

## STUDIES ON FASTNESS PROPERTIES OF INK JET PRINTS ON COATED PAPERS

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## STUDIES ON FASTNESS PROPERTIES OF INK JET PRINTS ON COATED PAPERS

Katri Vikman

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## PREFACE

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Espoo, May 28<sup>th</sup>, 2004

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## LIST OF PUBLICATIONS

The following publications are included in this thesis:

- I *Vikman, K. and Sipi, K.*, Applicability of FTIR and Raman Spectroscopic Methods to the Study of Paper-ink Interactions in Digital Prints. *J. Imag. Sci. Technol.*, 47(2003)2, pp. 139-148.
- II *Vikman, K.*, Fastness Properties of Ink Jet Prints on Coated Papers – Part 1: Effect of Coating Polymer System on Light Fastness. *J. Imag. Sci. Technol.*, 47(2003)1, pp. 30-37.
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The author's contribution to the appended joint publications:

- I Katri Vikman defined the research plan together with the co-author, performed the experimental work related to the ink jet print studies, analyzed the corresponding results, and wrote the manuscript. Moreover, she wrote the literature background related to paper and colorant research, and the experimental parts related to Raman spectroscopy.
- IV-V Katri Vikman defined the research plan together with the co-author, performed the experimental work, analyzed the corresponding results, and wrote the manuscript.
- VI Katri Vikman defined the research plan, performed the experimental work and analyzed the results together with the co-authors, and wrote the manuscript.

# CONTENTS

1	INTRODUCTION .....	1
1.1	Background .....	1
1.2	Objectives and scope .....	2
2	LITERATURE REVIEW .....	3
2.1	Ink jet coatings .....	3
2.1.1	Pigment-rich coatings .....	3
2.1.2	Resin-rich coatings .....	5
2.2	Fastness properties of ink jet prints on coated papers .....	6
2.2.1	Light fastness .....	6
2.2.2	Water fastness .....	8
2.3	Analytical methods in paper-ink interaction studies .....	10
3	HYPOTHESES .....	12
4	EXPERIMENTAL .....	13
4.1	Materials .....	13
4.1.1	Model coatings .....	13
4.1.2	Model inks .....	13
4.2	Methods .....	16
5	RESULTS .....	17
5.1	FTIR and Raman spectroscopic methods in ink jet print studies .....	17
5.2	Overview on ink jet print permanence .....	20
5.3	Mechanisms influencing water fastness of ink jet prints .....	21
5.3.1	Effect of coating composition .....	21
5.3.2	Physical properties of the coating layer .....	23
5.3.3	Chemical paper-ink interactions .....	25

5.4	Mechanisms influencing light fastness of ink jet prints.....	28
5.4.1	Effect of coating composition .....	28
5.4.2	Physical properties of the coating layer .....	29
5.4.3	Chemical paper-ink interactions .....	31
6	DISCUSSION.....	34
6.1	Water fastness .....	34
6.2	Light fastness.....	36
7	CONCLUSIONS .....	38
8	REFERENCES .....	40

APPENDICES:

ERRATA

PAPER I

PAPER II

PAPER III

PAPER IV

PAPER V

PAPER VI



# 1 INTRODUCTION

## 1.1 Background

Ink jet printing is one of the main imaging technologies because of its versatility. During recent years, its use has become more common particularly in small-scale color printing and in low-cost variable data printing applications (Lunde 1999, Londo 2000a, Glittenberg and Voigt 2001). Manifold criteria are generally set for ink jet print quality, eligible features typically including a large color gamut, sharp detail rendering, and excellent long-term fastness properties. These require fixation of the colorant to the paper surface and quick ink solvent absorption into the coating, commonly without the use of drying units (Lee et al. 1994, Yuan et al. 1997, Hauser and Bühler 1998, Lavery et al. 1998, Le 1998, MacLeod 1998, Thompson 1998, Chapman and Michos 2000, Bugner 2002). In consequence, ink jet print quality is remarkably dependent on the properties of papers and inks, and their mutual interactions (Lavery et al. 1998, Le 1998). Physical paper-ink interactions, such as wetting and penetration, govern primarily the setting and drying of a liquid ink on paper, whereas chemical interactions, e.g. ionic or hydrogen bonding, influence the final attachment of colorant to paper and the long-term stability of the prints (Lavery and Provost 1997).

The most common inks in desktop and large-format ink jet printing applications are low-viscous, aqueous blends, typically composed of 1-10 wt.% of colorant and 90-99 wt.% of multi-component carrier phase (MacLeod 1998, Thompson 1998, Bugner 2002). The nature of the ink thereby requires the use of an absorptive coated paper as a printing substrate to achieve high print quality. Currently, silica-based coatings represent the state of the art for high-quality ink jet papers. However, for economic reasons, other coating compositions are being sought to replace silica grades. For example, coatings consisting of the same components as conventional printing papers would be an interesting option also as an ink jet print medium, as they offer lower cost per printed page (Sangl and Weigl 1998, Lunde 1999, Ruy et al. 1999, Chapman and Michos 2000, Londo 2000a, Glittenberg and Voigt 2001, Cawthorne Jr. et al. 2003). However, when using conventional coatings in ink jet printing, disadvantages are the low affinity of ink jet colorants with the coating pigments, and their inability to absorb fluid ink jet inks because of their small pore volume and surface area. This results in low optical density, slow print drying, and eventually in poor overall print quality. Consequently, the composition of the conventional coating has to be modified to improve ink absorption and dye-binding capacity to the desired level (Lyne 1991, Borch 1993, Nakamura 1993, Hentzschel and Pelzer 1996, Chapman 1997, Lavery and Provost 1997, Sangl and Weigl 1998, Chapman and Michos 2000, Jopson 2001). So far, print quality on such modified conventional coatings has mainly been examined in terms of color density and geometrical properties of lines and dots (Londo 2000b, Huskey 2001, Jopson 2001, Hladnik and Muck 2002, Cawthorne Jr. et al. 2003). Meanwhile, systematic research and scientific publications on paper-ink interactions and long-term print quality are not currently available.

## 1.2 Objectives and scope

The first objective of this thesis is to evaluate the applicability of vibrational spectroscopy, or FTIR and Raman spectroscopic methods to studying ink jet prints. Secondly, an attempt is made to clarify the mechanisms contributing to the fastness properties of small-scale ink jet prints on coated papers. Light and water fastness in the time-scale of the print's end use are of particular interest. The research problem is contemplated by studying the physical properties of coatings and chemical paper-ink interactions, and their possible effects on the permanence of ink jet prints on coated papers using sample sets with known compositions and FTIR and Raman spectroscopy as the main analytical methods.

This Ph. D. thesis summarizes the findings of six scientifically refereed research papers with the following outline: in Chapter 2, a brief literature review is given on the topic, in Chapter 3 the hypotheses of the study are presented, and in Chapter 4, the experimental details are described. Results are summarized and discussed in Chapters 5 and 6. Chapter 7 presents the conclusions.

## 2 LITERATURE REVIEW

### 2.1 Ink jet coatings

Ink jet coatings are commonly divided into pigment- and resin-rich systems. The former are formulated above the critical pigment volume concentration (Chapman and Michos 2000), whereas polymers are the main components of the latter. Moreover, combinations of these systems also exist, like multi-layered structures representative of photopapers. These typically consist of an ink-receiving layer, and a thin, cross-linked protective layer on the top. Common substrates for ink jet coatings are papers, films and their composites (Nakamura 1993, Oka and Kimura 1995, Hentzschel and Pelzer 1996, Lavery and Provost 1997, Stockkamp 1997, Chapman and Michos 2000, Bugner 2002, Lavery and Spittles 2001).

#### 2.1.1 Pigment-rich coatings

In pigment-rich coatings, ink is absorbed into a porous pigment network (Chapman and Michos 2000). Amorphous silica is nowadays the most common pigment type in such systems (Bugner 2002) because of its large absorption capacity and hydrophilic nature (Walchli 1994, Withiam 1996, Sangl et al. 1997, Lunde 1998, Chapman and Michos 2000). The considerable absorbency of silica coating is based on its large specific surface area, which originates from the presence of both inter- and intra-particle pores. The former transport the carrier phase rapidly away from the surface of the coating, whereas the latter cause the eventual ink absorption because of the strong capillary pressure prevailing in narrow pores (Chapman 1997, Yoldas 1998, Bugner 2002). Moreover, silica particles are able to interact with the inks, owing to the reactive silanol groups and hydrated water on their surfaces. Indeed, silica has been shown to absorb ink solvents selectively in relation to the colorants, which results in partitioning of the colorant in the vicinity of the coating surface (Chapman 1997).

