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University of Technology

Katriina Mielonen

THE EFFECT OF CATIONIC-ANIONIC POLYELECTROLYTE MULTILAYER SURFACE TREATMENT ON INKJET INK SPREADING AND PRINT QUALITY

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in Auditorium 2310 at Lappeenranta University of Technology, Lappeenranta, Finland on the 10th of December 2015 at noon.

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Supervisor Professor Kaj Backfolk
LUT School of Energy Systems
Lappeenranta University of Technology
Lappeenranta, Finland

Reviewers Professor Jouko Peltonen
Laboratory of Physical Chemistry
Åbo Akademi University
Turku, Finland

Associate Professor Jonas Örtegren
Digital Printing Center
Mid Sweden University
Sundsvall, Sweden

Opponent Professor Jouko Peltonen
Laboratory of Physical Chemistry
Åbo Akademi University
Turku, Finland

Custos Professor Kaj Backfolk
LUT School of Energy Systems
Lappeenranta University of Technology
Lappeenranta, Finland

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ABSTRACT

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The focus of the work reported in this thesis was to study and to clarify the effect of polyelectrolyte multilayer surface treatment on inkjet ink spreading, absorption and print quality. Surface sizing with a size press, film press with a pilot scale coater, and spray coating, have been used to surface treat uncoated wood-free, experimental wood-free and pigment-coated substrates. The role of the deposited cationic (polydiallydimethylammonium chloride, PDADMAC) and anionic (sodium carboxymethyl cellulose, NaCMC) polyelectrolyte layers with and without nanosilica, on liquid absorption and spreading was studied in terms of their interaction with water-based pigmented and dye-based inkjet inks.

Contact angle measurements were made in attempt to explain the ink spreading and wetting behavior on the substrate. First, it was noticed that multilayer surface treatment decreased the contact angle of water, giving a hydrophilic character to the surface. The results showed that the number of cationic-anionic polyelectrolyte layers or the order of deposition of the polyelectrolytes had a significant effect on the print quality. This was seen for example as a higher print density on layers with a cationic polyelectrolyte in the outermost layer. The number of layers had an influence on the print quality; the print density increased with increasing number of layers, although the increase was strongly dependent on ink formulation and chemistry.

The use of nanosilica clearly affected the rate of absorption of polar liquids, which also was seen as a higher density of the black dye-based print. Slightly unexpected, the use of nanosilica increased the tendency for lateral spreading of both the pigmented and dye-based inks. It was shown that the wetting behavior and wicking of the inks on the polyelectrolyte coatings was strongly affected by the hydrophobicity of the substrate, as well as by the composition or structure of the polyelectrolyte layers.

Coating only with a cationic polyelectrolyte was not sufficient to improve dye fixation, but it was demonstrated that a cationic-anionic-complex structure led to good water fastness. A three-layered structure gave the same water fastness values as a five-layered structure. Interestingly, the water fastness values were strongly dependent not only on the formed cation-anion polyelectrolyte complexes but also on the tendency of the coating to dissolve during immersion in water. Results showed that by optimizing the chemistry of the layers, the ink-substrate interaction can be optimized.

Keywords: anionic polyelectrolyte, cationic polyelectrolyte, inkjet printing, multilayer surface treatment, print quality, surface sizing

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Lappeenranta, November 2015

Katriina Mielonen

LIST OF PUBLICATIONS

The thesis consists of a theoretical introduction and summary of the following publications referred to by their Roman numerals

I Mielonen, K., Geydt, P., Tåg, C.-M. and Backfolk, K. (2015). Inkjet ink spreading, absorption and adhesion on substrates coated with thin layers of cationic polyelectrolytes, Nordic Pulp and Paper Research Journal, 30(2) pp. 179-188.

II Mielonen, K., Lehto, R., Timonen, J. and Backfolk, K. (2014). Effect of alternating layers of anionic and cationic polyelectrolyte complexes on colorant fixing and liquid absorptions, Journal of Imaging Science and Technology, 58(4), pp. 040501-1- 040501-10.

III Mielonen, K., Geydt, P., Johansson, L.-S., Österberg, M. and Backfolk, K. (2015). Inkjet ink spreading on polyelectrolyte multilayers deposited on pigment coated paper, Journal of Colloid and Interface Science, 38, pp. 179-190.

IV Mielonen, K., Ovaska, S-S., Österberg, M., Johansson, L.-S., and Backfolk, K. (2016). Three-layered polyelectrolyte structures as inkjet receptive coatings: Part 1. Interaction with dye-based ink, Journal of Imaging Science and Technology, 60(3), 9p.

V Mielonen, K., Ovaska, S.-S., Laukala, T. and Backfolk, K. (2016). Three-layered polyelectrolyte structures as inkjet receptive coatings: Part 2. Interaction with pigment-based inks, Journal of Imaging Science and Technology, 60(3), pp. 030502-1- 030502-9.

VI Mielonen, K., Velling, K. and Backfolk, K. The effect of multilayer polyelectrolyte coating on inkjet ink water fastness and rub resistance. *Submitted to Nordic Pulp and Paper Research Journal 10/2015.*

AUTHOR’S CONTRIBUTION TO THE WORK PRESENTED IN THE LISTED PUBLICATIONS

I Planning the trials. Printing and testing paper samples together with a laboratory assistant and interpretation of results. Writing the manuscript with co-authors.

II Planning the experimental setup. Printing and testing paper samples together with laboratory assistant. Interpretation of results and writing the manuscript with co-authors.

III Planning the trials, printing and characterizing printed samples and writing the manuscript with co-authors.

IV Paper testing. Printing the samples, measuring and analyzing the results. Writing the manuscript with co-authors.

V Paper testing. Printing the samples, measuring and analyzing the results, Printing and testing paper samples, analyzing the results, writing the manuscript with co-authors.

VI Planning the experimental setup. Printing the samples, paper testing and print quality evaluation. Interpretation of the results and writing the manuscript.

SUPPORTING PUBLICATIONS

SI Mielonen, K., Ovaska, S.-S. and Backfolk, K. (2015). Potential of Coating Comprising Hydroxypropylated Starch for Dye-Based Inkjet Printing. 31th International Conference on Digital Printing Technologies. Portland, OR, USA. IS&T, Springfield, VA, USA, pp. 462-466.

SII Ovaska, S.-S., Mielonen, K., Lozovski, T., Rinkunas, R., Sidaravicius, J. and Backfolk, K. (2015). A Novel Approach for Studying the Effects of Corona Treatment on Ink-Substrate Interactions, Nordic Pulp and Paper Research Journal, 30(4), 8p.

SIII Mielonen, K., Ovaska, S.-S. and Backfolk, K. (2014). Tuning Liquid Absorption and Ink Spreading by Polyelectrolyte Multilayering on Substrates with Different Levels of Internal Sizing, 30th International Conference on Digital Printing Technologies. Philadelphia, PA, USA. IS&T, Springfield, VA, USA, pp. 357-361.

SIV Ovaska, S.-S., Mielonen, K., Saukkonen, E., Lozovski, T., Rinkunas, R., Sidaravicius, J. and Backfolk, K. (2014). A Novel Method to Study the Effect of Corona Treatment on Ink Wetting and Sorption Behavior, 30th International Conference on Digital Printing Technologies. Philadelphia, PA, USA. IS&T, Springfield, VA, USA, pp. 362-365.

ABBREVIATIONS

AFM	atomic force microscope
AKD	alkyl ketene dimer
ASA	alkyl succinic anhydride
BAA	Bristow absorption apparatus
C	cyan
CBS	concentric back scatter
CIJ	continuous inkjet
CLSM	confocal laser scanning microscope
DI	distilled water
DIM	diiodomethane
DMT	Derjaguin-Muller-Toporov theory
DOD	drop-on-demand
EG	ethylene glycol
HR-SEM	high resolution scanning electron microscope
HP	Hewlett-Packard
IAS	image analysis system
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
K	black
LbL	layer-by-layer
M	magenta
NaCMC	sodium carboxymethyl cellulose
PCC	precipitated calcium carbonate
PDADMAC	polydiallyldimethylammonium chloride
PEI	polyethylene imine
PIJ	piezoelectric inkjet
PPS	Parker print-surf
PVAm	polyvinyl amine
PVOH	polyvinyl alcohol
RH	relative humidity
RMS	root mean square

SA	styrene acrylate
SEM	scanning electron microscope
SFE	surface free energy
SIJ	super-fine inkjet
SiO_2	silicon dioxide
SMA	styrene maleic anhydride
SMAI	styrene maleic anhydride imide
SOHO	small office home office
TIJ	thermal inkjet
XPS	x-ray photoelectron spectroscopy
χ - Al_2O_3	transition phase of alumina
Y	yellow

TABLE OF CONTENTS

1 INTRODUCTION

1.1 Background

In recent years, digital printing and especially inkjet printing has shown a large market growth, for example in segments such as books, packaging, graphical printing and industrial decoration compared to traditional printing (Page 2011; Smyth 2011). The speed of inkjet printers has increased significantly, and substrate requirement and coating formulations have undergone changes, partly due to changes in inkjet ink formulations, although there is also a demand for low-cost substrates that provide good inkjet printability. Traditionally, inkjet printers have been used in the Small Office and Home Office market (SOHO), but in recent years inkjet has entered the industrial production printing market represented by wide format, packaging, label, transpromo and graphical printing. In the case of high-speed inkjet printing, a new business concept has developed for newspapers, magazines and books resulting in a substantial annual growth within high-speed inkjet printing (O'Brien 2013; HP 2014).

Nowadays, a lot of new innovations are being incorporated into high-speed inkjet printers, which makes them a serious competitor to both lithography and flexography in terms of print quality, productivity and cost-efficiency. High-speed inkjet printers (200m/min and more) have been launched by several equipment manufacturers such as Kodak, Hewlett-Packard (HP), Xerox, Océ and Riso (O'Brien 2013). Inkjet technology has made significant advances reducing drop size from more than 20 pL to less than 3 pL and drop sizes less than 1–2 pL can be made in production printing (Meier et al. 2009) and with super-fine inkjet (SIJ) printing (Murata 2003; Murata et al. 2005).

The composition of the paper surface has a significant impact on print quality and it has been demonstrated (e.g. Lee et al. 2002; Kettle et al. 2010; Lundberg et al. 2011) that surface modification of the paper can significantly reduce the required ink amount and make the print more durable and more environmentally friendly. Multilayer mineral or resin coatings have been used to improve print quality in high-quality photographic papers (Glittenberg et al. 2003; Jonckherree and Mabire 2003) and both barrier and printability properties have been developed by multilayer coating on fiber-based substrates (Bollström et al. 2009). According to the available literature, the potential for cationic-anionic polyelectrolyte multilayers to improve print quality in inkjet applications has not earlier been studied. The current development of paper surface treatment concepts and formulations is usually limited to the manufacturing technology.

The lack of suitable low-cost substrates for inkjet inks is still one of the challenges if high-speed inkjet printing is to be more cost-quality competitive. Although the composition of ink has developed, there is still a need to understand how to affect and control inkjet ink spreading and fixation on papers, preferably as a tool in designing a new range of papers that consume less ink, are more environment-friendly and provide high-quality and durable prints. However, the reformed high-speed inkjet printing technology with its recent hardware and ink development offers now more cost efficient prints on greater range of substrates.

1.2 Objective of the study

The objective of this work was to investigate ink-substrate interactions on a cationic-anionic multilayer polyelectrolyte surface coated on various paper substrates, and to clarify the roles of different polyelectrolytes, the effect of the order of addition, the number of multilayers, the role of nanosilica and the role of the substrate. Polyelectrolytes are polymers with a permanent positive or negative electric charge in an aqueous solution. Cationic and anionic polyelectrolytes cannot under ”normal conditions” be mixed in the same dispersion without achieving viscosity “shocks”, so the coatings were therefore prepared with intermediate drying or by using the wet-on-wet coating principle with a spray deposition system. Surface-treated papers were printed on various desktop printers which were selected in order to employ modern inkjet ink technology, and the print quality of the prints was evaluated.

The polyelectrolyte multilayers were characterized by e.g. contact angle measurements, atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) in order to determine the macroscopic and microscopic features of the surfaces, surface coverage or surface chemical properties. Ink-substrate interaction was assessed by ink spreading tests and by print density assessment. The base papers and surface-treated samples were printed on various desktop printers, using water-based pigment and dye colorants, selected in order to represent modern inkjet printers. The print quality was characterized by optical density, mottling, bleeding, wicking and water fastness. The results were analyzed to reveal information about the mechanism of ink absorption and spreading, and factors that affects print quality.

2 INKJET PRINTING

2.1 Inkjet technology

Inkjet technologies are divided into two main categories, continuous inkjet (CIJ) and drop-on-demand (DOD). Figure 1 shows how these two categories are divided into various subcategories. The DOD technology can be divided according to the method of generating the individual ink drops, the most common technologies being thermal inkjet (TIJ) and piezoelectric inkjet (PIJ), which basically differ only in their drop formation technology (Kipphan 2001).

In PIJ, a piezoelectric ceramic deforms in the ink chamber and decreases the volume of the ink chamber according to the digital page information. The volume of the ink chamber decreases and pushes an ink droplet or a specific amount of ink out of the nozzle. The firing frequency is then 10-20 kHz. The life of the head is long and the spot-size modulation is easy in PIJ. A wide range of different ink chemicals are approved for piezo inkjets, and inks having high pigment and high resin contents can be used. (Hakola and Oittinen 2009; Usui et al. 2002.) Grayscale printing with a PIJ printer was developed by e.g. Xaar (Manning and Harvey 1999) whose technology achieves high print quality by means of medium resolution combined with a grayscale, rather than by very high resolution binary printing by firing multiple droplets. Higher dot resolution and high print quality are achieved without using a large number of nozzles or multiple passes.

In TIJ, the drop is formed by heating the ink chamber rapidly to 300°C in less than 3 µs. Ink vaporizes and an air bubble is formed inside the ink chamber, which then forces the ink droplet out of the nozzle. When the heating element cools, the bubble collapses and the ink droplet breaks off. The ink refills back into the chamber and new drop formation begins. It takes 80 µs to run this whole process (Hakola and Oittinen 2009).

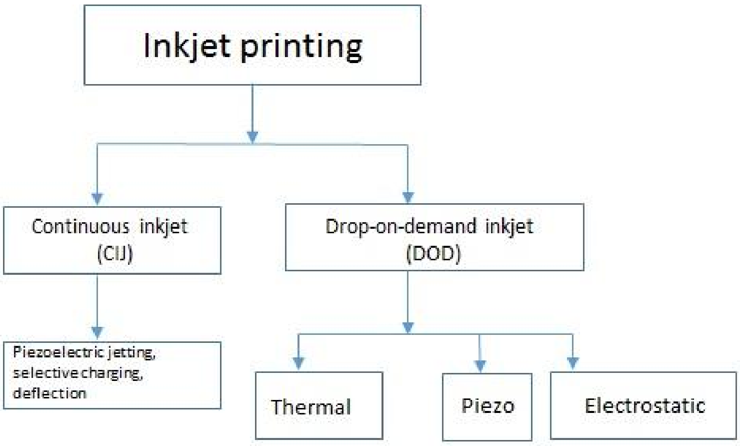

Figure 1 Inkjet technologies (Kipphan, 2001; Hakola and Oittinen 2009).

2.2 Inkjet inks

Inkjet inks can be classified according to the solvent system used or to the type of colorant. Different types of ink are used such as water-based and other solvent-based (organic solvents e.g. glycols and oils), hot-melt and UV-curable inks. Water-based inkjet inks are most commonly used (Hakola and Oittinen 2009) and they include both pigment-based and dye-based inks, although according to e.g. HP (2014), mixtures of dye and pigment colorants may be used as well.

Water-based inkjet inks have basically four main components: colorant (pigments, dyes), binder, vehicle and functional additives used to fine-tune the ink properties. Water-based inkjet inks are usually anionic and they have a very low surface tension and low viscosity, partly due to their high water content (almost 90%). They are not therefore usually suitable for use on standard commodity grade coated glossy offset paper since high and rapid water absorbency is usually required (Hakola and Oittinen 2009; Kipphan 2001). A dense or liquid-repelling surface and an anionic character of the coated paper provide few sites for interaction with inkjet colorants, but by incorporating microporous or nanostructured coatings or cationic additives, it is possible to retain the colorants on the surface and to fix dye-based colorants with a cationic mordant (Shaw-Klein 1998; Niemöller and Becker 1997; Kettle et al. 2010). Typical inkjet ink components, their purpose and formulations of DOD ink are presented in Table I.

Table I Inkjet ink components and their purpose and formulation of typical DOD ink. (Modified from Schmid 2009 and Kettle et al. 2010)

		Typical DOD office ink formulation	
Component	Purpose	Ingredient	%
Water	Primary solvent, carrier fluid	Water	84.0
Co-solvents (5–50%)	Prevent nozzles from drying out	Diethylene glycol	7.5
	Retain paper sheet flatness after printing		
	Enhance ink film formation		
Colorants (0.5–10%) - *Pigments, Dyes*	Produce vibrant, long-lasting images	Project Black	4.0
Polymeric binders (0–10%)	Increase durability of prints	Glycerine	2.1
	Increase gloss of prints		
Surfactants (0–2%)	Increase wetting by ink	2-pyrrolidinone	2.0
	Reduce “puddling” of ink on print head	Surfynol 104E	0.2
	Reduce resistor deposits		
Other additives - *Biocides*	Prevent growth of micro-organisms		
Chelating agents	React with free metals		
Anti-corrosion additives	Prevent corrosion	Urea	0.2

2.2.1 Pigment-based inks

Pigments used in inkjet inks are organic or inorganic colored, white, or black substances that are insoluble in the ink vehicle. They are present as solid particles and/or molecular agglomerates that must be held in suspension in the base liquid. The pigment particles are normally 0.1–2.0 μm in diameter and they can consist of several million molecules. Pigments consist of molecules that are cross-linked with one another as crystals. The particles are bounded to the paper surface with binder, but only around 10% of the molecules lie on the surface, and it is only these molecules and a few beneath them that can absorb light. Pigments disperse light and are opaque. They have a wide absorption band and are therefore not as “pure” as dyes, which have an extremely narrow absorption band. Depending on the color tone, the pigment content in the inkjet ink is between 5% and 30%. (Kipphan 2001; Fryberg 2005; Lamminmäki 2012.) Pigment inks have good light fastness and water fastness properties but poor ink stability, and they are sensitive to abrasion and may clog nozzles and increase corrosion in the inkjet printing heads. Dispersants and surfactants have been developed (Chang et al. 2003; Yoon and Choi 2008) to avoid the generation of agglomerate particles and to produce appropriate hydrophilicity.

2.2.2 Dye-based inks

Dyes in inkjet inks can be direct dyes, modified direct dyes, poorly water-soluble dispersion dyes or water-soluble acid dyes (Lavery and Provost 1997). Water-based soluble dyes are used in the SOHO area but also in high-speed inkjet printing. Dyes are soluble organic compounds and dye molecules are surrounded by solvent, so that almost every molecule can absorb photons, which leads to higher color intensity and more luminous colors. Dyes penetrate into the paper and are used in inkjet printing because of their ability to create high color brilliance and a large color gamut, although they have a lower permanence compared to pigment inks and they are prone to diffusion. Dyes have a larger range of colors, and ink formulation is easier than with pigment-based inks which need binders in the formulation. (Kipphan 2001; Fryberg 2005; Shang 2012; Lamminmäki 2012.)

