants present to reorient, and so permit wetting, may delay the passage of water, and thus the effective capillary pressure decreases. The equilibrium point comes much sooner with binder containing coatings, both due to reduced pore connectivity and surface chemistry effects, and these are reflected in the distance the liquid front finally travels. The measurement in the TLC analysis lasts up to 40 min, and the evaporation of eluent (water) has therefore an influence on the results. However, the evaporation study of water in Paper V indicated that evaporation has only a minor effect on the eluent movement in respect to the influence on the wetting force and viscous drag force. Only towards the very end of the experiment can we expect evaporation to be a further equilibrating factor additional to the wetting force-retardation balance.



**Figure 36.** The distance of eluent (water) front during the time in the chromatographic development. The coating pigment was "MCC large" and the eluent, water (de-ionized). Based on Paper V (Figure 8).

## 4.2.4 Inkjet ink penetration in coated papers monitored by electrical capacitance

In conventional contact printing methods, the external pressure has an important role to play in the penetration of low viscosity liquids, such as fountain solution in the offset process, or ink vehicle in low ink solids flexography. The exception is for the case of paste offset inks, where the penetration in the nip is minimal (Oittinen 1976). However, in inkjet printing, the only external pressure is occurring when the droplets hit the paper surface, and subsequently from the curvature of the ink droplet in relation to its surface tension. If a 15 pl dye-based inkjet ink droplet (density 1 000 kgm<sup>-3</sup>) arrives onto the paper surface with speed 15 ms<sup>-1</sup>, as in the Versamark<sup>®</sup> VX5000e technology, for example, the pressure of the droplet hitting the paper surface is a little under 0.10 bar. This pressure is soon dissipated in practice, and in the following experiments it is applied primarily to initiate stable wetting. A value of 0.10 bar is expected to be less that the capillary pressure in the fine pores. If the capillary pressure,  $p_c$ , of a liquid is calculated by the Young-Laplace equation (equation (10), considering a 100 nm diameter pore (nano-size pores), a contact angle of 50° (contact angle of water on the 7 pph PVOH containing "PCC large" coating, Figure 72) and a surface tension of 54 mNm<sup>-1</sup> (the cvan Versamark<sup>®</sup> VX5000e ink at 24 °C, Figure 10) we obtain for the Laplace capillary pressure, 13.9 bar, which is a lot higher than the used 0.10 bar. This means that the capillarity in the finest pores will act to cause the wetting. However, a capillary diameter of 1 µm develops a pressure which is ten times less, i.e. 1.39 bar, and 10 µm, 0.14 bar etc. So, the pressure of 0.10 bar forces ink by intrusion into pores which have a diameter of at least 13 µm. The studied coating layers have only a

few or none of this size pores, and therefore the coating structure will allow some very small amount of externally-driven permeation only. However, the 1.5 bar pressure forces liquid into over 1  $\mu$ m pores. This means that, at this pressure, the long term intrusion becomes dominated by permeation for many inkjet coatings. If the wetting force of 100 nm diameter pores is calculated, the equation  $\pi r^2 p_c$  gives 11 nN, which is a very low force despite the high pressures involved.

To illustrate the effect of pressure over a wider range, the study of inkjet ink penetration below has been divided into three different external over-pressures: 1.50 bar, 0.10 bar (inkjet droplets hitting pressure) and 0.02 bar (effectively no external pressure). By using different over-pressures, the separation between the effects of capillarity, permeability and diffusion can be detected. The work at high pressure permits to characterise the permeability, the medium pressure mostly capillary and diffusion, and the zero pressure capillary competing with diffusion of liquid and vapour. The results are based on *Paper II*.

### Absorption properties at 1.50 bar over-pressure

Figure 37 shows how the capacitance results at 1.50 bar external over-pressure changed when the amount of binder in the "PCC large" coating layer increased. The studied surface had two coating layers on the fine base paper. The precoating contained offset quality GCC and top-coating "PCC large" inkjet pigment. A series of top-coatings were thus tested having different amounts of partially hydrolvzed PVOH or styrene acrylate latex. In section 3.1.5 "Substrate: pre-coated base paper" has introduced the studied materials and in Table 8 the recipes of the coating colours are described. The coating which contained more binder had a slower capacitance change. The bimodal nature of the capacitance curve indicated the relative change from capillarity to permeability. Clearly, the highest binder level of PVOH dampened the capillary effect as the resulting graph becomes monotonic. It took from 2.4 s to 11.0 s for the inkjet ink to penetrate through the structure with PVOH containing coatings, whereas with SA containing coatings only from 0.9 s to 2.7 s. The fastest ink penetration speed through the pores was reached with lowest binder content and ink penetrated more quickly through the SA coating papers than through the PVOH papers.



**Figure 37.** Cyan dye-based ink (from Versamark<sup>®</sup> VX5000e) penetration through the "PCC large" coated papers at the external over-pressure of 1.50 bar, as measured with the Clara device: A – refers to the different content of PVOH and B – refers to the different content of SA latex, respectively. Based on Paper II (Figure 7).

We can calculate the penetration speed and depth from the capacitance results by assuming that the ink has gone through the whole paper structure as the highest capacitance values have been reached, as the method section indicated (Section 3.3.2 "Liquid penetration"). Figure 38 illustrates how the inkjet ink penetrated through these papers coated with "PCC large". The thicknesses of the coating layers together (both top- and pre-coating) were about 20 µm, but part of the pre-coating colour had probably penetrated during the consolidation into the top layer of the base paper, as we noticed earlier in Figure 25 with the 10 pph PVOH containing coatings. Therefore, we can assume that the effect of the coating layer can influence even as deep as 30 µm. The ink penetrated with higher speed through the SA latex containing coatings than through PVOH containing, and the penetration through the coating layer was lower as the binder content increased. The air permeance values of each comparable paper at a given binder amount were very similar, indicating that the PVOH blocked the capillarity-acting fine pores, whilst overall permeability comparing the binder systems appeared similar.

There appears a turning point in the curve of the inkjet ink penetration speed, which refers to a point located deep within the base paper. This supports the assumption that either the components of pre-coating or the polyvinyl alcohol of top-coating have penetrated deeply rendering the diffusion effect active throughout the sheet or the predicted over-pressure effect has created a significant difference in position between the wetting front relative to the coating saturation front, created by the permeation lead through the larger more connected pores, and that it requires further wetting front penetration before the saturation front has reached the base paper. In the coating layer consolidation, the PVOH can follow the liquid phase of the coating colour deeper into the paper structure and so affect the forming porosity. The pre-coating penetration into the base paper, as mentioned previously,

can also be an explanation. During the water-based ink imbibition, the penetrated PVOH swells under the influence of water, and this affects the absorption into the smallest pores by closing and/or diminishing them and this is reflected in the Clara results. The PVOH can also dissolve partially into the inkjet ink during the penetration process, as we shall later see in chapter 5 section 5.2.1 "Diffusion coefficient", and so affects for example the process viscosity and surface tension of penetrated liquid.



**Figure 38.** Cyan dye-based ink (from Versamark<sup>®</sup>VX5000e) penetration speed, as recorded by capacitance change, through the paper structures having PVOH and SA containing "PCC large" coatings at external over-pressure 1.50 bar. The coating variation refers here to the thickness differences of the coating layer: A – refers to PVOH and B – refers to SA latex, respectively. Based on Paper II (Figure 8).

### Absorption properties at the inkjet droplet hitting pressure

Figure 39 shows the capacitance results of the range of CaCO<sub>3</sub> pigment structures, as formed on the coated papers (same papers that were used before in the study at the 1.50 bar over-pressure), during imbibition of inkjet ink at 0.10 bar over-pressure. At the lowest binder amount (7 pph), the used cyan ink penetrated more rapidly in the SA latex containing "PCC large" coating than in the PVOH containing. The capacitance values of SA containing coating were still higher than the values of PVOH containing. When the binder amount increased, the curves of PVOH and SA coatings came closer to each other. We see that the bimodal nature of the curves is far less at the lower over-pressure than at the 1.50 bar, supporting the dominance in this case of capillary pressure over that of permeationdriven flow. At the 0.10 bar over-pressure, only in the coating with 7 pph of latex could any indication of bimodality be seen, and this supports the likelihood of there being greater permeability in this structural case, such that even at low pressure some external pressure-driven Poiseuille flow can be established. In the case of "PCC small" coatings (Figure 39D), the capacitance curves were very near each
other during the time of the first few seconds. The slope of PVOH containing coating was slightly higher in the beginning of the measurement indicating higher initial absorption rate of the coating layer. This indicates that the pre-diffusion of vehicle into the binder accelerates the penetration.





**Figure 39.** The effect of binder type and binder amount in the "PCC large" and "PCC small" coatings on the results of Clara. Measured with Versamark<sup>®</sup> cyan ink using 0.10 bar over-pressure: A, B, and C refer to 7, 12 and 30 pph binder levels in "PCC large" coatings, respectively, and D – refers to 7 pph PVOH and SA "PCC small" coatings. Based on Paper II (Figure 9).

#### Absorption in the non-pressurized regime

Figure 40 shows the capacitance results of the same coating layers at the external over-pressure of 0.02 bar (effectively no additional pressure). The 7 pph SA latex

"PCC large" coating produced again the higher capacitance results than PVOH containing, but the slope of the curves in the beginning of the measurements were already very similar. The capacitance results of 12 pph and 30 pph PVOH/"PCC large" coatings were seen to be at a higher level than the results of comparable SA latex containing (12 pph binder: PVOH 107-125 pF and SA 90-110 pF; 30 pph binder: PVOH 105-115 pF and SA 100-112 pF). It seems that the importance of inkjet ink diffusion into the binder and at the same time the swelling of the binder network increases as the coating colour has more binder and/or the external over-pressure decreases. This argument supports the conclusion that diffusion must compete against permeation-driven flow, which, under external pressure, can exceed the rate of diffusion into the water-swellable binder. The hydrophilic PVOH can absorb inkjet ink whereas the hydrophobic SA polymer latex matrix cannot. The bimodality can still be seen in the 7 pph SA coatings.



Figure 40. The effect of binder type and binder amount in "PCC large" coatings on the results of Clara at the external over-pressure 0.02 bar. Measured with Versamark<sup>®</sup> cyan ink.

#### Short-time and transition penetration in the coating structure

In the beginning of capacitance-based measurements, at 0.02 bar over-pressure, similar polar liquid inkjet ink penetration rate into the 7 pph SA containing coating and the 7 pph PVOH coating could be detected. When the binder amount increased to 12 pph or 30 pph, the PVOH containing "PCC large" coating produced a higher capacitance value than the comparable SA containing coatings. However, the situation changes when the external over-pressure is increased to the 0.10 bar, corresponding to the inkjet ink droplet hitting to the paper surface, or even higher, 1.50 bar. The pressure increase speeds up the penetration of the liquid

into the structures, and the penetration speed of SA latex containing coating increases more during the pressure increase than the PVOH coatings. The SA containing coatings had less binder interaction with the fine pores whilst permeability is maintained. At lower pressure, the ink penetration is controlled strongly by the nano-capillary absorption and diffusion into the PVOH. The pressure increase raises the speed of ink permeation more in large pores than in the small diameter pores because the capillary pressure of small pores is higher than the pressure in the large pores. At the higher external over-pressure, the permeation flow has the greater role to play in the liquid transfer than at the lower pressure.

We recall that the short timescale results of binder containing "MCC large" tablets in the microbalance measurement showed that PVOH containing coatings absorbed water quicker than SA latex coatings. However, this kind of difference could not be detected with the Clara measurements from "PCC large" coated papers at 0.10 bar external over-pressure, where inkjet ink penetrated quicker through the 7 and 12 pph SA containing coating layers than through the PVOH containing. There is also some variation in the results of Clara (Paper III) as well as in the microbalance, but by variation alone the differences in the results cannot be explained. Both pigments had very similar intra-particle pores and therefore the short timescale penetration speeds were expected to be similar while the chemistry of the structure remained similar. At the lowest 0.02 bar over-pressure, this kind of indication of slower penetration speed with the SA containing coatings than with the PVOH coatings could again be detected, especially at 12 and 30 pph binder content. The significance of diffusion increases, but primarily the permeability dominates whenever pressure is applied. Furthermore, the likely wetting delay caused by surfactant reorientation in the latex case is overcome once a small external pressure is applied, launching the system into absorption. The Clara results indicate, therefore, that the low pressure, which the inkjet droplets cause on initial contact at the paper surface, is high enough that at the beginning of the ink imbibition it significantly affects the inkjet ink movement in the top layer of the coating structure, i.e. it induces forced wetting.

The capacitance-based measurement at over-pressure 0.10 bar shows that there are turning points in the slope of capacitance results. The turning points located at a time of 0.02-0.20 s (Figure 39), and, on the basis of both 0.10 bar and 1.50 bar results, this is the moment when the capillary force-filled pores are starting to become saturated and the remaining larger pores fill under the external pressure. This changes the mechanism from capillary flow to permeation. This continues through the wetting of the base paper as the rate of base paper penetration is controlled by the permeability of the coating layer. If we now consider the absorption time of 0.36 s for the 7 pph SA-containing coating, as measured by DIGAT (Figure 29), we can conclude that the ink has already penetrated through the coating layers at the moment when the gloss of the 8 gm<sup>-2</sup> ink layer disappears.

At a binder amount of 12 pph and at the 0.10 bar external over-pressure, the SA latex containing "PCC large" coating absorbs the ink still more rapidly than PVOH. The effect of diffusion becomes more and more important when the external pressure decreases, and this acts to differentiate between the binders. At the

0.02 bar over-pressure, only the lower level of 7 pph SA binder containing "PCC large" coating remains at higher capacitance, from 115 pF to 130 pF, than the PVOH containing, from 105 pF to 115 pF (Figure 40).

#### Long-time penetration

The long timescale penetration means the time after the turning point in the capacitance results curve. In this regime, either the external pressure has forced the transition to permeation flow or the equilibrium has been reached at low external pressure between the capillary wetting force and the viscous retardation. The SA containing "PCC large" coatings had similar or even faster penetration speed of the inkjet ink than the PVOH containing coatings, depending on the external pressure. This result is very similar to that of the microbalance with "MCC large" coatings, and indicates that the permeability of the SA containing coatings is greater than that of the PVOH containing, once the external pressure dominates.

At the 0.10 bar over-pressure, the results varied depending on binder content, and at 1.50 bar the ink penetrated through the SA containing "PCC large" coatings quicker than through the PVOH containing coatings. One explanation for the slope variation at the over-pressure of 0.10 bar, consistent with the discussion above, can be that the structures combined with this inkjet ink might exhibit a critical pressure response in this region, where the normally dominating diffusion, combined with capillarity, becomes less important as the permeation starts to dominate.

# 4.3 The role of coating layer thickness in inkjet ink penetration

One way to affect the volume capacity where the inkjet ink can absorb is to increase the thickness of the coating layer. The research into this coating thickness effect was made by using "PCC small" or GCC pigment, and partially hydrolyzed PVOH as the binder. The binder amount was 7 or 15 pph. The coating colours were applied on plastic film using different coat weights to generate the different coating thicknesses. In section 3.2 "Designed coating structures and binder films, and their production", the production of these samples has been described more closely. Figure 41 shows first of all that the inkiet speciality "PCC small" pigment provided thicker coating layers on the plastic film surface than the offset standard GCC at equivalent coat weight (Paper III). The GCC pigment produces a more tightly packed coating layer structure, as the Si-oil porosity results indicated (Figure 20). Most of the Clara absorption result curves reached the maximum value of capacitance at the short time of 0.004 s (Figure 41). Inkiet ink has more or less penetrated through the coating layers which were applied on the plastic film surface, even though the thickness is up to 35 µm, during 0.004 s time. The pigment type or binder amount did not change the situation, as Paper III shows. The transit of the removable plate out of the measuring area lasted the first 0.0038 s, and so the relevant data are on the limit of stable detection.

The results show that, at longer time delays than 0.004 s, permeation flow dominates in the coating structures. The results agree very well with the results of Ridgway *et al.* (Ridgway *et al.* 2001, Ridgway *et al.* 2002). They calculated with a Pore-Core computer model of void structure how quickly alcohols and water move in the coating layer structure. Their results showed that smaller radius capillaries fill initially faster than larger ones. The fine capillaries filled faster until 0.00026 s to 0.00056 s, depending on the equation used in the calculation (Bosanquet inertia versus Szekely pore entrance energy loss), and only after this time do the larger pores start to fill at a faster rate.

The coating layer penetration results of the Clara device indicate, therefore, that the initial nano-capillary flow is too fast for the device. Using the Bosanquet absorption equation (Bosanquet 1923), which takes into account the inertial flow of liquid, the time of absorption into a 0.1  $\mu$ m length pore is below 10 ns (Ridgway *et al.* 2002). However, the Clara starts the detection of penetration from 1 ms. From this it can be concluded that the liquid in the coating has already passed via the first preferred pathway wetting front point in an idealised free access structure (non-permeability limited) to about the scale of a centimetre. The maximum coating thickness in this study was 35  $\mu$ m, which, since it is a complex network, probably does not exhibit direct *z*-directional centimetre scale pathways for ink, but is highly likely to have been traversed by the leading liquid front via a tortuous path through the complete sample thickness during this relatively long timescale in absorption terms.



**Figure 41.** The effect of coating layer thickness on the capacitance results. The inkjet speciality "PCC small" (A and C) and offset standard GCC (B and D) coatings are on a plastic film. The thickness of each coating layer has been added after the coat weight value. The ink was cyan dye-based ink from Versamark<sup>®</sup> VX5000e and the external over-pressure at the chamber 0.10 bar. The final capacitance level of Clara results depends on the variation of the plastic film (204–212 pF). Based on Paper III (Figure 7).

D

C

At the beginning of the measurement, it seems that the higher the coat weight the lower starts the values of the capacitance curves. This suggests that the thicker coating layer, in this case a higher coat weight on the plastic film, has more pore volume during the first few milliseconds of absorption than the thinner one. On the other hand, this can be an indication of the different kind of coating layer structures of the low and high coat weights. The thicker coating structure is less ink absorbing in the beginning stage of absorption. Laudone *et al.* (Laudone *et al.* 2006) found out that a high coat weight coating had lower porosity than a low coat weight coating because high coat weights tend to consolidate more. However, we

must remember that during the first 0.0038 s time the plate on the Clara device is still moving, and therefore the detected capacitance measurement area progressively increases. Additionally, the Clara is based on making an average dielectric permittivity assumption, and the thicker coating will have a higher permittivity weighting and so appear to accelerate the liquid passage in that region. Nonetheless, this provides more likely evidence for the preferred pathway wetting phenomenon as a greater proportion of pores are initially by-passed as the length of the sample increases.

The effect of coat weight on the paper surface was studied by applying the 7 and 15 pph PVOH (partially hydrolyzed) containing "PCC small" coating with a curtain coater on the commercially pre-coated fine paper surface (Paper III). Section 3.2 "Designed coating structures and binder films, and their production" introduces the coating procedure. The penetration distance results, which were calculated from the capacitance results, show (Figure 42) that in the beginning of the absorption into curtain-coated "PCC small" coatings, the distances have quite a linear relation to the square root of time, indicating either equilibrated Poisueille laminar flow according to the long timescale applicable Lucas-Washburn equation, and/or a Fick's Law diffusion response. There are two linear regions with respect to the square root of time during the first second timescale, with the turning point between them located at time 0.2 s (Figure 42), similarly as in the microbalance results though the turning point located at a different time moment. Ström et al. (Ström et al. 2008) had similar results in their study of PVOH containing coatings. In the first linear region of capacitance-based results, the properties of the coating structure predominantly affect the absorption, and in the second region the porous structure of the base paper dominates. This turning point seems to locate at a distance of 15 µm to 35 µm from the top of coating layer, depending on the coating layer thickness. The thicknesses of the applied curtain-coating layers were in the region of 2.5 µm and 8.5 µm. The thickness of the pre-coating layer was not measured, but it seems that the turning point locates neither in the pre-coating layer nor just under it. The turning point locates deeper within the base paper. The reason for this may again be in the PVOH polymer moving into the base structure and/or diluting or more likely the difference in preferred pathway wetting front and the line of saturation.



**Figure 42.** The penetration distance of dye-based ink (Versamark® VX5000e cyan) in the inkjet speciality "PCC small" coatings during square root of time clearly showing the two regimes of absorption. The external over-pressure at the chamber 0.10 bar. A – "PCC small" with 7 pph PVOH, B – "PCC small" with 15 pph PVOH. Based on Paper III (Figure 11).