Several silica grades are currently available, namely fumed, colloidal, precipitated, and gel types. Their particle sizes typically range from less than 100 nm to greater than 1  $\mu\text{m}$ . Colloidal, precipitated and fumed silica are composed of nonporous primary particles, whereas silica gel exists as rigid and porous three-dimensional networks, with a particle size up to 300 nm (Chapman and Michos 2000, Bugner 2002, Lee et al. 2002). Recently, a novel calcium-silica pigment has been developed (Johnston et al. 2002). This pigment has a nanophase structure, in which nanometer-sized platelets are joined together in an open framework, thus forming discrete particles about 0.5-2  $\mu\text{m}$  in size. The authors suggest the use of calcium-silica pigment in ink jet printing because of its high oil absorption capacity (400 g oil/100 g) and surface area (up to 350  $\text{m}^2/\text{g}$ ). Moreover, the surface of the pigment particles contains silanol groups and calcium ions, which should enhance the interaction with anionic dyes. In addition to the silica pigment, alumina is also used in ink jet coatings, especially in high-performance glossy coatings. It is available in similar particle sizes as silica. Pseudoboehmite ( $\text{AlO}_2\text{H}$ ) is a special type of commercial alumina, which is generally used as an aqueous dispersion of nanometer-sized particles. Furthermore, mixed oxides of silicon and aluminum can also be applied to ink jet coatings (Chapman 1997, Bugner 2002, Lee et al. 2002).

The coating polymer system selected for pigment-rich coatings is generally very important for the ultimate print quality, because the polymers immobilize the pigment particles and attach them to the base paper, and also absorb the carrier phase of the ink. With aqueous ink jet inks, the drying of the print on coated paper is therefore generally markedly dependent on the water absorption capacity of the binder. This can be influenced by choosing a polymer of suitable

chemical nature and molecular weight (Sargeant et al. 1995, Yuan et al. 1997, Lehtinen 2000). Theoretically, the larger the amount of water-absorptive polymers in the coating, the faster the print drying (Stockkamp 1997, Yuan et al. 1997). Consequently, the most common binders in pigment-rich ink jet coatings are water-soluble hydrophilic polymers, such as polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), and polyvinyl acetate (PVAc) (Pinto and Nicholas 1997, Yuan et al. 1997, Pinto et al. 1999, Bugner et al. 2002). Pre-eminently partially hydrolyzed, relatively low-molecular weight PVA grades have proven to be effective binders when combined with silica pigment (Lunde 1998, Hentzschel 2000). Moreover, owing to its non-ionic nature, PVA can be used together with most additives of coating colors, including cationic polymers and surface sizes (Hentzschel and Pelcher 1996, Boylan 1997, Hentzschel 2000). The use of a polymer-silica hybrid system in ink jet coatings has also been suggested (Dunlop-Jones et al. 2002). The hybrid system is produced with emulsion polymerization in the presence of colloidal silica, and the coating obtained with this system is reported to be micro-porous, glossy and water-resistant.

Besides rapid ink absorption, cationic water-soluble polymers, like PVP, offer high print density because of their capability to interact with both water and solvent (Pinto and Nicholas 1997, Pinto et al. 1999). For this reason, cationic polymers are commonly included as mordants in ink jet coatings. For example, polydiallyl dimethylammonium chloride (poly-DADMAC) and cationic PVA are known to improve dye attachment in addition to PVP. When used in combination with silica, the added amount is usually relatively low because of the drastic impact of cationic polymers on coating color rheology (Bugner 2002). Other binder types that have been applied to ink jet coatings are aqueous emulsions of styrene acrylic and styrene butadiene latexes (Hentzschel and Pelcher 1996, Yuan et al. 1997, Bugner 2002), as well as special binders like gelatin and its derivatives (Pörschke and Dolphin 1996). However, anionic latexes have proven to be rather unsuitable for silica coatings, since the stabilizing agents of latex particles may disturb the wetting process. In addition, the functioning of cationic additives may be disturbed (Hentzschel and Pelcher 1996).

At present, most pigment-rich ink jet coatings are composed of three primary ingredients: silica pigment, PVA binder and a cationic polymer additive (Lunde 1998, Yoldas 1998, Lunde 1999, Ruy et al. 1999, Chapman and Michos 2000, Glittenberg and Voigt 2001, Bugner 2002). Although this combination works very well in ink jet printing, certain disadvantages limit its usability. The biggest drawback of this blend is its expensiveness, which makes large-scale printing rather uneconomical. This is partly due to the high-priced ingredients, and partly the low-viscous nature of the silica-based coating colors. In silica coatings, the solids content is typically less than 20%, which makes high-speed coating quite complicated. In addition, considerable amounts of binders, often more than 40 wt.%, are needed because of the large specific surface area of silica. Silica papers also typically exhibit poor printability in other printing processes, which may restrict their applicability to hybrid printing processes involving a combination of conventional and ink jet printing techniques (Lee et al. 1994, Withiam 1996, Sangl et al. 1997, Lunde 1998, Ruy et al. 1999, Chapman and Michos 2000, Glittenberg and Voigt 2001).

Several approaches to obtain a coating that would combine the absorption properties of silica coatings with the lower cost of conventional coatings have been presented. For example, the use of ground or precipitated calcium carbonate and surface-enhanced aluminosilicate (SEAS) as a replacement for silica has been suggested (Lunde 1998, Londo 2000a, Londo 2000b, Bugner 2002). However, with SEAS, the use of a cationic additive proved to be necessary to achieve the surface and bulk coating properties required for high ink jet print quality (Cawthorne Jr. et al. 2003). In contrast, other studies (Donigian et al. 1998, Donigian et al. 1999) have shown that with cationic PCC pigment, binders are not necessary needed to

attach colorants. Chromatographic studies have indicated that the cationic PCC particles were able to fix the soluble dyes to their surfaces independently from the binder, and that the drying rate of the colorant increased rapidly as binder content was reduced. Moreover, the ink solvent was reported to be absorbed by the material beneath the coating layer unlike in silica coatings where the solvent was retained in the coating layer. Another novel PCC grade with platelet morphology has also been developed (Vučak et al. 2003). In addition, modification of traditional offset coating formulations with bentonite and PVP copolymer has been suggested to improve ink jet printability (Jopson 2001), as well as combining cationic starch with calcium carbonate pigments (Glittenberg and Voigt 2001, Glittenberg et al. 2003).

### 2.1.2 Resin-rich coatings

The main constituents of resin-rich coatings are water-swelling polymers, whereas pigments are present only in minor amounts. In consequence, resin-rich coatings function by absorbing ink-liquids mainly by a swelling mechanism. In contrast to pigment-rich coatings, evaporation or containment of liquids in pores is generally not involved. Drying of the print commonly occurs very slowly, because the coating absorbs moisture both from the ink and the atmosphere. As a result, the glass transition temperature  $T_g$  of the coating polymer decreases below room temperature, making the image tacky and prone to smudging. Eventually, the water evaporates, the ink co-solvents equilibrate within the ink receiving layer and the  $T_g$  rises back above room temperature. At a relative humidity below about 50%, drying commonly occurs within a short period of time. However, if the relative humidity or the amount of co-solvents in the ink increases, it may take several minutes for the print to equilibrate and become completely smudge-free (Yoldas 1998, Chapman and Michos 2000, Bugner 2002).

With coatings intended for water-based inks, biopolymers such as gelatins and polysaccharides (cellulose derivatives) have commonly been used, because they swell rapidly and absorb the aqueous carrier phase of the ink. Synthetic hydrophilic polymers such as PVA, PVP, polyethylene oxide (PEO), and poly-2-ethyl-2-oxazoline (POx) have also been proven to be well applicable. Moreover, polymer blends, multilayer coating structures or combinations of these consisting of several hydrophilic polymers have been used in resin-rich ink receiving layers as well (Yoldas 1998, Chapman and Michos 2000, Bugner 2002).

Besides absorptive polymers, resin-rich coatings contain several additives to improve their performance. The cationic mordants described in connection with pigment-rich coatings, or functionalized cyclodextrins are commonly added to resin-rich coatings to enhance dye attachment. Other typical ingredients are so-called matting agents, like silica or polymeric beads with a particle size typically ranging from 1  $\mu\text{m}$  to 50  $\mu\text{m}$ . Matting agents are generally present in relatively low concentrations, primarily providing some surface roughness without decreasing the perceived gloss of the coating. However, at higher concentrations they produce matte appearance in an inherently glossy coating (Bugner 2002).