2.2.3 Physical-chemical properties of pigment-based and dye-based inks

There are significant differences between pigment-based and dye-based inks with water as solvent which affect their behavior on a paper substrate. Dyes are soluble organic materials whereas pigment are insoluble and this leads to e.g. different degrees of water fastness. Most pigment- and dye-based inkjet inks used in thermal and piezo inkjet printers have a low viscosity (1−5 cP), a low surface tension (20−50 mN/m) and a low density 0.9−1.1 g/ml (Girard et al. 2006; Schmid 2009). Because of the high solubility in water of the dye-based inks, they usually have poor water fastness, although dye fixing agents are used to improve water fastness (Vikman and Vuorinen 2004). Pigments in general are more resistant to water damage, but keeping the surface charge of the pigments moderately low increases the water fastness. Dyes are monomolecular chromophores and each molecule contributes to the color, and the color they create is brighter. Pigments are groups of chromophores and only surface molecules interact with light, and this limitation decreases the transparency and the theoretical color gamut is smaller than with dye-based inks. Dyes penetrate into porous media and bind to coating components and that decreases the optical density of dye-based inks. Pigment-based inks, on the other hand, stay close to the surface and, in contrast to dye-based inks, the print density is increased. (Lamminmäki 2012; Fryberg 2005; Willis and Hudd 2015.)

2.3 Inkjet market development

Digital printing and especially inkjet printing has been growing in volume during recent years compared to traditional printing. Figure 2 shows the share of the different printing technologies in global markets (Bigianti and Lanter 2014) where digital printing is predicted to have 21% share of the global market by 2018. Inkjet printing together with dry and liquid toner electrophotography are the major contributors to the digital printing market, but inkjet is growing more rapidly and it is forecast that inkjet will overtake electrophotography after 2019 and that by 2024 inkjet will account for 56% of the value and 53% of the volume of the digital printing. (Smithers Pira 2014).

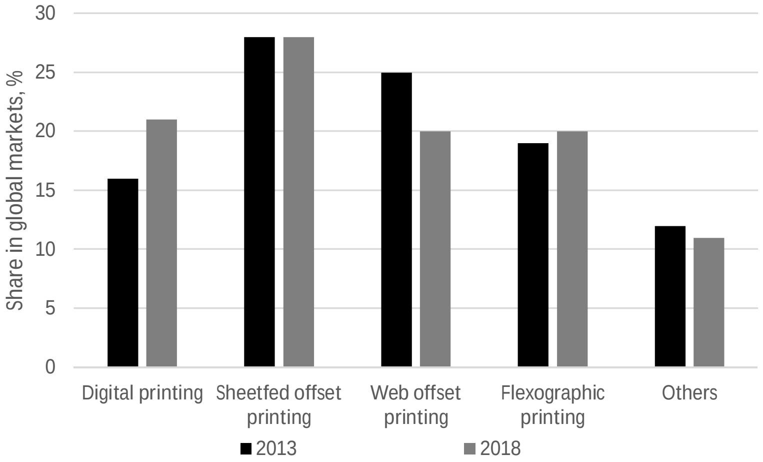

Figure 2 Shares of printing technologies in 2013 and in 2018 in relation to worldwide print production (Smithers Pira 2014).

During the past few years, there has been a vast amount of development such as new print heads and new ink dispersion systems. For example, Memjet has launched a printhead that is 222.8 mm wide and contains 70,000 print nozzles and uses “waterfall” technology where each nozzle produces 11,000 microdrops every second, making it possible to print up to 60 pages per minute (Lomond 2015). HP has launched ColorLok® papers where the pigment in the ink remains close to the paper surface and is rapidly immobilized increasing the optical density, increasing the color gamut and reducing color-to-color bleeding (HP 2012). HP has also developed a PageWide technology and a printer with more than 40,000 nozzles to produce high print quality (HP 2014). Kodak has launched Kodak’s Prosper S Series Imprinting Systems (Hamilton 2012) for hybrid newspaper printing applications, so that the user can take advantage of the special effects while also gaining the benefit of targeted or variable messaging and graphics in the prints. Landa (Landa 2015) has developed and launched Nanography^{TM}, a technology where nano-ink dispersion is first ejected onto a unique heated blanket where the ink dries, and then the ink is transferred from the blanket to the substrate in the form of an ultra-thin film.

3 DESIGN OF INKJET PRINTING SUBSTRATES

Inkjet printing is a very versatile technology and can be used to print on any surface or on various objects. However, the quality of the print is highly dependent on the ink-substrate interaction such as droplet spreading and absorption into the surface. The substrates recommended, for example, for high-speed inkjet and water-based inks are usually coated or surface treated with special ink-receptive layers formulated to provide suitable print quality and an adequate ink drying and absorption (Malla and Devisetti 2005; Stoffel 2007; Lundberg et al. 2010; Lundberg 2011).

Surface-treatment methods such as surface sizing, mineral or pigment coating, surface pigmentation, or priming are ways of improving the surface character of the paper substrate and hence the print quality. In most cases, the coating or surface treatment is a part of the papermaking process but new concepts also offer in-line treatment of substrates in the press before printing (Kodak 2010; Fu et al. 2014).

3.1 Ink-substrate interaction and ink drying

The ink setting and ink drying processes involve three different phases: spreading in the XY-direction, vehicle evaporation, and ink penetration in the Z-direction (Figure 3). The ink setting and drying processes are dependent on the kinetic energy and viscosity of the drop, the surface energy of the ink (Hakola and Oittinen 2009) as well as on the ink formulation and chemical and physical properties of the paper (Kipphan 2001).

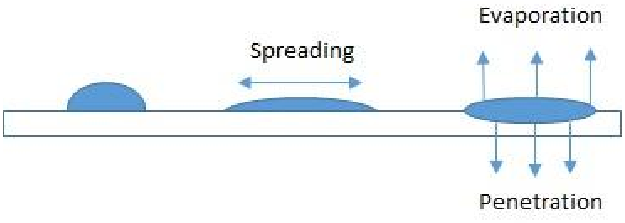

Figure 3 Ink setting and drying processes (Hakola and Oittinen 2009).

The interaction between the ink drop and the paper starts immediately after the ink drop contacts the paper. During the first ~10 μs, the initially spherical drop spreads out, bulging at the edges and then recoils. By ~20−80 μs, the drop reaches a static configuration, with a diameter roughly the same as the final spot size, and then begins to shrink as fluid penetrates into the paper and then evaporates. Time-scales for these processes depend greatly on the type of medium as well as on heating conditions, but for example, under ambient conditions, the ink drop takes 10−50 ms to fully penetrate into porous paper (Schmid 2009), although it has been shown by Bristow (1967) and later by Lyne and Aspler (1982) that there is a time delay in the wetting of paper with a polar liquid such as water. This "wetting delay" is usually a few seconds for sized papers. In contrast, such a drop may take 100−1000 ms to evaporate so that on porous paper most ink is absorbed before it evaporates (Schmid 2009). The coat weight or coating thickness also has an effect on the ink drying time: the higher the coat weight, the faster is the drying, indicating that the ink drying mechanism is dominated by the absorptive drying process (Yuan 1997). The complete drying of the ink might take hours (Agbezuge 1991).

The interaction between paper and inkjet ink has been evaluated in different ways, e.g. with the Bristow Absorption Apparatus (BAA) (Bares and Rennels 1990; Barker et al. 1992, Selim et al. 1997). Barker et al. (1992) used BAA together with contact angle measurements to calculate the substrate's roughness index and absorption coefficient, and they also predicted print quality (wicking) in inkjet printing and showed that the Bristow wheel test was the best predictive test of print quality. Selim et al. (1997) studied the evaporation of water-based ink and penetration into paper with the Bristow tester and found that in an office environment the rate of penetration was at least 20 times faster than the rate of evaporation. In contrast to this finding, Oko et al. (2011) studied the drying rates of pL size water droplets on uncoated and coated papers and found that imbibition dominated rather than evaporation on coated paper, but that evaporation dominated on uncoated paper. Svanholm (2007) developed a laboratory-scale microscopic drop absorption test equipment (MicroDAT) to study ink-coating interactions in inkjet-printing-like conditions. The impact and spreading of droplets was observed, and the droplet contact angle, height, and base for a duration of up to 8 seconds were measured. The dynamic surface wetting kinetics of sessile drops of water and ethylene glycol deposited on ink-jet papers were studied with hydrodynamic and molecular-kinetic models (Järnström et al. 2011) and it was concluded that the surface free energy (SFE) has a significant effect on the surface wetting dynamics of the paper samples.

3.2 Surface treatment for pigment-based inks

Substrates for modern water-based inkjet inks need to be sustainable, cost-efficient, and able to provide good and durable print quality. High-quality inkjet prints are usually obtained by using highly absorbing coatings based on resins or porous pigments or coating structures that promote a rapid uptake of colorant carrier liquid. Inkjet-printable substrates, for instance, for transpromo and direct mail require preferably a light surface treatment concept in order to be cost-effective and sustainable. Therefore different coatings have been developed and investigated, and the thickness of such coating layers obviously plays a crucial role in print quality development. A thin surface coating can be created to control lateral and vertical spreading and absorption and solvent uptake on rough fiber-based substrates.

Surface treatment with a cationic chemical such as starch (Moutinho et al. 2007; Costa et al. 2010), PDADMAC (Sousa et al. 2013), styrene maleic anhydride (SMA) (Batten 1995) or nanopigments (Wild et al. 2008) has been used to improve print quality. It has been demonstrated that a blend of cationic starch and minor quantities of four distinct copolymers of styrene enhanced print quality and also changed the hydrophobicity of the surface (Moutinho et al. 2011), whereas Sousa et al. (2013) showed that the paper modified with PDADMAC gave high print quality assessed as low bleeding and wicking and good dot quality. Batten (1995) and Moutinho et al. (2011) used SMA to improve the paper surface resistance to water. The use of nanopigment-based formulations (amorphous spherical silica) has been shown to result in high print density, dimensional stability, good water fastness and sharpness with aqueous inkjet inks (Wild et al. 2008).

Another efficient way of improving the fixation of a pigment colorant is by controlling the electrostatic interaction and colloidal stability with divalent or multivalent metal salts, as used by Lundberg et al. (2010), Hamada and Bousfield (2009) and Örtegren et al. (2011), preferably in combination with a tailored pigment surface modification as demonstrated by Yu and von Gottberg (2000). Oko et al. (2014) reported a series of aggregation and sedimentation experiments with commercial pigment-based inks, generic ink formulations and various specific ingredients, and they found differences in response to the presence of $MgCl_2$ or $CaCl_2$. Aggregation and sedimentation of inkjet ink components are thus linked to particle aggregation which affect the distribution of colorant pigments on inkjet prints.

3.3 Surface treatment for dye-based inks

Anionic dye colorants naturally react with cationic chemicals in the coatings, and cationic additives are usually used in coating formulations to improve the print quality and to fix the colorant molecules. A proper colorant fixation produces high optical density, brighter color and sharper lines, low bleeding and low print through and high rub and wet resistance (Kettle 2010).

Different chemicals e.g. PDADMAC (Lamminmäki et al. 2011), starch (Rahman 2003) and styrene maleic anhydride imide resin (SMAI) (Sreekumar et al. 2005a) have been tested on cellulose substrates to fix dye-based inks. Lamminmäki et al. (2011) used PDADMAC to produce cationicity when studying the effect of surface charge on dye-based ink penetration and on the resulting print quality. They showed that reduced bleeding and improved water fastness could be achieved when a cationic additive was used in pigment coating on a paper substrate. The application of a cationic additive to the coating layer surface retarded the dye-based ink penetration into the paper structure, by reducing the coating layer permeability and by bonding the anionic colorant in the top layer via electrostatic charge interaction. Rahman (2003) used e.g. cationic starch together with silica particles to improve the paper surface properties and found e.g. greater water fastness which was attributed to a specific interaction between the colorants and a receptive layer of the paper, an observation similar to that obtained with PDADMAC and PCC by Sreekumar et al. (2005a and 2005b). PDADMAC has also been used in a matte silica/polyvinyl alcohol coating (Ryu et al. 1999), and it has been shown that PDADMAC leads to superior fastness against water with a high print density of dye inks in inkjet printing (Shaw-Klein 1998).

The coating can also include a binder that swells when the solvent in the inkjet ink is absorbed (Svanholm 2007). A neutral resin or porous absorbent may provide good image quality (Hamada and Bousfield 2009; Donigian et al. 1999). Polyvinyl alcohol PVOH is the most commonly used binder in inkjet coatings (Khoultchaev and Graczyk 2001; Storbeck et al. 2005), and it usually has a positive effect on print quality (Lee et al. 2002; Lee et al. 2005a; Glittenberg et al. 2002). It seems that the colorants of dye-based inks are then more uniformly distributed in the coating structure since PVOH covers the pigment surfaces and masks any cationic surface of the pigments, as was recently demonstrated and proposed by Lamminmäki et al. (2009). Vikman and Vuorinen (2004) showed the role of cationic PVOH-PDADMAC binders and weakly cationic modified styrene-acrylate-latex-starch binders in pigment coatings on print quality and particularly on water fastness. The interfacial adhesion between ink and coating is more critical when the image is in physical contact in the presence of water or condensed moisture (Wexler 2001; Vikman 2004; Shi et al. 2004), and this emphasizes the role of the interactions. The binder should not only act as a fixative for the colorant but might also be designed to control the liquid phase absorption and chromatographic separation of colorants, which in turn affect the drying rate and print quality (Lamminmäki et al. 2010). Glittenberg et al. (2003) used starch as a binder together with PCC to create a coating formulation which enabled papermakers to develop new paper grades intermediate between uncoated and premium-grade qualities.

Good inkjet print quality with dye-based inks can also be promoted by silica pigment coatings which have a high porosity with micropores in the pigment particles and inter-particle pores and a large surface area providing rapid ink sorption and ink fixation. For dye-based ink colorants, micro-porous coatings (Storbeck et al. 2005) and coatings with SiO_2-Al_2O_3 (Lee et al. 2005b), colloidal silica (Chapman and Michos 2000) and fumed silica (Hladnik 2005: Chen and Burch 2007; Nelli 2007; Gong et al. 2010) have been investigated. Because of the high price of silica (Kettle 2010), alternative low cost pigments have been tested. Lamminmäki et al. (2013) studied porous olivine-silicate-based mineral pigments as coating pigments for matt inkjet papers. The coatings containing the experimentally produced silica gave print density, print-through, print gloss and bleeding results similar to those obtained with the commercial silica grade. A porous χ - Al_2O_3, one of the transition phases of alumina, which has a high porosity, high specific surface area, and positive surface charges, has been used as a coating pigment (Yu et al. 2012). A high dye-fixing ability was obtained, which was obviously due to the cationic character of the pigment and its porosity.

3.4 Surface treatment with polyelectrolyte multilayers

The layer-by-layer (LbL) assembly technique is based on sequential deposition of oppositely charged species on a charged substrates. The most common form of LbL deposition is based on ionic bonds between ionic species, although different types of chemical bonds may be involved in formation of the multilayer thin films (Montazami 2009). Figure 4 shows a schematic of formation of two bilayer via ionic attraction between two ionic polymers.

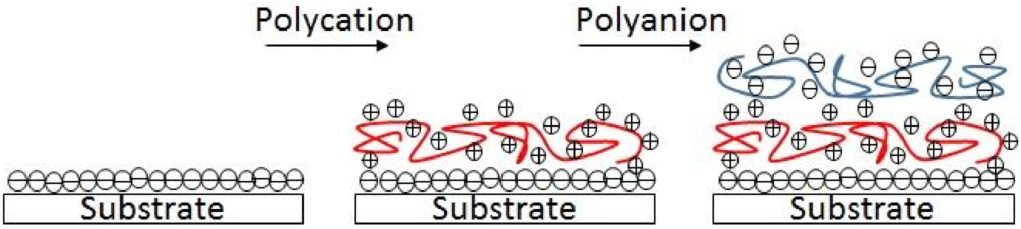

Figure 4 Formation of two bilayers of ionic polymers by LbL technique.

The use of a LbL assembly has been extensively studied over the past two decades (e.g. Srivastava and Kotov 2008; Kim et al. 2010; Chiono et al. 2012) with a particular focus on various barrier applications (Kim et al. 2006) and also to improve the surface properties of paper for example in relation to food packaging and paper coating (Priolo et al. 2010; Leterrier et al. 2009). However, it appears that LbL assembly in inkjet paper coatings has not earlier been studied.

There are several advantages, as well as challenges, in the scaling up of the LbL technique, particularly with high process speeds. LbL films can be made e.g. by dipping (Dubas et al. 2006; Park and Hammond 2004; Izquierdo et al. 2005), with a spin coater (Johnson et al. 2012; Priya et al. 2009; Johansson and Wågberg 2012) or by deposition with inkjet printers by employing inkjet technology to deliver the necessary quantities of LbL components required to build up the film without excess, eliminating the need for repetitive rinsing steps (Andres and Kotov 2010; Zhang et al. 2012).

3.5 Interaction between internal and surface sizing and its effect on inkjet print quality

In order to optimize liquid ink absorption, spreading and adhesion, it is essential to consider not only the effect of the surface size formulation but also the level and type of internal sizing, filler content and fiber mixture and, for example, base paper grammage and porosity (Kettle 2010; Sousa 2013; Desie and van Roost 2006)

Internal and surface sizing decrease the surface free energy sufficiently to make the paper surface more hydrophobic and suitable to retard the wetting and penetration of pigment ink into the structure. A certain amount of ink must penetrate the surface and at the same time ink must stay on the surface of the paper without spreading to achieve the desired print density. (Riebeling 1994; Kilpeläinen and Manner 2000; Hubbe 2007.)

The penetration depth of the dye-based ink can be significantly reduced by adding internal sizing chemical to paper to make the paper more hydrophobic (Yang et al. 2005). However, Kilpeläinen and Manner (2000) studied different formulations of internal sizing agents using alkyl succinic anhydride (ASA) and different levels of surface sizing using styrene acrylate (SA) and styrene maleic anhydride (SMA). They found out that good inkjet printing was obtained by optimizing the ASA amount and simultaneously the amount of the synthetic surface sizing polymer. The effect of internal sizing on inkjet print quality has also been reported for example by Pal et al. (2007) who showed that alkyl ketene dimer (AKD) has a negative effect on optical properties. A greater absorbency was observed in some samples when the amount of AKD was increased, even though the overall effect of surface sizing was to reduce the absorbency of the paper. Lundberg et al. (2011), on the other hand, studied the effect of ASA on inkjet print quality and found that internal sizing reduced the rate of absorption of water-based dye and claimed that the rate of evaporation affected the result. In the uncoated papers, internal sizing reduced the droplet spreading, the rate of ink absorption and the apparent surface energy. The coated inkjet papers exhibited relatively small pore sizes and low surface roughness and gave rise to rapid inkjet ink absorption and a cylindrical distribution of the colorant of the ink in the coating layer.

EXPERIMENTAL

4 MATERIALS AND METHODS

The experimental methods and materials used in this work are summarized here. More detailed descriptions are given in Papers I-VI.

4.1 Base papers, surface treatment methods and chemicals

Three different base papers and three different surface treatment methods were used in different combinations in this study. The experimental set-up of different studies and the surface-treatment chemicals used are presented in Table II

Table II The design of the studies in Papers I-VI.

	Paper I	Paper II	Paper III	Paper IV	Paper V	Paper VI
Base paper	Uncoated wood-free	Uncoated wood-free	Pigment-coated	Experimental wood-free	Experimental wood-free	Uncoated wood-free
Surface treatment method	Film press with pilot scale coater	Surface sizing with size press	Surface sizing with size press	Spray coating	Spray coating	Surface sizing with size press
Layers	1	5	5	3	3	5
Chemicals						
PDADMAC	x	x	x	x	x	x
NaCMC	x	x	x	x	x	x
PEI	x					
PVAm1	x					
PVAm2	x					
Nanosilica		x				x

PDADMAC, polydiallydimethylammonium chloride
NaCMC, carboxymethyl cellulose
PEI, polyethylene imine
PVAm, polyvinyl amine

The objective of Paper I was to clarify the effect of different cationic chemicals on print quality, and the absorption and wetting properties of the surface-treated papers. An uncoated wood-free base paper (Stora Enso Oyj, 80 g/m^2) was surface-treated on a pilot-scale sheet coater operated in the film press mode (DT Laboratory Coater, DT Paper Sciences, Turku, Finland), see Figure 5. The A4 size substrate was surface treated on one side following off-line IR drying. The coat weights were adjusted using various rod types between 0.2 mm – 1.0 mm. The chemicals used in the surface treatment were anionic NaCMC (Finnfix® 30, CP Kelco), cationic PDADMAC

(Catiofast® BP, BASF GmbH), high-molar-mass polyethylene imine PEI (Catiofast® SF, BASF GmbH) and two polyvinyl amines with different charge densities (PVAm1, Catiofast® VFH and PVAm2, Catiofast® VMP, BASF GmbH).