The turning point becomes more and more visible as the coat weight and binder amount increases, indicating a greater effect of the top-coating layer in the complete sheet construction on the apparent inkjet ink imbibition. This could, however, be an artefact of the measurement since the permittivity of the coating layer distance is different to that of the base paper, and in the Clara calculation it assumes an average permittivity throughout (section 3.3.2 "Liquid penetration"). The penetration rate apparently increased as the coating layer thickness increased (Figure 42). The higher pore volume combined with more nano-size pores (Figure 43) promotes the ink penetration into the coating layer structure, but the increased permeation resistance of the thicker coating should act eventually to slow progress. This evidence highlights the weakness of the Clara device in that it probably misinterprets the coating thickness effects on imbibition speed due to the ratios in permittivity of the different layers. The higher coat weight structure, nonetheless, has larger pore volume and therefore more nano-size pores, which will keep the high capillarity action active for longer.



**Figure 43.** The pore volume (A) and pore size distribution (B) of different coat weight "PCC small" coatings. Measured with mercury porosimetry. Based on Paper III (Figure 4).

The findings suggest that in the lower coat weight coating, the ink stays longer in the top-coating layer because the ink first penetrates quickly in the small nano-size pores of the structure caused by high capillarity and the Bosanquet inertial wetting regime, and the wetting front pins for a while in the interface between the small pore size fraction of the top-coating and the underlying pre-coating before it continues the penetration. The longer the ink front remains pinned in the top-coating means that inks have higher probability to mix with each other.

## 4.4 Summary of the coating structure effect on ink imbibition

All the results of absorption measurements, namely microbalance, thin layer chromatography and capacitance-based Clara measurement, indicate that the rate of liquid transport in the coating layer structures varies depending on the moment of detection. Each research method has a turning point of sorption, and before and after this point the penetration rate has a linear relationship to the square root of time. The moment of turning point depends on the sample preparation, tablet versus coating on film versus hand coating on pre-coated paper versus curtain coating, measuring principle, liquid being transferred upwards or downwards, from a supersource or a layer, including lateral spread or not, and the external pressure. The capacitance-based results show further that the over-pressure, caused by the inkjet ink droplet coming onto the paper surface, is in fact large enough to initiate wetting, but that we can consider it negligible in relation to capillarity but effective in promoting initial permeation. Therefore, in the ideal experimental situation the pressure should be removed after the start of the experiment, as of course happens in the real printing situation. Additionally, weaknesses in the capacity measurement theory, when based on the average assumption of constant permittivity throughout a coated paper, have been highlighted.

At the first instant of the liquid arriving onto the coating structure, the liquid penetrates more quickly into the very top-coating structure than later in the imbibition process. This is suspected to be an effective surface wetting phenomenon including the surface nanopores. After the liquid has wetted the coating surfaces, the major driving parameters for ink absorption into porous coating structures are capillarity and permeability in relation to the fine pores and the larger interconnected pores, respectively. The capillary force is active in the fine pores, and once the capillaries become saturated then permeability is the controlling factor for further imbibition to enable access to further unsaturated nanopores, indicating either equilibrated Poiseuille laminar flow according to the long timescale applicable Lucas-Washburn equation, and/or a Fick's Law diffusion response. In the case of inkjet ink imbibition, the polar ink vehicle firstly moves into the nano-size capillaries of the coating layer and forms the wetting front, where the colorant part of ink, if of the same charge as the pore walls is repelled or if of opposite charge is held by that charge, cannot transfer or does so only slowly by concentration-driven diffusion. Thus, anionic repulsion hinders the anionic colorant penetration into nanopores, and cationic attraction pins the colorant initially at the first contact point until concentration of colorant increases.

The permeation flow in coating layers becomes dominant as the resistive component after the first 0.004 s time. Depending on external pressure, the existence of fine nano-size pores either speeds up the sorption rate of the polar liquid ahead of the pore saturation front in the case of zero or low external pressure, or permeation dominates and the finest pores fill behind those of the larger connecting pores when sufficient external pressure is applied. In practice, external pressure only occurs at initial contact of the printing ink droplet. The results show that the coating with the dual-porosity structure provides an optimal balance of these two effects, i.e. it promotes the fast liquid absorption because it produces a coating structure with high permeability and it contains nano-scale pores that drive the liquid front forward, whilst the charge distribution defines the pinning and fixing characteristics of the colorant, thus supporting Hypothesis III.

**Hypothesis III** – the verity of Hypotheses I and II can be used to design porous coating structures, based on discretely bimodal pore size distributions, using binder and surface charge distribution characteristics to provide rapid fixing of ink colorant optimally close to the coating surface.

The pigment selection affects strongly the forming of the coating layer structure, but the binder type and its amount has also a major role in determining connectivity, permeability and interaction with liquid.

The DIGAT results from the gloss decay of a wet ink layer showed that the inkjet ink can initially stay on the top of the PVOH and SA latex containing coatings for a quite similar delay before it penetrates into the coated papers, but the ink penetration speed in the coating layer is higher in the SA bound coatings, especially under a high external pressure, indicating a permeability controlled difference between the structures using different binders – the particulate SA binder leading to a coating structure that is generally more permeable. The local-

ised hydrophobicity of SA containing coating slows firstly the inkjet ink penetration into the structure, related to the likely action of the wetting delay by surfactant. In the coating structure, the PVOH can locate in the intra-particle pores as well as on the surface of large pores, whereas SA latex remains in the large pores associated with the inter-particle interstices. Even a small binder addition, 1 pph, has a remarkable effect on the liquid movement in the coating structure as the TLC and microbalance measurements showed.

The PVOH polymer matrix can be diffused into by the polar liquid, as in the case of water-based inkjet ink, and the swelling of PVOH closes the nano-size pores in the coating structure and decreases the total porosity. Therefore, the ink can transfer in the PVOH containing coating structure but with lower speed than in the non-swelling SA containing coating. However, in the non-pressurized condition, and at the short timescale, the PVOH containing coating with nano-size pore structures absorbed polar liquid quicker than the SA containing structure. This indicates that the ink diffusion in the PVOH binder happens at the same timescale as the ink capillary flow in the SA coating. In parallel, the longer timescale absorption becomes permeability limited, and so the mechanism collapses back into equilibrium viscosity controlled flow. The quicker ink penetration speed (as measured by the capacitive method, Clara) and the same ionic charge of ink and binder in the SA latex containing coating structure causes colorant transport through to the top part of the base paper, and therefore print-through problems can occur, as we shall see in the print quality section.

The results showed that the nano-size pores are important in the polar liquid imbibition, but the pre-diffusion into binder is an additional short timescale phenomenon due to the location of the swellable binder in both those same nanopores and on the pore walls. The capillary flow controls the polar liquid imbibition in the short timescale, but the diffusion of water into binder polymer is taking an active part in this process. Water molecules diffuse into and within the hydrophilic PVOH polymer causing binder swelling, which closes some of the small pores and decreases the diameter of remaining pores, thus slowing the capillary flow as a function of time. The SA latex does not absorb the ink vehicle to the same extent as the PVOH, and therefore the dominating phenomenon in the coating structure is then capillary absorption and permeation. These findings support Hypothesis I.

*Hypothesis I* – inter molecular diffusion of the liquid phase of inkjet ink into polymers acts on a sufficiently fast timescale and in sufficient volume to compete with the permeation of ink through coating structures.

One way to increase the inkjet ink penetration speed is to apply a higher coat weight of an optimally designed absorbent coating structure on the paper surface. The higher coat weight produces more pore volume and a greater proportion of that optimally designed coating pore network structure, and so there is more space where a high inkjet ink amount can transfer. In this research, the coating pigment had intra-particle pores and therefore the higher coat weight means also more nano-size pores, which promote quicker ink penetration.

# 5. Mechanisms influencing liquid absorption in coating binders

#### 5.1 Liquid absorption by binder films

The diffusion of liquid into polyvinyl alcohol and on styrene acrylate latex binders, without the effect of coating pigments, was studied by using films formed using the binder polymers alone. The SA latex films were produced with a draw down coater and the PVOH films in the moulds. The study is based on Paper IV. In this research, the same styrene acrylate latex that was used in the coating studies and three polyvinyl alcohols - partially and fully hydrolyzed, and carboxylated - were used. Table 5 in chapter 3 shows the basic properties of the polymers. Besides the study of these polymer films, the effect of the addition of cationic or anionic additive in the soluble binders was clarified. To achieve this, the cationic poly-DADMAC or anionic sodium polyacrylate was added in an amount of 1 and 4 pph in the partially or fully hydrolyzed PVOH. The absorption of liquid into the films was mainly studied by using self formulated anionic and cationic ink, as well as commercial cyan ink (Versamark<sup>®</sup> VX5000e), but the behaviour of pure liquid was also considered in some measurements by using de-ionized water or hexane to provide contrast between a purely polar and purely dispersive (non-polar) liquid. The measuring method has been described in section 3.3.3 "Absorption of liquid into binder films". This section concentrates on the second hypothesis of this thesis work: *Hypothesis II* – the colorant follows ink vehicle into the binder polymer matrix, the vehicle acts as a colorant carrier, and this phenomenon competes with the surface adsorption of colorant.

Polyvinyl alcohol is a hydrophilic binder (Hara 2006, Pinto and Nicholas 1997), and absorbent. This is shown by the absorption results of the PVOH binder films (200–250  $\mu$ m) in the case of exposure to anionic and cationic aqueous dye-based inkjet ink, Figure 44. The ink absorption amount depends on the binder type and the degree of the polymerization of PVOH. The fraction of absorption (absorption capacity) of the fully hydrolyzed PVOH is seen to be in the region of 20–30 wt-%, and that of the partially hydrolyzed PVOH 30–40 wt-%. The carboxylated PVOH had the highest absorption capacity. The carboxylated PVOH also has the lowest degree of hydrolysis meaning that this polymer has more amorphous regions that

can hydrogen bond the ink. The amount of amorphous and crystalline regions in the polymer structure defines the content of absorbed liquid (Ricciardi et al. 2004, Hasimi et al. 2008). At certain relative moisture content, a polymer with a low crystallinity absorbs more moisture than one with high crystallinity (Hasimi et al. 2008, Salmén and Back 1980). The results of this study in Figures 44 and 45 illustrate that the more crystalline structures containing fully hydrolyzed PVOH (Kumaki and Nii 2010, Hasimi et al. 2008) absorbed less of the inkjet inks (or moisture) than the partially hydrolyzed. This confirms that the amorphous regions of the PVOH polymer can absorb water molecules and likely hydrogen bond readily, whereas the crystalline part cannot. The diffusion and fixing of water molecules to the amorphous region of the PVOH matrix causes the swelling of the polymer, whereas in the crystalline part either the water is excluded or the molecules penetrate through the PVOH structures without binding there. Iordanskii et al. (Iordanskii et al. 1996) introduced a third mechanism that can affect the water movement at the supermolecular level: collapse of domains or transformation in the interface layer of polymer. Water molecules form clusters in the range of 0.27-1.00 nm, depending on the amount of molecules in one cluster, (Topgaard and Söderman 2001), and these are small enough to fit into the polymer network without disrupting it. The order of the studied films remained the same regardless of absorption time, indicating no chemical change occurred. The standard deviation of the absorption results was at a maximum of 2.0 wt-%, but in most cases it was lower than 1.0 wt-%.

The least absorption of polar ink amongst the studied binders was shown in the case of the styrene acrylate latex film. The SA latex polymer has a hydrophobic nature, and it is the surfactants on the polymer surface that permit its dispersion in water and allow wetting of the polymer surface.



**Figure 44.** The absorption of anionic and cationic self formulated inks into the PVOH and SA latex films, expressed as the weight fraction of film weight. The standard deviation of absorbed ink amount was at maximum 2 wt-%, but in most cases it was under 1 wt-%. Cationic additive was polyDADMAC, and anionic additive sodium polyacrylate – the charge additives being dosed into the binder before film forming. Based on Paper IV (Figure 2).

The addition of cationic or anionic additive into the PVOH binder caused no significant differences in the absorption by the partially hydrolyzed PVOH, but in the case of fully hydrolyzed PVOH there were some differences, especially when the absorption results of films with 4 pph additive and binder films without additive were compared. This indicated that the additives either have very similar absorption properties for inks as those of partially hydrolyzed PVOH or the amount of additives were so low that they did not affect the results significantly indicating that the amorphous nature of the binder is the overriding factor. However, since they did affect the fully hydrolyzed PVOH, we can probably conclude that if there was an effect going to happen for the partially hydrolyzed it would have been seen. In common formulations of inkjet coatings, the amount of additives is usually within this same range. Thus, the charge additives probably disrupt the ordered hydrolyzed film structure forming, and therefore it is probable that they do not affect the diffusion into binder polymers if the binder itself is poorly absorbing unless this disruption takes place.

Since very similar absorption results were reached when the same binder films were immersed in either the anionic or the cationic dye-based ink (Figures 44A and 44B), we can conclude that the ionic charge of ink affects only the ink colorant fixing but not the absorption of ink vehicle. The same chemical groups of the polymer are involved in both cases, and the water-based ink vehicle hydrogen bonds to the groups of the binder.

As the absorption time increases, so the amount of ink absorbed into the films increases. The binder films will reach a stage of saturation if the absorption time is long enough, as Figure 46 shows with the partially hydrolyzed PVOH and SA latex films.

Figure 44 shows further that the amount of absorbed ink had a linear relation to the square root of time indicating that the polymer diffusion follows Fick's second law (chapter 2), where the liquid position is proportional to the square root of time and the position is related to the volume of ink and thus represents the mass of liquid uptake. All lines of absorption data in the PVOH films are parallel, indicating equal absorption rates. However, they locate at different heights in relation to the *y* axis. This is accounted for by differences in the moisture content of the binder films under ambient room conditions (23 °C and 50 %RH (relative humidity), Figure 45), but the greatest increase in the absorption results appears between the time moments 0 s and 5 s. These results indicate that another phenomenon has occurred prior to the first measurement time. It can only be speculated what this might be, but one may suspect a polymer swelling effect once exposed to moisture, which might be a selective molecular weight dependent phenomenon, i.e. low molecular weight species.



**Figure 45.** Moisture content of PVOH and SA binder films at 23 °C and 50 %RH. Cationic additive was polyDADMAC and the anionic sodium polyacrylate.

Besides water, inkjet inks contain other components, like glycols (Svanholm 2007), which affect the absorption properties of the binders, too. Figure 46 illustrates the absorption differences between water (polar), hexane (non-polar, i.e. purely dispersive or apolar) and commercial inkjet ink (cyan ink from Versamark<sup>®</sup> VX5000e) into the partially hydrolyzed PVOH film. The PVOH film absorbed 30.2 wt-% water at the 5 s absorption time and 4.3 wt-% non-polar hexane. The same PVOH film exhibited a 29.2 wt-% absorption when exposed to the commercial cyan dyebased ink for 5 s, and this value will be used in the theoretical calculations of section 5.5 "Binder swelling - impact on nano-size capillaries", where the effect of PVOH swelling on the coating pore diameters is studied more closely. The role of other components in the ink is usually to make the ink more controllable at the nozzle and to form a droplet quickly enough after the nozzle before contacting the media surface. The replacement of some small part of ink with less hydrophilic components causes this more desirable small drop size. The styrene acrylate latex film absorbed only 1.4 wt-% of cyan inkjet ink. The hydrophobicity of the underlying latex prevents absorption of the polar ink.



**Figure 46.** The absorption amount of polar and non-polar liquids into PVOH (partially hydrolyzed) and SA latex films. Assumed is a specific gravity for water of 1 and hexane 0.657, and the swelling fraction is given by (mass of liquid absorbed/mass of binder)\* 100. Water and Cyan dye commercial ink were polar liquids, and hexane non-polar. Based on Paper I (Figure 15).

# 5.2 Diffusion of liquid into coating binders

#### 5.2.1 Diffusion coefficient

The diffusion coefficient of liquid into binder films was studied by detecting the absorption data for water moisture into binder films using the techniques of Dynamic Vapour Sorption, DVS-1<sup>33</sup>, which is a gravimetric moisture sorption measurement. This has also been shown in *Paper VI*. The analyses were made with partially hydrolyzed PVOH and SA latex films using different moisture contents of surrounding air (Figure 47). The shape of the moisture absorption result curves are an inverse exponential, and therefore there has been applied the so-called Case II or Linear Driving Force Mass Transfer Model in the calculation of diffusion coefficient (Carslaw 1997). Carslaw considers an axially symmetrical system for heat transfer from the exterior to the centre of a material cylinder.

<sup>&</sup>lt;sup>33</sup> Surface Measurement Systems, 5Wharfside, Rosemont Road, Alperton, Middlesex, HA0 4PE, United Kingdom.



**Figure 47.** Absorption curves for water vapour diffusion for partially hydrolyzed PVOH and SA latex films. The broken line describes how the moisture content of surrounding air was changed. Based on Paper VI (Figure 8).



**Figure 48.** A schematic view of an isolated film cross section, i.e. symmetrical exposure to moisture from both sides. This corresponds in geometry to the cross-section of a cylinder through its central plane.  $M_0$  is the initial moisture content in the film,  $M_{Max}$  the maximum moisture content achievable when exposed to the moisture. Based on Paper VI (Figure 9).

Considering Figure 48, it can be seen that exposure of a single film to liquid on both sides adopts the same geometry as a single cross-section of a cylinder of absorbing material through its central axis. It is assumed that there exists an analogous substitution between heat transfer and moisture mass transfer (thermal diffusivity "*a*", normally found in the Carslaw/Mass Transfer Model equation, is replaced with moisture diffusion coefficient "*D*"), such that for cylindrical geometry

$$\frac{M(\tau)}{M_{\text{Max}}} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \cos\left(\frac{2n+1}{2}\pi \frac{x}{\delta}\right) \exp\left[-\left(\frac{2n+1}{2}\right)^2 \pi^2 \frac{D\tau}{\delta^2}\right]$$
(37)

where *r* is time, *D* the molecular diffusion coefficient and *n* the consecutive layers describing the build-up of the material around an axial symmetry. This is acceptable since both follow the diffusion equation. Thurn (Thurn 2008) used a similar equation in his study of the diffusion of water in silica coatings. The other variables are described in Figure 48. The equation (37) can be simplified for mass change of moisture in the middle of the plate-like film, i.e. at x = 0 and for n = 0.

$$\frac{M(\tau)}{M_{\text{Max}}} = 1 - \frac{4}{\pi} \exp\left[-\frac{\pi^2}{4} \frac{D\tau}{\delta^2}\right]$$
(38)

In equation (37) the factor  $4/\pi$  describes an axially symmetric system consisting of an infinite number of concentric layers, responding to pulse heating in the Carslaw case. Here, however, the geometry is planar, and so the factor is removed according to the boundary condition of zero absorption at zero time, i.e. at the initial time r = 0 the right side of the equation would become negative, but it should be 0. So, the following equation is used for diffusion coefficient estimation in the planar case considered here. The results are introduced in Table 13.

$$\frac{M(\tau)}{M_{\text{Max}}} = 1 - \exp\left[-\frac{\pi^2}{4}\frac{D\tau}{\delta^2}\right]$$
(39)

**Table 13.** The thickness of binder films and the diffusion coefficient calculated with equation (39).

Binder film	Thickness, m	Diffusion coefficient, m <sup>2</sup> s <sup>-1</sup>
PVOH (partially hydrolysed)	2.25E-04	3.0E-13
SA latex	2.84E-04	3.5E-13

Ideally, a calibration should be used to define the multiplicative factor in the exponential term, but since it is not possible to define the central position of the film thickness, i.e. impossible to define the absorbed mass at the centre experimentally, the term  $\pi^2/4$  is retained as an approximation.



**Figure 49.** The matching of model and measured data. A, B – the measured absorption amounts divided by the maximum absorption of PVOH or SA latex films and the values of the model (equation (39)), respectively. Based on Paper VI (Figure 10).

In this calculation, it was assumed that the diffusion happens into the plate-like film structure. This is actually valid for the PVOH binder, where water molecules diffuse into the polymer network, but not for the latex. In the case of latex, only a few water molecules can transfer onto the film (Figures 45–47), meaning that the diffusion is more a surface diffusion. If the thickness factor of the plate-like structure is decreased to near zero, the surface diffusion should be derivable. However, at the near-zero stage, the mass transfer becomes zero in equation (39), which cannot be true in the real liquid transfer, and so the problem changes to one of adsorption. Nonetheless, equation (39) fits the experimental diffusion data quite well, and it delivers a reasonable diffusion coefficient for latex, although the model is insufficient for the latex case.