## 2.2 Fastness properties of ink jet prints on coated papers

The fastness properties of ink jet prints can be described in terms of print durability and image stability. Print durability refers to the physical permanence of the paper, such as tear or scratch resistance. Therefore, it is mainly determined by the properties of the paper, and to a lesser extent by the type of ink. Image stability stands for the long-term permanence of the printed image, for example light or water fastness. The primary external factors affecting image stability are light, heat, humidity and air quality. In addition, the nature of the material with which the print is possibly in contact may also have an influence (Bugner 2002, Wypych 2003). Apart from the environmental elements, image stability is greatly influenced by the chemical and physical environment of the colorant in paper, which are determined by the nature of the coating and the other ink components (Lyne and Aspler 1984, Oka and Kimura 1995, Sargeant et al. 1995, Fryberg et al. 1997, Lavery and Provost 1997). Therefore, a proper match of an ink jet paper to a given ink set is critical to achieve good image stability (Bugner 2002). Beside, parameters influencing image stability do not act alone, instead they create an extremely wide range of conditions under which a material may have to perform (Wypych 2003).

### 2.2.1 Light fastness

There are several possible routes for photo-chemical reactions (Wypych 2003). Studies indicate that photodegradation of printed ink jet dyes cannot be explained by any single, well-defined mechanism (Steiger and Brugger 1998). On the contrary, it depends on several variables: numerous structural factors; the physical state of the absorbed dye, including the size and location of the associated particles; the chemical nature of the substrate; the extent of penetration of the dye and its concentration; the ease of diffusion of air, moisture, and gases; the energy of incident radiation; and the relative ease with which transient, reactive species are formed upon absorption of light (Kuramoto 1996, Csepregi et al. 1998, Doll et al. 1998, Lavery and Spittles 2001, Wypych 2003). The problem of colorant fading has been under extensive research for textiles and polymers, and the mechanisms identified in these studies have also been applied to studying the light fastness of ink jet dyes (Doll et al. 1998, Lavery et al. 1998, Wnek et al. 2002).

Photodegradation of azo dyes, which are typical ink jet colorants (Christie 2001), has been found to occur either by oxidation, reduction or by catalytic fading. These reactions are affected by the tautomeric equilibrium of the azo dye. In general, azo dyes occur in two tautomeric forms; azo ( $-N=N-$ ) or hydrazone ( $=N-NH-$ ). The latter is said to be more prone to oxidative fading, which is the most common photodegradation mechanism in the presence of light, moisture, and oxygen (Kuramoto 1996, Wnek et al. 2002). In photooxidation of 4-arylaazo-1-naphthol, singlet oxygen has proven to attack the hydrazone tautomer to form an unstable peroxide, which then decomposes to produce 1,4-naphthoquinone and toluene-p-diazonium ion. The results also indicated that the irradiation of 4-arylaazo-1-naphthol on solid silica gel with visible light in the presence of air results in the formation of identical reaction products (Griffiths and Hawkins 1972, Griffiths and Hawkins 1977). Under anaerobic conditions, azo dyes can be reduced to the corresponding amines by hydrogen donors produced on photoexcitation. The reduction route varies depending on the type of dye, but essentially it results in a hydrazo compound and eventually substituted anilines, and the original dye. This process is generally predominant in reductive environments typified by proteins such as wool and silk (Kuramoto 1996). Catalytic fading refers to a situation where certain dye combinations exhibit less stability if they are printed together rather than separately (Kuramoto 1996, Wnek et al. 2002). For example, the light fastness of blue, violet

or red dye commonly deteriorates when a yellow dye is added. Possible mechanisms suggested for catalytic fading are for example energy transfer processes and the formation of singlet oxygen in the dye mixture (Kuramoto 1996).

The nature and position of the substituents of the colorant molecule play a significant role as well (Csepregi et al. 1998), because they may have a major effect on the tautomeric equilibration, and thus on the photodegradation tendency of azo dyes. The azo group is an electron acceptor, and therefore it is stabilized by electron donating substituents, especially the methoxy group  $\text{OCH}_3$ . In contrast, the hydrazone tautomer is favored by electron withdrawing substituents, in particular the nitro group  $\text{NO}_2$ , because the imino group (NH) is an electron donor (Kishimoto et al. 1978). Further stabilization of the hydrazone tautomer is achieved with intra- or intermolecular hydrogen bonding. For example, an intramolecular hydrogen bond between an OH group at the o-position and the further nitrogen of the hydrazo group has proven to be favorable for light fastness, because oxygen forms a stronger hydrogen bond than nitrogen, and thus stabilizes the tautomer effectively. Intermolecular hydrogen bonding with the components of paper or the ink may have similar effects, but free interchange between the tautomeric forms is nevertheless restricted. Generally, the hydrazone tautomer is promoted by an increase in the polarity of the media (Wnek et al. 2002).

Besides the structure of the chromophore, the aggregation tendency of the colorant has also proven to be important for light fastness (Kuramoto 1996). Pigmented inks are known to have better stability than dye-based inks because of their crystalline structure. This can be attributed to several factors. In an aggregated colorant, the surface area per unit mass of dye available for attack by reactive species is diminished. Thus, there is a reservoir of intact dye left, even though the surface layers of the aggregates have been degraded. It has also been suggested that the lifetime of the dye's excited state is shorter in the aggregated state, allowing it less time to react (Skelton et al. 2002, Wnek et al. 2002). The reduction of the colorant's solubility can also be utilized in improving the light fastness of dye-based inks (Fryberg et al. 1997, Naisby et al. 2002, Wnek et al. 2002). This can be affected both by the nature of the substituents (Wight 2000) and the properties of the organic ink solvent (Fryberg et al. 1997). For example, the ionization degree of the acidic groups of the colorant can be suppressed and aggregation facilitated by using less basic solvent. This phenomenon may also occur in prints, if the media is acidic, causing the dye to precipitate upon contact. The effect of the carrier phase composition on the light fastness of ink jet prints has been studied by varying the types and amounts of colorant, organic co-solvent and surfactants (Hakola 2002). With dye-based inks, the type of colorant and the composition of the solvent proved to be the main factors, whereas surfactants did not have a marked influence. In general, light fastness decreased with an increase in the proportion of organic co-solvents in the ink blend. The addition of salts into the ink is also known to cause aggregation, because they reduce the thickness of the electrical double layer. Multivalent ions and cationic surfactants are particularly effective, and can also act as a bridge between two charged groups to bind the dye molecules (Wnek et al. 2002).

In addition to the ink-related factors, the properties of the media have a strong influence on light fastness. The polymer system of the coating is one of the main factors affecting the fastness properties of an ink jet print, since polymers can stabilize and immobilize the colorant both physically and chemically (Yuan et al. 1997, Khoultchaev and Graczyk 2001). For example, experiments carried out with thin-layer chromatography have shown that PVA provides some sites for dye binding when it is present in coating at high concentrations (Donigian et al. 1999). Ink jet photopapers usually contain a protective surface coating or polymer layer, which literally protects the chromophore from light and oxygen. This kind of

topcoat layer may contain UV absorbers such as benzophenones that absorb strongly UV light and release the energy nondestructively via a tautomeric process (Lavery and Provost 1997, Niemöller and Becker 1997, Wnek et al. 2002). However, it has been suggested that in highly porous ink receiving layers the chromophore may be vulnerable to extensive gas-fading (often ozonolysis) as well (Steiger et al. 2001, Wnek et al. 2002). In another study, the light fastness of three magenta azo dyes was found to be lower on microporous media than on the polymer-rich coating (Fryberg and Hofmann 2000). UV absorption can also create excited electrons, and consequently positive electron holes, which may migrate to the particle surface. Reactions with oxygen, water, and surface hydroxides may then lead to the formation of hydroperoxyl and hydroxyl radicals, which could attack the colorants. Antioxidants, such as a free radical scavengers and a peroxide decomposers, may be added to the medium to prevent this kind of behavior (Wnek et al. 2002). Singlet oxygen quenchers, like 1,4-diazabicyclo-[2,2,2]octane (DABCO), have also been found to inhibit the oxidative fading of azo dyes (Griffiths and Hawkins 1972, Griffiths and Hawkins 1977).