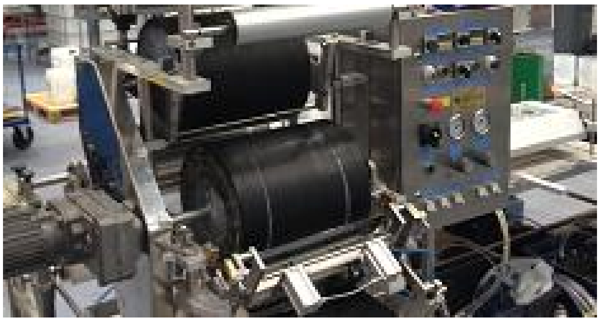

Figure 5 Pilot coater (DT Laboratory Coater, DT Paper Sciences, Turku, Finland).

In Papers II and VI, the same uncoated wood-free base paper as that used in paper I (Stora Enso Oyj, 80 g/m^2) was used and surface-treated using a conventional pilot-scale size press (Stora Enso Oyj, Research Centre Imatra). The size press was used with a nip pound operating at a speed of 70 m/min, with intermediate contact drying after each applied layer. The final moisture content was set to 5%. The multilayer structures were produced by treating the base paper five times with PDADMAC, five times with NaCMC, and five times alternately with PDADMAC and NaCMC. In a second surface-treatment experiment, also presented in Papers II and VI, the polymer solutions were mixed with various levels of anionic fumed nanosilica particles (AERODISP® W 7330N, Evonik Industries) in order to determine the effect of nanopigment.

In Paper III, a one-sided, glossy pigment-coated flexible commercial packaging paper for rotogravure, flexographic or offset printing (LumiFlex 90 g/m^2, Stora Enso Oyj) was surface treated using a pilot size press applicator operating at a speed of 100 m/min. The experimental set-up was similar to that used in Paper II except that the base paper was a mineral-coated paper instead of a wood free paper and no nanosilica was used.

In Papers IV and V, a base paper containing various amounts of internal sizing (ASA) was made on a pilot paper machine and surface sized with a cationic or an anionic polyelectrolytes. The wood free 80 g/m^2 base paper was made with a two-component retention system, 250 g/t cationic polyacrylamide (C-PAM, Percol® 47, BASF GmbH), and 1.5 kg/t bentonite

(Hydrocol® SH, BASF GmbH) starch and filler (precipitated calcium carbonate prepared by reacting CO_2 with calcium hydroxide). The targeted filler content was 25%. The level of ASA was 0 kg/t, 0.5 kg/t, 1.0 kg/t and 1.5 kg/ton of pulp. The A4 samples with different levels of internal sizing (ASA) were then multilayer-surface-treated using an automatized precision spray coater (Spalas Coating System, Nanotrons, USA). Various coating structures were made using NaCMC (Finnfix® 2, CP Kelco) and PDADMAC (Catiofast® BP, BASF GmbH) to form a three-layer coating without intermediate drying. The target coat weight for one layer was 1 g/m^2, which was determined gravimetrically according to ISO 536. NaCMC was diluted in tap water to a solids content of 4 wt-%, while the PDADMAC solution was diluted with tap water to a solids content of 5 wt-%. The Brookfield viscosity (100 rpm, spindle number 5) determined for the two samples was 16 cP.

4.2 Characterization methods

4.2.1 Physical properties of paper

The physical properties of the paper were tested at 23°C and 50% relative humidity. The Bendtsen roughness (ISO 8791–2), Print Surf roughness (ISO 8791–4), 75° gloss (TAPPI T 480 UM–85), grammage (ISO 536) and coat weight were determined after coating and air conditioning of the samples.

4.2.2 Atomic Force Microscope (AFM) and Scanning Electron Microscope (SEM)

The nano-scale topography and mechanical properties of the polyelectrolyte-surface-treated papers were measured using an atomic force microscope (Bruker Multimode 8 Scanning Probe Microscope, Bruker, USA). All images were captured in the PeakForce QNM mode at a spring constant of $k = 5$ N/m using probes with a tip radius < 8 nm. All AFM tests were carried out under ambient conditions (25 ± 3˚C, 40 ± 10% RH). The resolution of the images was typically 512x512 pixels and the scanning rate was between 0.1 and 0.3 Hz. Roughness values were calculated as root mean square (RMS) values for areas of 2 x 2 µm, 5 x 5 µm and 30 x 30 µm depending on the sample. Nanoscope Analysis 1.50 software was used to analyze images and RMS roughnesses. Changes in structure of the surface visible to the naked eye were confirmed in an optical microscope and further surface topography measurements were carried out with nano-scale resolution.

Cross-cut samples for microscope imaging were prepared using the Hitachi IM4000 Ion Milling System. Microscope images of the cross-cut samples were captured using a FEI Nova NanoSEM 450 field emission (Schottky emitter) scanning electron microscope with a 10.0 kV accelerating voltage and an 8 mm working distance. A retractable concentric back scatter detector (CBS) was used. The spot size was 3.5 and the image resolution for individual images was 3072 x 2048 pixels.

4.2.3 Contact angle and liquid absorption measurements

Apparent contact angles were determined to study the spreading and absorption of liquids and in order to calculate the SFEs of the samples. SFEs (γ) were calculated using the acid base approach, which allows closer characterization of solid (s) surfaces (Eq 1). The Acid-Base calculation is based on summing the three SFE components, Lifshitz van der Waals (LW), electron-acceptor (+), and electron-donor (-) components, and thus requires a three-equation system, which can be written as (Hejda et al. 2010):

$$(1 + cos\theta_i)\gamma_{li} = 2\left(\sqrt{\gamma_{li}^{LW}\gamma_s^{LW}} + \sqrt{\gamma_{li}^{+}\gamma_s^{-}} + \sqrt{\gamma_{li}^{-}\gamma_s^{+}}\right) \tag{1}$$

The contact angle measurements were made with an Attension Theta optical tensiometer (Biolin Scientific) using distilled water (DI), 99% diiodomethane CH_2I_2 (DIM, Alfa Aesar) and 99.8% ethylene glycol 1,2-ethanediol (EG, VWR Prolabo) and imaged with a 420 Hz camera (Basler A602F-2 with Navitar optics). The droplet volume was 0.8 µl and the contact angle was recorded immediately after the drop was released from the needle and contacted the surface. The size of the contact angle and the drop volume was measured repeatedly from initial contact to 10 seconds or complete wetting. Digital images were analyzed with the OneAttension image tool; the baseline was set manually for all the samples.

4.2.4 X-ray photoelectron spectroscopy (XPS)

The chemical composition of the surfaces made by the polyelectrolyte surface-treatment process were evaluated by X-ray Photoelectron Spectroscopy, XPS, using a state-of-the-art electron spectrometer (Axis Ultra by Kratos Analytical), monochromatic Al K_α X-rays and effective neutralization. The depth of analysis of the method was less than 10 nm. The elemental surface composition was determined from low resolution survey scans, while high resolution measurements of carbon C 1s and oxygen O 1s regions were utilized for a more detailed evaluation of the carbon compounds. CasaXPS software was utilized and, for the carbon regions, a specific four-component fitting routine tailored for cellulosic specimens was used (Johansson and Campbell, 2004). An in-situ reference sample of pure cellulose was measured with each sample batch.

4.2.5 Confocal laser scanning microscopy (CLSM) and optical microscopy

Confocal laser scanning microscope (CLSM) images were captured using an Olympus FV1000-IX81 microscope with a UPLSAPO 60x oil-immersion objective (NA=1.35). The fluorescence of the cellulose fibers (in the base paper) was measured with a 405-nm diode laser, and magenta ink with a 543-nm HeNe laser. Digital microscope images were taken from the Leica DFC450 microscope with an Olympus SZX9-camera. A pocket microscope (DPM 100, Fibro System AB) was used to determine the behavior (bleeding) of the ink. The same equipment was used to study droplet spreading on the different surface-treated papers. A droplet (2 µl) of ink was dispensed with a pipette, and images of the droplet were captured after 30 s and 240 s on the paper surface in order to determine the drop average diameter, and the average liquid phase migration distance.

4.3 Printing and print quality measurements

Polyelectrolyte-coated samples were conditioned at 23°C and 50% RH before being printed on an HP Office Jet Pro 8000 Enterprise inkjet printer (**printer 1**), a Brother MFC-J5910DW inkjet printer (**printer 2**) and a Lomond Evojet Memjet printer (**printer 3**), see Figure 6. The printer properties are described more in Table III. Table IV lists the printers used in the different studies.

Figure 6 (Left) HP Officejet Pro 8000 Enterprise printer, **printer 1**, (middle) Brother MFC-J5910DW printer, **printer 2**, and (right) Memjet, Lomond Evojet Office printer, **printer 3**.

Table III Printers and their properties according to manufacturers.

	HP Officejet Pro 8000 Enterprise [a)]	Brother MFC-J5910DW [b)]	Memjet, Lomond Evojet Office [c)]
	Printer 1	Printer 2	Printer 3
Printhead	Thermal inkjet	Piezo with 210 nozzles	Thermal inkjet, "waterfall" technique
Ink	Pigment-based CMYK	Dye-based CMY Pigment-based K	Dye-based CMYK
Max. Resolution	600 x 600 dpi	6000 x 1200 dpi	1600 x 1600 dpi
Min. Drop size	7–9 pL	1.5 pL	1 pL
Max. copy size	A4	A3	A4
Print speed	15 ppm	12ppm	60 ppm

a) http://www.hp.com/country/us/en/uc/welcome.html
b) www.brother.com/index.htm
c) evojet.lomond.com

Table IV Printers used in the different studies (Paper I-Paper VI).

Printer	Paper I	Paper II	Paper III	Paper IV	Paper V	Paper VI
Printer 1	x	x	x		x	
Printer 2			x		x	
Printer 3	x		x	x		x

The printed samples were studied with respect to print density (100% C, 100% M, 100% Y, and 100% K), mottling (100% C, 100% M, 100% Y and 100% K), bleeding and wicking. Print density (10 parallel measurements), was measured with an X-rite SpectroEye spectrophotometer, whereas mottling (unwanted unevenness), bleeding and wicking (4 parallel measurements for each) were determined with an Intelli IAS program with an Epson Expression 1680 scanner, based on the ISO/IEC 13660:2001 standard. Print density is a measure of a contrast between the printing ink and the substrate and is the logarithmic relation between the incoming light intensity and reflected light intensity (Puukko and Niemi 2009). Wicking was measured from the raggedness of the black and red printed lines on the base paper, and bleeding was measured from the raggedness of the black and red lines printed on white with a yellow boundary.

Some physical properties of the black pigment colorants in the inks from printer 1 (ink 1) and from printer 2 (ink 2) were determined using a Malvern Zetasizer Nano ZS, see Table V. It can be seen that the ζ-potential are relatively negative, which means that they were anionically charged even at relatively low pH values. The particle size values are at the same levels for both pigments, revealing nano-size pigments. Inks were diluted in a 0.026M NaCl (based on conductivity of the ink 2.6 mS/cm) solution and after dilution the pH was set to 8.3.

Table V Particle size and ζ-potential of the black pigment inks from printer **Printer 1** and **Printer 2**.

	Printer 1 (Ink 1)	Printer 2 (Ink 2)
Particle size, nm	130	120
pH	8.3	6.0
Conductivity, mS/cm	2.6	0.6
ζ-pot., pH 4	- 27.0	- 38.9
ζ-pot., pH 8.3	- 33.8	- 40.1
ζ-pot., pH 11	- 35.6	- 49.0

4.3.1 Dry and wet adhesion of ink

The wet adhesion of the ink was measured according to the water fastness test (Rahman, 2003), using a beaker with deionized water (water equilibrated for at least 5 min). The printed sheet was placed in the beaker for one minute and then removed and dried at room temperature. The optical densities of the black printed area before and after immersion were determined with respect to the original white area adjacent to the printed area. The ratio of the optical density of the water-soaked printed area to that of the unsoaked printed area expressed as a percentage gives the relative water fastness.

The dry adhesion of the printed substrates was determined for the 100% black print areas according IPC-TM 650.The printed samples were first dried and conditioned for 24 h at 23°C and 50% RH. A 3M tape was then pressed firmly onto the surface of the paper with a contact time of about 60 s. The tape was then peeled from the paper and the ink removed was visually evaluated with the naked eye.

4.3.2 Dissolution of the multilayer polyelectrolyte coating

The dissolution or water resistance of the multilayer polyelectrolyte surfaces was done by immersing the samples in tap water for 60 s, after which the amount of dissolved polymer was determined by measuring the chemical oxygen demand (COD) of the water according to the SFS 5504 standard.

5 RESULTS AND DISCUSSION

5.1 Effect of different cationic chemicals on wetting, absorption, and inkjet print quality (Paper I)

Four different cationic chemicals and one anionic chemical were studied in Paper I with regard to their effect on print quality and ink spreading, and the absorption and adhesion of pigment-based and dye-based inks. These mono-component coatings were prepared in order to provide a set of reference samples and values for subsequent evaluation and discussion.

5.1.1 Coating structure and characterization

The uncoated wood-free base paper was surface treated with four different cationic polyelectrolytes (PDADMAC, PVAm1, PVAm2, PEI) and with one anionic polyelectrolyte (NaCMC). The coat weights varied from 0.6 g/m^2 to 15.5 g/m^2, depending on the polymer and on the coating conditions. The main interest, with regard to the scope of this thesis, was the coat weight between 2 g/m^2 and 4 g/m^2. A significant difference between the samples was seen with respect to the surface energies or liquid (water, EG and DIM) absorption.

Figure 7 shows droplet base diameter as a function of contact angle on different substrates. The uncoated reference paper, the PDADMAC-treated surface (coat weight 6.1 g/m^2, SFE 43.0) and the PVAm2-treated surface (8.7 g/m^2, SFE 30.2 mN/m) showed a strong absorption of water, whereas the PEI-treated (7.0 g/m^2, SFE 25.3 mN/m) and NaCMC-treated (3.2 g/m^2, SFE 47.3 mN/m) surfaces showed a strong spreading of water.

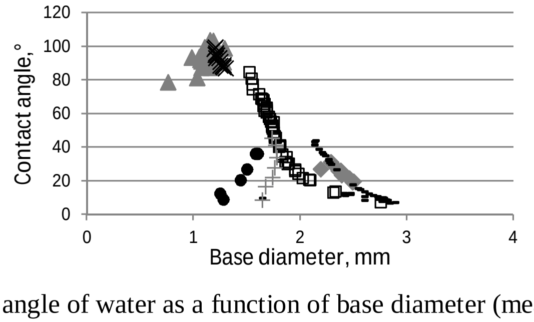

Figure 7 Contact angle of water as a function of base diameter (measurement time 6 s or less). Ref ●, CMC (1), (3.2 g/m^2) ♦, PEI (1), (7.0 g/m^2) □, PVAm1 (1), (5.4g/m^2) ▲, PVAm2 (1), (8.7 g/m^2) x, PDADMAC (2), (10.0g/m^2) - and PDADMAC (5), (6.1g/m^2) +.

The reference paper and surface-treated papers were relatively rough (5.5 µm – 6.4 µm) according to Print Surf method. The AFM modulus images show that the PVAm forms, at least locally, a film, which covers the surface and the structure of the fibers (Figure 8). The anionic polyelectrolyte, NaCMC, also seems to coat the paper surface, although a more fibrillar character can be identified, which presumably reflects the features of the base paper.

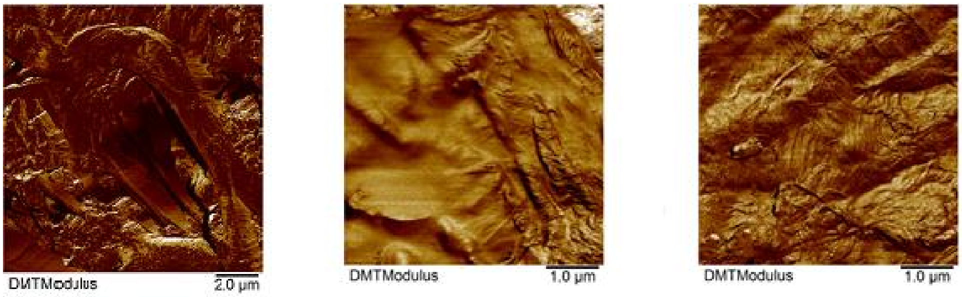

Figure 8 AFM images (DMTModulus) of (left) the base paper, (middle) a paper treated with PVAm1, coat weight 5.4 g/m^2 and (right) a paper treated with NaCMC, coat weight 0.6 g/m^2.

5.1.2 Interaction between substrate and pigment-based ink

The samples were printed on the desktop printer equipped with water-based pigmented ink (printer 1). PEI had a positive effect on print density and a clear increase in black print density was observed with increasing coat weight. Interestingly, a similar behavior was seen on the surfaces with the anionic NaCMC coating. The PDADMAC, on the other hand, had very little effect on the print density, even at high coat weight.

In the 100% areas, the mottling was reduced particularly for samples surface treated with PVAm1 and PEI, which is believed to be due to their high cationic charge density (11-12 meq/g) which promotes ink particle fixation (Hubbe et al. 2005). In addition to less print mottle, the substrates coated with PEI and PVAm2 showed less bleeding and wicking and the raggedness obtained were about 5 µm less than those for the reference sample, confirming that certain cationic polymers reduce lateral ink spreading and hence increase print uniformity.

Cationic polymers are known to improve the water fastness of inkjet prints in particular for dye-based inks (Vikman and Vuorinen 2004). In the present study, water fastness was measured for the pigment-based ink on various substrates and Figure 9 shows good wet adhesion for most of the samples (98%–100%). For the PVAm2- and PDADMAC-treated at high coat weights and the NaCMC-treated surfaces, the water fastness values were considerably less than 100%. Poor water fastness for samples having a high coat weight is due to dissolution of the coating immersion in water during water fastness test, so that ink is removed. AFM imaging of the samples before the water fastness tests revealed agglomerated pigments fixed on the surface as a filter cake (Figure 10a), whereas after the water fastness test some areas were substantially free from ink particles (Figure 10b), confirming that ink particles are detached during the water fastness test.

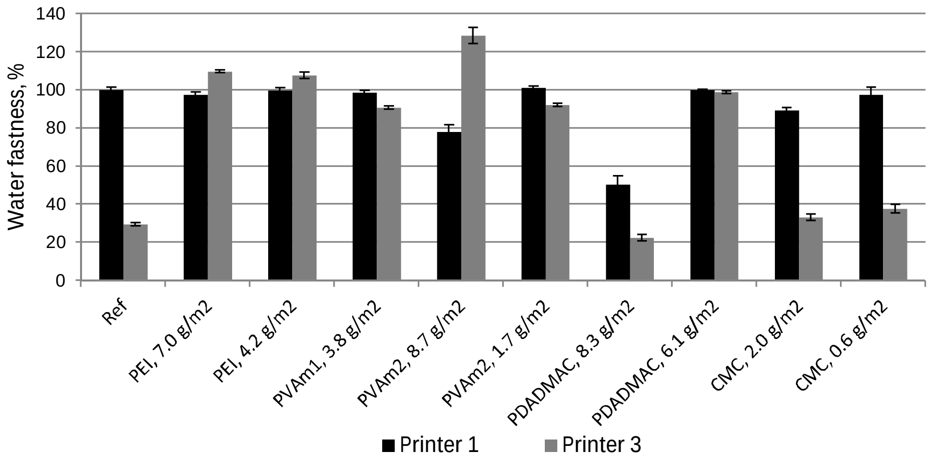

Figure 9 Water fastness results for black ink (black = pigment-based ink and grey = dye-based ink).