The results of diffusion coefficients for water vapour in films made from the PVOH and SA latex binders are both close to 3.0.10<sup>-13</sup> m<sup>2</sup>s<sup>-1</sup>, whereas in the coating structures, such as the "MCC large" plament with 1 pph of PVOH or SA, they are each about 2.5 10<sup>-11</sup> m<sup>2</sup>s<sup>-1</sup>. Hill et al. (Hill et al. 2011) show that by crosslinking the binder polymer (PVOH and polyvinyl pyrrolidone) the diffusion coefficient for binders can be increased to the range of 1.7-4.4 10<sup>-11</sup> m<sup>2</sup>s<sup>-1</sup>. Thurn (Thurn 2008) showed that a thermally-grown silica coating had a minimal swelling whereas the corresponding evaporated and physical vapour deposited (sputtered) coatings swell significantly. The diffusion coefficient for the sputtered silica coating in the Thurn case was 1.10<sup>-15</sup> m<sup>2</sup>s<sup>-1</sup>, a factor of hundred times smaller than in the case of the polymers here, and Riegel et al. (Riegel et al. 1997) showed that the diffusion constant of water into a silica aerogel was 3 10<sup>-10</sup> m<sup>2</sup>s<sup>-1</sup>. Is seems that the polymer film allows water diffusion at the same rate as silica. In comparison, for cellulose fibres the water vapour diffusion coefficient is also about 10<sup>-11</sup> m<sup>2</sup>s<sup>-1</sup> (Topgaard and Söderman 2001), and for paper, with porosity of 20 %, 10<sup>8</sup> m<sup>2</sup>s<sup>-1</sup> (Hellén et al. 2002). The porous structure of a fibre mat structure enables the higher diffusion because there are more surfaces accessible by permeation by the vapour where the diffusion into the fibre body can happen. Therefore, it can be concluded that the permeability of the coating structure enhances the diffusion rate beyond that of a single binder film alone.

On the other hand, the water phase type, i.e. separate molecules, clusters or films, seems to differ between the cases of the PVOH and SA latex films. The results of differential scanning calorimetry (DSC) made on water absorbed binder films, Figure 50, show that the SA latex film had proportionally more free water than the PVOH film at both 1.0 % and 4.0 % moisture content. In the DSC measurement, the difference in the amount of heat required to increase the temperature of a sample by a defined amount is detected. In the measurement, the freezing of unbound water was analyzed by the latent heat effect at -0.5 °C. The bound water was then identified as the total moisture content of the film found during drying by heating minus the amount of unbound water. The water molecules diffuse in the polyvinyl alcohol polymer network and they can hydrogen bond to the hydrophilic groups of the amorphous region of PVOH (Kumaki and Nii 2010, Lavery and Provost 1997, Hodge et al. 1996). Latex does not have chemical groups that can fix the water molecules to the same extent as the PVOH. This kind of difference in the fixing capability between the binders must also exist during practical inkjet ink imbibition.



**Figure 50.** The water type (bound versus unbound) in PVOH (partially hydrolyzed) and SA latex films, as measured with DSC for 1 % and 4 % moisture containing films. The dissolving of PVOH has likely some effects on the results. Based on Paper IV (Figure 3).

The water-solubility of PVOH polymer means that during the contact of inkjet ink some of the PVOH can also dissolve out of or within the film. Figure 51 shows that from the studied partially hydrolyzed PVOH film several wt-% of polymer can disappear during the liquid absorption test, whereas the SA latex film lost far less

polymer than the PVOH. In the latex case it can be assumed that surfactant and/or residual monomer may have dissolved. The polymerised SA latex does not dissolve into the polar liquid, unlike PVOH.



**Figure 51.** The disappeared (dissolved) binder amount during the liquid absorption test. The PVOH (partially hydrolyzed) and SA latex films have been immersed in water or cyan dye-based ink (Versamark<sup>®</sup> VX5000e) for 30 s or 300 s.

#### 5.2.2 Colorant penetration

The colorant location in the binder films after the absorption test was studied by producing cross-section images from all three polyvinyl alcohols (partially hydrolyzed, fully hydrolyzed and carboxylated) (Paper IV). The same binders and binders with cationic or anionic additive were studied, as above in the absorption amount study, and the ink was again the self formulated anionic or cationic ink. Figure 52 shows the location of cyan colorant in the PVOH binder films after the 5 s absorption time. The ink colorant has penetrated into the binder film, regardless of colorant ionic charge, but not completely through the film, and the narrowest colorant layer in both ink cases located on the top part of the fully hydrolyzed PVOH film which had also the lowest absorption amount of the respective inks, Figure 44. The results demonstrate that the colorant has moved into the PVOH matrix with the ink vehicle (mainly water). The vehicle diffuses into the binder film and bonds to the amorphous regions of PVOH and therefore the polymer structure opens so that the colorant fits into the interpolymer structure. The result is in good agreement with the observations of Oka and Kimura (Oka and Kimura 1995) and Svanholm and Ström (Svanholm and Ström 2004). The z-direction figures indicate further that there is more colorant at the top part of the film than deeper in the colorant containing layer. During the absorption test, the top part of the film is first in contact with the ink and as the absorption time increases the deeper the ink vehicle, as well as ink colorant, penetrates, producing a concentration gradient of colorant.



Carboxylated PVOH Partially hydrolyzed PVOH Fully hydrolyzed PVOH

**Figure 52.** Anionic (upper image series) and cationic (lower image series) dye colorant location in the z-direction of PVOH binder films (cross-section figures). Based on Paper IV (Figure 8).

The colorant location in the partially hydrolyzed PVOH was also studied with Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS), using commercial ink (Versamark® VX5000e cyan water-based dye) as the colorant provider. The similar PVOH film as was used in the previous absorption study was immersed in cyan dye or cyan dye with an addition of 1 gdm<sup>-3</sup> lithium for 5 min exposure time. It was assumed that the lithium, with its very low molecular weight (small atomic radius), followed the water molecules, and so could be used as a tracer for the vehicle imbibition path decoupled from that of the larger radius dye molecules. The ink colorant contained copper and sodium, and with these elements it was additionally tried to provide a trace for the colorant. The colour immersed sample was dryed at 50 %RH and 23 °C overnight. The sample was embedded, crosssectioned, covered with platinum and finally polished before the ToF-SIMS analysis, as has been descibed in Paper IV. Figure 53 shows the distributions of sodium, copper and lithium atoms, and the figure on the extreme right shows the total ion map of the analyzed sample. The amount of copper and sodium, however, was so low that it was very difficult to detect the colorant with certainty. On the other hand, Figures 53 and 54 indicate that the tracer lithium can be found deeper in the binder film structure than copper. There was also a concentration gradient of colorant as well as lithium, indicating water movement within the film and the highest copper concentration located on the top of the film. Thus, there is a chromatographic separation of colorant, and hence penetration differential of colorant into the polymer network. The results converge well with the results of cross-section figures shown before. These results confirm that the ink vehicle

absorbs into the binder polymer network and it behaves as a colorant carrier during the liquid absorption, as Hypothesis II argues.



PVOH film with cyan ink



Interestingly, in Figure 54B, the picture is not so clear regarding the sodium trace. If the results of sodium curves in Figures 54A and 54B are compared, the sodium distribution appears to penetrate deeper into the layer than into the non lithium containing layer. This suggests that sodium in the ink is released from a complex in partial exchange equilibrium with the lithium.



**Figure 54.** The location of ink (Cu and Na) and water (Li) in the PVOH film layer. Ink was cyan dye from Versamark<sup>®</sup> VX5000e. Measured with ToF-SIMS. Base on Paper IV (Figure 5).

Figure 55 shows a ranking by cyan colouring. The carboxylated PVOH produced the darkest cyan colour after the 5 s ink absorption time, then came the partially hydrolyzed PVOH and the SA latex film did not have cyan colour at all. The result demonstrates that the higher the ink absorption amount the higher was the colorant content in the binder polymer, and the higher amount of cyan colorant means further that the structure contains more of the colour producing components. Again, the capability to absorb the polar liquid, as inkjet ink, enhances the opening of the polymer matrix where the colorant moves more readily and the greatest absorption produced the darkest cyan colour. The high absorption amount means as well there have been more possibilities for the ink colorant to transfer into the polymer matrix. The SA latex did not have blue colour at all indicating that polymer does not have chemical groups that can bind the colorant at the timescale of 5 s in the inkjet ink immersion. The latex did not absorb water molecules and so the binder polymer structure remained closed to colorant uptake. These contrasting effects of binder could be expected to influence print density distribution properties in inkjet coatings.



**Figure 55.** The cyan colour darkness of PVOH and SA latex films after 5 s absorption time. Ink was anionic cyan aqueous-based dye.

Figure 56 shows the SA latex films after 5 s and 60 s of cationic and anionic self formulated ink absorption. The films were produced with the film coater and dried in an oven (105 °C, 5 min). *Paper IV* describes the details of this study. Figure 56 shows that the cationic ink colorant has fixed to the anionic film after 5 s absorption and the film becomes darker blue as the absorption time increases. The opposite ionic charge of binder film and colorant enables the ionic attraction. More colorant molecules have fixed to the binder polymer film structure, when adsorption exposure time was longer, 60 s, and therefore the film had a darker blue colour. The situation is different when the ink colorant has the same ionic charge as the latex binder film. After 5 s adsorption, the SA film did not have any colorant, and after 60 s some small amount only, but not as much as in the case of cationic ink. The light cyan colour of SA latex film at the 60 s exposure time might have a connection to the latex dispersion stabilising surfactant. Altogether, the ionic interactions are the main forces acting in respect to the colorant fixing onto the SA latex.



Cationic ink

Anionic ink

**Figure 56.** The colour of SA latex films after the immersion of 5 s or 60 s time in the anionic and cationic self formulated inks. Based on Paper IV (Figure 6).

The addition of cationic additive (polyDADMAC) in the PVOH polymer fixed the anionic colorant effectively into the top part of the film, whereas in the case of non-additive or anionic additive containing films the colorant penetrates deeper into the films and there forms a chromatographic colorant separation (Figure 57). The Coulombic forces bind the opposite charges of the chemical groups effectively to each other.



**Figure 57.** The anionic colorant location in the partially hydrolyzed PVOH films where have been added 1 pph or 4 pph (more) cationic or anionic additive. Cationic additive is polyDADMAC and anionic additive anionic sodium polyacrylate.

# 5.3 Water and colorant in the binder film structure

In the polyvinyl alcohol binder, the water molecules diffuse into the polymer matrix and form hydrogen bonds with the hydrophilic groups of the amorphous region of polymer whilst some of them remain as free water in the network as DSC results show. The water molecular diffusion causes the swelling of the polymer matrix and the further opening of the PVOH network microstructure so that the colorant molecules subsequently fit into the binder structure. The transfer of ink vehicle promotes the movement of colorant molecules into the PVOH matrix. The SA latex polymer microstructure has less chemical groups that can fix the water molecules and therefore during the absorption test there is more free water at a given liquid content than bound water on the surface network of SA binder - assumed to be related to surfactant or surface carboxylation. Figure 55 shows that, after 5 s absorption time of dye-based ink, the SA latex film did not have any ink colorant at all, whereas all PVOH films had a blue colour. On the other hand, the results of the absorption by binder films showed that PVOH films took up anionic aqueous dye-based ink more than SA latex film. The high binding capacity of PVOH means that the polymer attracts (absorbs) the water molecules and the concentration of water in the PVOH is therefore higher than in the latex, although the diffusion rate of water vapour in relation to the polymer itself remains similar, albeit bulk diffusion in the case of PVOH and surface diffusion in the case of SA latex. This means that in the case of PVOH the diffusion happens in the polymer network structure, whereas in the latex the diffusion occurs mainly on the surface of the polymer network (Figure 58). It might also be so that the surface active polymers of latex that have been used in the polymer production extend for a small but significant distance from the actual surface into the outer bulk.

We may conclude that at the beginning of ink imbibition into PVOH containing coatings, the dominating diffusion will be surface diffusion and osmosis, followed by Knudsen diffusion when the polymer swelling has decreased the effective coating structural pore diameters. In the SA latex containing coatings, the role of Knudsen diffusion must be insignificant and the diffusion is mainly surface diffusion. The next section will now illustrate the validity of this conclusion.





#### 5.4 Diffusion in the coating layer during inkjet ink absorption

During the coating layer consolidation, the PVOH molecules can form a binding layer on the coating pigment surfaces as well as binding "bridges" between the pigments, but they can fit also in the intra-particle pores of a porous pigment, such as the CaCO<sub>3</sub> inkjet coating pigments, as Figure 24 in chapter 4 shows. The SA latex binder instead remains sited in the inter-particle pores, because the particle size of latex is usually over 100 nm (in this research SA latex had 180 nm) and the intra-particle pores are in the region of 20-60 nm. If the same "MCC small", "MCC large" and "PCC small" pigment coatings with 10 pph PVOH are studied, as in section 4.1 "Impact of coating pigment type and binder selection on the structure formation of the coating layer" on the pilot pre-coated paper (Paper I), it can be noticed that the commercial cyan dye from Versamark® VX5000e has distributed guite uniformly through the "MCC large" and "PCC small" coating layers (Figure 59). This could indicate that PVOH has covered the pigments and colorant is predominantly in the PVOH. The zeta-potential of these coating layers was 13.1 mV and 1.6 mV, respectively. These findings suggest that either the ink does not encounter the cationic nature of the pigment or the coating is too permeable to provide surface contact for all the colorant as it flows through the structure. However, in the GCC coating, which had anionic charge -9.0 mV, the anionic cyan colorant seems to locate more on the top part of the coating layer. The anionicity has prevented colorant location in the coating structure other than on the coating layer top. The low pore volume and anionic nature, combined with the thicker PVOH binder layer on the pigment surface, have prevented the colorant penetration deeper into the structure. These results show that the diffusion potential for ink vehicle into the coating binder does not alone guarantee the optimal colorant location. If the coating is highly permeable, then either the flow through the coating is too fast for bulk diffusion to occur and/or the anionic surface of the pigment provides a long range Coulombic repulsion. If, however, the permeability is low, the same ionic repulsion, and volume loss by binder swelling, confines the colorant to the top part of the coating layer, but of course absorption of vehicle is too slow for satisfactory ink drying. The porosity and permeability of the coating structure are very important in determining the final colorant location.



MCC large

PCC small

50 µm

**Figure 59.** The cross-section images from GCC, "MCC small", "MCC large" and "PCC small" containing coatings that had 10 pph of PVOH (partially hydrolyzed). Papers had been printed with Versamark<sup>®</sup> VX5000e. Based on Paper I (Figure 19).

The results of TLC (Paper V). Clara device (Paper II) and microbalance (Paper V). shown previously in section 4.2, "The effect of coating structure and binder selection on liquid imbibition rate", demonstrate that the binder can nonetheless have an effect, even with a small amount, on the inkjet ink imbibition speed. The use of 1 pph PVOH in the "MCC large" pigment containing coating decreased the rate of absorption front rise of a water/colorant mixture on the coated TLC plate clearly from 0.050 mm·s<sup>-1</sup> in dispersed "MCC large" pigment to 0.017 mm·s<sup>-1</sup> in dispersed "MCC large" with PVOH. The capacitance-based results corroborate this lower rising rate in such a way that the PVOH containing coatings had longer penetration time through the coated papers than in the case of the SA latex containing, and as the binder amount increased so the penetration rate decreased. In the microbalance research, a similar lower absorption rate of water was detected at the long timescale absorption, again indicating a permeability controlled mechanism. Although the volume of the liquid uptake of PVOH containing coating structure, related to PVOH swelling, can be smaller than the structure of SA latex containing coating, it acts to dominate the comparative inkjet ink imbibition.

The similar diffusion coefficient for PVOH and SA latex means that the flux of water vapour in these coatings is dominated by the pore structure of the coating, and thus also the local liquid concentration difference across the wetting front during the imbibition time. This supports the findings of Gane and Ridgway (Gane and Ridgway 2008), who presented moisture pickup results from pigment tablets of dispersed GCC of various particle size distributions. They concluded that the initial moisture absorption rate of pigments depends on the permeability of the structure. Once access of vapour to the pore structure has occurred, contact with absorbent binder provides the transition to bulk diffusion within the polymer network.

At the short timescale absorption of the inkjet ink, in the form of polar liquid, the role of diffusion is also significant in the capillaries of the coating layer when containing hydrophilic, water-swellable binders. Figure 60A illustrates the predominant forces in the case of such a hydrophilic absorbing surface. The absorption study with the microbalance shows that up to 2 s timescale the PVOH containing "MCC large" and "PCC small" coatings absorbed water at a quicker rate than the SA containing coating (Figure 31). This illustrates the absorption of ink into the polymer as well as surface diffusion on the interface of the pore wall of the PVOH containing coatings. The appearance of swelling means that the absorptiondescribing mechanism, in our discussion here being exemplified by the Bosanquet equation (12), would require two additional components that describe the diffusion of polar inkjet ink into the binder component and modification of the structure by swelling, respectively. This can already be partially taken into account in the external pressure part and the inertial drag, if the dynamic radius change of capillaries, r(t), is considered (Figure 60A). Above all, this becomes important in the nanoscale capillaries, which have been shown to be very advantageous for fast penetration of the inkjet ink vehicle into the coatings.

Thus, in the case of hydrophilic swelling binder, the Bosanquet equation becomes a convolution of the situation in a static structure with the structural change, i.e.

$$\left[\frac{\mathrm{d}}{\mathrm{d}t}\left(\pi r^{2}\rho x\frac{\mathrm{d}x}{\mathrm{d}t}\right)+8\pi\eta x\frac{\mathrm{d}x}{\mathrm{d}t}\right]\otimes swelling = \left[p_{\mathrm{e}}\pi r^{2}+2\pi r\gamma_{\mathrm{lv}}\cos\theta\right]\otimes diffusion \quad (40)$$

and, if the diffusion is expressed as in equation (39) and the dynamic changes of capillaries are assumed to be in cylindrical form, the model can be formed as two simultaneous equations,

$$\frac{\mathrm{d}}{\mathrm{d}t} \left( \pi r^{2}(t) \rho x \frac{\mathrm{d}x}{\mathrm{d}t} \right) + 8\pi \eta x \frac{\mathrm{d}x}{\mathrm{d}t} = p_{\mathrm{e}} \pi r^{2}(t) + 2\pi r(t) \gamma_{\mathrm{lv}} \cos\theta$$

$$r(t) = r_{0} - \frac{r_{0}^{2} - r^{2}(t)}{2r(t)}$$

$$(41)$$

where the volume of water diffused across unit capillary surface in time *t* is given by the second term in the second of the simultaneous equations above

$$\frac{\Delta V(t)}{A_{\text{capillary surface}}} = \frac{\pi (r_0^2 - r^2(t))x}{2\pi r(t)x}$$
(42)

and is related to the diffusion coefficient by a rearrangement of equation (39), including a reduction of the diffusion coefficient by an approximate factor  $\frac{1}{2}$  since the access to the binder film is one sided only,

$$\Delta V(t) = V_{\text{tot}} \left\{ 1 - \exp\left[ -\frac{\pi^2}{4} \frac{\frac{1}{2}Dt}{r^2(t)} \right] \right\}$$
(43)

where  $V_{tot}$ , the total absorbed volume per unit capillary surface area, can be determined experimentally. For example, the swelling of PVOH was shown to reach ~30 %.

In the above description, the term r(t) describes the radius during the time t,  $\rho$  density of fluid, x distance where the fluid progresses in the capillary,  $\eta$  liquid viscosity,  $p_e$  external pressure,  $\gamma_{lv}$  surface tension at the liquid-vapour interface,  $\theta$  dynamic contact angle and D diffusion coefficient. Although this algorithm is not applied in this work, it forms the basis of the analysis in the next section where the nanopores are reduced in radius and volume due to the swelling of the PVOH, and the absorption affected as a result.

In the case of internally hydrophobic binders, at the beginning of inkjet imbibition, the hydrophobicity prevents the polar ink penetration (Tiberg *et al.* 2000) as the results of the microbalance measurement indicated (Figure 32A). After a while, the penetration starts as surfactants permit surface wetting, and it is faster than in the hydrophilic swelling binder containing coatings due to greater permeability of the non-swelling binder case, as the results of the microbalance and the capacitance-based measurements showed (Figures 32B and 37). The diffusion on the hydrophobic coating binder surface is more or less a surface diffusion related to surfactant/carboxylation and this affects the surface wetting force,  $\gamma_{hv}\cos\theta$ , and thus the effective frictional resistance by producing a concentration gradient of ink vehicle molecules (Figure 60B). This has probably a connection to the Marangoni effect, where the molecular motion occurs in the edge areas between liquid and solid material, connected by the surfactant(s) associated with the latex. The counter force for the diffusion in this case is the hydrophobic resistance of the non-swelling binder/capillary wall. However, these forces caused by the diffusion must be small in the SA containing coatings compared with the other forces during the inkjet ink imbibition, and so the local changes in surface energy are impossible to capture in such a spatially averaged model.