Materials with a high proportion of hydroxyl functionality, like PVA and cellulose derivatives, have been found to promote light stability, owing to their capability to act as free radical quenchers (Yuan et al. 1997). PVA is also known to be a good barrier against oxygen (Wnek et al. 2002). Moreover, an increase in the hydrogen bonding capability of the host polymer has proven to reduce the fading of certain azo dyes (Clifton and Nugent 2000). Studies have indicated that an azo dye containing sulphonic acid groups shows good stability in contact with PVA binder without marked dye aggregation, suggesting other prevailing stabilizing mechanisms (Naisby et al. 2002). In addition to polymers with hydroxyl functionalities, alkyl groups and ethyl cellulose have been found to enhance the light stability of some colorant pigments (Wing-sum Kwan 1999). Conversely, polymers containing UV light absorbers, like styrene, may destabilize the azo colorants (Wing-sum Kwan 1999), which also applies to coating layers containing cationic compounds (Yuan et al. 1997, Lavery et al. 1998). For example poly-DADMAC, which is a common mordant (Niemöller and Becker 1997, Shaw-Klein 1998, Ruy et al. 1999), has been found to be detrimental to light fastness (Shaw-Klein 1998). This behavior has been explained by the location of the colorant in the cationic coating - as the dye is fixed on the surface of the substrate, it is more vulnerable to UV light and thus to photodecomposition (Lavery and Provost 1997). It has also been proposed that the aggregating tendency of some ink jet dyes is reduced if the dyes get into contact with nitrogen-containing polymers such as PVP (Wang et al. 1999).

### 2.2.2 Water fastness

Two of the most critical elements for the water fastness of ink jet prints are the ink formulation and the composition of the receiving media. Typical ink jet dyes have significant water solubility, and if there are no strong binding forces holding the dye to the receiving medium, the dye will dissolve when the image comes into contact with water or moisture (Wexler 2001). It is a well-known fact that pigmented inks, because of their crystalline structure, have better water fastness than dye-based inks. The use of water-insoluble dyes in ink jet inks in conjunction with water-soluble polymers has also been suggested as a means to improve water fastness (Taniguchi and Oyama 1997). As in the case of light fastness, controlled dye aggregation in the ink-receiving layer improves water fastness (Fryberg et al. 1997, Wnek et al. 2002). Another study (Hakola 2002) which discussed the effect of ink composition on fastness properties of ink jet prints gave indications that the water fastness of dye-based inks was dependent mainly on the type of colorant and the composition of the solvent, whereas surfactants did not have a marked effect. This study also implied that the use



of an organic solvent in the ink, or an increase in its hydrophobic nature, would improve water fastness further.

The components of the coating contribute strongly to water fastness (Fryberg et al. 1997). To prevent dissolution of the attached colorant, the paper surface should be charge-regulated. In other words, the dissociation constant of the surface should be adjusted to ensure that a large maximum repulsion is generated at intermediate distances between the water molecules and the surface, whereas at smaller distances the attraction should be large (Wnek et al. 2002). Besides the attachment of the dye to the coating, the cohesion of the coating itself (or solubility of the coating components) is a critical factor (Yuan et al. 1997, Khoultaev and Graczyk 2001). The use of anionic colloidal silica as a co-pigment with porous silica has been suggested as a means to improve the dry and wet surface resistance of silica coatings. This has been explained by better use of the binder polymer molecules, for example owing to the reduced penetration and loss of PVA macromolecules into the silica pore structure. A further improvement can be achieved with cationic colloidal silica particles, which are surrounded by positive electrical charges. These enable direct fixation of ink jet dyes to the pigment particles, unlike in a coating containing cationic polymers. Moreover, the use of cationic colloidal silica reportedly reduces the coating color interactions responsible for the increases in viscosity, or the adverse quenching effects of anionic optical brightening agents (Jonckherree and Mabire 2003). Other possibilities for improving water fastness are to use for example cationized calcined kaolin clay (Chen and Godfrey 2000) and cationic precipitated calcium carbonate PCC (Donigian et al. 1998, Donigian et al. 1999). The use of water-insoluble fine particles containing amino groups (Moronuki et al. 2001) and a combination of porous macroparticles and fully dense fine particles (Tang et al. 1999) has also been suggested as a means to enhance water fastness.

The polymer system of the coating is decisive for the fastness properties of ink jet prints (Yuan et al. 1997, Khoultaev and Graczyk 2001). In porous ink jet coatings, pigment particles are bonded together by a binder. Hence, the water fastness is inevitably a function of the pigment-binder ratio. The level of water fastness of the coating is dependent on the amount of free polymer in the coating. At low binder contents, all the polymer binder is adsorbed on the particle surfaces, which limits its configuration and mobility. As a result, the binder will be insoluble in water, allowing good water fastness to be achieved (Tang et al. 1999). The ability of porous ink jet papers to absorb ink readily, but repel water, is probably related to the differential wettability of the pores, as the surface tensions of pure water and typical ink jet inks are different (Bugner 2002). As the amount of free polymer increases, the coating loses its water fastness because unbound polymer dissolves in water (Tang et al. 1999). Particularly the water-soluble polymers, which are used in most ink jet media as binders to absorb ink vehicles, will swell and be washed away when in contact with water for extended periods of time. Therefore, a careful balance between hydrophilic and hydrophobic components in the ink receptive coating is needed to give both a good image and water resistance (Yuan et al. 1997, Khoultaev and Graczyk 2001).

When striving to enhance water fastness with polymers, dye mordants, such as cationic polymers, have often been used. For example poly-DADMAC is commonly used because of its capability to form ionic complexes with anionic dyes (Niemöller and Becker 1997, Shaw-Klein 1998, Ruy et al. 1999, Wexler 2001, Bugner 2002, Jonckherree and Mabire 2003). The water fastness of a coating containing a hydrophilic binder can also be improved by using hardening agents capable of cross-linking the binder (Kasahara et al. 2000). In addition to this, the use of cationic latexes has been suggested in the literature (Sugiyama 1983, Wexler 2001, Bugner 2002). However, the use of cationic polymers may also have adverse effects. These include prolonged ink drying because of reduced ink absorption speed, possible poor

compatibility between the coating color and cationic fixatives, which may increase the coating color's viscosity, and decreased print quality and light fastness. Moreover, cationic polymers may cause quenching of optical brightening agents (Jonckherree and Mabire 2003). The water fastness of the coating layer and printed area can also be improved by crosslinking its water-soluble components such as PVA or starch, for example with the aid of glyoxal-based resins. In addition, hydrophobic polymers, like styrene acrylate or ethylene vinyl acetate-based copolymers, can be used as a partial or total replacement for water-soluble binders (Jonckherree and Mabire 2003).

## 2.3 Analytical methods in paper-ink interaction studies

As has become evident from the previous chapters, paper-ink interactions contribute strongly to both short- and long-term print quality. Detailed information on such interactions cannot be obtained solely with traditional print quality measurement methods. Analytical methods capable of detecting both physical and chemical paper-ink interactions are therefore needed.

Physical paper-ink interactions, like aggregation or penetration of the ink into the paper, have been investigated with various microscopic methods, often combined with thin-cuts of paper (Pinto and Nicholas 1997, Shaw-Klein 1998, Stübbe et al. 1998, Pinto et al. 1999, Preston et al. 2000). However, in most cases these techniques do not give direct information on the chemical structure of the interface. On the other hand, chemical paper-ink interactions have been studied with a number of methods. Chromatographic techniques in particular (Oliver and Kale 1985, Donigian et al. 1999) have been used in experiments related to ink jet printing to obtain information on interactions between solutes, solvents and solid surfaces. Still, because of the large amount of ink solvent present, they do not enable studies of real prints and therefore do not simulate the actual printing situation. Thermal analysis (Sargeant et al. 1998), absorbance measurements and zeta potential measurements (Oka and Kimura 1995) have also been used in interaction studies. Electron spectroscopy for chemical analysis (ESCA) has been utilized in examining both the chemical structure of the paper surface and print properties (Farrow et al. 1982), because it gives information on the electronic structure and bonding of single atoms. The main disadvantage of ESCA in relation to ink jet printing is its extreme surface sensitivity, which may complicate the detection of the paper-ink interface. Moreover, the inability of ESCA to detect hydrogen atoms may limit the possibilities of analyzing the hydrogen bonding of the colorant. In addition, even minor sample impurities may cause serious errors in the results obtained with ESCA.

Vibrational spectroscopic methods, or Fourier transform infrared (FTIR) and Raman spectroscopy, were selected as the main analytical methods for the paper-ink interaction studies of this thesis. Their most remarkable benefit is probably the possibility of examining prints as such, and thereby obtain information on the actual paper-ink interactions. Owing to the versatility of the available detection methods, the samples can also be examined in any physical state. Hence, both inks and papers can be examined without destructive and often tedious sample preparation. A third very advantageous feature of vibrational spectroscopy in print analyses is that it allows both surface and depth profiling measurements. However, despite their numerous favorable properties in connection with print studies, there are only a few publications on the suitability of FTIR and Raman spectroscopy specifically for ink jet print studies. Instead, both techniques have been used extensively for identifying paper components and possible contaminants, and for studying the photoyellowing of pulps and papers (Agarwal and Atalla 1995, Forsskåhl et al. 1995, Friese and Banerjee 1995). FTIR methods have also been applied in investigating archeological findings (Lang et al. 1998),

classifying document papers (Kher et al. 2001) and studying the chemical composition of coatings (Halttunen et al. 1999, Kenttä et al. 2000, Halttunen et al. 2001). Raman spectroscopy has been mainly utilized in analyzing coated paper mottling (Guyot and Amram 1993) and in depth profiling and lateral mapping of paper coatings and offset prints (Vyörykkä et al. 2001, Vyörykkä et al. 2002).