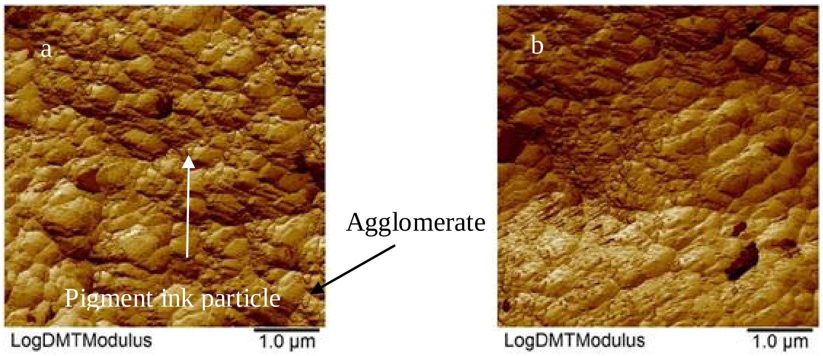

Figure 10 AFM images (LogDMTModulus) of NaCMC (2) (2.0 g/m^2) surfaces, printed with pigment-based ink, (a) before and (b) after immersion in water.

5.1.3 Interaction between substrate and dye-based ink

The same set of samples was printed on a desktop printer using a water-based dye-based ink (printer 3). The print density of most of the samples was on the same level as that of the reference sample when using a small amount of polyelectrolyte (3–6 g/m^2). The prints on the PEI sample gave higher density values but this was probably because the PEI turned yellowish on the surface of the paper. All the surface-treated samples gave higher print mottle and greater bleeding than the reference paper and this was visible to the naked eye. Bleeding of the black dye ink was greater on the surface-treated surfaces than on the reference sample, which was surprising since e.g. Lamminmäki et al. (2011) claimed that "The opposite charges of the coating components and dye molecules bind the colorant most effectively to the top part of the coating layer, producing less bleeding and improved water fastness" and this should apply when PDADMAC was used. On the other hand, Svanholm (2007) showed that a cationic additive can sometimes be transferred deeper into the base paper and it cannot then effectively take part in the binding of the colorant, and this may be the reason for the high bleeding values obtained in this study. The wicking of the black dye ink decreased when the coat weight of PDADMAC was increased. With a coat weight of 6-10 g/m^2, the raggedness was approximately at the same level as that of the untreated sample. At low coat weights, the coverage is obviously not sufficient to provide a homogeneous coating, and it is possible that at a higher coat weight the coating is not sufficiently even to give low bleeding or raggedness values. Low bleeding was obtained only on samples coated with large amounts of PEI or PVAm1, and thus may be due to the high cationicity. On the other hand, the sample coated with PVAm1, was relatively hydrophobic according to the contact angle measurements. This may, however, favor ink vehicle spreading and improve the dye fixation. The low bleeding on the PEI surface may be explained by an electrostatic interaction between the anionic dye and the highly charged PEI (Kallio et al. 2006).

Water fastness values (Figure 9) for the dye-based inks are depended on the surface treatment and coat weight. The highest water fastness was achieved with PVAm2 (coat weight 8.7g/m^2) and PEI (coat weights 7.0 g/m^{2}and 4.2 g/m^2). A water fastness result greater than 100% has previously been ascribed to a migration of colorant to the surface (Khoultchaev and Graczyk 2001), and this may explains the values greater than 100% found here. The dye-based inks are absorbed into the coating and are thus more prone to inter-diffusion. The lowest water fastness result was obtained with a high coat weight of PDADMAC (water fastness 22.4%, coat weight 8.3 g/m^2) and NaCMC (water fastness 33.1%, coat weight 2.0 g/m^2). The results obtained with the anionic NaCMC are in good agreement with results presented by Vikman (2004), who claimed that, the hydrogen bonding is a prevailing mechanism for the attachment of the colorant to anionic pigment coatings, whereas ionic bonds between dye inks and the surface developed with cationic coatings.

Figure 11 shows the water fastness for both dye-based and pigment-based inks plotted as a function of coat weight for PDADMAC. These results suggest that there is an optimal coat weight (approximately 6–7 g/m^2) giving the best water fastness. The PDADMAC-treated surface dissolved in water and ink was removed the same time. Deinkability would presumably be favored by such an ink detachment mechanism.

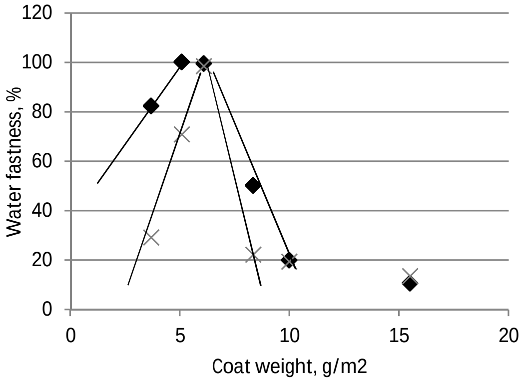

Figure 11 Water fastness of the black pigment-based ink (♦) and dye-based ink (x) on the PDADMAC surface. Lines have been added to indicate the optimal coat weights.

5.2 Effect of polyelectrolyte multilayers on print quality and on the absorption and wetting by ink (Paper II, Paper VI)

The scope of papers II and VI was to study the effect on ink spreading and absorption of alternating cationic and anionic layers, the role of the number of coating layers and the interaction of alternating layers with inkjet pigment-based and dye-based colorants and the subsequent print quality.

5.2.1 Coating structure and characterization

The uncoated wood-free base paper was surface-treated and multilayer structures were produced the base paper being treated five times with PDADMAC (CCCCC), five times with NaCMC (AAAAA) and five times alternately with PDADMAC and NaCMC (CACAC). Each symbol represents an intermediate coated sample (Table VI) and these single- (C), double- (CA), tri- (CAC) and tetra- (CACA) coated samples were also studied and printed. PDADMAC is indicated by C and NaCMC is indicated by A.

Table VI The design of the multilayer structures produced together with their sizing formulations and cumulative coat weights after each coating layer.

Surface		Coat weight, g/m^2/layer				
Compound	Layer structure	1	2	3	4	5
PDADMAC	CCCCC	0.4	1.5	2.4	3.9	4.7
NaCMC	AAAAA	0.3	1.8	2.3	3.4	4.0
PDADMAC	CACAC	1.1		2.9		5.0
NaCMC			2.0		4.0	
PDADMAC	CACAC + silica 1:2	0.9		2.9		4.6
NaCMC			1.3		3.4	

The paper surface was characterized by means of roughness and gloss. Bendtsen and Print-Surf (PPS) roughness values were at the same level for all the samples (Bendtsen roughness approximately 350 ml/min and PPS roughness 5.6–6.0 µm) and it was therefore, concluded that the macroscopic roughness properties of the paper surfaces remained similar even when the five times coated samples had 4-5 g/m^2 of polymer coating.

The multilayer polyelectrolyte surface treatment had a clear effect on the absorption of water, EG and DIM. Based on the liquid absorption of water on five samples and two reference samples, it is evident that the CCCCC treatment increased the absorption time but that no lateral spreading occurred. Anionic surface treatment (AAAAA) and layering five times (CACAC) did not greatly increase the contact angle. Some absorption occurred on the CACAC-treated sample but it was much slower than in the other samples (CCCCC, AAAAA and CACAC). Surprisingly, the surface spreading was reduced on the AAAAA-treated sample and practically no absorption could be determined.

The contact angle and absorption rate values for DIM on the CCCCC coating showed no significant differences from the reference paper. However, the absorption of the non-polar DIM was completely blocked by the AAAAA and CACAC coatings, which shows that polyelectrolyte multilayers can be tailored to selectively promote or prevent rapid liquid absorption. The absorption rates and contact angles determined for EG were very similar on all the samples. Contact angle of water was slightly higher on the cationic (CCCCC) or cationic-anionic (CACAC) coatings than on the anionic coating (AAAAA).

5.2.2 Interaction between substrate and pigment-based ink

When prints were made with printer 1, it was noticed that some of the print properties improved when the number of layers of cationic and anionic polymers was increased. Multiple coating layers had a positive effect on the print density of, e.g., black pigment-based ink, for which the optical density was increased by 0.4 units, i.e. from 1.5 to 1.9 after the introduction of cationic and anionic layers, respectively, see Figure 12a. The effect of interfacial chemistry in a multilayer polyelectrolyte-treated surface was weak for the black ink, but strong for the yellow (Figure 12b). Compared to the reference one-component coating in the case of the yellow ink, the anionic polymer reduced whereas the cationic polymer increased the print density. Cationic polymers (CCCCC-treatment) slightly decreased the mottling, while multilayers (CACAC) increased the mottling but this effect could clearly be attributed to specific ink–surface interactions showing less mottling on cationic layers (C, CAC and CACAC) than on anionic layers (CA and CACA).

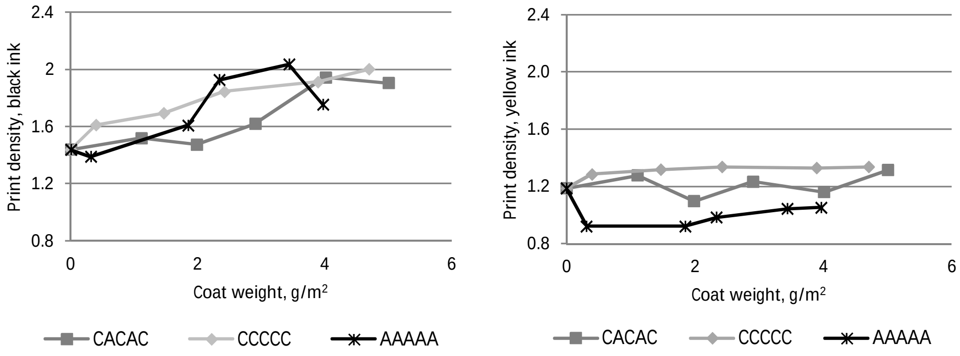

Figure 12 Print density of (a) black ink (printer 1) and (b) yellow ink (printer 1). Standard deviation was 0.01–0.08.

Ink spreading on the coated surface was studied by means of ink bleeding and wicking. Figure 13 shows the effect of polyelectrolyte multilayering on the line raggedness. The multilayer structure seem to slightly increase the bleeding behavior which is ascribed to a slower absorption of the ink, which was confirmed by absorption experiments with water. Contact angle data indicate that absorption by a CACAC-treated surface is much slower than the absorption by other surfaces, while the base diameter of the drop remained the same during measurement. The use of PDADMAC, on the other hand, reduced the vertical and horizontal bleeding of all colors in comparison with the untreated reference sample, see Figure 13. The PDADMAC gave a greater improvement, but an increase in the coat weight seemed to have only a minor effect on ink bleeding.

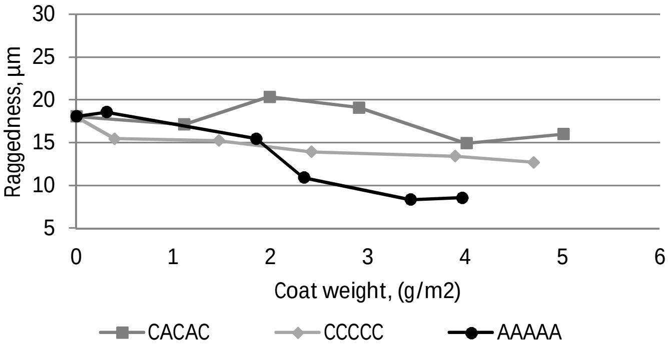

Figure 13 Horizontal line bleeding of the black ink (printer 1). Standard deviation was 0.3 –1.1.

The CLSM images in Figure 14 show how the magenta ink (red boundary layer) was set on the paper surface when the surface had been treated with a cationic or anionic chemical. The setting of the ink on the reference paper was less even. The continuous ink layer obtained on the NaCMC-treated paper is obviously due to the viscous character of the polymer, which gave a more even coating and at least partially sealed the surface reducing the interlayer diffusion of the ink and its penetration into the base paper. For the cationic PDADMAC, the coating seems to be very efficient locally in capturing ink pigment particles, but it could be expected that its low viscosity would create a more heterogeneous coating. It seems that surface treatment with a cationic polymer does not charge the structure sufficiently to create a highly ink-fixing substrate.

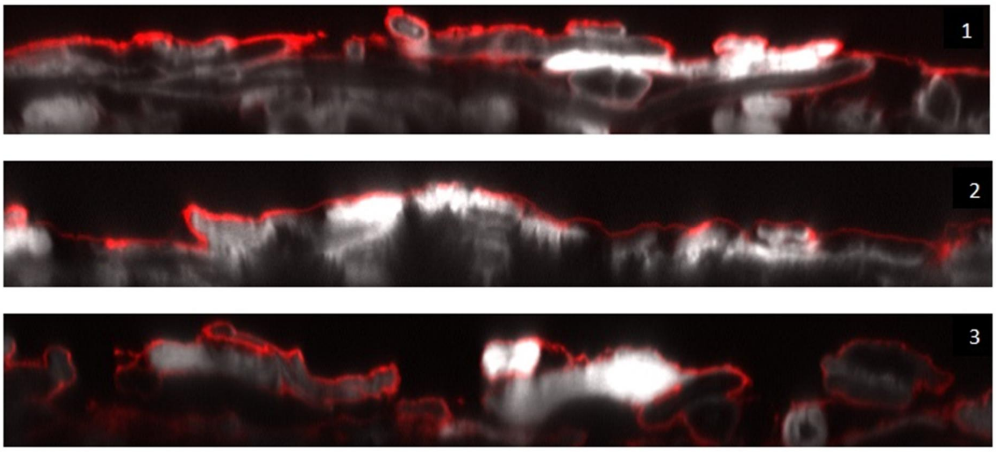

Figure 14 Cross-section CLSM-images of papers with a cationic (top panel) and an anionic (middle panel) coating and of a reference paper (bottom panel). All the papers were printed with magenta ink.

5.2.3 Interaction between substrate and dye-based ink

Figure 15a shows print density data for the prints made with printer 3 showing that surface treatment with cationic-anionic multilayers had only a minor effect on the print density. For the cationic (CCCCC) coating, the print density was slightly higher, but it increased by only 0.2 units, indicating that the cationic polymer did not efficiently fix the dye ink. However, it was recently demonstrated that with specially developed inkjet coating, the print density for this particular ink reached almost 2.5, which demonstrates that higher density levels are achievable (Mielonen et al. 2015). The print evenness and print mottle increased with increasing number of cationic-anionic polyelectrolyte layers (Paper VI).

Ink bleeding results (raggedness values) for the vertical red line in contact with a border of yellow ink are presented in Figure 15b. Polyelectrolyte surface treatment increased the raggedness of the red ink, which became obvious after the second coating, i.e. the CA-layer. For the cationic polyelectrolyte coating, the color-to-color ink bleeding remained on the same level as that of the reference. Lamminmäki (2011) showed that the use of cationic PDADMAC reduced dye-based ink bleeding, which is in agreement with our results. For the surface coated with anionic polyelectrolyte, AAAAA, bleeding increased at low coat weights (A-AAA), but decreased with higher coat weights finally reaching almost the same level as the uncoated reference paper. Too low an absorption speed into the coating means that the colorants in the inks have more time to mix together and bleeding therefore increases (Lamminmäki 2011; Moutinho et al. 2007). The contact angle measurements showed the hydrophobic character of the CACAC-treated surface and hydrophilic character of the CCCCC-treated surface. Thus, higher raggedness values were obtained on the sample with a higher hydrophobicity (CACAC-treated surfaces) and a lower value was obtained on the more hydrophilic sample (CCCCC-treated surface), although the effect of surface charge should also be considered.

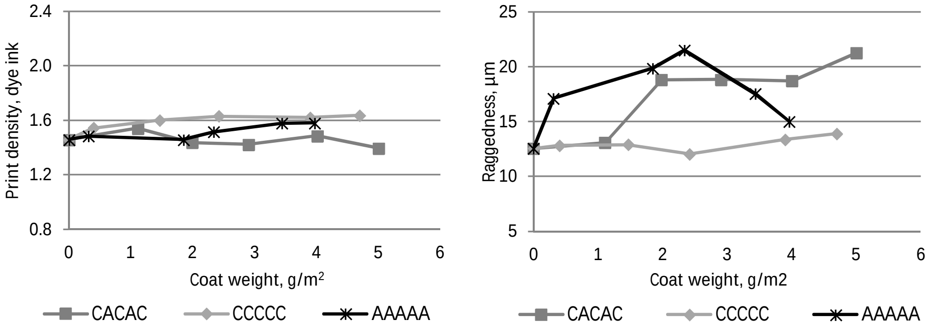

Figure 15 (a) Print density for the black ink and (b) horizontal bleeding (raggedness) of the red ink line. The standard deviation was 0.01–0.06 for the print density and 0.2–1.3µm for the bleeding.

With a CCCCC or AAAAA polyelectrolyte surface treatment the prints with dye-based ink showed little or no water fastness as was also demonstrated in Paper I. Both anionic and cationic coatings dissolve when immersed in water leading to detachment of the dye particles. An optimal coat weight of cationic polymers in respect to water fastness was found. At higher coat weights, the cationic layers dissolve in water together with the polymer coating. Water fastness properties for the cationic-anionic CACAC multilayer coating increased significantly, as shown in Figure 16, confirming that the multilayer structure creates a domain-like structure (Müller 2014) with electrostatic interaction between NaCMC and PDADMAC.

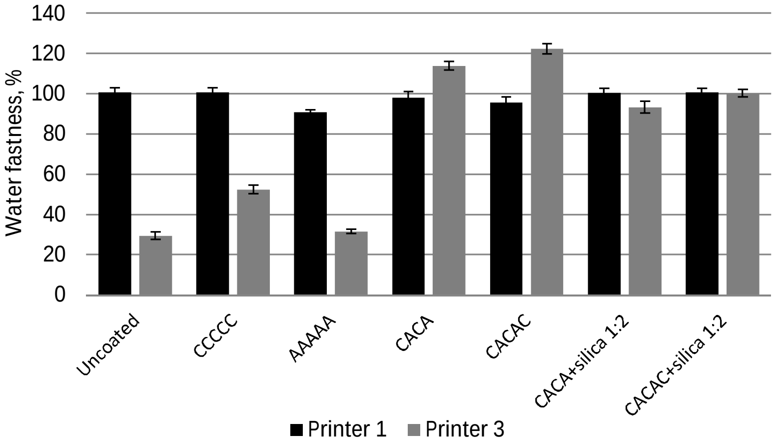

Figure 16 Water fastness values for the black pigment-based ink from printer 1 and dye-based ink from printer 3.

5.3 Print quality, absorption and wetting by ink when silica nanoparticles were added to polyelectrolyte multilayers (Paper II, Paper VI)

The aim of this study was to clarify how addition of nanoparticles in cationic-anionic polyelectrolyte multilayers influenced the liquid wetting properties, ink-substrate interactions and print quality.