**Figure 60.** The effect of the diffusion of inkjet ink (polar) into/on the capillary wall that contains hydrophilic (PVOH, A) or internally hydrophobic (SA latex, B) binder at the beginning of inkjet ink imbibition.

#### 5.5 Binder swelling – impact on nano-size capillaries

The significance of swelling on the conditions of the high-speed inkjet printing press was clarified with a theoretical calculation. In *Paper I* a description was introduced to describe how the swelling affects the closing of nano-size pores. The mercury porosimetry results show that the PVOH binder can go into the intra-particle (Figure 24) as well as the connecting pores, and covers the surface of the larger interparticle pores as Boisvert and Guyard (Boisvert and Guyard 2003) and Wedin *et al.* (Wedin *et al.* 2006) assumed in their studies. At sufficiently high levels, the interactions between the binder and the liquid phase of the ink become important, not only in the structural modification of pore volume but in the diffusion of liquid into the polymer network. In the case of PVOH and inkjet ink this relates to binder swelling.

In this theoretical calculation, the binder layer thickness is considered to be present on the pigment surface as a homogeneously distributed layer, and its thickness will depend on the specific surface area of pigment (thicker binder film on a lower specific surface area pigment). The geometry of the pore is assumed to be simple: the binder forms a uniform layer on the interior surface of the circular equivalent capillary (Figure 61, left side), thus controlling the capillary diameter. In this way, it can be calculated how the round pore entrance area changes during the binder swelling process. The pore volume and amount of binder represents that to be found in 1 g of coating structure, and the coating formulation proportion was taken into account. The right side of Figure 61 shows how the delay in pore area growth as a function of original pore diameter increases with binder addition. The first line on the left (Figure 61, right side) is the pore area when the structure has been formed from pigments alone. The addition of 10 pph binder into the coating colour decreases the pore diameters, they being reduced by the absorbed layer of PVOH binder on the pigment surface by a diameter amount of 13 nm when the PVOH is dry. The inkjet ink caused a 29.2 % swelling of PVOH, as Figure 46 shows. This swelling closes further the pore diameter by 5 nm. The point at which the pore diameter is closed increases at the same time from 19 nm to 24 nm, i.e. the swelling renders the pores finer than this original diameter value as they become progressively closed. This leads to complete blocking of the finest pores, reduction in pore size in general and loss of connectivity in the structure when the binder is concentrated at pore nodes. A higher amount of binder produces a thicker binder layer on the pore wall, and thus the effect of swelling also increases. The calculations show that the swelling affects the intra-particle pores region in the pore size distribution. If higher specific surface area pigments are used, the thickness of binder layer on the pigment surface decreases, and therefore the pore area growth curves move toward the direction of lower pore diameters. For example, at a specific surface area of 70 m<sup>2</sup>g<sup>-1</sup>, and a 30 pph PVOH binder content, the swelling closes up the under 10 nm diameter pores.



**Figure 61.** The theoretical calculation of PVOH swelling effects. The coating amount was 1 g and density of PVOH 1.26 g·cm<sup>-3</sup>. The swelling of PVOH film was 29.2 % after 5 s (cyan dye). Specific surface area of pigment 10 m<sup>2</sup>g<sup>-1</sup>. Based on Paper I (Figure 16).

The calculations show that the binder swelling can affect the absorption of inkjet inks through the closing up of small pores in the timescale of 5 s. Table 14 shows the time delays in the inkjet printing machine Versamark<sup>®</sup> VX5000e. At 100 m·min<sup>-1</sup> speed, the delay between the first inkjet nozzles and the beginning of drying is 2.6 s, and to the end of drying 3.8 s. The 5 s time considered in the calculations is within this same timescale. At the printing speed 15 m·min<sup>-1</sup>, the swelling of binder polymer has clearly a strong influence on the closing of capillaries. The effect of swelling diminishes when liquid has less time to affect the binder, and therefore we can assume that swelling has a smaller role to play at higher printing speeds, but it will not totally disappear. Thus, diffusion into polymer networks is a relevant phenomenon within the timescale of current inkjet printing, even in the high-speed printing domain.

Position on the inkjet press	Speed 15 m <sup>-</sup> min <sup>-1</sup>	Speed 100 m <sup>-</sup> min <sup>-1</sup>
Cyan print head to yellow print head (CMKY)	5 s	0.8 s
Yellow print head to beginning of drying	12 s	1.8 s
From beginning to the end of drying	8 s	1.2 s
SUMMARY	25 s	3.8 s

Table 14.	Time delays in the Versamark <sup>®</sup>	VX5000e printing press.

# 5.6 Summary of diffusion mechanisms in coating binders

Inkiet ink penetration into the coating layer structure depends on the type of binder used in the coating colour. The hydrophilic PVOH binder allows the diffusion of the inkjet ink vehicle into the polymer matrix and this causes the swelling of the polymer. This acts to close and/or diminish the number of active nano-size pores and therefore slows down the capillary flow of ink in the coating structure. At the same time, the pore volume decreases as the binder swells. On the other hand, the calculations of the water moisture diffusion coefficient show that the hydrophilic partially hydrolyzed PVOH film has a very similar diffusion coefficient as that of the surface diffusion on the internally hydrophobic SA latex film. This result together with the different water phase-structure types shows that the water molecules diffuse into the PVOH polymer matrix whereas they stay on the SA latex network surface, meaning that the mechanism of water diffusion is different in the PVOH and SA latex binders. The SA latex does not absorb the ink vehicle, and therefore the dominating phenomenon in the SA containing coating structure is then structural only and impacts the static structural capillary absorption, with only a minor effect arising from the latex dispersion stabilising surfactant acting to delay wetting. In the case of PVOH, the diffusion can start via surface diffusion and osmosis, followed by Knudsen bulk diffusion, and these diffusion regimes compete at the beginning of inkjet ink imbibition with the capillary flow and later with the capillary and permeation flow, respectively.

The speed of sorption is determined by the porosity and permeability of the coating layer structure, but in the case of hydrophilic coating binder, the swelling of polymer will affect this rate strongly. The short timescale results, less than 2 s, of the microbalance indicate that the diffusion of water into PVOH binder can speed up the sorption. The coating structures that contained nano-size pores absorbed polar liquid initially quicker when the coating contained PVOH than when it contained SA latex. Thus, during inkjet ink sorption into the hydrophilic binder containing coating structure, the diffusion is acting as a short timescale rate determining phenomenon, and so could be represented in a description of the absorption dynamic, such as that offered by the Bosanquet equation.

*Hypothesis I* – inter molecular diffusion of the liquid phase of inkjet ink into polymers acts on a sufficiently fast timescale and in sufficient volume to compete with the permeation of ink through coating structures.

The opening of the PVOH polymer matrix during the swelling allows furthermore that the colorant molecules can fit into the binder polymer matrix. The ink vehicle acts as a carrier of the colorant as is hypothesised in Hypothesis II. There develops a concentration gradient of colorant in the binder layer and the largest amount of colorant remains on the top of the PVOH binder film.

*Hypothesis II* – inter molecular diffusion of the liquid phase of inkjet ink into polymers, acting as a colorant carrier, is a competing mechanism to the surface adsorption of ink dye.

The research, where the anionic or cationic additive was mixed with the binder polymer, shows that the produced cationic charge of the film surface fixes the anionic colorant effectively to the top layer of the film, promoting partially the Hypothesis III. The opposite ionic charge of film binds the colorant to the surface via the Coulombic forces. However, the additional few parts of additives have very minimal effect on the inkjet ink absorption amount.

*Hypothesis III* – the verity of Hypotheses I and II can be used to design porous coating structures, based on discretely bimodal pore size distributions, using binder and surface charge distribution characteristics to provide rapid fixing of ink colorant optimally close to the coating surface.

# 6. Inkjet ink colorant fixing and transfer into the coating layer

## 6.1 Colorant fixing to the anionic or cationic coating layer

The predominating driving force for the adsorption of azo dyes is found to be electrostatic (Coulombic forces) and/or hydrophobic interaction (Kallio *et al.* 2006, Lavery and Provost 1997). The coating layer is usually highly charged, and this promotes the attraction between the anionic colorant and the inorganic pigmented layer. These interactions of course depend on the charges of the coating components used in relation to the ionic charge of the dye. Donigian et al. (Donigian et al. 1998) hypothesized that the most important chemical groups of a colorant for the fixing of the dyes are carboxylic and sulphonic acid groups. Vikman and Vuorinen (Vikman and Vuorinen 2004a) showed further that the most important chemical groups supporting the ink colorant fixing mechanism to the coating layer components are hydrogen and ionic bonds. In this research work, the fixing of the colorant is studied in the context of thin layer chromatography, adopting UV-VIS analysis and ToF-SIMS.

#### 6.1.1 Thin layer chromatography

The target of the thin layer chromatography study, TLC (*Paper V*), was to detect how the ionic charge of the model coating structure affects the colorant and eluent movement and colorant fixing, respectively, in an inkjet coating. In this study, "MCC large" pigment coatings were applied on a glass plate. The coating colours were defined either as pigment alone or with binder additives. In the case of pigment alone, the "MCC large" pigment was dispersed either with 0.5 pph anionic sodium polyacrylate or 0.5 pph cationic poly(diallyl dimethyl ammonium chloride) (polyDADMAC). The differently dispersed coatings were also formed with either 1 pph polyvinyl alcohol (partially hydrolyzed PVOH) or 1 pph SA latex. All TLC coating layers had about 100 gm<sup>-2</sup> coating colour. The eluent was de-ionized water, into which were added different amounts of anionic dye-based colorant.

Table 15 shows the zeta-potential of the studied coating colours. The highest negative charge was seen for the coating colour formulations having anionically
dispersed "MCC large" alone or anionic "MCC large" pigment with SA latex. The anionicity of latex showed to be on the same level as the dispersing agent provided on the pigment. The addition of PVOH decreased the anionic charge, although the PVOH has a non-ionic nature. Probably the PVOH polymer has covered the anionic pigment surface so that ionic charge remains ineffectively under the non-ionic polymer or the addition of an uncharged soluble species simply reduces the average zeta-potential leaving the particles themselves charged as before. This suggests that if interacting according to the first option, the PVOH is associating with the charged groups of the dispersed pigment. The "MCC large" pigment with cationic dispersing produced the highest cationic zeta-potential, 24 mV, and the addition of PVOH to the cationic dispersed pigment decreased the zeta-potential value to 11 mV. This promotes the idea that the PVOH polymer may be capable of covering the pigment surface, and so it decreases the externally effective ionic charges on the surface of the pigments, most likely in the final coated layer.

Table 15.	Zeta-potential of	of "MCC la	arge" pig	ment c	colours.	Measured	with	Acous-
toSizer II.								

Pigment system	Zeta-potential, mV			
MCC large powder in water	21			
Anionic MCC large	-37			
Anionic MCC large + 7 pph PVOH	-12			
Anionic MCC large + 7 pph SA	-37			
Cationic MCC large	24			
Cationic MCC large + 7 pph PVOH	11			

The section 4.2.3 "Liquid and colorant movement – impact of charge on chromatographic separation in the coating layer" illustrates how the liquids become transported through different distances, and how the ink colorant fixed differently to the anionic and cationic coatings. The thin layer chromatography results (Figure 35) show that, as expected, there was no ink colorant binding to the coating layer when the colorant and the coating layer had the same sign of ionic charge. The colorant follows the eluent wetting front up the coated plate because there are no attractive ionic forces between the coating components and colorant molecules. On the other hand, opposite ionic charge fixes the colorant to the coating layer, related to the attractive force and diffusion of colorant, and the anionic colorant stayed at the bottom edge of the cationic TLC coating layer. This observation agrees with many other equivalent results, such as those in (Lavery and Provost 1997, Donigian et al. 1998, Pond 2000, Vikman and Vuorinen 2004 a and b, Kallio et al. 2006). However, the results show further that the anionic colorant started to rise up the cationic TLC coating after ten minutes exposure to the supersource of colorant solution had elapsed (Figure 62). The fixed bottom edge appeared to fill with colorant molecules. Clearly, the surface area of the pigment associated with the cationised pores takes part in adsorption, and only when the surface area is saturated can the colorant move forward into the structure. This sorption control is effectively a titration measure of specific charge density per unit TLC length.



Figure 62. Anionic colorant (5 wt-%) movement on the cationic "MCC large" TLC plate. Based on Paper V (Figure 7).

As the eluent rose up through the TLC coatings, the gray level changes were detected. The gray value of the coating layer without any eluent was set to 150. Figure 63 shows how at first the gray value decreased because the eluent first arrived at the detection area and then occupied it progressively little by little. The eluent changed the coated plate by reducing the light scatter as pores filled, making the appearance darker and therefore the gray value decreased. For the cationically dispersed "MCC large" structure it took 2 min to cover the whole detection area, whereas for PVOH containing coatings it took 4 and 5 min, respectively. The swelling of PVOH causes a decrease of pore volume, and importantly connectivity, in the coating layers, and therefore it takes more time for liquid to transfer through the whole detection area, as the distance results indicated before in chapter 4.





**Figure 63.** The effect of anionic cyan dye at the levels of 0, 0.12 and 5 % on the gray values in the TLC development. A – cationically dispersed "MCC large" pigment, B – the cationically dispersed "MCC large" pigment with 1 pph PVOH, C – the anionically dispersed "MCC large" pigment with 1 pph PVOH. The time 2, 4 and 5 min describe the moments when the eluent front has occupied the detection area totally. Based on Paper V (Figure 9).

Figure 63 shows that the gray level values of cationic surfaces remained on a higher level than those of anionic layers. The cationic coatings fix the anionic colorant to the bottom of the TLC plate and the changes of gray value are caused at first expressly by the eluent water, whereas, in the case of anionic coating, the colorant follows water immediately just after the wetting front, contributing to the darkening effect. The filling of the colorant at the bottom edge can be seen on the cationically dispersed "MCC large" coating as the gray value which starts to decrease at the 25 min development time (Figure 63A). The addition of 1 pph PVOH did not change the gray level, indicating that the cationic charge combined with the

very small amount of PVOH fixed the colorant effectively to the bottom of the coating plate until colorant ad- and absorption saturation were reached.

In the case of the anionic coating, the ionic repulsion dominates, and the colorant diffusion into the small amount of PVOH binder is insufficient to capture a high colorant saturation level. If the binder amount had been higher, then the anionic repulsion of the pigment charge would have been at least partly compensated. The transfer of colorant molecules into the binder film by following the ink vehicle competes with the anionic repulsion.

#### 6.1.2 Absorption and/or adsorption of coating components

The colorant absorption into and/or adsorption onto the coating components were studied more closely with the UV-VIS spectroscopic method (Paper VII). The pigment coating structure systems used in this part contained the same "MCC large" pigment as above. The dispersions were made by using either the anionic or cationic dispersing agent (0.5 pph) as previously described. Besides the dispersed coating pigment system, the anionic pigment was used in coating colours with either 7 pph partially hydrolyzed PVOH or 7 pph SA latex. The cationic pigment was similarly studied together with 7 pph PVOH (partially hydrolyzed). All these coating colours were dried and ground as described in section 3.3.4 "Absorption/adsorption of liquid colorant by coating components". The concept of grinding is largely to avoid the extended pore network structure or chromatographic separation effect present in coating cakes or TLC layers, thus enabling the structure surface-related phenomena to be isolated from the permeability characteristics. However, the grinding of the coating layer may act undesirably to expose more surfaces by breaking the binder polymer bridges or by pealing/debonding the binder polymer away from the pigment surface. By adopting a relatively low energy of grinding, this effect is expected to be minimal. The ground powder was screened and 5 g of powder was mixed with 10 cm<sup>3</sup> anionic dye-based self formulated ink at different time delays (5 min, 30 min, 2 h and 18 h). After that the mixture was centrifuged and the filtrate was analyzed by ultraviolet-visible (UV-VIS) spectroscopy. The idea was that the inkjet ink colorant absorbs and/or adsorbs in/onto the coating structure system during their mixing, and this can be detected as a change of colorant absorbance in the liquid phase remaining after centrifugation with the UV-VIS. Thus, the absorbance result arising from the colorant in the supernatant liquid solution phase has an inverse relation to the absorbed/adsorbed colorant amount depending on the prior contacted surrounding surface chemistry: the higher the optical absorbance, the less dye colorant has been absorbed/adsorbed onto the pigment system. The term "absorb" is used in the case for the interaction with PVOH, relating to the molecular motion of ink vehicle into the binder polymer network (diffusion), affecting the uptake of colorant.

Figure 65 shows that the "MCC large" pigment ground powder alone adsorbed some of the colorant molecules because that UV-VIS absorbance results from the supernatant were clearly on a lower level (2.3–2.9) than the maximum value 3.7

(ink value without the pigment system adsorption, Figure 64). This indicates that the dry powder has some cationic sites on the pigment surface already before extra dispersing agent addition.



Figure 64. An example of UV-VIS result curves from different concentrations of colorant dye.

The "MCC large" pigment dispersed with extra cationic dispersing agent produced the lowest absorbance value in the supernatant indicating that the colorant sorption was clearly greater with this cationic system than in any anionic system, and even in the original cationic pigment case without the extra charged polymer addition. This refers again to the action of Coulombic attraction. The addition of PVOH to the cationically dispersed "MCC large" had only a minimal effect on the absorbance results, and importantly in the ground materials, the added PVOH does not prevent the colorant sorption. It seems that the cationic charge of the pigment system binds the anionic colorant effectively. The lower zeta-potential (11 mV), when the non-ionic PVOH polymer was added, suggesting that it is either on the pigment surface, and/or within the intra-particle pores and/or distributed throughout the structure, did not change the situation. This shows that the adsorption dominates over absorption, in that the action of Coulombic attraction over a distance onto a high surface area exceeds the amount undergoing diffusion into the binder polymer matrix. However, the diffusion of the water molecules into the hydrophilic PVOH network persists, and the colorant will transfer into the polymer network by absorption, especially if in excess of the pigment surface adsorption capacity.

The addition of an anionic dispersing agent in the coating pigment system increased the absorbance results from the supernatant to the level 3.1. The anionic components have fixed to the cationic parts of the pigment surface and there are clearly less available cationic groups which can bind colorant molecules. The addition of anionic SA latex did not change the absorbance, but as the polyvinyl alcohol was added to the anionic coating colour the absorbance of colorant decreased, illustrating the diffusion absorption of colorant into PVOH. This finding promotes the Hypothesis II of this work. It is possible that the colorant is trapped in the PVOH polymer network. Thus, the results show that in the anionic, PVOH containing, coatings the dye colorant is associated with the binder, whereas in the cationic, PVOH containing, coatings the dye undergoes both ionic attachment to the pigment surface and association with the PVOH polymer matrix when adsorption capacity is reached.



**Figure 65.** The UV-VIS light absorbance of supernatant liquid containing anionic cyan dye after the mixing procedure of different "MCC large" pigment systems. Self formulated anionic dye-based ink. Extra charged polymer is used to define either anionic or cationic coatings. Based on Paper VII (Figure 3).

The results in Figure 65 show further that the long mixing time did not significantly release the colorant from the cationic "MCC large" pigmented coating colour systems. However, with regard to the anionic dispersion, the dispersed pigment powder and the pigment with PVOH showed an increase in the supernatant absorbance value over time. This might be an indication that a dissolution or release of polymer species from the coating colour mix may occur. The results in Figure 51 showed already that some of the PVOH film disappeared during the measurement of liquid absorption. To confirm this, the centrifuged material was re-suspended in de-ionized water, filtered, diluted and repeatedly washed. After each washing, the dissolved fraction in the filtrate was measured by drying and weighing.

Figure 66 illustrates how strongly the dispersing agent polyDADMAC has adsorbed and become fixed to the "MCC large" pigment by studying the polymer content in the filtrate after progressive washing of the dispersed pigment powder system. Some of the cationic polyDADMAC was seen to be released from the mix, and from the data it was possible to calculate that 15.7 % of the originally added 24.9 mg·g<sup>-1</sup> was recovered during washing. Thus, some of the cationic polymer is released, but probably not from the charged pigment surface, but rather because it is in excess of the surface adsorption capacity of the anionically charged sites on the pigment. However, the UV-VIS measurements showed that despite this cationic polymer loss the fixed colorant remains with the cationized surface, passing into the deposit after the centrifugation such that the filtrate remains clear. This further supports the suggestion that the lost polyDADMAC was in excess of the surface adsorption site capacity.