Besides studies related to pulp and paper, FTIR and Raman spectroscopy have been applied to colorant research. FTIR methods have been used in identifying colorants (Kaplanová and Cerný 1997, Kaplanová 1998), in characterizing the functional groups of carbon black pigment (Prest Jr. and Mosher 1982), in measuring the light absorption of very thin ink layers (Kushelevsky and Slifkin 1987) and in studying dye-polymer interactions (Slark and Hadgett 1998, Slark and Hadgett 1999). Moreover, FTIR methods have proven to be useful in studying reactive dye states on cotton fabric (Kokot et al. 1997b). Raman methods have been applied extensively to analyzing pigment structures and the degradation of historical documents and fabrics (Edwards and Falk 1997, Clark and Gibbs 1998, Lyon et al. 1998, Mulvaney and Keating 2000), in studying interactions between reactive dyes and cotton fibers (Kokot et al. 1997a) and in discriminating colorants from paper surfaces (Kenton and Rubinowitz 1990). Both FTIR and Raman spectroscopy have also been widely utilized in studying azo compounds (Hadži 1956, Trotter 1977, Kelemen et al. 1982, Biswas and Umaphathy 2000), which are typical colorants used in ink jet inks. Recently, NIR-FTR (Fourier transform Raman spectrometry using near-infrared excitation) and SERRS (surface-enhanced resonance Raman scattering) were used for detecting ink jet dyes on paper surfaces (Rodger et al. 2000, Littleford et al. 2003). The colorants could be detected with both methods, but it was concluded that fluorescence may pose a problem in NIR-FTR, whereas in SERRS the spectra arise from an interaction between the colloidal surface and the dye, and not from the bulk. This may be a problem particularly with thick ink films. Moreover, in SERRS the required pre-treatment of the sample with metal prevents the prints from being studied as such.

### 3 HYPOTHESES

This thesis discusses the effects of physical properties of coatings and chemical paper-ink interactions on the light and water fastness of ink jet prints on coated papers using sample sets with known compositions. Mechanisms that are expected to contribute to the permanence of ink jet prints based on the pertinent literature are summarized in Table 1. Also included are the factors that are presumed to have relevance for the suggested fastness mechanisms.

*Table 1. Suggested mechanisms of water and light fastness of ink jet prints on coated papers.*

<b>Suggested fastness mechanism</b>	<b>Factors influencing water fastness</b>	<b>Factors influencing light fastness</b>
<b>Protective layer</b> (Physical properties of the coating)	Porosity Roughness Wettability Dye distribution in z-direction	Porosity Roughness Polarity Dye distribution in z-direction
<b>Chemical stabilization</b> (Chemical paper-ink interactions)	Ionic interactions Dye distribution in z-direction	Hydrogen bonding Dye distribution in z-direction

Firstly, it is postulated that the physical properties of the coating have an impact on ink jet print fastness. More specifically, it is hypothesized that the coating is able to form a protective layer against exposure to environmental factors, thereby reducing photodegradation or dissolution of colorant. Porosity and wettability are presumed to be the most important physical properties contributing to this, because low porosity and low wettability are expected to counteract the penetration of light, surrounding air or water into the coating. Roughness and polarity may also have some relevance. The effects of the physical properties of the coating are studied using conventional methods for measuring paper properties. In addition, spectroscopic depth profiling is used to examine the penetration of the ink into the coating.

The second hypothesis is that apart from the physical properties of the coating, chemical paper-ink interactions also have an effect on print permanence. Certain coating components are expected to be able to stabilize the colorant once it is printed onto the paper. In particular, polymers containing hydroxyl moieties are presumed to be capable of forming hydrogen bonds with the colorants, thereby suppressing photodegradation. In addition, the presence of ionic interactions between the dyes and the coating components is postulated to promote the water fastness of soluble dyes. The chemical paper-ink interactions are examined with vibrational spectroscopic methods.

## 4 EXPERIMENTAL

Detailed descriptions of the materials and methods used in the experiments included in this thesis are given in Papers I-VI.

### 4.1 Materials

#### 4.1.1 Model coatings

The thesis concentrates on the effects of the physical properties of the coatings and of the chemical paper-ink interactions on the light and water fastness of ink jet prints. To investigate this, two model coating sets were generated, in which the polymer system (Papers II and III) and the pigment composition (Papers IV-VI) were used as variables.

The structural properties of the coatings were varied using three different types of pigment: SPS kaolin (Papers II and III), and modified kaolin and PCC, which were tailored to ink jet coatings (Papers IV-VI). The absorption properties of the model coatings were altered using different types and amounts of binder. These were hydrophilic polyvinyl alcohol (PVA), hydrophobic styrene acrylate latex (SA), and weakly cationic SA latex. The net charge of the coatings was modified using different dispersants for the kaolin pigment. These were anionic carboxymethyl cellulose (CMC), oxidized starch, weakly cationic starch, and cationic polydiallyl dimethyl ammonium chloride (poly-DADMAC). In all model coating sets, the base paper was surface-sized copy paper with 80 gm<sup>-2</sup> grammage, and the target amount of coating was 10 gm<sup>-2</sup>. All the coated papers were uncalendered. In studying the applicability of the spectroscopic methods (Paper I), an experimental offset paper was also used as a printing substrate. Table 2 summarizes the compositions of the model coatings and their abbreviations added to the grouping used later in this compendium.

#### 4.1.2 Model inks

Model inks with known compositions were used in the studies to better understand the paper-ink interactions occurring in the prints. The inks consisted of colorant, co-solvent and distilled water.

Three soluble azo colorants with different chemical properties, and one pigment dispersion were chosen for the inks. Magenta azo colorant C.I. Acid Red 249 (AR249) shown in Figure 1 is an acid dye, whereas yellow anionic azo colorant C.I. Direct Yellow 86 (DY86) presented in Figure 2 belongs to the class of direct dyes. The other magenta colorant C.I. Direct Violet 107 (DV107) is a modified direct azo dye with enhanced fastness properties. Information on the molecular structure of DV107 is not publicly available. The fourth colorant used in the study is an azo pigment, C.I. Pigment Yellow 83 (PY83), see Figure 3. The added co-solvents were 2-pyrrolidone (2-p), diethylene glycol (DEG) and tetraethylene glycol (TEG). To simplify the analysis of the paper-ink interactions, surfactants were not used in the model inks. Consequently, the inks do not necessarily behave as typical commercial ink jet inks, as far as physical and chemical paper-ink interactions are concerned.

Table 2. Abbreviations, compositions and grouping of the model coatings.

Coating code	Pigment		Binder		Dispersant		Coating group
	Type	Amount (pph)	Type	Amount (pph)	Type	Amount (pph)	
PVA5CMC	SPS kaolin	100	PVA	5	CMC	1	Anionic
PVA10CMC				10			
PVA15CMC				15			
SA5	SPS kaolin	100	Anionic SA latex	5	-	-	Anionic
SA10				10			
SA15				15			
SA20				20			
SA10xSt	SPS kaolin	100	Anionic SA latex	10	Oxidized starch	4	Anionic
CSA10CSt	SPS kaolin	100	Weakly cationic SA latex	10	Weakly cationic starch	4	Weakly cationic
PVA5PoD	SPS kaolin	100	PVA	5	Poly-DADMAC	3	Cationic
PVA10PoD				10			
P0:100	Modified PCC and kaolin	PCC:kaolin 0:100	PVA	10	Poly-DADMAC	3	Cationic
P20:80		20:80					
P40:60		40:60					
P60:40		60:40					
P80:20		80:20					
P100:0		100:0					
S0:100	Modified PCC and kaolin	0:100	Weakly cationic SA latex	10	Weakly cationic starch	4	Weakly cationic
S20:80		20:80					
S40:60		40:60					
S60:40		60:40					
S80:20		80:20					
S100:0		100:0					

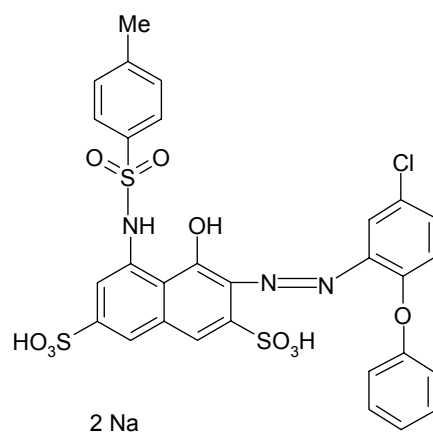


Figure 1. Molecular structure of C.I. Acid Red 249.