5.3.1 Coating structure and characterization

Nanoparticles were mixed with cationic (PDADMAC) and anionic (NaCMC) polymer solutions in ratios of silica of 1:1 and 1:2 and multilayer polyelectrolyte surfaces were prepared as shown in Table VI, but only results when silica was added in a ratio of 1:2 are presented here. Figure 17 shows AFM images of the uncoated base paper (Figure 17a) revealing the microfibrillar structure of the fibers. Figure 17b shows that after the paper had been coated five times with alternating cationic and anionic polyelectrolyte (CACAC), a smooth polymeric film was obtained that covered the characteristic structure of the base paper. However, when fumed nanosilica was added to the corresponding cationic-anionic polyelectrolyte coating layers (Figure 17c), the structure of the paper surface became more textured disclosing fumed nanosilica on the surface of the paper.

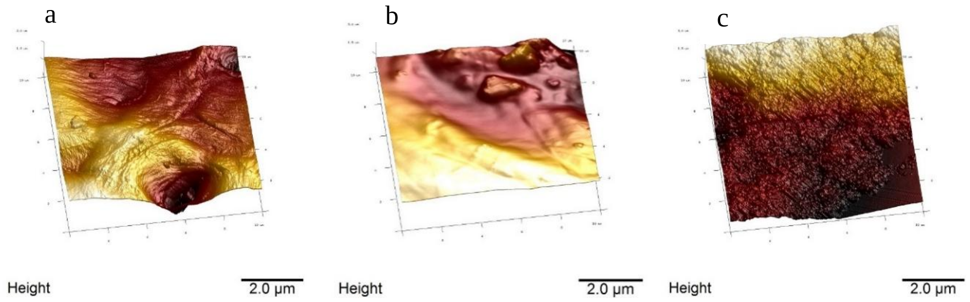

Figure 17 AFM images (height) of (a) base paper, (b) paper treated with CACAC and (c) a paper treated with CACAC + silica 1:2.

Surface spreading and absorption were assessed by determining the contact angles of water, EG and DIM on the surfaces. A study of the contact angles as a function of time (Figure 18a) indicated that some liquids displayed two or three different regimes, where the first linear regime was predominantly related to interfacial-driven spreading and absorption, while the later regimes were related to swelling and dissolution of the coating. The presence of silica particles in the CACAC coating reduced the contact angle, and facilitated a fast absorption of water because of increased wetting (Figure 18b). For these samples, the absorption times were similar to that of the reference sample, unlike the sample with CACAC treatment without silica. This enhanced wetting may be either because silica particles create less self-assembly between the polyelectrolyte layers or because the nanosilica enhances the pinning effect on the edge of the liquid drop (Starov et al. 2003, Fleischman et al. 2012). It has been demonstrated that the wettability of the surface can be controlled by the design of the multilayer structure (Yoo et al. 1998). We noticed here that the multilayer structure had a clear effect on wettability and liquid spreading. When silica was added to the cationic and anionic polyelectrolytes and when the coating was composed of five layers, the spreading of a water drop was significantly less than on a coating composed of only cationic or of cationic and anionic layers without the addition of silica particles.

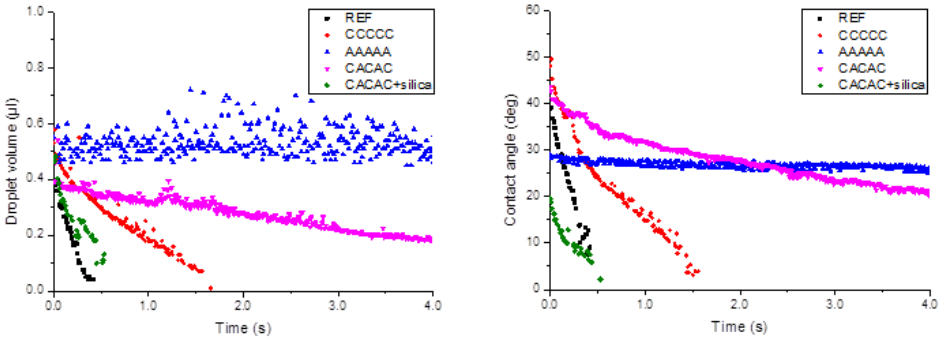

Figure 18 (a) volume of water droplet as a function of time and (b) contact angle of water as a function of time on the paper surface.

5.3.2 Interaction between substrate and pigment-based ink

When nanosilica was added to the polyelectrolyte layers in a ratio of 1:2, a reduction in print density was seen. On the fifth layer CACAC, the drop in print density of black print from printer 1 was 0.4 units when nanosilica was present (1.9 on CACAC and 1.5 on CACAC + silica 1:2). This reduction was probably due to the smaller effective amount of polymer in the coating.

The effect on mottling of added nanosilica can clearly be seen in Figure 19, where mottling values for the 100% black, yellow, magenta and cyan tone areas are presented. There is less mottling on the cationic than on the anionic surface. The fact that the pigment was fixed unevenly on the anionic surface suggests that anionicity and a dense surface may cause colorant particle depletion and flocculation. It is known that a disadvantage of using silica is that it may cause mottled inkjet prints (Hladnik 2005) and in Figure 19 it can be seen that mottling of the black ink is in all cases higher when the polyelectrolyte coatings comprise silica.

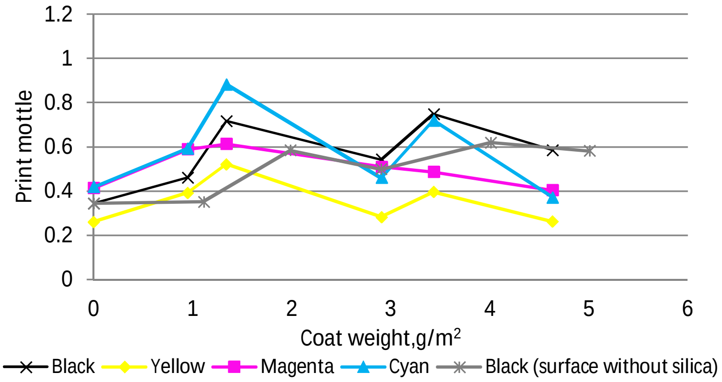

Figure 19 Mottling of the 100% black, yellow, magenta and cyan prints on C-, CA-, CAC, CACA- and CACAC- treated surfaces with nanosilica added in a ratio of 1:2 and for the black prints on the CACAC-treated surface without silica. Samples were printed with a pigment based ink. Standard deviation was 0.009-0.07.

With alternate layers of the cationic and anionic coating, bleeding of a horizontal line was somewhat unexpected. Strong bleeding was observed with a large number of cationic-anionic polyelectrolyte coating layers as seen in Figure 20. This bleeding could not be attributed solely to the chemistry of the ink-coating system but rather to the interaction between the alternating layers, and was probably due to the structuring effect, i.e., a change in the microscale roughness of the surface indicated by the contact angle results supports this finding, where larger amounts of nanosilica led to a faster lateral spreading of water seen here as inter-color bleeding.

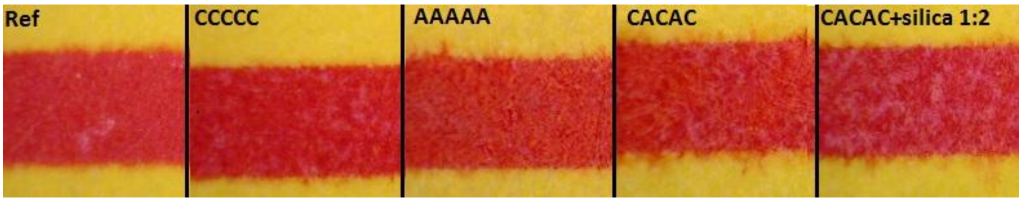

Figure 20 Photomicrographs of the lateral bleeding of red ink.

5.3.3 Interaction between substrate and dye-based ink

The print quality of the samples with added nanosilica printed with dye-based ink (printer 3) was evaluated in paper VI. When the number of layers increased from one (C) to five (CACAC), the print density increased from 1.4 to 1.7 (Figure 21). The nanosilica led to an increase in print density particularly on the fifth cationic-anionic layer (CACAC), an increase from 1.4 to 1.7

(Figure 22). Surface sizing with a fumed silica dispersion gave a more homogeneous pore structure, so that ink was absorbed more uniformly and efficiently (Batz-Sohn et al. 2009; Müller et al. 2014) leading to a higher print density. Nanosilica-based polyelectrolyte coatings also reduced the mottling with the dye-based ink by 50%, as shown in Figure 22. Vertical bleeding of the red ink on the fifth layer (CACAC) was 6 units smaller than on the sample without added silica.

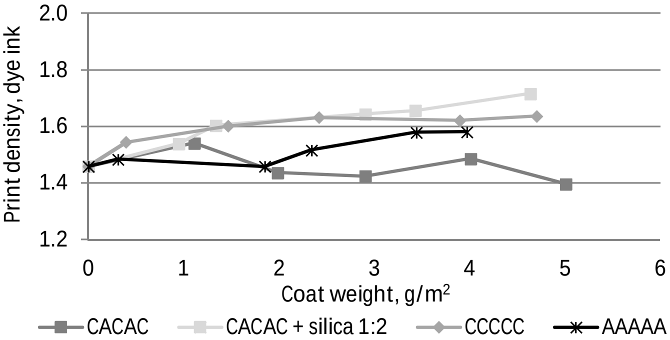

Figure 21 Print density values for the black dye-based ink. The standard deviation was between 0.01–0.06.

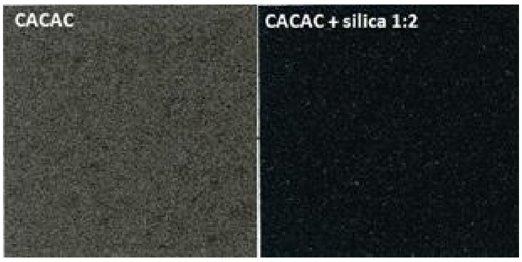

Figure 22 Scanned images in from sample from the 100% black ink areas printed on CACAC surfaces with and without silica.

Water-fastness of the dye-based ink on the multilayer-polyelectrolyte-treated surface was lower when nanosilica was incorporated than on papers without nanosilica, but the water fastness results were still at a good level, 93% on the CACA-treated surface and 100% on the CACAC-treated surface (Figure 15). Chen and Burch (2007) have studied different methods to convert the surface charge of fumed silica and they found that increasing the level of treatment improved only the water fastness and reduced bleeding, while the image quality and other deteriorated. In our study, bleeding of the black ink decreased slightly, but the bleeding of red ink increased.

5.4 Effect of a mineral-coated substrate on cationic-polyelectrolyte structure and the print quality (Paper III)

Commercial mineral-coated papers were surface-treated with cationic and anionic polyelectrolytes (CACAC) to determine the mechanism of ink absorption and spreading and the print quality.

5.4.1 Coating structure and characterization

The coatings were prepared with a size-press unit on a commercial one-side mineral-coated paper. The total amounts picked-up was determined but the different absorptivities and roughnesses of the top and reverse side, required another approach to determine the coat weight. Cross-section SEM images (Figure 23) showed that the amount of the CACAC coating layer was 0.5–1.0 g/m^2. The coat weights for three times (CAC) and four times (CACA) surface-treated papers were assessed to be in the range of 0.1–0.3 g/m^2, estimated from the total pick-up during surface sizing.

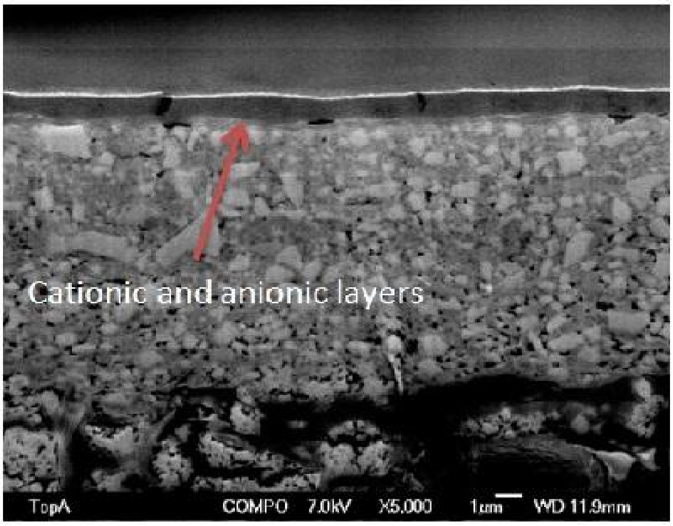

Figure 23 Cross-section SEM image of the five-time surface-treated CACAC sample printed with pigment ink 1.

XPS was used to determine the coverage of the NaCMC and PDADMAC on the mineral-coated side. Table VII shows the relative coverage of three different chemicals, PDADMAC, $CaCO_3$

and clay based on XPS measurements. The first PDADMAC layer (C) covered 30% of the surface and the coverage increased up to 60% with further cationic layers (CAC and CACAC). The PDADMAC surface coverage of the CACAC was almost identical to that of the CAC sample, which may depend on the surface sensitivity of XPS. As expected, the nitrogen amount did not increase greatly when the NaCMC was added (CA and CACA layers) but the clay and $CaCO_3$ signals diminished, indicating that at this point the CA and CACA did indeed cover most of the surface.

Table VII Relative surface coverages of PDADMAC, $CACO_3$ and clay.

Sample	Relative PDADMAC surface coverage (%) (based on N)	Relative PDADMAC surface coverage (%) (based on Cl)	Relative $CaCO_3$ coverage (%)	Relative clay coverage (%)
Ref	<1	<1	19	46
C	32	32	10	18
CA	40	31	4	4
CAC	56	62	3	<1
CACA	54	52	2	<1
CACAC	59	63	2	<1

Contact angles of water, EG and DIM were determined. Figure 24 shows that the hydrophilic character of the cationic-anionic layers was more evident when the number of coating layers increased. With DIM, the contact angle remained at approximately the same level of 50°, even for the CACA and CACAC layers. The drop volume remained unchanged during the measurement, indicating that the surface was relatively stable towards the non-polar liquid. The contact angle for EG was more dependent on the surface composition. The contact angle increased after deposition of the cationic polyelectrolyte (C), but decreased after deposition of the anionic NaCMC (CA). The change in contact angle was significant, although the coat weights for the anionic coating seemed to be relatively low. When the number of cationic–anionic polyelectrolyte layers was increased, the contact angle when the surface was cationic increased from 70° (C) to 85° (CACAC). The thin film apparently resisted absorption because the volume of the droplet remained the same during the measurement although the diameter of the droplet increased. XPS together with AFM and contact angle measurements showed that the thin polyelectrolyte complex layers change the surface chemistry and the wetting behavior.

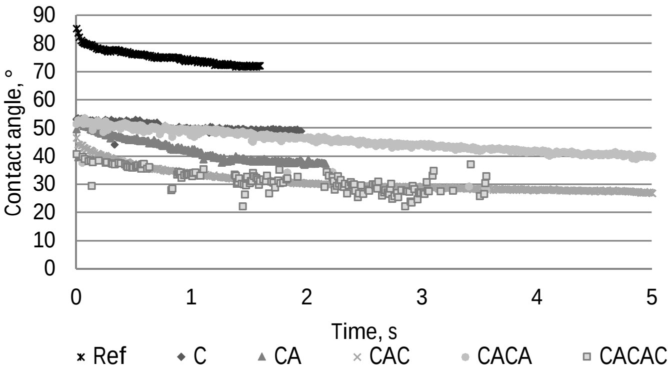

Figure 24 Contact angle of water as a function of time.

5.4.2 *Interaction between substrate and pigment-based ink*

The cationic–anionic polyelectrolyte surface treatment on the coated paper affected the print density, mottling and wicking particularly with the pigment-based ink. Figure 25 shows that the print density of the 100% black prints with ink 1 (printer 1) and ink 2 (printer 2) decreased with increasing numbers of multilayer polyelectrolyte surface treatments. There is a clear difference in density between these two pigment-based prints, probably related to a difference in the formulation of the inks. The print density of the black ink 1 was more dependent on the polyelectrolyte coating chemistry than the print density of ink 2. With an anionic polyelectrolyte on top of the cationic polyelectrolyte coating (CA, CACA), the print density was 3.0, which is very high on a coated paper. On the other hand, the dry adhesion test revealed that the adhesion of the ink was poor on these surfaces. The best ink adhesion was obtained with the CACAC surface, especially for the samples printed with ink 2. Tests revealed that the adhesion of the pigment-based inks was dependent on the surface chemistry and on the coat weight: the more hydrophilic the surface the stronger is the ink adhesion (surface energy in sample C 40.5 mN/m, in sample CA 47.0 mN/m and in sample CACAC 43.2 mN/m).

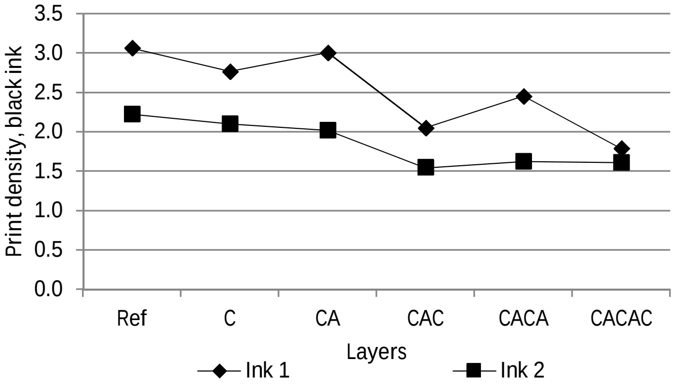

Figure 25 Print densities for the black prints made with ink 1 and ink 2. Standard deviation was between 0.01–0.08.

The degree of mottling on the black areas was clearly affected by the cationic-anionic polyelectrolyte surface treatment. The prints with ink 1 initially showed a decrease in print mottle, on the first two multilayers (C, CA) the mottling decreased from 0.65 to 0.45, but with further multilayers and particularly the cationic CAC and CACAC multilayers showed higher mottling values (1.1 on CAC and 1.7 on CACAC). This was considered to be partly due to substantial changes in the ink spreading behavior, causing discontinuities in the ink layer, as shown in Figure 26. One of the reasons for the cracking of the black and cyan printed surfaces (Figures 26a and 26b) might be spinodal dewetting behavior (Xie et al. 1998). Similar observations have also been reported by Ryu et al. (1999) who claimed that PDADMAC produces a hard, inflexible coating structure that tends to crack during drying. Khoultchaev and Graczyk (1999) gave no detailed explanation of the phenomenon of crack formation on prints made with pigment-based inks, but later (2001) they showed that a short drying time (60 s) can lead to crack formation on media printed with pigment-based inks.

The macro-roughness in unprinted and printed areas of the substrates prepared in this study (Paper III) was determined in order to see whether surface roughening induced by the surface treatment with polyelectrolytes affected the print evenness. RMS roughness values on the inked samples (black ink 1) were between 21 nm and 52 nm, so no clear effect on the surface cracking was found. With ink 2, on the other hand, no cracking behavior was noticed.

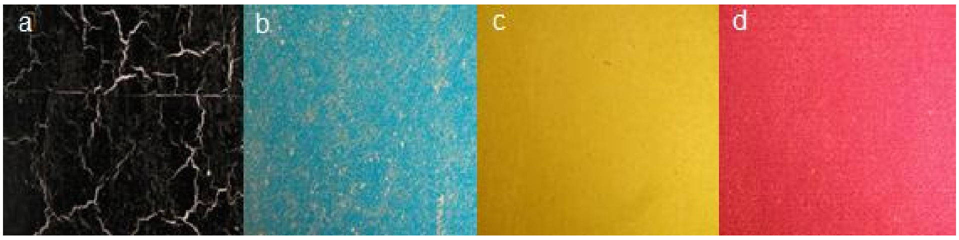

Figure 26 Photomicrographs of the CACAC samples printed on printer 1, 100% tone area; (a) black, (b) cyan, (c) yellow and (d) magenta. Magnification was 12.6 x.