**Figure 66.** The content of polyDADMAC in the filtrate after washing. At first, 5 g of pigment (dispersed with 0.5 pph of polyDADMAC) was mixed with de-ionized water (20 cm<sup>3</sup>) for 1 min, followed by transferring to a Büchner funnel and filtering. The filtrate was dried and the dry weight content was measured. After that a further 20 cm<sup>3</sup> of water was added to the filtercake and the filtrate therefrom again analyzed. The procedure of water addition was repeated eight times with analysis made after each dilution (called here "washing"). It was assumed that the pigment remained on the filter paper (the filtrate after each washing was transparent). Based on Paper VII (Figure 4).

The anionic ink location was also detected within the printed coated papers. By imaging the printed anionic colorant location in the cationic "MCC large" pigment, with 10 pph PVOH (13.1 mV) double coated on the non pre-coated fine paper surface, Figure 67, the anionic colorant was seen not to have fixed totally into the top layer of cationic coating, contrary to what might have been expected on the basis of different ionic charges between the coating layer and the ink colorant. The cationicity did not prevent the colorant penetration into the bottom part of the coating layer. Thus, either speed of transit of the ink vehicle flow into the pore structure was too high for the capture to occur and/or the colorant was in excess of the local adsorption charge capacity of the surface of the coating structure. Similar effects were noticed by Svanholm and Ström (Svanholm and Ström 2004) in their study. However, the UV-VIS results indicated that the 7 pph PVOH containing "MCC large" coating structure system (11 mV) had very similar absorbance results to that of the cationically dispersed "MCC large" coating. This supports the case that

the reason for the colorant passage deep into the coating layer itself, is that the competing electrical attraction is not high enough to attract all the colorant molecules in the timescale available. The coating is so permeable that the permeation flow dominates too much during the ink penetration, and it cannot provide enough time for the colorant to bind onto the coating surfaces. Thus, there must be some kind of optimum between the ink flow rate and the ionic attraction where the inkjet ink colorant fixes optimally to the top layer of coating components.



**Figure 67.** The cross-section of high-speed inkjet printed (Versamark<sup>®</sup> VX5000e) 10 pph PVOH containing "MCC large" coating. Anionic cyan colour located very uniformly in the cationic coating layer, indicating a rate limited adsorption or colorant amount exceeding the adsorption capacity of the pigment surface. Based on Paper I (Figure 19).

## 6.2 Colorant transfer into the binder

The ToF-SIMS studies with partially hydrolyzed PVOH films and commercial cyan dye-based ink, and with the same ink with lithium addition (chapter 5, *Paper IV*), showed that the dye-based colorant separates from the water vehicle of ink during the ink absorption/adsorption into and within the PVOH film. Figure 54 (chapter 5) shows the ToF-SIMS results expressing the colorant location in the PVOH film, and this proves that the low molecular weight lithium follows the water molecules, and the colorant follows the ink vehicle (water) into the film. This finding agrees well with the results of Oka and Kimura (Oka and Kimura 1995). The water molecules open the polymer matrix, and, after that, the colorant, about 1.3 nm in diameter (calculated by taking account of the length of different bonds in the Cu phthalocyanine colorant molecule and assuming the molecule is planar), fits into the binder network. Figures 52 and 54 (chapter 5) each shows further that most of the longest in contact with the inkjet ink. There is, therefore, a chromatographic separation of colorant molecules from the ink vehicle. Moreover, the added cationic

additive in the binder films fixed the anionic dye more in the top layer. The results of ToF-SIMS and cross-section images, therefore, promote Hypothesis II.

## 6.3 Summary of colorant fixing and movement

Hypothesis II assumed that the diffusion of inkjet ink vehicle carries the ink colorant into the polymer matrix component(s) in the coating layer. The results of the PVOH film verified that the water molecules diffuse into the binder polymer and the colorant follows them, and there happens a chromatographic separation. The colorant becomes trapped in the PVOH binder matrix structure after the evaporation of water.

*Hypothesis II* – inter molecular diffusion of the liquid phase of inkjet ink into polymers, acting as a colorant carrier, is a competing mechanism to the surface adsorption of ink dye.

The ionic charge of dye colorant and the surface charge capacity of the coating colour combined with diffusion into the binder determine the adsorption potential for dye colorant. The porosity and permeability in turn define the bulk absorption rate and compete in speed with the adsorption and diffusion mechanisms in relation to the end position of colorant during the print drying process. The opposite charge of the coating components and colorant molecules binds the colorant effectively to the coating layer, as Hypothesis III argues. However, the colorant binding requires that the opposite charge is available in the coating structure. The effect of Coulombic attraction can be partially overcome by rapid passage of the ink due to a too large permeation flow of the inkjet ink through the pore network. The addition of polymeric soluble binder, such as PVOH, acts to reduce the permeability and provides additional diffusion absorption and interpolymer matrix fixing of the colorant. Thus, there is an optimum imbibition rate for the ink such that the colorant has sufficient time to bind to the available oppositely charged surface chemical groups and to be drawn into the soluble binder polymer network by vehicle diffusion. To aid the control of imbibition rate, the design of pore structure based on discretely bimodal pore structures, i.e. porous particles packed together, has been proposed and demonstrated by way of particle size combinations (Ridgway et al. 2011). Thus, we can support Hypothesis III:

*Hypothesis III* – the verity of Hypotheses I and II can be used to design porous coating structures, based on discretely bimodal pore size distributions, using binder and surface charge distribution characteristics to provide rapid fixing of ink colorant optimally close to the coating surface.

# 7. Factors influencing the print quality of dye-based ink prints

The target of the printing trials was to verify how the produced structural as well as ionic charge and hydrophilic changes of the coating layers influence the performance in a high-speed inkjet printing environment and in the final print quality. A Versamark<sup>®</sup> VX5000e high-speed inkjet press was used in *Papers I, II* and *III*. The selected printing conditions of these studies have been described in section 3.3.6 "Print quality". The printing nozzles of the press work by the continuous jetting principle. Aqueous dye-based inks were used, which were heated in the nozzle to a temperature of 40 °C. A further inkjet printer was used for testing, namely a desk-top printer (HP DeskJet 3940), which was applied in the last paper (*Paper VII*), because the previous print press was not available at this stage of the work.

## 7.1 Coating layer structure

Different coating layer structures were constructed for study using five different calcium carbonate pigments, in each case adopting 10 pph partially hydrolyzed PVOH as binder. The coating pigments had different diameters, ranging from nano-size (20–30 nm in the fine fraction of "PCC small") to the largest (2.7  $\mu$ m ("MCC large")), and displayed different morphological structures, namely with and without internal (intra-particle) pores. The porosities of the coating layers ranged from 17 % to 48 %. The coatings were applied with a semi-pilot scale coater, and the details of the coating procedure have been described in section 3.1.5 "Substrate: pre-coated base paper". Each coating colour was applied as two separate application layers on the fine paper surface as the target coat weight of 10 gm<sup>-2</sup> was not achievable with a single coating application on the semi-pilot coater. The details of the coating layers and their analyses are described in *Paper I*. The printing conditions, as stated above, are described in 3.3.6 "Print quality".

Figure 68 shows the print densities of dye-based inks (Versamark<sup>®</sup> VX5000e) on the different CaCO<sub>3</sub> coated papers. The "PCC small" pigment provided the highest print density and "MCC large" the lowest. The "PCC small" is virtually an optically inert pigment (Figure 69A), whereas the other pigments affect the print density formation more due to their intrinsic light scattering. According to the theory

of Kubelka-Munk (Kubelka and Munk 1931) those particles which have a diameter of the order of the wavelength of light (0.1–1.0 µm) affect strongly the light scattering of the structure. The opacity and light scattering coefficient of the studied "PCC small" pigment coating (Figure 69B) remains on a lower level than those of the other pigments because the size of the pigment is so small, 20-30 nm. Figure 69 illustrates further that the other pigments produced quite similar opacities on glass plates as well as on the fine paper surface. On the basis of these results, it can be expected that coating containing "PCC small" would provide a higher print density (McFadden and Donigian 1999). The cross-section figures (Figure 70) show that despite the different coating laver structures the ink colorant remains in the coating layers and does not penetrate into the base paper. In the case of the "PCC small" pigment, the colorant remaining in the coating layer complements the optical weakness of the coating pigment, providing sufficient print density due to the lack of coating light scattering - reduced background white noise and improved image signal to noise ratio. Therefore, there is still enough colorant present so that it can participate in the print density formation. It can also be expected that the coatings with high pore volume produce more light reflecting surfaces and so have an effect on print density formation. The correlation between the pore volume of the whole paper and print densities was in the range -0.904--0.949, whereas correlation between the pore volume of the coating layer alone and print density was as low as -0.050--0.217. This shows that the whole paper structure, therefore, takes a part in the print density formation, not only the coating layer. This of course depends on the nature of the base paper.

The lowest inter-colour bleeding results, indicating sufficient absorption balanced against surface spreading, were seen for the "PCC large" coating, and then somewhat higher values for the "MCC large" and "PCC small" pigment coatings. The "MCC small" and standard GCC showed the most bleeding tendency. "MCC large" and "PCC large" coatings provided the coating layers with the highest porosity, and they had the largest inter-particle pores but also nano-size pores associated with the particle structure. The bleeding distance (Figure 68B) depends on the rate of absorption, available pore volume and surface wetting of the coating layer. The high pore volume provides more volume where the applied ink can transfer from the surface to the internal structure. Although the "PCC small" coating contained the most nano-size pores, and thus the highest capillarity on the short timescale, the porosity was only on a medium level, thus limiting both permeability (assuming a connective structure) and total absorption capacity. The observation that the bleeding was also on a medium level promotes the importance of nanosize pores in quick inkjet ink sorption into the coating layer structure so that the ink colorant mixing can be prevented. The quickest absorption (DIGAT) of an inkjet ink application was also reached with coating structures containing these nanosize pores (Figure 29).



**Figure 68.** The print density (A) and inter-colour bleeding (B) of CaCO<sub>3</sub> pigment coated fine papers. Printed with Versamark<sup>®</sup> VX5000e with printing speed 100 m·min<sup>-1</sup>, and drying drum plus hot air dryer at 80 °C. Ink amount was constant. The coatings had 10 pph PVOH (partially hydrolyzed) and they were double-coated having in total 10 gm<sup>-2</sup> coating. The print density was measured from 70 % half tone dot area by using GretagMacbeth D196 spectrophotometer. The bleeding was measured from compact (100 % half tone dot) printed area. The porosity of each coating structure has been added under the name of each pigment in (B). The bleeding is defined as a line width between 10 % of the maximum and 10 % of the minimum of grey value. Based on Paper I (Figure 18 and 21).



**Figure 69.** The opacity of CaCO<sub>3</sub> coatings which contained 10 pph PVOH (partially hydrolyzed) on a glass plate (A) and on a fine paper (B). Coat weight on glass plate was 100 gm<sup>-2</sup>. During the measurement of  $R_{\infty}$ , a white board was placed behind the coated glass plate, having an opacity of 94.8 % and ISO-brightness 91.3 %. Based on Paper I (Figure 17).



**Figure 70.** The cross-section images of dye-based ink (cyan) printed on the various  $CaCO_3$  coated fine papers. Printed with Versamark<sup>®</sup> VX5000e using constant ink amount. Based on Paper I (Figure 19).

### 7.2 Binder amount and type

The effect of binder diffusion on the print quality formation was studied in Papers I and *II* by changing the amount of binder and using alternately a diffusion inert and diffusion promoting coating binder. The coating colours studied were based on the "PCC large" pigment including 7, 12 or 30 pph of either partially hydrolyzed PVOH or SA latex and were applied on the pilot pre-coated fine base paper surface. The printing was performed with the Versamark<sup>®</sup> VX5000e using a constant ink amount for all the tests. Figure 71A shows that the coating binder amount had a minimal influence on the print densities of the cyan dye-based ink, at least for this ink amount per printed area. The only exception was the 7 pph SA coating that produced a higher print density than the other coatings, although the strike-through (describing the penetration of the colorant through the coated paper structure) was clearly higher with the SA containing coatings than with the PVOH containing. These results emphasize once again the importance of the optical properties of the complete coated paper in respect to the resultant print density formation. The coating with 7 pph SA latex had the highest ISO-brightness and opacity, as Figure 72A shows.

The bleeding in this case was illustrated by the line edge-area distance (width) and the results show that the 12 and 30 pph SA latex containing coatings produced greater bleeding than the other printed surfaces (Figure 71B). All the SA latex containing coating layers were clearly surface wetting resistant, i.e. pseudo hydrophobic in respect to contact angle (Figure 72B), but clearly not actually hydrophobic in respect to pore chemistry as absorption proceeded without hindrance (Figures 29B and 37). Figure 73 shows the printed lines on the half tone dot area 65 %. The black line on the 30 pph SA containing coating has clearly wicked more than on the 7 pph SA containing coating. Since the apparent contact angle was greater than 90°, the image bleed must have been via sub-surface wicking/capillarity. The 12 pph and 30 pph binder containing coatings had similar absorption time (DIGAT) for dye-based ink (8 gm<sup>-2</sup> ink amount, Figure 29B), indicating that the dye absorbs into the coating layer structures with the same speed. The porosity values alone cannot explain this result, because the 30 pph SA latex containing coating had even higher air permeance than the coating containing the same amount of PVOH (Figure 29C). The capacitance-based results (Figures 37 and 38) show that the inkjet ink is imbibed at a faster rate in the SA containing coating layer paper than in the PVOH containing. Therefore, these results indicate that the higher bleeding results have a connection to the surface wetting resistance of SA containing coatings, and likely to the surfactants on the latex polymer surface that have been used in latex production. The surfactants could aid lateral transport of colorants within the top part of the coating, although the penetration speed of the ink is in principle quick enough normally to have prevented the appearance of colour bleeding.



**Figure 71.** Print density (A) and bleeding (B) against strike-through of dye-based ink printed "PCC large" coating surfaces containing different amounts of PVOH or SA latex. Coat weight was 8 gm<sup>-2</sup>. Printed with Versamark<sup>®</sup> VX5000e (speed 100 m·min<sup>-1</sup>, drying at 80 °C), constant ink amount. The print density was measured with GretagMacbeth D196 spectrophotometer. Bleeding definition: 15 % of minimum and maximum grey value. Based on Paper II (Figure 10 and 11).



**Figure 72.** The ISO-brightness, opacity (A) and contact angle of water (B) as function of increasing amount of PVOH (partially hydrolyzed) and SA latex containing "PCC large" coatings, respectively. Coat weight was 8 gm<sup>-2</sup>.



7 pph SA latex

30 pph SA latex

**Figure 73.** Printed black lines on cyan 65 % half tone dot area on the 7 pph SA and 30 pph SA containing coating layers. Printed with Versamark® VX5000e (speed 100 m  $\cdot$  min<sup>-1</sup>, drying 80 °C).

All of the dye colorant was found to locate in the coating layer (Figure 74, 7 pph binder figures were also shown previously in Figure 28), and takes part in defining the print density formation. Nonetheless, the distribution of colorant within the coating is very different in the case of the 7 pph PVOH containing "PCC large" pigment coating compared with the case of the higher binder level 30 pph PVOH containing. In theory, if the lateral cyan colorant distribution in the 30 pph coating had been more uniform, it would probably have produced higher print density as it was seen to be located more on the top of the coating layer, and the opacity of the 30 pph binder coatings was somewhat lower than that of the 7 pph binder containing results. The 30 pph PVOH coating image (Figure 74) shows a place in the coating layer where the ink colorant has penetrated as far as the base paper. This could

be a position in the coating layer where the PVOH, having formed initially a filmlike structure, has subsequently developed a hole in the drying film as it shrank (Figure 75).

In the case of SA latex containing coatings, the cyan colorant can be seen to have penetrated as far as into the top of the base paper. The greater permeability as well as the anionic nature of the SA containing coatings allows the anionic colorant to penetrate freely through the structure together with the ink vehicle. There are no colorant-fixing cationic groups and the high permeability provides pathways for ink to transfer deep into the structure. This explains why the SA latex containing coatings had higher strike-though results than the PVOH containing (Figure 71). However, despite the colorant location in the bottom part of the coating layers, no decrease in print density was observed. The cross-section images of the SA coating structures show that the colorant also locates partly within the coating layers. The explanation for satisfactory print density can, therefore, be related to the ink amount. Probably sufficient ink has been applied that there still remains enough colorant within the coating layer to produce a similar print density as in the case of PVOH containing coating.



7 pph PVOH

30 pph PVOH



**Figure 74.** Cross-section images of 7 and 30 pph PVOH or SA containing "PCC large" coatings that have been printed with cyan dye (Versamark<sup>®</sup> VX5000e using speed 100 m·min<sup>-1</sup> and drying temperature 80 °C), constant ink amount. Coat weight was 8 gm<sup>-2</sup>. Based on Paper 1 (Figure 23).





Figure 76A shows how the uniformity of the printed PVOH containing surfaces varied the most in the resolution area of 0.34 mm and 0.67 mm. This is the area where the pigment size and state of flocculation affect the result the most. As the binder amount of "PCC large" coatings increased, so grew the mottling values at this resolution. The non-uniform coating layer structure and the holes in the 30 pph binder containing coating produce the highest mottling values as the ink penetrates very unevenly into the coating layer. The use of "PCC small" pigment, in contrast, produced the lowest mottling values. The "PCC small" pigment provides a coating layer structure with nano-size pores and the colorant transfers into this kind of structure more uniformly. In the case of SA containing coatings, a similar mottling increase was detected as the binder amount increased (Figure 76B). However, the maximum values located in the coarser resolution area (0.67–1.34 mm), indicating large size variation on the cyan printed surface.



**Figure 76.** The mottling (mottling index) of cyan ink (C70 – 70 % halftone dot area) printed "PCC large" and "PCC small" coating surfaces. The PVOH (A) or SA latex (B) content varied between 7 and 30 pph. Coat weight was 8 gm<sup>-2</sup>. Printed with Versamark<sup>®</sup> VX5000e by using printing speed of 100 m·min<sup>-1</sup> and drying temperature 80 °C. Based on Paper I (A: Figure 24).

Important print quality properties, from the point of view of the printed inkjet paper user, are water fastness and rub resistance. The print should be resistant to exposure to water and the ink colorant should stay in/on the prints without transferring to the user's fingers or spreading on the printed surface when touched. Figure 77 shows the water fastness of 70 % half tone dot cyan dye-based ink prints (CIELab\*) on the different PVOH and SA latex content "PCC large" coatings after they had been treated by immersing for 5 min in water. The PVOH containing coatings produced clearly lower density change values after the exposure to water than the SA latex containing, indicating that the water treatment changed less the colour of the prints on PVOH containing coatings. PVOH contains chemical groups which can bind colorant molecules, and/or the polymer structure can permit diffusion by the ink, so that it is subsequently more difficult to get colorant molecules out of the coating structure during the water fastness test. All PVOH containing coatings had slightly cationic charge (zeta-potential about 2 mV) that promotes ionic adsorption of the dye, and the hydrophilicity of PVOH binder means that hydrogen bonds can also take a part in the colorant fixing. The colorant thus becomes trapped within the binder polymer structure after ink vehicle evaporation. In the SA latex containing coatings, the same sign of ionic charge of coating layer and colorant molecules causes an anionic repulsion between the binder and colorant. There is no diffusive motion into the binder polymer (the diffusion is surface diffusion only) that could otherwise assist colorant movement into the binder structure.



**Figure 77.** The water fastness of cyan dye-based ink printed on "PCC large" surfaces with different content of PVOH (partially hydrolyzed) or SA latex as a binder. Coat weight was 8 gm<sup>-2</sup>. Printed with Versamark<sup>®</sup> VX5000e (speed 100 m·min<sup>-1</sup> and drying temperature 80 °C), constant ink amount. Based on Paper II (Figure 12).