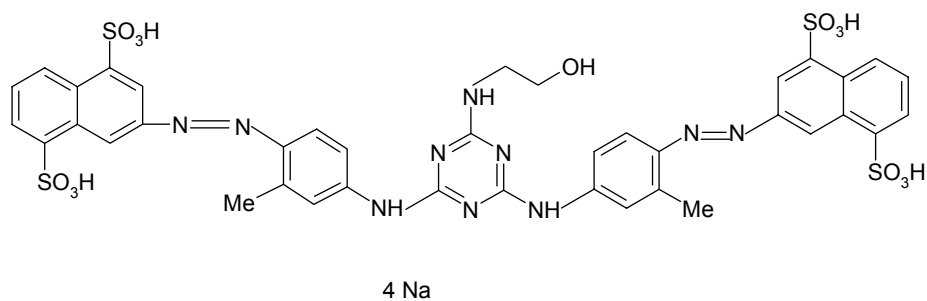


Figure 2. Molecular structure of C.I. Direct Yellow 86.

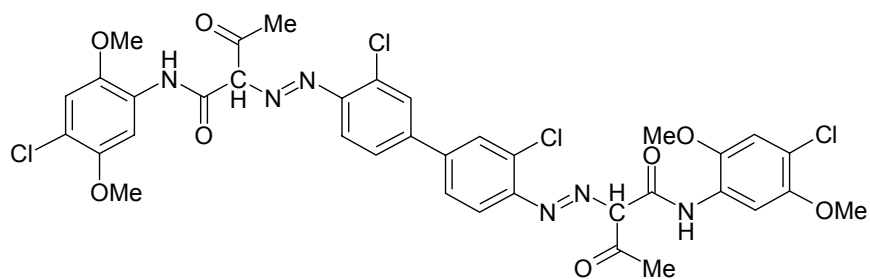


Figure 3. Molecular structure of C.I. Pigment Yellow 83.

## 4.2 Methods

Coated papers were analyzed to determine their roughness, porosity, wettability, and polarity, and the model inks to determine their pH, surface tension and viscosity (Papers II-V).

To examine the paper-ink interactions contributing to the light and water fastness of ink jet prints, solid single-color areas were printed on the experimental papers with a thermal ink jet printer (Papers I-III) and a piezo ink jet printer (Papers IV-VI) using the model inks. The compositions of the model inks were not optimized for the printer's performance, so the printed areas were generally extensively striped, instead of being completely solid. This unevenness may have caused unexpected variation in the measured print quality parameters. Moreover, the exact amount of ink on the paper is unknown, and therefore only colorant-paper interactions are considered in this study. Water fastness was measured by immersing the prints into de-ionized water for 5 minutes without agitation (Paper III). Light fastness of the prints was measured by exposing them to artificial sunlight emitted by a Suntest CPS+ xenon arc lamp for 100 hours (Paper II), according to the common practice (Wypych 2003). The spectral composition of the xenon arc lamp corresponds approximately to that of sunlight. The device was equipped with an optical filter system, which cuts off the wavelengths below 310 nm.

FTIR-ATR, NIR-Raman, UV resonance Raman (UVRR) and Kerr-gated resonance Raman spectra of unprinted and printed samples were recorded to get more information on the chemical composition of the samples and conceivable paper-ink interactions affecting the fastness properties.

The analyses of the measurement data (Papers IV-VI) were accomplished with multivariate data analysis methods, namely projection to latent structure (PLS) and principal component analysis (PCA). The mathematical background of these chemometric methods is described in the literature (Eriksson et al. 2001). The effect of the physical properties of the coating on the fastness properties was evaluated with the PLS method. The data were not mathematically manipulated except for the unit variance scaling prior to the PLS analyses. The use of the PLS method for prediction and modeling purposes requires a large number of variables and observations in order to get reliable results. In this study, the sample sets were rather small, so the calculated models should not be used in predicting fastness values. The PLS analysis is nevertheless justified here, as it gives a compact representation on the effects of all the studied X variables on all Y variables and their mutual relationships. Principal component analysis (PCA) was utilized in the interpretation of the spectroscopic data. Reading of the resultant plots of PLS and PCA (score plots, loading plots) is explained in Paper IV. Further examples on the use of these methods in the analysis of print and spectroscopic data are found from the literature (Kokot et al. 1997b, Hladnik and Muck 2002, Hladnik et al. 2002).



## 5 RESULTS

### 5.1 FTIR and Raman spectroscopic methods in ink jet print studies

The applicability of FTIR and Raman spectroscopic methods to the analysis of ink jet prints on coated papers was evaluated in the first part of this thesis (Papers I and VI). The emphasis in the evaluation of methods was placed on light fastness studies, though both spectroscopic techniques allow the water fastness of ink jet prints to be studied as well. In light fastness experiments, the most intensive exposure is typically directed towards the printed surface of the sample (Wypych 2003). Therefore, detailed analysis of the topmost layers of the print is essential. This can be accomplished by combining the information obtained from surface analysis and depth profiling measurements carried out with vibrational spectroscopic techniques. In this study, the FTIR methods used for analyzing unprinted coated papers and prints were attenuated total reflectance (FTIR-ATR) and step scan photoacoustic measurement (FTIR step scan PAS). The evaluated Raman methods were confocal near infrared Raman (NIR-Raman), UV resonance Raman (UVRR) and Kerr gated resonance Raman spectroscopy.

The results indicate that both FTIR and Raman methods are capable of detecting the light-induced changes in the spectra of ink jet prints (Papers I and VI). The main advantage of the evaluated FTIR methods in analyzing ink jet prints proved to be the possibility of investigating many kinds of paper coatings independently of their composition, and to characterize the hydrogen bonding between ink and paper components. However, the detection of printed soluble dyes from the coating using FTIR spectroscopy was found to be rather difficult, regardless of the selected measurement mode, which complicated the interaction analysis. In most cases, spectral subtraction was required to bring out the bands of dye-based colorants from the FTIR spectrum of the printed sample. The principal component analysis (PCA) method proved to be a very convenient way of analyzing spectral data, because even minor differences between the spectra could be observed with this method (Paper IV). Among the evaluated FTIR measurement techniques, the micro-ATR technique turned out to be the most convenient FTIR method for analyzing unprinted papers and printed samples (Paper I).

In contrast to the FTIR methods, even minor amounts of ink jet dyes and their light-induced changes could generally be detected with the evaluated Raman measurements (Papers I and VI). UV Resonance Raman spectroscopy (UVRRS) was found to be a particularly promising method for studying the photodegradation of ink jet prints, owing to its sensitivity to aromatic structures and conjugated double bonds (Papers I and V). An example of this is presented in Figure 4, which presents the 1750-1500  $\text{cm}^{-1}$  region of the UVRR spectra of unprinted SB latex-CaCO<sub>3</sub> coating, and yellow prints treated with different amounts of light energy. In the spectrum of the unprinted coating (a), the bands at wavenumbers 1647 and 1602  $\text{cm}^{-1}$  likely originate from the aliphatic and aromatic C=C stretching modes of the SB latex (Lin-Vien et al. 1991), respectively. As a result of printing (b), slight changes in the wavenumbers and the intensities of these bands can be observed suggesting interaction between the colorant and the coating. Moreover, a new band likely originating from the dye arises at 1572  $\text{cm}^{-1}$ . Light exposure for 100 hours (c) results in marked changes in the UVRRS spectrum of the yellow print. The intensity of the band at 1644  $\text{cm}^{-1}$  decreases and a new band can be detected at the wavenumber 1682  $\text{cm}^{-1}$ . In addition, the band at 1607  $\text{cm}^{-1}$  shifts to wavenumber 1602  $\text{cm}^{-1}$ , and the dye band at 1572  $\text{cm}^{-1}$  to 1575  $\text{cm}^{-1}$ . These spectral changes would imply alterations in the chemical compositions of both the dye and the latex.