Wicking of the black ink lines was determined and results are presented in Figure 27, which shows that the two inks used in this work behaved quite differently. The effect on the surface structure of the cationic-anionic polyelectrolyte surface treatment is more obvious with ink 1 where wicking was, quite surprising, greater on layers with the cationic polyelectrolyte on top of the coating. These results indicate that there is a relationship between the charge character of the coating layer (cationicity/anionicity) and the contact angle. It has been claimed that measurement of the contact angle is an efficient way to evaluate printing behavior (Moutinho et al. 2007; Park et al. 2007). In our study, a more rapid absorption of water by the base paper and the anionic CA layer corresponded to lower wicking values, while the CACA surface, which had a more hydrophobic character, also showed low wicking values. This confirms that a thin polyelectrolyte coating affects the print quality through electrostatic interaction, but the print quality also obviously depends on the absorption behavior. Strong bleeding (raggedness approx. 70µm) was observed for the ink 1 on first layer (C), but bleeding decreased with number of layers although it was still at a high level (35 µm on CACAC surface). Multilayer polyelectrolyte surface treatment had no effect on the bleeding of ink 2.

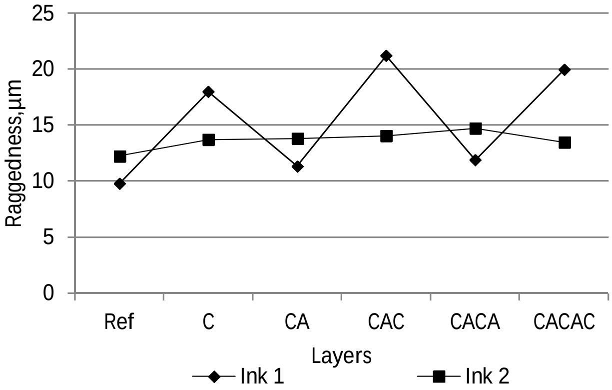

Figure 27 Wicking for the vertical black lines for ink 1 and ink 2. The standard deviation was between 0.3 and 2.0.

5.4.3 Interaction between substrate and dye-based ink

The print density of the 100% black print from printer 3 increased after the first (C) and second coating (CA), and then remained at the same level (approximately 2.0). The same behavior was seen for mottling and wicking, i.e. the first two layers affected the mottling and wicking. Bleeding increased on the first cationic layer and subsequent polyelectrolyte surface layers decreased the ink bleeding. Raggedness values decreased from 50 µm to 30 µm and were 20 µm smaller than those for the reference pigment-coated paper. There was no significant difference in bleeding between the CACA and CACAC samples suggesting that the cationicity or anionicity of the outermost layer did not affect the dye-based ink bleeding behavior, although it is known (e.g. Sreekumar et al. 2005b) that cationic additives improve line sharpness.

The cationic–anionic multilayer had a remarkable effect on the wet adhesion of the inks. The water fastness results shown in Figure 28 showed that with dye-based ink, cationic-anionic layers improved water fastness. Interestingly, the water fastness of the dye-based ink was highest on the surfaces where the top polyelectrolyte coating was anionic. This might be due to diffusion of the dye into the coating which thus protect the colorant to dissolve in water fastness tests. Water fastness results also showed that dissolution of the polyelectrolyte coating tended to occur when the amount of polyelectrolyte cationic-anionic coating layers increased. The roughness of the surface may influence the water fastness results (Vikman 2004), but the present results emphasize the role of interfacial adsorption sites for colorant fixation and the role of dissolution of the coatings, which thus requires sufficient anion–cation interdiffusion and subsequent cross-linking between NaCMC and PDADMAC to give a three-dimensional network (Müller 2014).

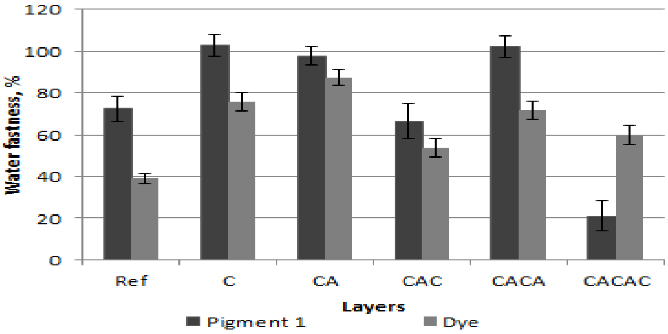

Figure 28 Water fastness results determined for the black pigment-based ink from printer 1 and the black dye-based ink from printer 3.

5.5 Effect on print quality of polyelectrolyte layer structure and level of internal sizing in the base paper (Paper IV and Paper V)

The aim of Papers IV and V was to determine the role of base substrate hydrophobicity on polyelectrolyte coating structure and its interaction with pigment-based (Paper IV) and dye-based (Paper V) inkjet inks. The wetting and spreading of the inks were studied with contact angles and XPS (Paper IV), with ink spreading tests (Paper V) and with SEM images (Paper IV and Paper V) and the print quality by means of print density, bleeding, wicking and water fastness was evaluated.

5.5.1 Coating structure and characterization

A wood-free 80 g/m^2 base papers containing different levels of internal sizing (alkyl succinic anhydride, ASA) was used as a substrate. The ASA dosage was 0, 0.5, 1.0 and 1.5 kg per ton of pulp. Three-layer surface treatments were carried out on the various substrates according to the wet-on-wet principle, *i.e.* AAA, CCC, CAC and ACA. The coat weight of the three-layers surface treated samples are presented in Table VIII.

Table VIII. Total coat weights of the three-layer coated samples.

ASA amount, kg/t	-	0.5	1.0	1.5
Total coat weight, g/m^2				
AAA	4.7	5.1	6.1	5.3
CCC	4.5	4.5	4.7	4.6
ACA	3.0	3.5	3.3	3.0
CAC	3.3	3.9	3.4	3.0

The non-impact spray-coating process and the three-layer coatings should provide good coverage, although the low viscosity of the liquids might lead to uneven spreading of the coating liquids. XPS was used to evaluate the surface compositions and coating coverages of the polyelectrolyte surface-treated samples, and it seemed that the coating layer distribution was not relatively even and that the spray treatment may lead to some absorption into the substrates and that this absorption is strongly affected by the viscosity of the coating solutions. With a single polyelectrolyte (AAA or CCC), the anionic coating was found to cover the substrate better, but the coverage was far from complete, even after three layers when the total coat weight was between 4.5 g/m^2 and 6.1 g/m^2. The oppositely charged polyelectrolyte coatings (ACA and CAC), on the other hand, gave clearly better coverage even though the coat weights were lower (3.0 g/m^2 and 3.9 g/m^2), which could be ascribed to stronger electrostatic interactions occurring during the wet-on-wet coating, leading to polyelectrolyte complex formation (Hubbe et al. 2005; Müller 2014) and subsequently gel formation with a high viscosity. However, the presence of the cationic polyelectrolyte, which has a greater affinity to the cellulose, will lead to a different coating structure and substrate coverage.

Contact angles were determined to characterize the wetting properties of the base paper and surface-treated papers. The internal sizing clearly gave a more hydrophobic surface especially at an ASA dosage of 1.0 kg/t and higher, with substantially no absorption or surface spreading on a short-time scale (< 5 s). It is known that internal sizing decreases the wetting by water and other fluids. With no internal sizing, the water droplet was absorbed very rapidly (on a time scale shorter than what we could measure with the current system) i.e. as soon as the droplet touched the paper surface (Figure 29a). Figure 29b, on the other hand, shows the contact angles of water (< 1 s) determined on surface-treated surfaces of substrates containing 0.5 kg/t of ASA. The three-layer PDADMAC coating (CCC), slightly decreased the hydrophilicity of the paper, since the contact angle for water increased. With the other multilayered polyelectrolyte coatings (ACA, CAC, AAA) the initial contact angle dropped from ca 70° to values between 25° and 30°.

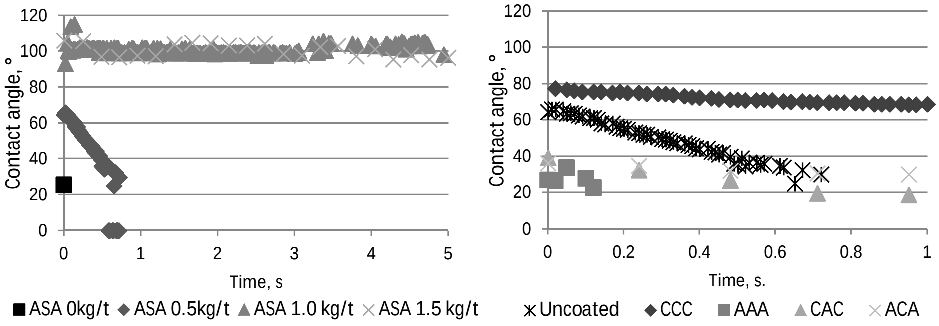

Figure 29 Contact angle of water determined on a) uncoated paper and b) multilayer polyelectrolyte surface-treated substrates with an internal sizing level of 0.5 kg/t.

5.5.2 Interaction between substrate and pigment-based ink

Print densities were measured on both untreated and coated papers. On the untreated paper, there were some differences in density value between the prints obtained with printer 1 and 2. There was no significant effect of the internal sizing on the densities of C, M, Y or K prints made with printer 1 (ink 1), but the highest print density value (1.6) was obtained for the black print from printer 2 (ink 2) on the substrate with 0.5 kg/t of ASA, although the level of internal sizing seemed to have only a small effect on the print density. These results thus disagree with the previous statement that highly sized papers give a high optical density with pigment-based inks (Pal et al. 2007).

The densities of the 100% black prints of the two inks on substrates having different levels of internal sizing and different polyelectrolyte multilayers are shown in Figure 30. The print density for the ink 1 tended to increase, with increasing internal sizing, but when the amount of ASA was 1.0 kg/t or higher, the density did not increase further (Figure 30a). The cationic polyelectrolyte (CCC and CAC) treatment gave the highest print density for a given level of internal sizing. This is in agreement with result reported in Paper II showing that cationic chemicals on the surface of the paper increase the print density.

Figure 30b shows, however, the opposite behavior with ink 2. CCC treatment gave the lowest print density when the amount of ASA in the base paper was high, and the same trend of decreasing print density with increasing internal sizing can be seen for the CAC-treated surface. An increase in density of prints with ink 2 with increasing level of internal sizing was observed only for the uncoated substrate and for the substrate coated with AAA, where the print density reached a maximum level when the ASA amount was 1.0 kg/t.

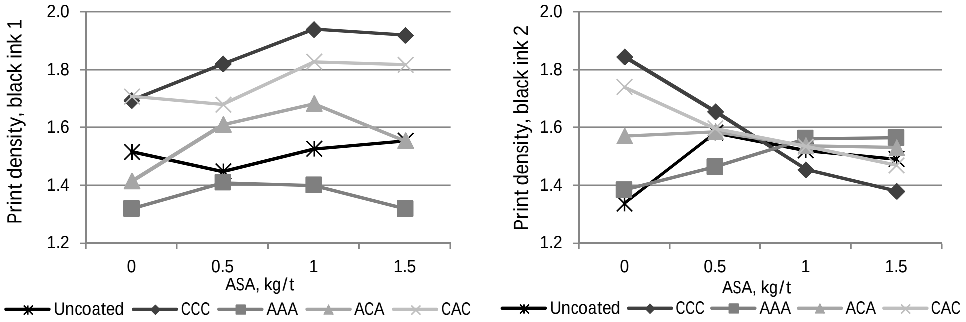

Figure 30 Print densities for (a) ink 1 and (b) ink 2 for the 100% black tone areas. The standard deviation was 0.03–0.10 for ink 1 and 0.02–0.11 for ink 2.

Mottling was determined for the black prints (100% areas) on the surface-treated papers. With both inks, the print mottle was lower on the surfaces containing cationic polyelectrolytes (CCC or CAC). The mottling on the uncoated reference was almost at the same level. On the substrate with an anionic coating (AAA), however, the mottling increased significantly with increasing amount of internal sizing (ASA) suggesting that a higher level of internal sizing leads to an uneven absorption and levelling of the inks. This suggests that ink spreading is strongly dependent on the evenness of the coating, and that this is in turn is affected by the hydrophobic character of the base substrate.

Although the print mottle increased indicating uneven ink absorption, the wicking decreased on the AAA sample prepared on the highly sized base substrate. Ink 1 showed low wicking on the cationic CCC and CAC samples. The values decreased with increasing level of internal sizing. Ink 2 behaved differently from ink 1 and the internal sizing dosage did not greatly affect the results. The raggedness of the lines was lowest on the uncoated base paper, so that in this case the surface treatment increased wicking. On the other surfaces, the raggedness values were very similar (15–20 units). Bleeding results for ink 2 were similar to the wicking results, the lowest values being obtained on the uncoated base paper.

Figure 31 shows photomicrographs illustrating the spreading behavior of the inks after 30 s and 240 s on the uncoated and surface-treated paper when the ASA dosage was 1.5 kg/t. On the AAA surface, ink 1 is probably absorbed through the paper and does not separate like the other droplets, the droplet diameter being the same (4.4 mm) after 30 s and 240 s, see Table 4. However, the boundary line of the droplet on the AAA-surface is uneven compared with that on the CCC- and CAC- surfaces. This is in agreement with the wicking values where the boundary line was even and the ink vehicle spread laterally. The greatest spreading after 240 s was on the CAC (1.99 mm) and CCC (1.69 mm) surfaces, but the edge of the droplet is most even suggesting that internal sizing reduces the ink penetration but that a cationic surface binds the ink pigment and the water-based vehicle spreads laterally. These result are in line with those of Riebeling (1994) who showed that internal and surface sizing lower the paper surface energy and make the paper surface sufficiently hydrophobic to retard wetting and penetration into the structure by the black ink.

The spreading of ink 2 is also in line with the wicking results, showing that the drop boundary spreads unevenly on every surface with a tendency to feathering. On the cationic CCC surfaces, the drop diameter was relatively small confirming that the cationic coating is able to capture the pigment particles. In this case, the ink was immobilized whereas the ink vehicle spread on the surface. On the AAA and ACA samples, spreading of the liquid phase can be seen and there is also a strong tendency for the pigment to spread, which means that the ink particles are not trapped by the coating. On the CAC coating, a behavior intermediate between that on the AAA and CCC coatings was observed.

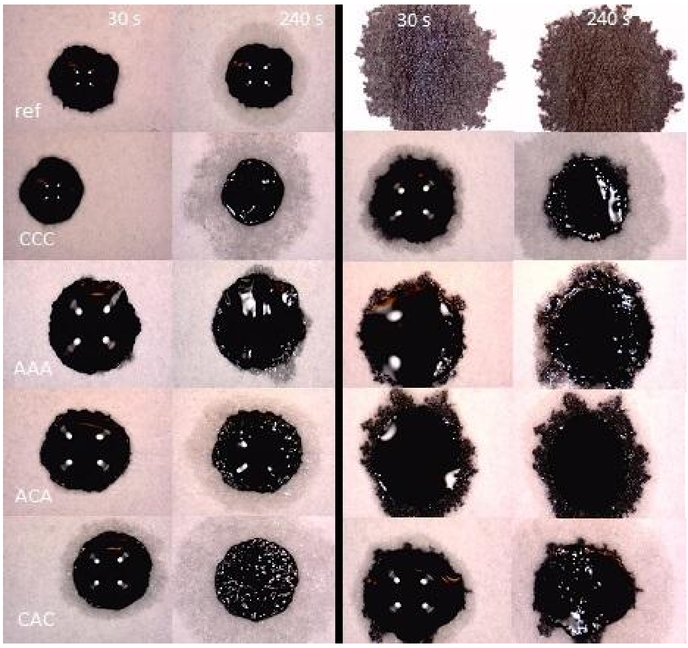

Figure 31 Spreading of ink droplet (volume 2µl) after 30 s and 240 s on surface-treated substrates with on internal sizing level of 1.5 kg/t. On the left ink 1 and on the right ink 2.

Figure 32a shows that the water fastness of the ink 1 was almost 100% on the uncoated and surface-coated samples regardless of the level of internal sizing, except for the sample with the anionic AAA coating. The water fastness of ink 2 (Figure 32b) was similar to that of ink 1 but the water fastness for the CCC-coated sample increased from 100% to 130% with increasing level of base paper hydrophobicity. This is probably because the cationic polyelectrolyte is not absorbed into the paper but stays on the top of the internal sized paper and causes a post-levelling effect of the ink (Shaw-Klein 1998) which was more obvious when the hydrophobicity of the base paper was higher.

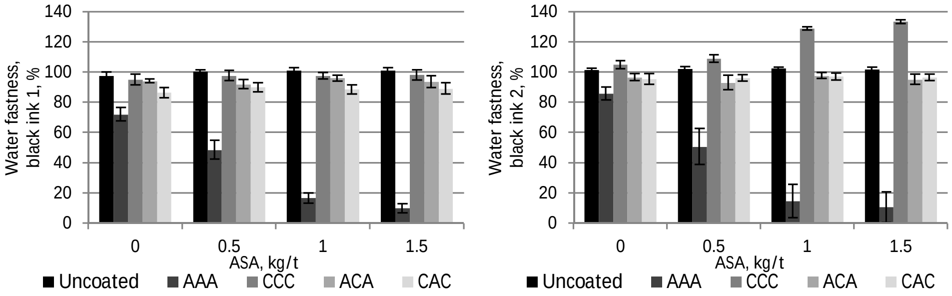

Figure 32 Water fastness values for (a) black ink 1 and (b) black ink 2.

High resolution cross-section SEM images (Figure 33a) confirmed that, after the water fastness test, the thin AAA coating layer (ASA dosage 1.5 kg/t) printed with ink 1 had been removed from the top of the paper. Both prints on the ACA-coated papers revealed good water fastness behavior, which was confirmed in SEM images (Figure 33b). The cross-section images confirm that the ACA layer is still present after the water fastness test and the cationic layer in the middle of the multilayer structure probably binds the pigment ink.

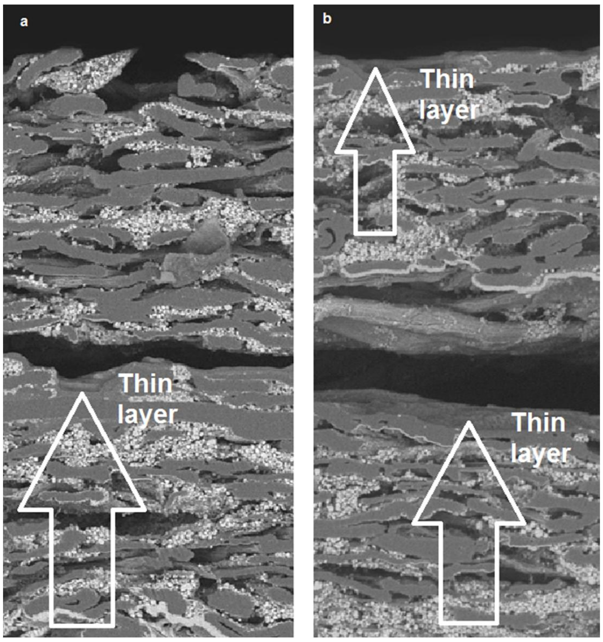

Figure 33 Cross-section SEM micrographs for the printed, a) AAA-treated sample and b ACA-treated sample before (bottom) and after (top) the water fastness test.

5.5.3 Interaction between substrate and dye-based ink

The print density of the dye-based black prints made with printer 3 on the uncoated substrates was not greatly affected by the ASA dosage. The density level was less than 1.4, implying relatively low dye retention on the surface of the substrate (Figure 34). With other inks (C, M, Y) the print densities were unchanged, when the internal sizing dosage was changed. This partly contradicts the results of other studies which have reported that internal sizing reduces ink penetration (Yang et al. 2005). A plausible explanation of this disagreement is a difference in compositions of the inkjet inks.