## 7.3 Coat weight

The effect of coat weight was studied in Paper III by using the coatings that contained the inkjet pigment, "PCC small", and 15 pph of PVOH (partially hydrolyzed). The coatings were applied with a pilot-scale curtain coater on the top of precoated fine paper. The printing was carried out on the Versamark<sup>®</sup> VX5000e using the same ink feed during the whole printing series. The printing speeds were 50 and 100 m min<sup>-1</sup>. The on-line camera images in Figure 78 show how much the inkiet inks have mixed together on the different coat weight "PCC small" coatings during printing. All images show wicking paths where the black ink has moved into the area of the cyan colour. The highest coat weight coatings produced the narrowest and the most uniform printed black line next to the cyan ink. There is enough pore volume in these coatings where the ink can penetrate quickly and sufficiently, in regard of ink mixing. Figure 43 illustrates that the higher coating weight paper has more pore volume and it contains more nano-size pores. If the coating layer has a constant pore structure (pore size distribution) and the only variable is the thickness of coating layer, a thicker layer would have more pore volume where the ink can penetrate quickly than the thinner layer. In the low coat weight coating, the ink arrives at the interface between the coatings and base paper earlier, and it pins there for a while. This means that at a certain moment there is more colorant that can spread in the lateral direction, whereas in the thicker coating case the ink still continues to move in the z-direction. The printing speed increase expected in high-speed inkjet presses means that the time delays between the nozzles become shorter, and the sorption rate of ink into the coating layers becomes even more important.



**Figure 78.** On-line images of intercolour bleeding from "PCC small" coatings that contained 15 pph PVOH (partially hydrolyzed) using printing speeds of 50 and 100 m·min<sup>-1</sup>. The time delay between cyan application and the on-line camera system was 2.2 s ( $50 \text{ m·min}^{-1}$ ) and 1.1 s ( $100 \text{ m·min}^{-1}$ ), respectively. The time delay between cyan and black nozzles was 1.1 s and 0.54 s depending on printing speed, respectively. Based on Paper III (Figure 13).

The results of paper analyses show that the highest coat weight (10 gm<sup>-2</sup>) of curtain-coated "PCC small" with 15 pph PVOH surface produced the highest total paper porosity, and, hence, greatest pore volume, with the 20-60 nm diameter pores providing for the quickest inkjet ink absorption rate. All these findings relate to the simple relationship between the top-coating proportion and the total sheet weight. On-line images collected on the press show further how inkjet inks mixed together less if the coating layer has high coat weight. However, on the 70 % halftone dot area the 4 gm<sup>-2</sup> coat weight produced higher print density than the 10 gm<sup>-2</sup> coat weight (Figure 79). Nilsson and Fogden (Nilsson and Fogden 2008) noticed also the print density decrease on PVOH containing spherical polystyrene plastic pigment coatings, which had nominal particle diameter of 0.14 µm, when the coat weight increased from 5 gm<sup>-2</sup> to 20 gm<sup>-2</sup>. The colorant remains in the coating layer and therefore the lower coat weight structure has relatively more colorant molecules in the coating volume than the higher coat weight structure. In the high coat weight case, the colorant has moved deeper into the coating layer structure, and therefore there are less colorant molecules that can take part in print density formation. From the print density point of view, when the coating colour has an anionic charge like that of the dye, the coat weight should be low. To minimise the colorant spreading in the x, y-direction it is, however, necessary to have sufficient pore volume in the coating, which requires the adoption of high coat weight.



**Figure 79.** Cross-section images of printed 15 pph PVOH (partially hydrolyzed) containing speciality coatings (70 % half tone dot area). Printed with Versamark<sup>®</sup> VX5000e, 100 m·min<sup>-1</sup>, drying 70 °C, constant ink amount. Coat weights 4, 8 and 10 gm<sup>-2</sup>. Based on Paper III (Figure 14).

## 7.4 Cationic additive applied directly onto the top of coating surface

One way to design coatings for controlled dye-based ink colorant penetration and fixing is to use a multi-layer structure where each coating layer has a specific purpose. From the colorant fixing point of view, the top applied layer should have an opposite ionic charge than the colorant such that the desired high print density and good colour gamut is usually achieved by ensuring that the colorant will stay in the top part of the layer structure. This kind of layer structure was studied in Paper VII. In this research, a cationic polyDADMAC was applied as a post treatment conversion with a draw down coater on the "PCC large" top-coating layer that contained either 7 pph of SA latex (anionic) or 7 pph of PVOH (partially hydrolyzed) - the base paper was pilot pre-coated fine paper. The penetration properties of the surfaces for ink were measured with the capacitance-based device (Clara) using water and cyan dye ink (Versamark® VX5000e), the water being at the temperature of 23 °C and the dye ink at 23 °C and 40 °C. The 2.0-3.2 gm<sup>-2</sup> application of cationic polymer on the surface slowed down the speed of water and dye-based ink absorption into the structure (Figure 80), as expected. The polymer reduced the permeability of the surface so that it took more time for liquid to penetrate into the surface. The lowest capacitance results, i.e. slowest imbibition, were shown by water, then the anionic dye-based ink at the temperature of 23 °C, and the quickest was seen with the same ink at the higher temperature. The surface tension of water at 23 °C is 72 mNm<sup>-1</sup>, and cyan dye at 24 °C is 54 mNm<sup>-1</sup> and at 40 °C, 49 mNm<sup>-1</sup>, which promotes the faster penetration rate. Additionally, the temperature affects viscosity. The viscosity of the cyan dye ink decreases from 1.05 mPas (23 °C) to 0.80 mPas (40 °C) which also promotes a faster absorption. Figure 81 shows two examples of the various Clara results, and they confirm that the differences in the results are reproducible and cannot be explained by random variations.



**Figure 80.** The capacitance changes of papers, having a top-coat of anionic "PCC large" + 7 pph SA latex, and same surface where polyDADMAC (cationic) has been post-applied plotted against time. The penetration of water (23 °C) and dye-based inks (23 °C and 40 °C) into the anionic "PCC large" coating at the timescale of 1 s (A) and polyDADMAC treated surface at 1 s (B). The external over-pressure was 0.10 bar. Based on Paper VII (Figure 6).



**Figure 81.** The progression of the capacitance values of anionic "PCC large" + 7 pph SA latex with the polyDADMAC (cationic) treated surface in the Clara device. External over-pressure was 0.10 bar and the liquid was anionic dye at 40 °C (A) and water at 23 °C (B). Based on Paper VII (Figure 7).

The higher temperature (40 °C) affects the diffusion velocity of ink component molecules, such that the macromolecular motion depends on temperature, viscosity of the surrounding fluid and size of particle/macromolecule, according to the equation of Stokes-Einstein (Mehaffey and Cukier 1977). The diffusional motion of macro-molecules is greater at 40 °C than at 23 °C, and therefore the ink imbibition is accelerated by use of a warmer ink, as viscosity also falls exponentially with temperature (Figure 10 in section 3.1.4 "Inkjet inks and printing devices"). Another

advantage of using higher temperature ink is the possibility to speed up the final drying of the ink. In the real printing process, the use of warmer ink is limited by the printing nozzles. The ink must not be allowed to start to dry in the nozzles or accumulate on the nozzle exit edge area. The surface tension of the ink, in addition, depends on temperature, especially if this is defined by surfactant action, which itself is diffusion dependent.

The surfaces with and without polyDADMAC treatment were also printed using an HP DeskJet 3940 printer, and the print quality was analyzed. The bleeding was measured from the magenta line (Figure 82), which was either printed as the first colour laid on the paper surface (line spreading on the coating surface) or onto a pre-printed yellow surface (ink mixing). The application of cationic polyDADMAC on the surface decreased the line width, both for the single colour and the magenta on yellow cases. The cationic additive application did not decrease the raggedness of the magenta/yellow line, but the magenta line on the coated paper alone had less raggedness on the polyDADMAC treated surface than on the 7 pph SA-containing coating without treatment. The cationic components of polyDADMAC prevented the anionic colorant spreading, although the added polymer partially closed the structure. The opposite charge of surfaces (electrostatic forces) binds the anionic colorant effectively on the surface so that the colorant cannot spread on the xyplane of the surface. Svanholm (Svanholm 2007) showed that the addition of cationic additive into the coating colour did not always diminish bleeding tendency of dye-based inkjet ink printed coatings. The cationic additive in the coating layer does not necessarily locate on the top part of the coating layer, because, during the consolidation process, the additive can transfer deeper into the coating layer, or even to the base paper, and so it cannot effectively take part in the binding of the colorant. On the other hand, the porosity of the coating layer affects the ink spreading, and in the cationic additive containing coating layer the capillary and permeation flow competes more strongly with the ionic interactions than in the polyDADMAC polymer coated layer, as we saw in section 6.1.2 "Absorption and/or adsorption of coating components". Thus, the additive must locate on or very near the top of the coating layer to fix the colorant quickly enough to the surface so that bleeding problems cannot appear. The only exception could be detected with the magenta ink on the yellow surface, where the raggedness was higher with the cationically treated surface than with the SA containing coating. This indicates that once the ink is isolated from the cationic layer by a previously applied colour, and, as the absorption of ink vehicle is slowed by the presence of the polymer reducing the permeability, the dye can migrate more freely.



**Figure 82.** The line width (A) and raggedness (B) of a magenta line printed on the "PCC large" coated paper surface with and without cationic post-treatment (cat.), and on the same surface with a pre-printed yellow compact area. C - a schematic illustration of printed magenta line on the pre-printed yellow and on the non preprinted paper surface. Printed with HP Deskjet 3940, which had dye-based inks. Based on Paper VII (Figure 9).

The water fastness was measured for this coating series, as before, by detecting the print density changes and  $\Delta E^*$  of cyan 100 % printed surface after immersion for 5 min in water (23 °C). The results are shown in Figure 83. The print density differences between before and after water treatment were greater on the SA containing coatings than on the PVOH containing surfaces. The water treatment of printed SA coating releases the colorant out of the printed surface because the colorant has no effective binding to the latex, whereas in the PVOH containing coating there forms hydrogen bonding and/or colorant trapping, and the slightly cationic charge of the coating, about 2 mV, provides for ionic interactions. If the SA latex containing coatings with different binder content are compared, somewhat larger changes in  $\Delta E^*$  were seen with the 30 pph SA containing structure than with the 7 pph SA containing. The 30 pph SA containing coating has fewer surfaces where the colorant can bind and therefore more colorant can release out of the coating. On the 7 pph PVOH containing coatings, the cationic additive application had quite minimal influence on the change in print density results, indicating an adequate colorant fixing to the PVOH polymer. No large differences were observed between the different PVOH content coatings. A similar value was recorded for the  $\Delta E^*$  values.

On the SA coatings, the polyDADMAC treated surface produced the lowest  $\Delta E^*$  value, and the results were very similar to those of PVOH containing coatings. The cationic additive treated SA containing coating fixes the anionic colorant more permanently to the coating layer than the anionic SA latex containing coating alone. The ionic interactions (Coulombic attraction) fix the colorant effectively to the treated surface. The difference between the slightly cationic PVOH containing coating and the cationic polyDADMAC treated PVOH coating surface is small. This indicates that polyDADMAC and the PVOH containing surface behaved very similarly in the water fastness test. The cationicity of the surface does not promote stronger colorant binding more than the diffusion of colorant into the PVOH polymer. The slightly cationic nature combined with the suitable inter-polymer matrix diffusion capability of the coating binder seems to be sufficient for an adequate colorant fixing, so that the colorant does not release out of the surface during the water fastness test as used here.



**Figure 83.** The water fastness of surfaces: print density (100 % cyan) before and after water treatment (A) and the corresponding  $\Delta E^*$  (B, 100 % cyan surface). High fastness implies small  $\Delta E^*$ . Printed with HP Deskjet 3940 which had dye-based inks – the coating had "PCC large" pigment with 7 or 30 pph PVOH (partially hydrolyzed) or SA latex with and without cationic post-treatment (cat.). Measurements were made with SpectroEye spectrophotometer. Based on Paper VII (Figure 10).

## 7.5 Summary of print quality formation

Beside the selection of printing press variables, inkjet print quality depends on the selection of coating components as well as the amount of each component in the formulation. The main coating layer properties that affect the bleeding formation are the pore volume and the pore size distribution in respect to connectivity and permeability, and thereby the penetration rate of inkjet ink.

If the coating layer contains latex, in this case study styrene acrylic (SA), the surfactants of the latex assist the sub-surface colorant lateral motion but the penetration speed of ink is high enough to prevent colour bleeding. The SA latex containing coatings have no chemical groups that can fix the colorant quickly to the coating layer. However, in the combination studied here, the optical properties of the speciality coating layer alone play only a minor role in the print density formation of the high-speed inkjet printed surface. The optical properties of the whole fine paper structure dominate in the print density formation.

In the case of PVOH containing coatings, the ink vehicle diffuses into the hydrophilic polymer network, causing polymer matrix swelling, and this acts to close the nano-size pores thus reducing the ink penetration rate, as was seen previously for the model coating structures. The diffusion transfer seems to be high enough to prevent bleeding problems in the studied coating layers indicating that the diffusion of the liquid phase of inkjet ink into the absorbing polymers acts on a sufficiently fast timescale (Hypothesis I).

*Hypothesis I* – inter molecular diffusion of the liquid phase of inkjet ink into polymers acts on a sufficiently fast timescale and in sufficient volume to compete with the permeation of ink through coating structures.

The ink colorant locates within the PVOH containing coating layer, thus supporting the idea that colorant transfers into the polyvinyl alcohol matrix by following the ink vehicle (Hypothesis II). Although generally positive, a too high PVOH binder content in the coating colour when applied to paper can produce film-like structures in the coating layer and shrinkage of the wet film during drying can lead to surface defects/holes. During printing, the inkjet ink can penetrate through these holes as far as the base paper, and, as a result, the print uniformity suffers. The PVOH containing coatings on paper had good water fastness results, despite the slightly cationic charge of the coating bulk, as was also seen for the model coatings, indicating that the diffusion of ink colorant into the binder polymer matrix and hydrogen bonding to the polymer matrix is sufficient that the water treatment cannot release the colorant from the structure.

*Hypothesis II* – inter molecular diffusion of the liquid phase of inkjet ink into polymers, acting as a colorant carrier, is a competing mechanism to the surface adsorption of ink dye.

In the case of anionic SA latex containing coatings, the surface has no chemical groups that can bind the anionic colorant and/or allow the colorant molecules to

diffuse into the binder matrix, and therefore water can release colorant from the printed surface during the water fastness test. This lack of adsorption can also be seen as the anionic colorant partially penetrates through the SA bound coating structure to the top of the base paper, and therefore print-through problems occur. The hydrophobicity of the latex polymer, as well as the action of surfactants on the SA latex surface, affects the molecular motion on the coating surface.

The use of higher coat weight is illustrated by the 15 pph PVOH containing "PCC small" pigment coatings. Higher coat weight in this case speeds up the ink penetration into the coating layer because of the greater pore volume of the absorbent top coating layer. The high pore volume means that ink transfers continuously in the *z*-direction of the coating layer for longer, and therefore there appears less lateral colorant motion. Despite this positive effect on bleeding, at the same time, the print density decreases because the colorant can transfer deeper into the coating layer.

By application of a small amount of cationic polymer onto an already formed anionic coating layer surface, the bleeding tendency of the ink can be decreased, although the absorption rate of the ink also decreases due to the presence of the polymer. The opposite ionic charge of cationic additive and that of the ink colorant fixes (Coulombic attraction) the colorant molecules within the top part of the coating structure. However, there was no clear connection between the cationic nature of the surface and the print density. Furthermore, once a print colour has been applied, it acts to mask the applied cationic charge, such that subsequent ink colorant application has greater freedom to bleed. The improvement in single colorant fixing is reflected additionally in respect to the water fastness properties in the case of latex containing coatings. The cationic additive application on the PVOH containing coating layer, on the other hand, had quite minimal influence on the water fastness results, indicating the adequate fixing effect of PVOH alone.

The use of higher temperature ink allows quicker diffusion of the ink molecules into the polymer structure of PVOH, and therefore the ink sorption rate can be increased.

## 8. Conclusions

# 8.1 The effect of coating structure, binder properties and surface adsorption on inkjet ink imbibition and colorant distribution

### 8.1.1 The interplay of capillarity and diffusion

The porosity and pore size distribution, in respect to the connected wettable pore network structure of an inkiet paper coating, dominates the imbibition properties for ink vehicle during high-speed inkjet printing. The wetting force of capillaries drives the ink into the coating layer structure, whilst the viscous drag as the network fills resists it. At first, there forms a wetting front of ink vehicle where the capillary flow drives the ink forward through a selective pathway depending on the ratio of pore diameter, with the finest pores acting on the shorter timescale. As the viscous drag increases in proportion to the length over which the liquid flows within the structure, and to the inverse of the fourth power of typical equivalent capillary size (Poiseuille effect), there comes a point when the drag equals the wetting force. However, this equilibrium point is never reached within the dimensions of paper coatings and permeation can continue, even through the coating into the basepaper. In the case where hydrophilic soluble binder is used in the coating formulation, the polar ink vehicle (water) diffuses into the binder polymer matrix. As a result, the polymer swells, and this has an effect on the capillary flow by decreasing the pore diameters leading to closure of the smallest pores. As a result, even during the short timescale absorption, the capillary flow becomes reduced and progressively substituted locally by the diffusion into the swelling-generated inter-polymer space. When the smallest capillaries have been filled by a combination of free liquid and liquid bound between the binder polymer chains, the inkjet ink continues to transfer along the large pore structure according to permeation flow. In the case of dve-based inks, the dve follows the vehicle, and, if encountering surface adsorption sites, becomes chromatographically separated from the bulk flow. Dye transport occurs also within the binder polymer network if diffusion is additionally driving absorption into the binder, such that dye becomes bound or trapped within the polymer matrix. In the case of vehicle-repellent binder polymers,

both vehicle and colorant are excluded from the binder, and interaction with ink is limited to the action of surface carboxylation and/or surfactants used to stabilise the otherwise hydrophobic binder particle.

#### 8.1.2 Detailed role of binder

During the ink transfer process, the hydrophilicity/hydrophobicity of binder has a strong effect on the diffusional movement of vehicle and dye. The work here illustrated the impact of binder type in more detail by focusing on two examples, partially hydrolyzed PVOH and styrene acrylic latex. In all cases, the presence of binder slows the absorption rate compared to pure coating pigment. However, at short timescale, the diffusion mechanism in hydrophilic PVOH speeds up the polar liquid absorption relative to the "diffusion-inert" SA latex, which acts to slow the polar liquid movement primarily due to its modification of the surface chemistry by means of associated surfactant used in the emulsion polymerisation process producing the latex. The structural effect of latex is to reduce permeability less than in the case of soluble binder. As a hydrophilic polymer, such as PVOH, absorbs the inkjet ink, the polar ink vehicle (mainly water) diffuses in the polymer network structure and opens it by the action of swelling. The vehicle changes the amorphous region of the polymer. The ink colorant follows the vehicle that acts as a colorant carrier into the polymer matrix. The colorant forms either hydrogen bonding with the chemical groups of PVOH and/or becomes trapped into the structure after ink water evaporation. There is a chromatographic separation, and the dye colorant fixes to the polymer and the vehicle of the ink transfers deeper into the polymer structure proceeding with a depletion of the colorant. The highest content of colorant can be seen on the binder surface that has been longest in contact with the ink. The swelling occurs at a few seconds timescale, which is of similar timescale to the delay that can occur in high-speed inkjet presses between the nozzles and dryers. In the case of effectively non-swelling SA latex, the water and colorant remain excluded from the polymer matrix, and the colorant cannot fix other than by external charge interaction if present. The hydrophobic nature of latex prevents the diffusion of the polar liquid into the polymer structure, but wetting still occurs, once again probably related to the surfactant and/or carboxylation used to stabilize the latex when in suspension. However, the diffusion coefficient in contact with PVOH and SA latex films seems to be similar, although the mechanisms of bulk diffusion and surface diffusion are different. The main polar liquid driving phenomena in the SA latex containing coatings are related to the capillary flow, and the diffusion acts as a molecular motion on the interface of capillary wall and liquid phase, i.e. surface diffusion.

On the longer timescale the diffusion still continues, but the dominating inkjet ink (polar) transport happens in the large pores, and the resulting permeation flow is the most dominant mechanism defining the resistance/competition to capillarity and molecular translation toward diffusion absorbing and charge adsorbing surfaces. One thing that should not be forgotten during inkjet ink imbibition into PVOH containing coatings, i.e. in the general case of soluble binders, is the dissolution of PVOH itself into the inkjet ink, and this has an effect on the viscosity and surface tension of the ink and further ink and binder transport.

#### 8.1.3 Adsorption and dye fixation

The results of thin layer chromatorgraphy (TLC) show that a surprisingly small amount of binder (1 pph) affects the liquid transfer through (along) the coating layers. The capillary flow is again shown to be the main inkjet ink driving phenomenon in the coating structure. However, the swelling of the PVOH polymer acts on the short timescale liquid absorption, due to the short nano-scale distances involved in the finest pores, despite it being a diffusion-controlled process. The permeation flow offers the resistance to the capillary and diffusion-controlled driving forces in the continuing liquid mass transfer, and swollen binder acts to impede that flow. The latex containing coating carries the water further along a TLC plate than in the PVOH containing. The slightly larger pores of the SA containing coating structure and the non-swelling nature of latex allows a quicker liquid permeation, rather than the smaller pores and reduced connectivity of the PVOH containing coatings.