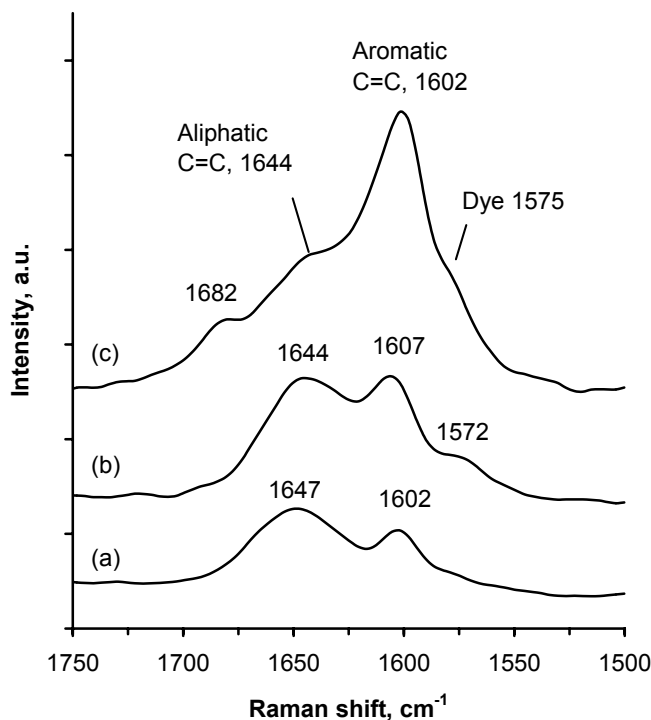


Figure 4. Effect of light exposure on UV Resonance Raman spectra of yellow ink jet prints. (a) Unprinted and unexposed coating, (b) printed and unexposed coating, and (c) printed and light-exposed (100h) coating. The spectra are vertically shifted for clarity.

The main difficulty in the Raman measurements was the obtrusive fluorescence originating from most studied ink jet colorants and the kaolin pigments. This phenomenon could be somewhat alleviated by using an immersion objective in the confocal Raman measurement (Paper I). However, substantially more effective quenching of the fluorescence could be achieved by using the Kerr gate fluorescence rejection method in conjunction with resonance Raman spectroscopy (Paper VI). The results indicated that Kerr gated resonance Raman spectroscopy is eminently applicable to studying the photodegradation of ink jet prints, owing to the effective damping of sample-related fluorescence as shown in Figure 5. Besides, the possibility of obtaining resonance enhancement of the desired chemical groups of the colorant by proper selection of the wavelength, and the method's apparent sensitivity to light-induced changes in prints further increase its attractiveness.

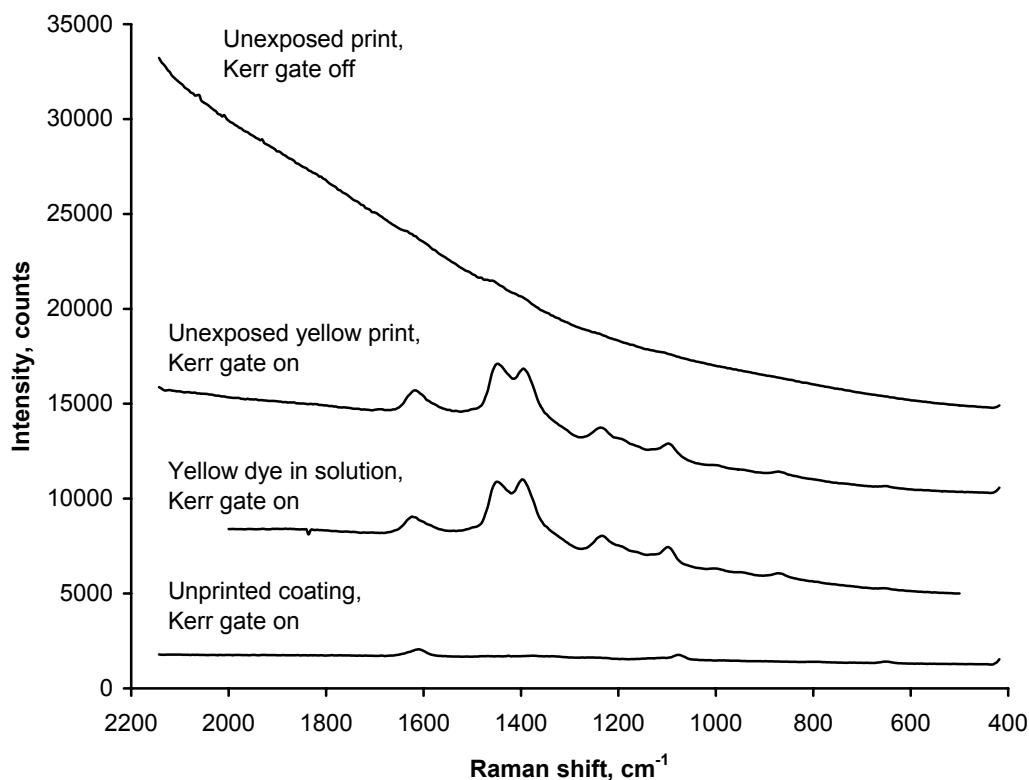


Figure 5. Effect of Kerr gate on resonance Raman spectra of ink jet prints. Colorant DY86, coating P80:20. The curves are vertically shifted for clarity.

Two depth profiling methods were also studied, namely FTIR step-scan PAS and the confocal Raman technique. Of these, confocal Raman spectroscopy proved to be better applicable to studying the light fastness of dye-based ink jet prints than FTIR step-scan PAS (Paper I). This was because of its sensitivity to the chemical structures of the ink jet colorants, the good S/N-ratio of the spectra determined from the topmost surface layers of the print, and the knowledge on the exact probing depth.

## 5.2 Overview on ink jet print permanence

In the second part of this thesis, the effects of the physical properties of the model coatings and chemical paper-ink interactions on the ink jet print permanence were investigated. The relation between water and light fastness values measured as color differences  $\Delta E^*$  for all colorant-coating combinations is presented in Figure 6. The corresponding data can be found in Papers II-V.

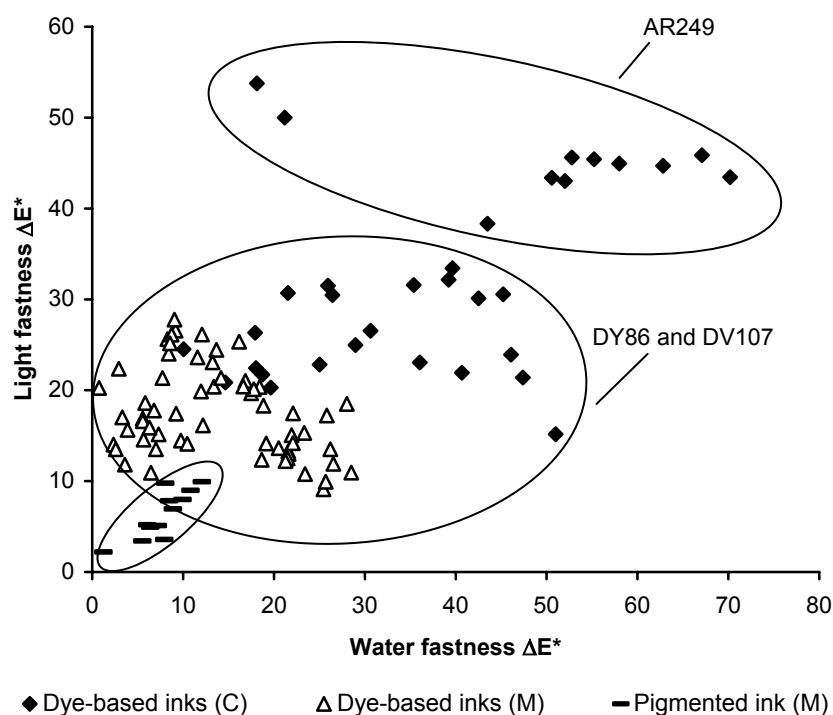


Figure 6. Relation between water and light fastness values of all ink-coating combinations. The letter C in the legend denotes the conventional kaolin coatings and M the modified coatings containing pigments tailored for ink jet printing.

As Figure 6 illustrates, light and water fastness values of ink jet prints depend markedly on both the coating composition and the type of ink. The lowest print permanence (large  $\Delta E^*$  values) was generally obtained with dye-based inks on conventional kaolin coatings (Papers II and III). Within this sample set, the differences in water and light fastness values were quite drastic and depended largely on the type of dye. The permanence of the two direct dyes DY86 and DV107 was clearly better than that of the acid dye AR249. With modified conventional coatings containing pigments tailored for ink jet printing (Papers IV and V), the water fastness of the dye-based inks was clearly improved compared to the conventional kaolin coatings. However, the effect on light fastness was not equally straightforward. Instead, it seemed to be more dependent on the ink-coating combination in question. With modified coatings, light and water fastness values were nevertheless mostly within a relatively small range compared to the conventional kaolin coatings, which suggests that the role of the coating composition is reduced. The data presented in Figure 6 further indicate that superior print permanence is obtained with pigmented ink on modified coatings and that the differences between the observations are small (Papers IV and V). This holds true for both water and light fastness.