On the AAA-, CAC- and ACA-surface, the print density was lower than on the CCC surface which is in agreement with paper VI where it was shown that a cationic surface increases the print density and the ability to fix the dye colorant. When the level of ASA was increased, the density of the print on the CCC-surface increased and was 0.4 units higher than on the uncoated surface when the ASA dosage was 1.5 kg/t. The polyelectrolyte complexes (CAC and ACA) are obviously not sufficiently cationic to provide enough fixation sites for the dye colorants. The results demonstrate that a cationic or cationic-anionic three-layer structure is sufficient to give a common targeted density level of 1.5 for the black ink (Kipphan 2001) and this is also in agreement with the density data Papers III and VI where the same density level was achieved after a three-layer treatment.

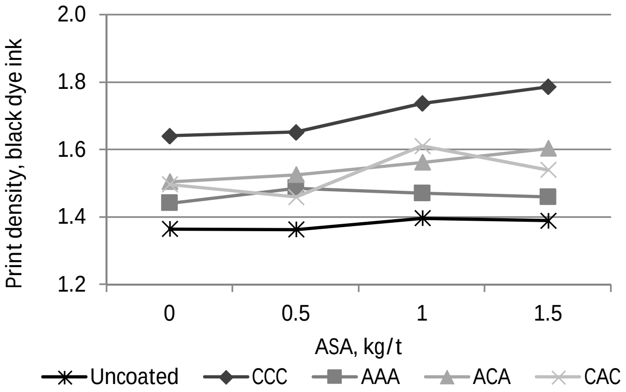

Figure 34 Print density of the dye-based ink in the 100% black tone areas. The standard deviation was between 0.01 and 0.07.

The mottling values for the black ink were lowest (0.38 units) on the uncoated reference. On the AAA-surface, the mottling increased with increasing ASA dosage, being highest (1.0 units) when the ASA dosage was 1.5 kg/t. This is probably caused by the hydrophobic character of the paper surface in combination with the uneven structure and coverage of the anionic NaCMC. The effect of uneven ink spreading on the hydrophobic paper substrate and on regions with amphiphilic NaCMC was pronounced and both the contact angle data and the XPS results revealed low coverage. Bleeding and wicking on the AAA-surface was much higher (raggedness approx. 20 µm) than on the CCC-treated surface (the raggedness approx. 12 µm) which is in line e.g. the study by Stankovska et al. (2014) who showed that cationic treatment improves the line sharpness. This is also in agreement with the contact angle measurements which show that the cationic CCC layers created a hydrophobic surface while the AAA-treated surface was hydrophilic. CAC and ACA gave a hydrophilic character to the surface but the absorption rate was lower than that with the AAA surface, which is probably because PDADMAC probably cross-links with NaCMC (Lefebvre and Grey, 2005). On the other surfaces (uncoated, CAC and ACA), multilayer polyelectrolyte surface treatment had practically no effect on ink spreading or mottling.

The water fastness for the black dye-based ink on the CAC and particularly on the ACA surface (Figure 35a) was substantially higher than that on the CCC surface, which further suggests that the water fastness is strongly dependent on the interfacial coating chemistry, the solubility of coating and its ability to absorb the colorant. This is in line with the water fastness results presented in Paper III. Adding a cationic substance to the coating layer retarded the ink penetration into the paper structure by reducing the coating permeability and bound the anionic colorant at the top layer by charge interaction (Lamminmäki et al. 2011). However, it was surprising to see that the cationic surface treatment (CCC) was not sufficient to improve the dye fixation when the printed materials was immersed in water. This is claimed to be caused by dissolution of both anionic dye molecules and the cationic polymer, which occurs particularly at higher coat weights when the interfacial coating between the substrate and ink is dissolved (Paper I). It has also earlier been shown by Hoogeveen et al. (1996) that, for stable multilayers of strongly charged cationic and anionic polyelectrolytes, the influence of the substrate is restricted to only the first few layers. In our study, we had only three anionic-cationic layers, e.g. CAC and ACA, and there was some dependence of the water fastness on the base paper hydrophobicity. It is assumed that the colorant-capturing mechanism is affected more by the presence and structure of the polyelectrolyte complexes rather than by the ability of the polyelectrolyte coating to charge-neutralize the colorant molecules.

The amount of organic compounds as COD values in dilution after the water fastness test are presented together with the water fastness results in Figure 35b. The greater the amount of organic compounds, the lower is the water fastness, indicating that AAA and CCC surface layers are dissolved in water during the water fastness test. ACA treatment creates a surface that binds the anionic ink to the cationic middle layer.

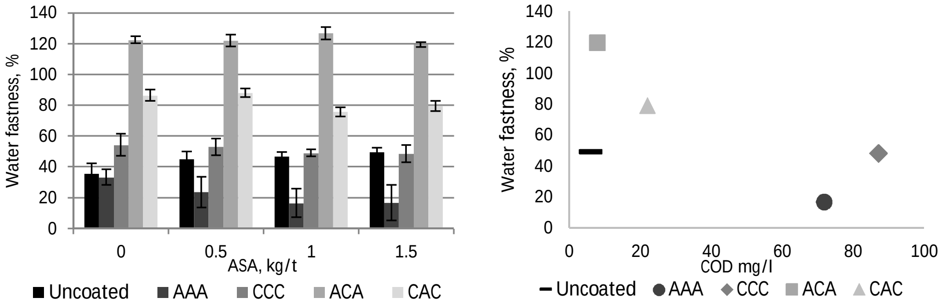

Figure 35 (a) Water fastness values for the black dye-based ink and (b) water fastness plotted against the COD values for the samples when ASA amount is 1.5 kg/t.

6 CONCLUDING REMARKS

The goal of this work was to clarify the mechanism of a cationic-anionic multilayer polyelectrolyte surface treatment on a paper surface and its effect on inkjet print quality and on ink absorption and spreading. The roles of multilayer structures, coat weights and number of layers of the coatings of particularly anionic NaCMC and cationic PDADMAC were determined. In addition to gaining an understanding of how to design a surface for inkjet inks, this work demonstrated that the alternating cationic and anionic multilayer method can be used as a tool to investigate ink spreading and absorption phenomena on fiber-based substrates.

Surfaces were characterized and absorption and wetting properties were studied through contact angle determinations and AFM, SEM and CLSM analyses. It was shown that number and order of the polyelectrolyte layers have an effect on both water absorption and spreading. For example, when the surface was treated with the cationic polyelectrolyte, the absorption time slightly increased and when the surface was coated with cationic-anionic layers, the absorption of water was much slower indicating more complex wetting behavior. On the other hand, by using different base paper, different results were obtained emphasizing the role of base substrate on wetting behavior. The contact angle of water on the anionic surface was usually smaller than that on the cationic surface, indicating fast spreading and wetting.

The print quality was characterized by means of optical density, mottling, bleeding, wicking and water fastness. Table IX presents summary of how the various coatings affected the quality of prints made from pigment-based and dye-based inks. It shows that there are differences in the effects of cationic chemicals with different charge densities. The cationic-anionic surface treatment affects the print density, mottling and line raggedness particularly with pigment-based inks. With dye-based inks, the effects of polyelectrolyte multilayers on print quality were less pronounced.

It was shown that a small amount of cationic chemicals is sufficient to improve the print quality. If the coat weight or the number of layers is too high, the print quality may decline and the adhesion become poorer which was demonstrated with water fastness tests. In most cases, a three-layer cationic-anionic treatment was sufficient to produce a surface with good printability properties, although the base paper hydrophobicity also affected the print density results. The order of layers in the multilayer structure plays an essential role, particularly with regard to the ink adhesion and colorant fixation, and it was shown that water fastness is better, especially for the dye-based inks, if the cationic-anionic polyelectrolyte treatment is used instead of a totally cationic or totally anionic treatment and that water fastness was better on the ACA-treated surface than on the CAC-treated surface. It was confirmed that alternating cationic and anionic layers provide alternating surface-charge characteristics and this helps to understand the mechanisms of ink fixation and by optimizing the chemistry of the layers, the important ink–substrate interactions can be optimized.

It was demonstrated that the addition of fumed nanosilica to the coatings significantly increased the rate of absorption of the ink, which could be attributed to the effect of the nanostructure of the coating on the wetting front. The effect of the fumed silica in the alternating polycationic and polyanionic layers on the ink-substrate interaction was less pronounced, but it seemed to result in enhanced solvent absorbency. Nanosilica in the coating played a more important role when the prints were made with dye-based ink and the print density could be increased by adding nanosilica to the polyelectrolyte layer.

Finally, the study showed that multilayer polyelectrolyte surface treatment of paper substrates with different levels of internal sizing had various effects on the water absorption and spreading assessed from contact angle measurements. When a surface is treated with cationic-anionic polyelectrolytes, the effect on the surface hydrophobicity or hydrophilicity depends on the order and number of layers.

Table IX Summary of the effects of coating structure and composition on the properties of the printed samples.

	Role of various polyelectrolytes, Paper I	The effect of the order of addition Paper II- Paper VI	Number of multilayers Paper II- Paper VI	The role of nanosilica Paper II and Paper VI	Role of the base substrate hydrophobicity Paper IV, Paper V
Property	Pigment-based black ink				
Density	PEI-coating increased print density NaCMC increased print density PDADMAC had no significant effect	Higher print density on cationic top coatings, e.g. CAC is better than ACA and CCCCC is better than CACAC In some case also anionic treatment increased density	Highest print density was achieved after two layer (CA) In Paper II the max. print density was achieved after four layers	Print density increased when nanosilica was used	Base substrate hydrophobicity had an effect on density, which depended on ink type
Mottling	PEI and PVAm1 decreased mottling	Mottling increased on totally cationic surface (CCCCC) Cationic-anionic-treatment increased	Mottling increased when the number of layers increased	Mottling increased	Mottling increased on AAA surface and when hydrophobicity increased
Bleeding	PEI and PVAm2 increased bleeding	Bleeding decreased when surface was cationic, but depends on pigment ink type	No significant effect on bleeding	Bleeding slightly decreased	Decrease when hydrophobicity increased
Wicking	PEI, PVAm1 and PVAm2 decreased wicking	Cationic surface but also anionic treatment in some cases reduced wicking	Wicking increase when the layer increased	Wicking increased	Wicking decreased when the hydrophobicity increased
Water fastness	PEI, PVAm1, PVAm2 and PDADMAC had a good water fastness when the coat weight was not too high	Anionic treatment only decreased, cationic-anionic-treatment increased the water fastness	Three layers were enough to achieve good water fastness	Water fastness improves	On AAA-treated surface, decrease when the hydrophobicity increased
Property	Dye-based black ink				
Density	PEI and PDADMAC slightly increased print density	Print density was higher on totally cationic surface, in some case, anionic treatment increased the print density	Print density was higher on first two layers, then decreased	Print density increased when nanosilica was used	Print density slightly increased on CCC-treated surface when the hydrophobicity increased
Mottling	Mottling increased on all surfaces	Mottling higher on anionic surfaces	Mottling increased when number of layers increase	Mottling decreased compared to sample without silica	Increase on AAA surface when hydrophobicity increased
Bleeding	Bleeding increased on all surfaces	Bleeding decreased when the surface was cationic and increased when it was anionic	Number of layer increased bleeding	Lower than the same sample without silica but higher than the reference	No effect on bleeding
Wicking	PEI and PVAm1 decreased wicking	Cationic treatment increased wicking	Decreased when the number of layers increase	Wicking increased	No effect on wicking
Water fastness	PVAm2 and PEI had good water fastness	ACA gives better water fastness that CAC Cationic-anionic structure is needed	Three layers were sufficient (CAC vs. CACA or CACAC)	Water fastness improved	No effect on water fastness

7 REFERENCES

Agbezuge, L. (1991). *Drying of Ink Jet Images on Plain paper - Falling Rate period* In: NIP7: International Conference on Digital Printing Technologies, Society for Imaging Science and Technology, Portland, Oregon, USA. p. 173.

Andres, C. M. and Kotov, N. A. (2010). Inkjet deposition of layer-by-layer assembled films. *Journal of the American Chemical Society*, 132(41), pp. 14496–14502.

Batten, G.L., Jr. (1995). Effects of SMA surface sizes on paper end-use properties. *Tappi journal* 78(1), pp. 142–146.

Bares, S.J. and Rennels, K.D. (1990). Paper compatibility with next generation's ink-jet printers. *Tappi journal*, 73(1), pp. 123–125.

Barker, L. J., dePierne, O. S. and Proverb, R. J. (1992). Effects of Surface-size on Printability of Alkaline Paper in Inkjet Print Tests. 1992 International Printing and Graphic Arts Conference. Pittsburgh, PA, USA, pp. 355–359.

Batz-Sohn, C. Nelli, L. and Müller, A. (2009). *Improving Inkjet Print Performance of Plain Sized Paper with Nanostructured Pigments*. In: NIP25 and Digital Fabrication, Society for Imaging Science and Technology, Louisville, Kentucky, USA, pp. 539–542.

Bigianti M. and Lanter A. (2014*). Digital Printing Leads to Print Finishing Opportunities, The Binding edge, Digital Printing Leads to Print Finishing Opportunities*. [Retrieved Apr. 1, 2015], url: http://www.thebindingedge.com/stories/112614/digital-printing-leads-print-finishing-opportunities.shtml#.VS5ZqWP3T5o

Bollström, R., Määttänen, A., Tobjörk, D., Ihalainen, P., Kaihovirta, N., Österbacka, R., Peltonen, J. and Toivakka, M. (2009). A multilayer coated fiber-based substrate suitable for printed functionality. *Organic Electronics*, 10(5), pp. 1020–1023.

Bristow, J. A. (1967). Liquid Absorption into Paper during Short Time Intervals, Svensk Papperstidning 70(19), 623–629.

Chang, C. J., Chang, S. J., Tsou, S., Chen, S. I., Wu, F. M. and Hsu, M. W. (2003). Effects of polymeric dispersants and surfactants on the dispersing stability and high-speed-jetting properties of aqueous-pigment-based ink-jet inks. *Journal of Polymer Science Part B: Polymer Physics*, 41(16), pp. 1909–1920.

Chapman, D. M. and Michos, D. (2000). Novel silica gels for glossy, ink-receptive coatings. *Journal of Imaging Science and Technology*, 44(5), pp. 418–422.

Chen, T. and Burch, E. (2007). *High Performance Porous Inkjet Media Derived from Fumed Silica.* In: NIP23 and Digital fabrication, Society for Imaging Science and Technology, Anchorage Alaska, USA, pp. 110–113.

Chiono, V., Carmagnola, I., Gentile, P., Boccafoschi, F., Tonda-Turo, C., Ballarini, M., Ventsislava, G., Georiev, G. and Ciardelli, G. (2012). Layer-by-layer coating of photoactive polymers for biomedical applications. *Surface and Coatings Technology*, 206(8), pp. 2446–2453.

Costa, T. G., Gamelas, J. A., Moutinho, I. M., Figueiredo, M. and Ferreira, P. J. (2010). The influence of paper surface sizing on inkjet pigment penetration. *Appita Journal*, 63(5), p. 392.

Desie, G. and van Roost, C. (2006). Validation of ink media interaction mechanisms for dye and pigment-based aqueous and solvent inks. *Journal of Imaging Science and Technology*, 50(3), pp. 294–303.

Donigian, D. W., Wernett, P. C., McFadden, M. and G. McKay, J. J. (1999). Ink-jet dye fixation and coating pigments. *Tappi Journal*, 82(8), pp. 175–182.

Dubas, S. T., Kumlangdudsana, P. and Potiyaraj, P. (2006). Layer-by-layer deposition of antimicrobial silver nanoparticles on textile fibers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 289(1), pp. 105–109.

Fleischman, M. S., Lee, B. S., Rodriguez-Santiago, V., Chhasatia, V., Sun, Y. and Pappas, D. D. (2012). Hybrid method involving atmospheric plasma treatment and inkjet deposition for the development of conductive patterns on flexible polymers. *Surface and Coatings Technology*, 206(19), pp. 3923–3930.

Fryberg, M. (2005). Dyes for ink–jet printing. *Review of Progress in Coloration and Related Topics*, 35(1), pp. 1–30.

Fu, X., Pal, L. and Zhou X. (2014). Post-treatment solution for digital inkjet printing, US 20140141212 A1 patent.

Girard, F., Attane, P. and Morin, V. (2006). A new analytical model for impact and spreading of one drop: application to inkjet printing. *Tappi journal*, *5*(12), pp. 24–32.

Glittenberg, D., Voigt, A. and Becker, A. (2002). *Available Options for Mass Production of High-Grade Ink-Jet Papers*. In Proceedings from TAPPI Metered Size Press Forum, Atlanta, GA, USA. pp. 229–233.

Glittenberg, D. Voigt, A. and Donigian, D. (2003). Novel pigment-starch combination for the online and offline coating of high-quality inkjet papers, *Paper Technology*, 44(7), pp. 36–42.

Gong, R. Fleming, P.D. and Sonmez, S. (2010). *Application of Nano Pigments in Inkjet Paper Coating*. In: NIP26 & Digital Fabrication Conference. Society for Imaging Science and Technology, Austin, Texas, USA, pp. 507–511.

Hakola, E. and Oittinen, P. (2009). Principles of digital printing. In: Oittinen P. and Saarelma H. Eds. *Papermaking Science and Technology*, Book 13, Fapet Oy, Jyväskylä, pp. 147–172.

Hamada, H. and Bousfield. D. W. (2009). Effect of cationic additives on ink penetration. *Journal of Pulp and Paper Science*, 35(3-4), pp. 118–122.

Hamilton, J. (2012). High-Speed Monochrome and Color Inkjet in Hybrid Configurations, InfoTrends, [Retrieved Aug. 17, 2015], url: http://www.infotrends.com/public/content/freedownloads/downloadfiles/kodakhybrid.pdf

Hejda, F., Solar, P. and Kousal, J. (2010). Surface Free Energy Determination by Contact Angle Measurements–A Comparison of Various Approaches. In: *WDS* 10 pp. 25–30.

Hewlett-Packard Development Company, HP. (2014). Inks for HP PageWide Technology, Technical white paper, [Retrieved Aug. 12, 2015], url: http://www.hp.com/hpinfo/newsroom/press_kits/2014/DesignjetProduction2014/PageWide_Inks.pdf

Hewlett-Packard Development Company, HP. (2012). ColorLok® Backgrounder, [Retrieved Aug. 12, 2015], url: http://www.hp.com/hpinfo/newsroom/press_kits/2014/DesignjetProduction2014/PageWide_Inks.pdf

Hladnik, A. (2005). Use of Specialty Pigments in High End Inkjet Paper Coating, *Journal of Dispersion Science and Technology*, 25(4), pp. 481–489.

Hoogeveen, N. G., Cohen Stuart, M. A., Fleer, G. J. and Böhmer, M. R. (1996). Formation and stability of multilayers of polyelectrolytes. *Langmuir*, 12(15), pp. 3675–3681

Hubbe, M. A., Moore, S. M. and Lee, S. Y. (2005). Effects of charge ratios and cationic polymer nature on polyelectrolyte complex deposition onto cellulose. *Industrial & engineering chemistry research*, 44(9), pp. 3068–3074.

Hubbe, M. A. (2007). Paper's resistance to wetting–A review of internal sizing chemicals and their effects. *BioResources*, *2*(1), pp. 106–145.

Izquierdo, A., Ono, S. S., Voegel, J. C., Schaaf, P. and Decher, G. (2005). Dipping versus spraying: exploring the deposition conditions for speeding up layer-by-layer assembly. *Langmuir*, 21(16), pp. 7558–7567.

Johansson, L.-S. and Campbell, J. M. (2004). Reproducible XPS on biopolymers: cellulose studies. *Surface and interface analysis*, 36(8), pp. 1018–1022.

Johansson, E. and Wågberg, L. (2012). Tailoring the mechanical properties of starch-containing layer-by-layer films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *394*, pp. 14–22.