The studies with the anionic dye and anionic coating layer on the TLC plates show that there is a colorant-free wetting front and behind that a concentrated ink colorant containing layer followed by a lighter colorant area. The surface area associated with the finest pores in these structures is either not available for adsorption of the dye or the charge similarity leads to an exclusion of colorant at the pore entry points. The concentrated colorant layer existing behind the wetting front suggests that charge exclusion is the more likely mechanism. In the case of a cationic coating layer, the anionic colorant fixes immediately into the first contact layer of coating on the TLC plate and remains there until the coating layer specific adsorptive surface area is saturated totally by the colorant, after which the colorant begins to migrate further into the coating.

The penetration of dye-based inks was also studied by means of recording the capacitance change induced by the liquid filling the porous structure. This technique allows the application of an external pressure range, namely 0.02, 0.1 and 1.5 bar in this study. The results measured from the coatings of both standard offset-quality ground calcium carbonate and an inkjet purpose designed precipitated calcium carbonate, combined with different PVOH contents and applied on a plastic film, showed that after as short a time as 0.004 s the permeation flow becomes established in the coating layer when external pressure is applied. The capillary flow, however, acts continuously as the internal driving force throughout. The pigment type, the binder amount or the coating layer thickness (up to 35 gm<sup>-2</sup>) did not influence this mechanistic result even though their interaction with ink vehicle controls the permeation rate. Similar sorption rate differences were also noticed between the PVOH and SA latex containing coatings as in the TLC, and direct microbalance measurements also confirmed this finding. However, the turning

points between short and long timescale absorption were located at different times depending on the measurement system used. The differences in the nonpressurised microbalance and the slight overpressure applied in the capacitance technique were related directly to the pressure difference, in that the overpressure forced the imbibition into an early permeation mode. The external overpressure caused by an inkjet ink droplet hitting the paper surface is quite low, being approximately equivalent to the capacitance study using 0.10 bar, but it is large enough to have a meaningful effect on the initial sorption results causing an initial wetting by forced surface permeation.

The use of higher temperature ink in the capacitance-based measurement allows a quicker diffusion of the ink molecules into the polymer structure. Additionally, higher temperature lowers the surface tension and viscosity of the ink, and therefore the ink wets and flows more readily.

## 8.2 Print quality – factors relating to the identified interaction mechanisms

The coating layer structural properties have an effect on the print quality via the ink absorption speed and the pore volume capacity. Too low ink absorption speed into the coating structure means that the colorant of the inks has more time to mix together and bleeding problems are more visible. The optical properties of the *whole coated paper* dominate the print density formation. The reason behind this is that inkjet coating pigments are generally designed to have low scattering potential, and so the base paper, if optically active, has a strong effect in respect to show-through in the coating layer.

The coat weight study shows that absorption speed is not the only criterion for preventing intercolour bleeding during inkjet ink drying, but the combination of the continuity of absorption over time coupled with sufficient total pore volume within the rapidly absorbing layer is the key factor. The only way to decrease the coat weight of speciality inkjet coating layers and still have satisfactory print quality, therefore, is to use pigments that produce a structure with a high proportion of nano-pores and high permeability. The presence of diffusion controlling binder is seen as a limiting factor to achieving optimal inkjet coatings at low coat weights in the case where pore structure derived from the pigment alone is properly designed. The PVOH binder swelling, however, was shown to have a quite minimal influence on the bleeding results. The SA latex on the other hand with its associated surfactant(s) on the latex polymer surface, stabilising the latex in suspension, increased the bleeding results strongly despite the SA containing coating having higher penetration rate than the PVOH containing coating.

Furthermore, the binder type strongly affects the water fastness properties of the inkjet printed surface. The PVOH binds and/or traps the anionic dye colorant molecules so that it is difficult to get them out of the coating structure during exposure to water in the water fastness measurement. The results show that the SA latex can neither bind ink colorant nor prevent bleeding upon wetting. The postapplication of cationic polyDADMAC polymer on the surface of SA latex containing anionic coating decreases the bleeding and produces improved water fastness results, indicating better colorant fixing to the surface despite the slower absorption rate through the surface. The opposite ionic charge of the surface binds the ink colorant molecules in the top part of the structure by Coulombic forces, and the lack of colorant penetration seems not to prevent this rapid fixing of the dye colorant.

The adsorption of colorant in the fixing process can be detrimentally limited if too great a permeation flow of inkjet ink occurs during the imbibition. Especially the fixing of colorant by PVOH containing coatings showed that the dynamics of colorant hydrogen bonding following diffusion into the binder polymer network and/or Coulombic forces acting at pore surfaces can be slower than the bulk flow transport of the colorant past the relevant adsorption sites. These results suggest that, for good colorant fixing, there is an optimum in the ink sorption flow rate into the coating structure, such that the colorant has sufficient time to bind to the available opposite charge and/or binder chemical groups.

## 9. Suggestions for future work

The results of this study show that the diffusion-driven and ionic charge interactions between the components of the coating layer and the ink colorant are complex, and that they are strongly dependent on the coating formulation and how the coating layer structure is produced, i.e. in terms of drying, porosity, or use of multilayer structures. At the same time, the results suggest that there would be an optimum absorption permeation rate for inkjet inks in terms of colorant fixing. Further studies to generate a better understanding of ionic charge location and polymer distribution in/on the coating layer structure is therefore identified as a potential means for helping inkjet substrate designers in their search for inkjet coating colour formulations for the rapidly emerging market in high-speed inkjet printing.

There are identifiable trends in the inter-colour bleeding results that suggest the outermost surface and immediate sub-surface energy of the coating layer(s) can influence the inkjet ink mixing tendency. This discovery certainly needs more comprehensive research to define the effects more thoroughly, and probably would lead to further correlations with the ionic properties of the coating layer. This is a research area where some work has already been made, but the connections between surface energies and print quality aspects have not been shown in sufficient detail. This research could include the role of surfactant action associated with latex.

One aspect that has not been studied in this thesis is the drying of inkjet prints: how the coating layer with absorbing binder combined to the structural variation affect the drying rate, and, if the water is held by the diffusive mechanism in the coating, how does it effect to the final drying of printed surface. Thermal properties of the various formulations in respect to efficient heat transfer could be connected to this.

The research work in this thesis concentrated on dye-based aqueous inkjet inks. There are now many developing applications that use pigment-based aqueous inks, and the interest in pigment inks is increasing all the time. The currently reducing cost of pigment-based inks is pushing their development further, but still the ink does not work reliably enough in the nozzles and produces at best only similar print quality to the dye-based inks, in respect to colour gamut, in highspeed inkjet printing. Nevertheless, the growth in pigment-based inks will continue, partly due to the improved holdout properties and reduced demand for extremely high absorbency in the coating, and so the understanding of their setting interactions on coating layers and the surface sized structures is important for application at high printing speeds. The other area, in respect of the inks likely to be used for high-speed inkjet printing, is the behaviour of UV-curing inks on coated surfaces and especially how the coating components affect the UV-curing.

In the case of the use of a swelling binder, changes to the absorption dynamic are identified, e.g. modification of the Bosanquet equation as applied to pore networks, but a detailed development was not undertaken in this thesis. To capture such an effect in an algorithm would be a subject for later work, and could, for example, be applied to a time-evolving network model. In effect, the absorption driver of diffusion, although positively active, is, however, giving a negative feedback and so reducing the capillary-driven absorption.

Perhaps one of the most important aspects to consider now and in the future is the recycling potential of inkjet printed papers. A control of the interaction of ink and substrate will be a key feature for developing optimally recyclable substrates. It is hoped that such future work will benefit from the findings presented in this thesis.

## References

- Adair, P. C.: Ink jet coatings for pigmented inks, IS&T NIP14: International Conference on Digital Printing Technologies, October 18–23, 1998, Toronto, Canada, IS&T: The Society for Imaging Science and Technology, Springfield, USA, 1998, 146–149.
- Agbezuge, L., Gooray, A.: Drying of ink jet images on plain papers falling rate period, IS&T's NIP7: International Conference on Digital Printing Technologies, 1991, Portland, USA, IS&T: The Society for Imaging Science and Technology, Springfield, USA, 1991, 173–184.
- Ahlen, A.T.: Diffusion of Sorbed Water Vapor Through Paper and Cellulose Film, Tappi Journal 53(1970)7, 1320–1326.
- Alleborn, N., Raszillier, H.: Spreading and sorption of a droplet on a porous substrate, Chemical Engineering Science 59(2004)2, 2071–2088.
- Alleborn, N., Raszillier, H.: Dynamics of films and droplets spreading on porous substrates, Tappi Journal 6(2007)3, 16–23.
- von Bahr, M., Tiberg, F., Zhmud, B.: Spreading Dynamics of Surfactant Solutions, Langmuir 15(1999)20, 7069–7075.
- von Bahr, M., Kizling, J., Zhmud, B., Tiberg, F.: Spreading and Penetration of Aqueous Solutions and Water-borne Inks in Contact with Paper and Model Substrates, Advances in Printing Science and Technology –Advances in Paper and Board Performance, 27th Research Conference of the International Association of the Research Institutes for the Printing, Information and Communication Industries (Iarigai), 2000, Graz, Austria, 87–102.
- von Bahr, M., Tiberg, F., Zhmud, B.: Oscillations of sessile drops of surfactant solutions on solid substrates with differing hydrophobicity, Langmuir 19(2003)24, 10109–10115.
- von Bahr, M., Seppänen, R., Tiberg, F., Zhmud, B.: Dynamic wetting of AKDsized papers, Journal of Pulp and Paper Science 30(2004)3, 74–81.
- Batz-Sohn, C., Lembach, A., Nelli, L., Müller, A., Roisman, I., Tropea, C.: Speed of ink absorption on modified paper surfaces, IS&T's NIP26 International Conference on Digital Printing Technologies, 2010, Austin, USA, IS&T: The Society for Imaging Science and Technology, Springfield, USA, 2010, 503–506.

- Bauer, W., Baumgart, D., Macholdt, H.-T., Zoeller, W.: Lightfast colorants for ink jet applications, Ink World 4(1998)10, 52–58.
- Bermel, A. D., Bugner, D. E.: Particle size effects in pigmented ink jet inks, Journal of Imaging Science and Technology 43(1999)4, 320–324.
- Biry, S., Dietliker, K. [online]: UV ink jet printing: Market and technology, <u>http://www.ciba.com/pf/docMDMS.asp?targetlibrary=CHBS\_ce\_MADS&d\_ocnumber=3272</u>, 2006, 14 p. [Cited: 12.02.2008].
- **Boisvert, J.-P., Guyard, A.**: Influence of structural properties of nanoporous silica-polymer materials on ink absorption, Nordic Pulp and Paper Research Journal 18(2003)2, 210–216.
- **Bosanquet, C. H.**: On the flow of liquids into capillary tubes, Philosophical Magazine, Serie 6, 45(1923)267, 525–531.
- Carslaw, H. S.: Conduction of heat in solids, Clarendon Press, Oxford, UK, 1997, p. 100.
- Cawthorne, J. E., Joyce, M., Fleming, D.: Use of a Chemically Modified Clay as a Replacement for Silica in Matte Coated Ink-Jet Papers, Journal of Coatings Technology 75(2003)937, 75–81.
- Chapman, D. M.: Coating structure effects on ink-jet print quality, Tappi Coating Conference, 1997, Philadelphia, USA, Tappi Press, Atlanta, USA, 73–93.
- Colour Index: [online] Colour Index Numbers (CIN). Available online at: <u>http://www.artiscreation.com/Colour\_Index\_International\_ci.htm</u>, [cited: 7.12.2011]
- Darcy, H.: Les fontaines publiques de la ville de Dijon, V. Dalmont (ed.), Paris, 1856, 647.
- Desie, G., Deroover, G., De Voeght, F., Soucemarianadin, A. (a): Printing of dye and pigment-based aqueous inks onto porous substrates, Journal of Imaging Science and Technology 48(2004)5, 389–397.
- Desie, G., Deroover, G., De Voeght, F., Claes, R. (b): Fundamental mechanisms in ink media interactions for aqueous, UV-curing and solvent based inks, IS&T's NIP20: International Conference on Digital Printing Technologies, 2004, Salt Lake City, USA, IS&T: The Society for Imaging Science and Technology, Springfield, USA, 2004, 774–779.
- **Desie, G., Van Roost, C.**: Validation of ink media interaction mechanisms for dye and pigment-based aqueous and solvent inks, Journal of Imaging Science and Technology 50(2006)3, 294–303.
- Donigian, D. W., Wernett, P. C., McFadden, M. G., McKay, J. J.: Ink jet dye fixation and coating pigments, Tappi Coating/Papermakers Conference, 1998, New Orleans, USA, Tappi Press, Atlanta, USA, 393–412.
- Gane, P. A. C., Kettle, J. P., Matthews, G. P., Ridgway, C. J.: Void Space Structure of Compressible Polymer Spheres and Consolidated Calcium Carbonate Paper-Coating Formulations, Industrial and Engineering Chemistry Research 35(1996)5, 1753–1764.
- Gane, P. A. C., Matthews, G. P., Schoelkopf, J., Ridgway, C. J., Spielmann, D. C.: Observing fluid transport into porous coating structures: Some novel findings, TAPPI Advanced Coating Fundamentals Symposium, 1999, Toronto, Canada, Tappi Press, Atlanta, USA, 1999, 213–236.
- Gane, P. A. C.: Mineral Pigments for Paper: Structure, Function and Development Potential (Part II), Wochenblatt für Papierfabrikation 129(2001)4, 176–179.
- Gane, P. A. C., Ridgway, C. J.: moisture pickup in calcium carbonate coating structures: role of surface and pore structure geometry, TAPPI 10th Advanced Coating Fundamentals Symposium, 2008, Montreal, Canada, Tappi Press, Atlanta, USA, 24 p.
- **Girard, F., Attané, P., Morin, V.**: A new analytical model for impact and spreading of one drop: application to inkjet printing, Tappi Journal 5(2006)12, 24–32.
- **Glittenberg**, **D.**, **Voigt**, **A.**: Economic formulations for improved quality ink-jet papers, Paper Technology 42(2001)9, 24–29.
- **Glittenberg, D., Voigt, A., Donigian, D.**: novel pigment-starch combination for the online and offline coating of high-quality inkjet papers, Paper Technology 44(2003)7, 36–42.
- Hara, K.: Specialty PVOH in ink jet coating formulations, Paper Technology 47(2006)3, 27–30.
- Hamada, H., Bousfield, D. W.: The effect of cationic additives on ink penetration, Journal of Pulp and Paper Science 35(2009)3–4, 118–122.

- Hartus, T.: Adsorption and Desorption Behaviour of Ink Jet Dye on Paper, Graphic Arts in Finland 27(1998)3, 3–9.
- Hasimi, A., Stavropoulou, A., Papadokostaki, K. G., Sanopoulou, M.: Transport of water in polyvinyl alcohol films: Effect of thermal treatment and chemical crosslinking. European Polymer Journal 44(2008)12, 4098–4107.
- Haverinen, H. M., Myllylä, R. A., Jabbour, G. E.: Inkjet printing of light emitting quantum dots, Applied Physics Letters 94(2009)7, 073108, 3 p.
- Hayes, R. A., Ralston, J.: The molecular-kinetic theory of wetting, Langmuir 10(1994)1, 340–342.
- **Heilmann, J., Lindqvist, U.**: Effect of drop size on the print quality in continuous ink jet printing, Journal of Imaging Science and Technology 44(2000)6, 491–494.
- Hellén, E. K. O., Ketoja, J. A., Niskanen, K. J., Alava, M. J.: Diffusion through fiber networks, Journal of Pulp and Paper Science 28(2002)2, 55–62.
- Hill, D. J. T., Whittaker, A. K., Zainuddin: Water diffusion into radiation crosslinked PVA-PVP network hydrogels, Radiation Physics and Chemistry 80(2011)2, 213–218.
- Hladnik, A.: Use of Specialty Pigments in High-End Ink-Jet Paper Coatings, Journal of Dispersion Science and Technology 25(2004)4, 481–489.
- Hodge, R. M., Edward, G. H., Simon, G. P.: Water absorption and states of water in semicrystalline poly(vinyl alcohol) films, Polymer 37(1996)8, 1371–1376.
- **Iordanskii, A. L., Razumovskii, L. P., Krivandin, A. V., Lebedeva, T. L**.: Diffusion and sorption of water in moderately hydrophilic polymers: From segmented polyetherurethanes to poly-3-hydroxybutyrate, Desalination 104(1996)1–2, 27–35.s
- Josserand, C., Zaleski, S.: Droplet splashing on a thin liquid film, Physics of Fluids, 15(2003)6, 1650–1657.
- Kallio, T., Kekkonen, J., Stenius, P.: Acid/base properties and adsorption of an azo dye on coating pigments, Journal of Dispersion Science and Technology, 27(2006)6, 825–834.

- Kang, H. R.: Water-based ink-jet ink. 1. Formulation, Journal of Imaging Science 35(1991)3, 179–188.
- Kettle, J., Lamminmäki, T., Gane, P.: A review of modified surfaces for high speed inkjet coating, Surface and Coatings Technology 204(2010)12–13, 2103–2109.
- Khoultchaev, K., Graczyk, T.: Polymer-polymer and polymer-pigment interactions – implications on ink jet universal media, Tappi Coating Conference, 1999, Toronto, Canada, 155–168.
- Klang, J. A., Balcerski, J. S.: UV Inkjet Technology: Issues for Inkjet Formulations, Ink Maker online, September 2002, 7 p.
- Klass, C.P.: New modified natural zeolite, Paper360°, August 2007, 24-26.
- Koenig, M. F., Yang, S., Hartman, R. R., Schultz, S., Stoffel, J., Tran, H., Askeland, R., Sperry, W. R., Gibson, L.: Recording sheet with improved image dry time, International Paper Company, USA. U. S. Pat. 2007/0087138, Available online at: <u>http://www.patents.com/us-20070087138.html</u> [cited: 9.12.2011]
- Kubelka, P., Munk, F.: Ein Beitrag zur Optik der Farbanstriche, Zeitschrift für technische Physik 12(1931)11a, 593–601.
- Kumaki, K., Nii, S.: Polyvinyl alcohol in ink jet coatings, Tappi PaperCon, 2010, Atlanta, USA, Tappi Press, Atlanta, USA, 27 p.
- Van Laethem, J.: New security printing possibilities with industrial digital presses, International Conference on Digital Production Printing and Industrial Applications, 2003, Barcelona, Spain, 124–126.
- Lamminmäki, T., Puukko, P.: New ink absorption method to predict inkjet print quality, Advances in Printing and Media Technology, 34<sup>th</sup> International Research Conference of Iarigai, 2007, Grenoble, France, 231–239.
- Lamminmäki, T., Lampinen, H., Hyvärinen, S., Kataja, K.: Measuring the Penetration Properties of Starch-Treated Wood-Free Paper, Nordic Pulp and Paper Research Journal 25(2010)3, 372–379.
- Larsson, L. O., Trollsås, P. O.: Genomtrycket och dess komponenter, Svensk Papperstidning 75(1972)8, 317–321.

- Laudone, G. M., Matthews, G. P., Gane, P. A. C.: Coating shrinkage during evaporation: observation, measurement and modelling within a network structure, Tappi 8th Advanced Coating Fundamentals Symposium, Chicago, USA, 2003, Tappi Press, Atlanta, USA, 116–129.
- Laudone, G. M., Matthews, G. P., Gane, P. A. C.: Effect of Latex Volumetric Concentration on Void Structure, Particle Packing, and Effective Particle Size Distribution in a Pigmented Paper Coating Layer, Industrial and Engineering Chemistry Research 45(2006)6, 1918–1923.
- Lavery, A., Provost, J.: Color-media interactions in ink jet printing, IS&T's NIP13: International Conference on Digital Printing Technologies, 1997, Seattle, USA, IS&T: The Society for Imaging Science and Technology, Springfield, USA, 1997, 437–442.
- Lee, H.-K., Joyce, M. K., Fleming, P. D., Cameron, J. H.: Production of a Single Coated Glossy Inkjet Paper Using Conventional Coating and Calendering Methods, Tappi Coating and Graphic Arts Conference and Trade Fair, 2002, Orlando, USA, 24 p.
- Lee, H.-K., Joyce, M. K., Fleming, P. D.: Influence of Pigment Particles on Gloss and Printability for Inkjet Paper Coatings, IS&T's NIP20: International Conference on Digital Printing Technologies, 2004, Salt Lake City, USA, IS&T: The Society for Imaging Science and Technology, Springfield, USA, 2004, 934–939.
- Lee, H.-K., Joyce, M. K., Fleming, P. D., Cawthorne, J. E.: Influence of silica and alumina oxide on coating structure and print quality of ink-jet papers, Tappi Journal 4(2005)2, 11–16.
- Liang, B., Fields, R. J., King, C. J.: The mechanisms of transport of water and npropanol through pulp and paper, Drying technology 8(1990)4, 641–665.
- Lundberg, A., Örtegren, J., Alfthan, E., Ström, G., Microscale droplet absorption into paper for inkjet printing, Nordic Pulp and Paper Research Journal 26(2011)1, 142–150.
- Malla, P. B., Devisetti, S.: Novel Kaolin Pigment for High Solids Ink Jet Coating, Paper Technology 46(2005)8, 17–27.
- Marmur, A.: Kinetics of penetration into uniform porous media: Testing the equivalent-capillary concept, Langmuir 19(2003)14, 5956–5959.

- Massoquete, A., Lavrykov, S., Ramarao. B. V.: Non-fickian behaviour of moisture diffusion in paper, Journal of Pulp and Paper Science 31(2005)3, 121–127.
- McFadden, M. G., Donigian, D. W.: Effects of coating structure and optics on inkjet printability, Tappi Coating Conference, 1999, Toronto, Canada, Tappi Press, Atlanta, USA, 169–177.
- Mehaffey, J. R., Cukier, R. I.: Kinetic-Theory Derivation of the Stokes-Einstein Law, Physical Review Letters 38(1977)19, 1039–1042.
- Miller, G. D., Cook, G. R.: Polyvinyl alcohol a specialty polymer for specialty papers, Tappi Short Course, Boston, USA, Tappi Press, Atlanta, USA, 1990, 43–70.
- **Morea-Swift, G., Jones, H.**: The use of synthetic silicas in coated media for ink-jet printing, Tappi Coating Conference and Trade Fair, 2000, Washington, USA, Tappi Press, Atlanta, USA, 317–328.
- **Mowiol**: Mowiol Polyvinyl Alcohol, procure of the chemical, Clariant, Available online at: <u>http://www.kuraray-am.com/pvoh-pvb/downloads/Mowiol\_broc</u> <u>hure\_en\_KSE.pdf</u>, 2003, [cited: 1.11.2012]
- Mäkinen, M. O. A., Happonen, J., Sahivirta, J., Hartus, T., Paltakari, J., Jääskeläinen, T., Parkkinen, J.: Color difference model for estimating real perceived print-through, Journal of Pulp and Paper Science 33(2007)1, 35–43.
- Nguyen, H. V., Durso, D. F.: Absorption of water by fiber webs: an illustration of diffusion transport, Tappi Journal 66(1983)12, 76–79.
- Nilsson, H., Fogden, A.: Inkjet print quality on model paper coatings, Appita 61(2008)2, 120–127.
- **Oittinen, P.**: Fundamental rheological properties and tack of printing inks and their influence on ink behaviour in a printing nip, Dissertation, 1976, Helsinki University of Technology, Helsinki, Finland.
- **Oka, H., Kimura, A.**: the physicochemical environment of acid red 249 insolubilized in an ink-jet paper, Journal of Imaging Science and Technology 39(1995)3, 239–243.
- Oliver, J.F.: Wetting and penetration of paper surfaces, in Colloids and Surfaces in Reprographic Technology, M. Hair, M. D. Croucher, 1982, American Chemical Society, Washington, USA, 435–453.

- Pajari, H., Juvonen, K., Jokio, M., Koskela, H., Sneck, A.: Dynamic measurement of coating colour consolidation with a new laboratory coater, 23rd PTS Coating Symposium, 2007, Baden-Baden, Germany, Paper 28, 13 p.
- Pan, Y.-L., Yang, S.: Wetting and liquid absorption characteristics of ink jet paper, IS&T's NIP 12: International Conference on Digital Printing Technologies, 1996, San Antonio, USA, 399–402.
- Pinto, J., Nicholas, M.: SIMS studies of ink jet media, IS&T's NIP 13: International Conference on Digital Printing Technologies, 1997, Seattle, USA, IS&T: The Society for Imaging Science and Technology, Springfield, USA, 1997, 420–426.
- Pond, S.: Inkjet technology and product development strategies, USA 2000, 406 p.
- Radhakrishnan, H., Chatterjee, S. G., Ramarao, B. V.: Steady-state moisture transport in a bleached kraft paperboard stack, Journal of Pulp and Paper Science 26(2000)4, 140–144.
- von Raven, A., Strittmatter, G., Weigl, J.: Cationic coating colors a new coating system, Tappi Journal 71(1988)12, 141–148.
- **Reynolds, P. A., Goodwin, J. W.**: Direct measurement of the translational diffusion coefficients of aggregated polystyrene latex particles, Colloids and Surfaces 11(1984)1-2, 145-154.
- Ricciardi, R., Auriemma, F., Gaillet, C., De Rosa, C., Laupretre, F.: Investigation of the Crystallinity of Freeze/Thaw Poly(vinyl alcohol) Hydrogels by Different Techniques. Macromolecules 37(2004)25, 9510–9516.
- Ridgway, C., Schoelkopf, J., Matthews, G. P., Gane, P. A. C., James, P. W.: The Effects of Void Geometry and Contact Angle on the Absorption of Liquids into Porous Calcium Carbonate Structures, Journal of Colloid and Interface Science 239(2001)2, 417–431.
- Ridgway, C. J., Gane, P. A. C.: Controlling the absorption dynamic of water-based ink into porous pigmented coating structures to enhance print performance, Nordic Pulp and Paper Research Journal 17(2002)2, 119–129.
- Ridgway, C. J., Gane, P. A. C., Schoelkopf, J.: Effect of Capillary Element Aspect Ratio on the Dynamic Imbibition within Porous Networks, Journal of Colloid and Interface Science 252(2002)2, 373–382.

- Ridgway, C. J., Gane, P. A. C.: Bulk density measurement and coating porosity calculation for coated paper samples, Nordic Pulp and Paper Research Journal 18(2003)1, 24–31.
- Ridgway, C. J., Gane, P. A. C.: The Impact of Pore Network Structure on the Absorption of Pigmented Inkjet Inks, Tappi Coating Conference, 2005, Toronto, Canada, Session 6, Tappi Press, Atlanta, USA, 15 p.
- Ridgway, C. J., Gane, P. A. C.: Correlating pore size and surface chemistry during absorption into a dispersed calcium carbonate network structure, Nordic Pulp and Paper Research Journal 21(2006)5, 563–568.
- Ridgway, C. J., Schoelkopf, J., Gane, P. A. C.: Competitive absorption of polar and non-polar liquids into latex bound porous structures of fine ground calcium carbonate, Transport in Porous Media 86(2011)3, 945–964.
- Riegel, B., Hartmann, I., Kiefer, W., Gross, J., Fricke, J.: Raman spectroscopy on silica aerogels, Journal of Non-Crystalline Solids 211 (1997)3, 294–298.
- Romano, C. E. JR., Schlicsman, L. J. JR., Niemiec, J. P.: Inkjet recording medium, Newpage Corporation, USA, U. S. 2011, Pat. 2011/0037818.5 p.
- Rousu, S., Gane, P., Spielmann, D., Eklund, D.: Separation of off-set ink components during absorption into pigment coating structures, Nordic Pulp and Paper Research Journal 15(2000)5, 527–535.
- Rousu, S., Gane, P., Eklund, D.: Print quality and the distribution of offset ink constituents in paper coatings, Tappi Journal 4(2005)7, 9–15.
- Salminen, P.: Studies of water transport in paper during short contact times, Dissertation, 1988, Department of Chemical Engineering, Åbo Akademi, 94 p.
- Salmén, N. L., Back, E. L.: Moisture-dependent thermal softening of paper, evaluated by its elastic modulus, Tappi J. 63(1980)6, 117–120.
- Schoelkopf, J., Ridgway, C. J., Gane, P. A. C., Matthews, G. P., Spielmann, D. C.: Measurement and Network Modeling of Liquid Permeation into Compacted Mineral Blocks, Journal of Colloid and Interface Science 227(2000)1, 119–131.
- Schoelkopf, J., Gane, P. A. C., Ridgway, C. J., Matthews, G. P.: Practical observation of deviation from Lucas–Washburn scaling in porous media, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 206(2002)1–3, 445–452.

- Shaw, D. J.: Introduction to colloid & surface chemistry, 4th edition, Reed Educational and Professional Publishing Ltd, 1996, 306 p. ISBN 0 7506 1182 0
- Shaw-Klein, L., Wexler, A., Giacherio, D., Demejo, L.: Materials for high-quality inkjet papers, PTS 23rd Coating Symposium, 2007, Baden-Baden, Germany, 8 p.
- Shi, J., Schuman, T. P., Stoffer, J. O.: Ink-jet printing paper with improved waterfastness, Journal of Coating Technology Research 1(2004)3, 225–234.
- Shore, J.: [online] Colorants and auxiliaries, Organic Chemistry and Application Properties, Volume 1 – Colorants. Available online at: <u>http://www. scribd.com/doc/50173889/3/COLOUR-INDEX-CLASSIFICATION</u>, [cited: 7.12.2011]
- Smyth, S.: The Future of Inkjet Printing to 2015, Global Market Forecasts, Pira International Ltd, 2010, 208 p.
- Sorbie, K. S., Wu, Y. Z., McDougall, S. R.: The Extended Washburn Equation and Its Application to the Oil/Water Pore Doublet Problem, Journal of Colloid and Interface Science 174(1995) 2, 289–301.
- Sundquist, J.: Tekstiiliväriaineet, Kemia Kemi, 11(1985)11, 937–944.
- Svanholm, E., Ström, G.: Influence of polyvinyl alcohol on inkjet printability, International Printing and Graphic Arts Conference, Vancouver, BC, Canada, 2004, PAPTAC, 187–207.
- Svanholm, E.: Printability and Ink-Coating Interactions in Inkjet Printing, Doctoral thesis, Karlstad University, Faculty of Technology and Science, Chemical Engineering, 2007:2, Karlstad 2007, 48 p.
- **Thurn, J.**: Water diffusion coefficient measurements in deposited silica coatings by the substrate curvature method, Journal of Non-Crystalline Solids 354(2008)52–54, 5459–5465.
- Tiberg, F., Zhmud, B., Hallestensson, K., von Bahr, M.: Capillary rise of surfactant solutions, Physical Chemistry Chemial Physics 2(2000)22, 5189–5196.
- Topgaard, D., Söderman, O.: Diffusion of Water Absorbed in Cellulose Fibers Studied with H-NMR, Langmuir 17(2001)9, 2694–2702.
- Varnell, D. F.: Composition and method for improved ink jet printing performance, US6207258 B1, 2001, 12 p.

- Vikman, K.: Fastness Properties of Ink Jet Prints on Coated Papers Part 2: Effect of Coating Polymer System on Water Fastness, Journal of Imaging Science and Technology 47(2003)1, 38–43.
- Vikman, K., Vuorinen, T. (a): Water Fastness of Ink Jet Prints on Modified Conventional Coatings, Journal of Imaging Science and Technology 48(2004)2, 138–147.
- Vikman, K., Vuorinen, T. (b): Light Fastness of Ink Jet Prints on Modified Conventional Coatings, Nordic Pulp and Paper Research Journal 19(2004)4, 481–488.
- Wallqvist, V., Claesson, P. M., Swerin, A., Schoelkopf, J., Gane, P. A. C.: Interaction forces between talc and hydrophobic particles probed by AFM, Colloids and Surfaces, A: Physicochemical and Engineering Aspects 277 (2006)1–3, 183–190.
- Walther, M., Ortner, A., Meier, H., Löffelmann, U., Smith, P. J., Korvink, J. G.: Terahertz metamaterials fabricated by inkjet printing, Applied Physics Letters 95(2009)25, 251107, 3 p.
- Ward, N.: A primer on inkjet presses, Printing Impressions 53(2010)3, 32, 34–35.
- Washburn, E. W.: The Dynamics of Capillary Flow, Physical Review 17(1921)3, 273–283.
- Wedin, P., Svanholm, E., Alberius, P. C. A., Fogden, A.: Surfactant-Templated Mesoporous Silica as a Pigment in Inkjet Paper Coatings, Journal of Pulp and Paper Science 32(2006)1, 32–37.
- Yip, K. L., Lubinsky, A. R., Perchak, D. R, Ng, K. C.: Measurement and Modeling of Drop Absorption Time for Various Ink-receiver Systems, Journal of Imaging Science and Technology 47(2003)5, 388–393.
- Young, T.: An Essay on the Cohesion of Fluids, Philosophical transactions of the Royal Society of London, 1805.



Title	The comparative dynamics of bulk liquid flow and interpolymer diffusion during inkjet ink imbibition in porous coating structures
Author(s)	Taina Lamminmäki
Abstract	The focus of this thesis is to establish the timescale of interactions, physical and chemical, during dye-based inkjet ink imbibition into calcium carbonate (CaCO <sub>3</sub> ) pigmented coatings. Comparison is made between conventional offset quality CaCO <sub>3</sub> , and special inkjet qualities in the form of either modified or precipitated CaCO <sub>3</sub> combined with swelling diffusion driving or non-swelling diffusion-inert binder. The selection of pigment is based on the control of pore volume, pore size distribution and connectivity of the coating layer. Pigments with nano-size pores (intra-particle) are primarily exemplified. The final coating layers display discrete pore size bimodality in relation to the intra-particle and inter-particle pores. Polyvinyl alcohol (PVOH) is used as the diffusion sensitive binder and styrene acrylate latex (SA) as the bulk diffusion-inert binder. By changing the coating structures and using the contrasting binders, the roles of liquid diffusion, capillary pressure and permeation flow are clarified both in the short and long timescale imbibition. The wetting force within the finest capillaries drives the ink into the porous structure, whilst the viscous drag within the structure resists the movement. The nano-size capillaries initiate absorption of the ink vehicle, though typical impact pressure of an inkjet droplet is shown to provide forced wetting. During the flow, the hydrophilic binder swells, acting to close the smallest pores and reduce the remaining pore diameters. The total pore volume decrease competes with the initial capillarity. The diffusion is shown to have a marked effect on the polar liquid absorption rate into the PVOH-containing coatings over different timescales. The swelling opens the polymer matrix so that the colorant fits into the binder structure and can either hydrogen bond or become mechanically trapped. The diffusion potential. The competing decrease on the colorant has insufficient time to translate under the Coulombic attraction toward the cationic adsorption sites o
ISBN, ISSN	ISBN 978-951-38-7455-1 (soft back ed.) ISSN 2242-119X (soft back ed.) ISBN 978-951-38-7456-8 (URL: http://www.vtt.fi/publications/index.jsp) ISSN 2242-1203 (URL: http://www.vtt.fi/publications/index.jsp)
Date	March 2012
Language	English, Finnish abstract
Pages	187 р. + арр 89 р.
Name of the project	
Commissioned by	
Keywords	Diffusion, absorption, permeability, porosity, ionic charge, coating binder, coating, inkjet printing
Publisher	VTT Technical Research Centre of Finland P.O. Box 1000, FI-02044 VTT, Finland, Tel. 020 722 111



Nimeke	Liuoksen virtausdynamiikka ja polymeerien diffuu- sio mustesuihkuvärin asettumisessa huokoisiin päällysterakenteisiin
Tekijä(t)	Taina Lamminmäki
Tiivistelmä	Tämän väitöskirjan tavoitteena on selvittää liukoisen inkjet-värin asettumisessa vallitsevien vuorovaikutusten, sekä fyysisten että kemiallisten, aikaskaaloja kalsiumkarbonaattipigmenttipäällysteissä (CaCO <sub>3</sub> ). Pigmentteinä on käytetty sekä perinteistä offset-laadun että eritysiä inkjet-laadun CaCO <sub>3</sub> -pigmenttejä, jotka ovat joko modifioituja tai saostettuja CaCO <sub>3</sub> -pigmenttejä ja näihin on yhdistetty turpoava, diffundoiva tai ei-turpoava, diffundoimaton sideaine. Pigmentti on valittu siten, että päällysteisiin saadaan erilaisia huokostilavuuksien ja -kokojakaumien rakenteita. Inkjet-päällysteissä käytetään usein pigmenttejä, joissa itse pigmenttipartikkelissa on nanokoon huokosia (sisäisiä huokosia). Lopullisessa päällystekerrokseessa on sekä pigmentin sisäisiä että ulkoisia huokosia. Polyvinyylialkoholia (PVOH) käytetään työssä diffuusioherkkänä sideaineena ja styreeni-akrylaatti-lateksia (SA) diffundoimattomana sideaineena. Päällysteen diffuusion, kapillaari- ja permeaatio-virtauksen merkityksiä lyhyen ja pitkän aikajakson värin asettumisessa selvitetään käyttämällä erilaisia päällysterakenteita ja sideaineita. Pienimpien kapillaarien kastumisvoimat ajavat värin huokoiseen rakenteeseen, kun taas viskoottiset hidastusvoimat rakenteessa vastustavat nesteen liikettä. Nanokoon kapillaarit käynis-tävät värin liuotinosan absorption, kun taas inkjet-jisaran iskeytymisen aikaansaama voima lisää kastelevuutta. Virtauksen aikana hydrofiilinen sideaine turpoaa sulkien pienimpiä huokosia ja pienentäen huokosten halkaisijoita. Koko huokostilavuuden pieneneminen kilpailee alkuperäisen kapillaarisuuden kanssa. Työssä osoitetaan, että diffuusiola on merkittävä vaikutus polaarisen nesteen absorptionopeuteen PVOH-sisältävissä päällysteissä eri ajanhetkinä. Lisäksi turpoaminen avaa polymerimattiisia niin, että värin väriaine mahtuu sideaineen rakenteen sisään ja voi joko muodostaa vetysidoksia tai jäädä rakenteeseen värin kuivuttua. PVOH- tai SA-lateksi-filmin veden diffuusiokerroin on samaa suuruusluokkaa, tosin polymeerien d
ISBN, ISSN	ISBN 978-951-38-7455-1 (nid.) ISSN 2242-119X (nid.) ISBN 978-951-38-7456-8 (URL: http://www.vtt.fi/publications/index.jsp) ISSN 2242-1203 (URL: http://www.vtt.fi/publications/index.jsp)
Julkaisuaika	Maaliskuu 2012
Kieli	Suomi, englanninkielinen tiivistelmä
Sivumäärä	187 s. + liitt. 89 s.
Projektin nimi	
Toimeksiantajat	
Avainsanat	Diffusion, absorption, permeability, porosity, ionic charge, coating binder, coating, inkjet printing
Julkaisija	VTT PL 1000, 02044 VTT, Puh. 020 722 111

## The comparative dynamics of bulk liquid flow and interpolymer diffusion during inkjet ink imbibition in porous coating structures

The focus of this thesis is to establish the timescale of interactions. physical and chemical, during dye-based inkjet ink imbibition into calcium carbonate (CaCO<sub>3</sub>) pigmented coatings. Comparison is made between conventional offset quality CaCO<sub>2</sub>, and special inkjet qualities in the form of either modified or precipitated CaCO<sub>3</sub> combined with swelling diffusion driving or non-swelling diffusion-inert binder. Polyvinyl alcohol (PVOH) is used as the diffusion sensitive binder and styrene acrylate latex (SA) as the bulk diffusion-inert binder. The nanosize capillaries initiate absorption of the ink vehicle, though typical impact pressure of an inkiet droplet is shown to provide forced wetting. During the flow, the hydrophilic binder swells, acting to close the smallest pores and reduce the remaining pore diameters. The total pore volume decrease competes with the initial capillarity. The diffusion is shown to have a marked effect on the polar liquid absorption rate into the PVOH-containing coatings over different timescales. The swelling opens the polymer matrix so that the colorant fits into the binder structure and can either hydrogen bond or become mechanically trapped. The diffusion coefficient of water in PVOH and on SA latex films is shown to be similar, despite the difference in geometry. The competing mechanisms of liquid flow and ab/adsorption are seen as crucial to developing a high quality print. High speed inkiet print density depends on the colorant location in the structure and the optical properties of the whole coated paper.

ISBN 978-951-38-7455-1 (soft back ed.) ISBN 978-951-38-7456-8 (URL: http://www.vtt.fi/publications/index.jsp) ISSN 2242-119X (soft back ed.) ISSN 2242-1203 (URL: http://www.vtt.fi/publications/index.jsp)