Johnson, P. M., Yoon, J., Kelly, J. Y., Howarter, J. A. and Stafford, C. M. (2012). Molecular layer-by-layer deposition of highly crosslinked polyamide films. *Journal of Polymer Science Part B: Polymer Physics*, 50(3), pp. 168–173.

Jonckherree, E. and Mabire, F. (2003). Improving the waterfastness of high quality matt and glossy ink-jet printing papers. *Paper technology*, 44(6), pp. 38–44.

Järnström, J., Järn, M., Tåg, C. M., Peltonen, J. and Rosenholm, J. B. (2011). Liquid Spreading on Ink-Jet Paper Evaluated by the Hydrodynamic and Molecular-Kinetic Models. *Journal of Adhesion Science and Technology*, 25(6-7), pp. 761–779.

Kallio, T., Kekkonen, J. and Stenius, P. (2006). Acid/base properties and adsorption of an azo dye on coating pigments. *Journal of dispersion science and technology*, 27(6), pp. 825–834.

Kettle, J., Lamminmäki, T. and Gane, P. (2010). A review of modified surfaces for high speed inkjet coating, *Surface and Coating Technology*, 204(12–13), pp. 2103–2109.

Khoultchaev, K and Graczyk, T. (1999). *Polymer–polymer and polymer-pigment interactions-implications on Ink Jet*. Universal Media, TAPPI Coating Conference.

Khoultchaev, K. and Graczyk, T. (2001). Influence of Polymer-Polymer Interactions on Properties of Ink Jet Coatings. *Journal of Imaging Science and Technology*, 45(1), pp. 16–23.

Kilpelä, T. and Manner, H.J. (2000). *Internal and surface sizing of inkjet printing papers printing and graphic arts*. In: Conference, International printing and graphic arts TAPPI Press. Pp. 245–250

Kim, D. W., Ku, B. C., Steeves, D., Nagarajan, R., Blumstein, A., Kumar, J., Gibson, P. W., Ratto, J. A. and Samuelson, L. A. (2006). Hydrophobic barrier: Molecular self-assembly of amphiphilic polyacetylenes within aluminosilicate nanoplatelets. *Journal of membrane science*, 275(1), pp. 12–16.

Kim, B. S., Lee, S. W., Yoon, H., Strano, M. S., Shao-Horn, Y. and Hammond, P. T. (2010). Pattern transfer printing of multiwalled carbon nanotube multilayers and application in biosensors. *Chemistry of Materials*, 22(16), pp. 4791–4797.

Kipphan, H. (Ed.). (2001). *Handbook of print media: technologies and production methods*. Springer, Germany. 1207 p.

Kodak. (2010). Kodak Announces Comprehensive Paper Strategy for KODAK PROSPER Press Platform [Retrieved Aug. 13, 2015], url: http://www.zieglerpapier.com/en/home/kom-archiv.htm?id=6900

Landa. (2015). The Nanographic Printing® Process, White paper, [Retrieved Aug. 13, 2015] url: http://www.landanano.com/nanography/nanoink, 12 p.

Lamminmäki, T. (2012). *The comparative dynamics of bulk liquid flow and interpolymer diffusion during inkjet ink imbibition in porous coating structures*. VTT Technical Research Centre of Finland.

Lamminmäki, T., Kenttä, E., Rautkoski, H., Bachér, J., Teir, S., Kettle, J. and Sarlin, J. (2013). New Silica Coating Pigment for Inkjet Papers from Mining Industry Sidestreams. *Journal of Surface Engineered Materials and Advanced Technology*, 3(3), pp. 224–234.

Lamminmäki, T. T., Kettle, J. and Gane. P. A. C. (2011). 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(1), pp. 79–88.

Lamminmäki, T., Kettle, J.P., Puukko, P., Gane, P.A.C. and Ridgway, C. (2009). Inkjet print quality: The role of polyvinyl alcohol in speciality $CaCO_3$ coatings. *Journal of Pulp and Paper Science*, 35(3-4), pp. 137–147

Lamminmäki, T. Kettle, J. Puukko, P. Ketoja, J. and Gane, P. (2010). The role of binder type in determining inkjet print quality. *Nordic Pulp and Paper Research Journal*, 25(3), pp. 380–390.

Lavery, A. and Provost, J. (1997). *Color-media interactions in ink jet printing*. In: NIP13: International Conference on Digital Printing Technologies, The Society for Imaging Science and Technology, Seattle, Washington, USA, pp. 437–442.

Lee, H. K., Joyce, M. K. and Fleming, P. D. (2005a). Influence of pigment particle size and pigment ratio on printability of glossy ink jet paper coatings. *Journal of Imaging Science and Technology*, 49(1), pp. 54–60.

Lee, H.-K., Joyce, M.K., Fleming, P.D. and Cameron, J. (2002). *Production of a single coated glossy inkjet paper using conventional coating and calendaring methods*, Proceedings of the TAPPI Coating Conference, 24 p.

Lee, H-K. Joyce, M. Fleming, P. and Cawthorne, J. (2005b). Influence of Silica and Alumina Oxide on Coating Structure and Print Quality of Ink. *Tappi Journal*, 4(2), pp. 11–16.

Lefebvre, J. and Gray, D.G. (2005). AFM of adsorbed polyelectrolytes on cellulose I surfaces spin-coated on silicon wafers, *Cellulose*, 12(2), pp. 127–134.

Leterrier, Y., Singh, B., Bouchet, J., Månson, J. A., Rochat, G. and Fayet, P. (2009). Supertough UV-curable silane/silica gas barrier coatings on polymers. *Surface and Coatings Technology*, 203(22), pp. 3398–3404.

Lomond (2015). Memjet technology. [Retrieved Aug. 17, 2015] url: http://evojet.lomond.com/en/technology_memjet

Lundberg, A. (2011). *Ink-Paper Interactions and Effect on Print Quality in Inkjet Printing*, Thesis for the degree of Licentiate, Mittuniversitetet, Sweden, 28 p.

Lundberg, A., Örtegren, J. and Alfthan, E. (2009). *On the Effect of Variations in Paper Composition on Inkjet Print Quality*. In: NIP25 and Digital Fabrication, Society for Imaging Science and Technology, Louisville, Kentucky, USA Society for Imaging Science and Technology, pp. 316–319.

Lundberg, A., Örtegren, J., Alfthan, E. and Ström, G. (2011). Microscale droplet absorption into paper for inkjet printing. *Nordic Pulp and Paper Research Journal*, 26(1), pp. 142–150.

Lundberg, A., Örtegren, J., Norberg, O. and Wågberg, K. (2010). *Improved Print quality by Surface fixation of Pigments*. In: NIP & Digital Fabrication Conference. Society for Imaging Science and Technology, Austin, Texas, USA, pp. 251–255.

Lyne, M.B. and Aspler, J.S. (1982). Wetting and the sorption of water by paper under dynamic conditions. *Tappi journal*, 65(12), pp. 98–101.

Malla, P. B. and Devisetti, S. (2005). Novel kaolin pigment for high solids ink jet coating. *Paper technology*, 46(8), pp.17–27.

Manning, H. J. and Harvey, R. A. (1999). *Xaar greyscale technology*. In: NIP15 & Digital Fabrication Conference, Society for Imaging Science and Technology, Orlando, Florida, USA, pp. 35–39.

Meier, H., Löffelmann, U., Mager, D., Smith, P. J. and Korvink, J. G. (2009). Inkjet printed, conductive, 25 µm wide silver tracks on unstructured polyimide. *Physica status solidi (a)*, 206(7), pp. 1626–1630.

Mielonen, K., Ovaska S.-S. and Backfolk, K. (2015). *Potential of Hydroxypropylated Starch-Comprising Composite Coatings for Dye-Based Inkjet Printing*, In: NIP31 Digital Fabrication and Digital Printing, Society for Imaging Science and Technology. Portland, OR, USA. IS&T, Springfield, VA, USA

Montazami R. (2009) *Fabrication and Characterization of Layer by Layer Assembled Single and Dual-Electrochrome Electrochromic Devices*, M.Sc. Thesis, Virginia Polytechnic Institute and State University, USA. 68 p.

Moutinho, I. M., Ferreira, P. J., Figueiredo, F. and Margarida L. (2007). Impact of surface sizing on inkjet printing quality. *Industrial & Engineering Chemical Research*, 46(19), pp. 6183–6188.

Moutinho, I. M., Ferreira, P. J., Figueiredo, F. and Margarida, L. (2011). Paper surface chemistry as a tool to improve inkjet print quality, *BioResources*, 6(4), pp. 4259–4270.

Murata, K. (2003). *Super-fine ink-jet printing for nanotechnology*. In MEMS, NANO and Smart Systems, 2003. Proceedings. International Conference IEEE. pp. 346–349.

Murata, K., Matsumoto, J., Tezuka, A., Matsuba, Y. and Yokoyama, H. (2005). Super-fine ink-jet printing: toward the minimal manufacturing system. *Microsystem technologies*, 12(1-2), pp. 2–7.

Müller, A. Batz-Sohn, C. and Evonik Industries. (2014). Products for the paper and film industry, p. 8 in ``*Inorganic material for print media'', Industry information 2243*, [Retrieved Aug. 17, 2015] url: https://www.aerosil.com/sites/lists/IM/Documents/II-2243-Products-for-the-Paper-and-Film-Industry-EN.pdf

Müller, M. (2014). Sizing, shaping and pharmaceutical applications of polyelectrolyte complex nanoparticles. In: *Polyelectrolyte complexes in the dispersed and solid state II*. Springer Berlin Heidelberg, Germany, pp. 197–260.

Nelli, L. (2007). *Improving Inkjet Print Performance with Fumed Silica at the Size Press.* In: NIP23 and Digital Fabrication, Society for Imaging Science and Technology, Anchorage, Alaska, USA, 603–607.

Niemöller, A. and Becker, A. (1997). *Interactions of ink jet inks with ink jet coatings*. In: NIP 13, International Conference on Digital Printing Technologies, Society for Imaging Science and Technology Seattle, Washington, USA, pp. 430–436

O'Brien K. (2013). *High Speed Production Inkjet*: *Progress Marches on in 2013*, [Retrieved Jul. 6 2015], http://info.outputlinks.com/american-printer/bid/83157/High-Speed-Production-Inkjet-Progress-Marches-on-in-2013

Oko, A., Claesson, P. and Swerin, A. (2011). Imbibition and evaporation of water droplets on paper and solid substrates. *Journal of Imaging Science and Technology*, 55(1), pp. 10201–1.

Oko, A., Swerin, A., Brandner, B. D., Bugner, D., Cook, W. and Claesson, P. M. (2014). Aggregation of inkjet ink components by Ca and Mg ions in relation to colorant pigment distribution in paper. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 456, pp. 92–99.

Page, A. (2011). *Global Print Markets to 2016*. Pira Executive Retreat, Global Print Markets. Nice, France. 34 p.

Pal, L., Agate, S. and Fleming, P. D. (2007). *Effects of paper manufacturing factors on inkjet print quality and lightfastness*. In: NIP & Digital Fabrication Conference, Society for Imaging Science and Technology, Anchorage, Alaska, USA, pp. 749–754

Park, J. and Hammond, P. T. (2004). Multilayer Transfer Printing for Polyelectrolyte Multilayer Patterning: Direct Transfer of Layer-by-Layer Assembled Micropatterned Thin Films. *Advanced Materials*, 16(6), pp. 520–525.

Park, H., Kang, S. W. and Ryu, S. (2007). *Wicking process of penetrants and inkjet inks on printing media*. In: NIP23 and Digital Fabrication, Society for Imaging Science and Technology, Anchorage, Alaska, USA, pp. 121–125.

Priolo, M. A., Gamboa, D., Holder, K. M. and Grunlan, J. C. (2010). Super gas barrier of transparent polymer− clay multilayer ultrathin films. *Nano letters*, 10(12), pp. 4970–4974.

Priya, D. N., Modak, J. M. and Raichur, A. M. (2009). LbL fabricated poly (styrene sulfonate)/TiO2 multilayer thin films for environmental applications. *ACS applied materials & interfaces*, 1(11), pp. 2684–2693.

Puukko P. and Niemi K. (2009). Instrumental measurement of print quality. In: Oittinen P. and Saarelma H. Eds. *Papermaking Science and Technology*, Book 13, Fapet Oy, Jyväskylä, pp. 318–332.

Rahman, L. (2003). *Factors affecting the performance of inkjet papers*. Proceedings from Spring Technical Conference & Trade Fair, Chicago, IL, USA, 19 p.

Riebeling, H. U. (1994). *Improving inkjet printability through surface sizing*, Sizing Science and Technology II. In Paper Technology Seminar, Ludwigshafen. 25(4).

Ryu, R., Gilbert, R. and Khan, S. (1999). Influence of cationic additives on the rheological, optical, and printing properties of ink-jet coatings. *Tappi Journal*, 82(11), pp. 128–134.

Shang, S. (2012). Process control in printing of textiles. Majumdar, A., Das, A., Alagirusamy, R. and Kothari, V. K. Eds. *Process control in textile manufacturing*. Elsevier. 355 p.

Schmid, C. (2009). Formulation and Properties of Waterborne Inkjet Inks, In: Magdassi, S. Ed, *The Chemistry of Inkjet Inks*, Publishing Co. Pte. Ltd., Singapore. pp. 123-140

Selim, M. S., Yesavage, V F., Chebbi, R., Sung, S. H., Borch, J. and Olson, J. M. (1997). Drying of Water-Based Inks on Plain Paper, *Journal of Imaging Science and Technology*, 2(7), pp. 152–158.

Shaw-Klein, L. (1998). *Effects of mordant type and placement on inkjet receiver performance*. In: NIP14: International Conference on Digital Printing Technologies, Society for Imaging Science and Technology, Toronto, Canada., USA, pp. 129–132.

Shi, J., Schuman, T. and Stoffer, O. (2004). Ink-jet printing paper with improved waterfastness. *Journal of Coating Technology and Research*, 1(3), pp. 225–234.

Smithers pira (2014). *Growth in Digital Printing to Remain Strong until 2024*. [Retrieved Apr. 1, 2015], url: http://www.smitherspira.com/news/2014/april/digital-printing-to-remain-strong-until-2024

Smyth, S. (2011). *The Future of Digital Printing to 2021, Strategic market and technology forecasts*, Pira International Ltd, UK. 160 p.

Sousa, S., Gamelas, J., de Oliveira Mendes, A., Fiadeiro, P. and Ramos, A. (2013). Interactions of ink colourants with chemically modified paper surfaces concerning inkjet print improvement. *Materials Chemics and Physics*, 139(2), pp. 877–884.

Sreekumar, J., Sain, M. and Farnood, R. (2005a). *Effect of Styrene Maleic Anhydride Imide Resin (SMAI) on Ink-jet Paper Coating Suspension Rheology*. 91st Annual Meeting Preprints - Pulp and Paper Technical Association of Canada.

Sreekumar, J., Sain, M. Farnood R. and Dougherty, W. (2005b). Styrene maleic anhydride imide resin (SMAI): a novel cationic additive in paper coating for ink-jet printing, *Pulp & Paper Canada*, 106(3), pp. 38–41.

Srivastava, S. and Kotov, N. A. (2008). Composite layer-by-layer (LBL) assembly with inorganic nanoparticles and nanowires. *Accounts of chemical research*, 41(12), pp. 1831–1841.

Starov, V. M., Zhdanov, S. A., Kosvintsev, S. R., Sobolev, V. D. and Velarde, M. G. (2003). Spreading of liquid drops over porous substrates. *Advances in Colloid and Interface Science*, 104(1), pp. 123–158.

Stankovska, M., Gigac, J., Letko, M. and Opálená, E. (2014). The effect of surface sizing on paper wettability and on properties of inkjet prints. Wood Research, 59(1), pp. 67–76.

Stoffel, J. (2007). *Improving the Performance of InkJet and Laser Printing through Paper Modification*. In: NIP23 and Digital Fabrication, Society for Imaging Science and Technology, Anchorage, Alaska, USA. p. 577–579.

Storbeck, W., Dietrich, D. and Schneider, R. (2005). *Fixation of Pigmented Black Ink on Matte Coated Ink-Jet Substrates*. In: NIP25 and Digital Fabrication Conference, Society for Imaging Science and Technology, Baltimore, Maryland, USA, pp. 306–311.

Svanholm, E. (2007). *Printability and Ink-Coating Interactions in Inkjet Printing*, PhD Thesis. Karlstad University, Sweden.

Usui, M., Hayashi, H., Hara, K. and Kitahara, T. (2002). *The development of pigment ink for plain paper*. In: 18th International Conference on Digital Printing Technologies, Society for Imaging Science and Technology, San Diego, California, USA, pp. 369–373.

Vikman, K. and Vuorinen, T. (2004). Water fastness of ink jet prints on modified conventional coatings. *Journal of Imaging Science and Technology*, 48(2), pp. 138–147.

Vikman, K. (2004). *Studies on Fastness Properties of Ink jet Prints on Coated Papers*. Doctoral Thesis, Helsinki University of Technology, Laboratory of Forest Products Chemistry, 47 p.

Wexler, A. (2001). *Latex complexes as stabilized colorant*. Kodak Polychrome Graphics, USA. U.S. Pat. 6297296 B1.

Wild, P. Wildlock, Y. Andersson, K. and Lindgren, E. (2008). *A novel coating formulation for silica inkjet layer coatings*. In: NIP24 and Digital Fabrication, Society for Imaging Science and Technology, Pittsburgh, Pennsylvania USA, pp. 383–386.

Willis, M. and Hudd, A. (2015). *Inkjet ink materials and dispersions*. IMI Inkjet Printing Summer School, 22.-23.6.2015 Munich, Germany.

Xie, R., Karim, A., Douglas, J. F., Han, C. C., & Weiss, R. A. (1998). Spinodal dewetting of thin polymer films. *Physical Review Letters*, 81(6), pp. 1251–1254.

Yang, L., Fogden, A., Pauler, N., Sävborg, Ö. and Kruse, B. (2005). A novel method for studying ink penetration of a print. *Nordic Pulp & Paper Research Journal*, 20(4), pp. 423–429.

Yoo, D., Shiratori, S. S. and Rubner, M. F. (1998). Controlling bilayer composition and surface wettability of sequentially adsorbed multilayers of weak polyelectrolytes. *Macromolecules*, 31(13), pp. 4309–4318.

Yoon, C. and Choi, J. H. (2008). Syntheses of polymeric dispersants for pigmented ink-jet inks. *Coloration Technology*, 124(6), pp. 355–363.

Yu, P. C., Chen, C. I., Yang, R. J., Yen, F. S. and Max Yen, S. T. (2012). Porous χ-Al_2O_3 Flake Powder as Dye-Fixing Materials for Inkjet Printing Paper. *Journal of the American Ceramic Society*, 95(7), pp. 2124–2126.

Yu, Y. and von Gottberg, F. (2000). *Surface Modified Color Pigments for Ink Jet Ink Application*. In: NIP16 International conference on Digital Printing, Society for Imaging Science and Technology, Vancouver, Canada, USA, pp. 512–515.

Yuan, S., Sargeant, S., Rundus, J., Jones, N. and Nguyen, K. (1997). *The Development of Receiving Coatings for Inkjet Imaging Applications.* In: NIP 13 International conference on Digital Printing, Society for Imaging Science and Technology, Seattle, Washington, USA, pp. 413–417.

Zhang, H., Xie, A., Shen, Y., Qiu, L. and Tian, X. (2012). Layer-by-layer inkjet printing of fabricating reduced graphene-polyoxometalate composite film for chemical sensors. *Physical Chemistry Chemical Physics*, 14(37), pp. 12757–12763.

Örtegren, J., Norberg, O. and Lundberg, A. (2011). Aggregation of color pigments by surface fixation treatment. *Journal of Imaging Science and Technology*, 55(5), p. 50605–1.

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