The distribution of the colorant in the z-direction was evaluated with Raman spectroscopy; an example of the results is presented in Figure 7. With conventional kaolin coatings, Raman depth profiles measured from the samples printed with the modified direct dye DV107 indicated that the dye that has penetrated into the coating layer is primarily in contact with the coating polymers, irrespective of the polymer system (Paper II). This was a common behavior observed for all studied dye-based colorants, regardless of the carrier phase or the coating composition (Paper IV). The results nevertheless implied that the pigmented model ink tends to behave somewhat differently on the coating surface compared to the dye-based model inks (Paper IV). As Figure 7 illustrates, the dye-based DY86 colorant has penetrated deeper into the coating than the pigmented ink PY83, as the widths of the colorant profiles differ. In the case of DY86, the main profile is approximately 10  $\mu\text{m}$  wide, whereas with PY83, it is only about 5  $\mu\text{m}$ .

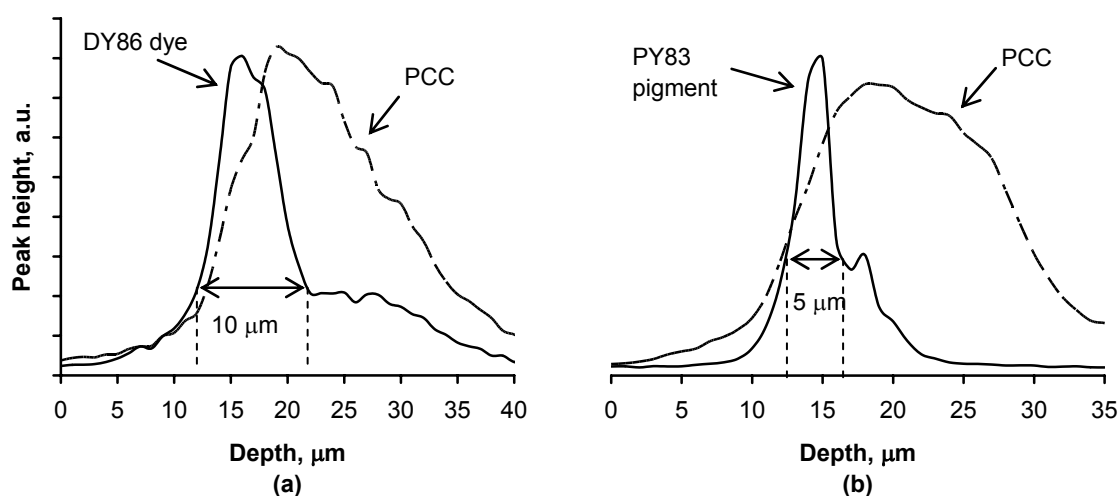


Figure 7. Distributions of (a) direct dye DY86 (co-solvent 20 wt.% 2-pyrrolidone, and (b) pigmented ink PY83 on a PVA-poly-DADMAC model coating containing 100 pph PCC. The printed samples were untreated.

In the following chapters the mechanisms influencing the water and light fastness of ink jet prints are evaluated. The emphasis is placed on dye-based inks, because within the present sample set the composition of the coating appears to be rather irrelevant for the fastness properties of the pigmented model ink, PY83. Furthermore, the studies of chemical paper-ink interactions focus on AR249 and DY86 colorants, as their detailed chemical structures are known.

## 5.3 Mechanisms influencing water fastness of ink jet prints

### 5.3.1 Effect of coating composition

The print permanence data presented in Figure 6 and in Papers III and IV indicated that the water fastness of dye-based inks is strongly dependent on the compositions of both the coating and the ink. To explore the overall effect of the coating composition on the water fastness of the dye-based model inks, a PCA analysis was conducted for the water fastness values of DY86 2p20 and DV107 inks on the model coatings (Table 2). The results presented here represent the general behavior observed. The PCA score plot presented in Figure 8 illustrates the influence of the coating composition on water fastness.

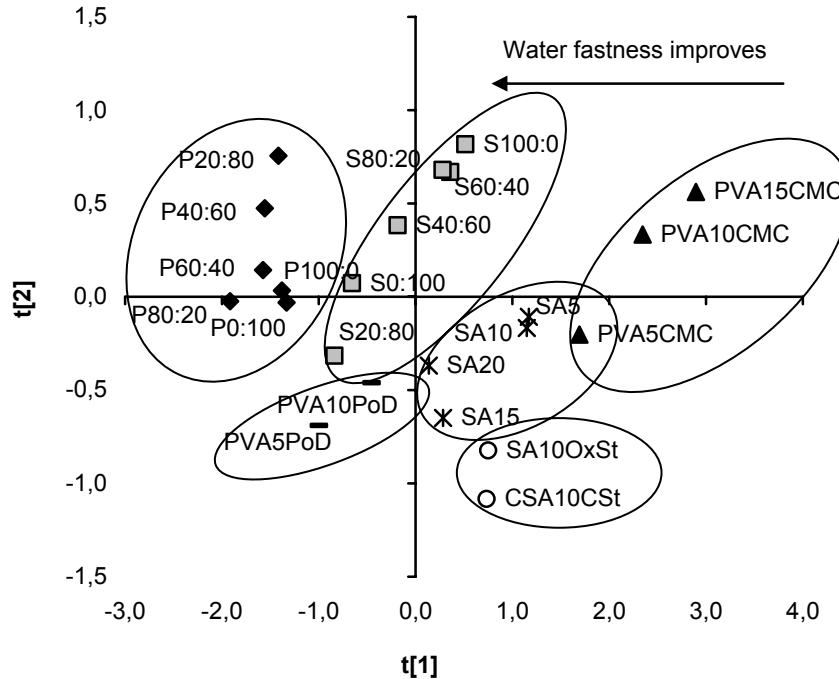


Figure 8. Grouping of coating compositions as a function of water fastness values. Keys to the abbreviations denoting the observations are listed in Table 2.

The PCA score plot demonstrates that the coating composition has a distinct influence on the water fastness of dye-based ink jet prints. The first principal component PC1 separates well the observations, with the water fastness improving as a function of decreasing score value  $t[1]$ . Various coating polymer and pigment combinations are distinctly grouped, and certain trends can also be found within each group. The highest water fastness is typically obtained with the cationic model coating sets, namely PVA-poly-DADMAC coatings containing modified PCC and kaolin (P0:100...P100:0) and conventional SPS kaolin as pigments (PVA5PoD, PVA10PoD). The pigment composition (PCC:kaolin ratio) of the modified PVA-poly-DADMAC coatings does not have a clear influence on water fastness. On the other hand, on conventional PVA-poly-DADMAC coatings water fastness deteriorates as the amount of PVA binder increases.

The water fastness of the two dye-based model inks on coatings containing anionic or weakly cationic SA latex (S0:100...S100:0; SA5...SA20; SA100xSt and CSA10CSt) is generally somewhat lower than on cationic PVA-poly-DADMAC coatings. With weakly cationic SA latex-starch coatings containing modified PCC and kaolin (S0:100...S100:0) the effect of the pigment ratio is now more pronounced compared to the modified PVA-poly-DADMAC coatings, such that water fastness improves as the amount of kaolin in the coating increases. If ink jet kaolin is replaced with SPS kaolin (CSA10CSt), water fastness is impaired. The lowest water fastness is obtained with anionic coatings containing PVA-CMC as a polymer system and conventional SPS kaolin (PVA5CMC...PVA15CMC). With this set, an increase in the binder content results in decreased water fastness, whereas the opposite is true for the anionic but hydrophobic SA latex coatings (SA5...SA20). An SA latex coating containing oxidized starch (SA100xSt) slightly improves water fastness compared to an anionic SA latex coating with an equal amount of binder (SA10).

### 5.3.2 Physical properties of the coating layer

The effects of the physical properties of the coating on water fastness were explored by performing PLS analyses with cationic, weakly cationic and anionic coatings groups (Table 2) separately. The coating-related variables (X variables) selected for the analysis were Bendtsen air permeability (B\_air\_p), average pore diameter (Av\_PoreD), total pore area (Tot\_PoreA), Bendtsen roughness (B\_rough),  $\theta_a$  micro roughness ( $\theta_a$ , inclination of the roughness profile),  $R_a$  micro roughness ( $R_a$ , the arithmetic mean of the deviations from the mean line of the roughness profile), contact angle (Cont\_ang) and polarity of the coating (Polar). Water fastness variables (Y variables) were the color difference values of DY86 2p20 and DV107 model inks. The data on the physical properties of the coatings and the calculated water fastness values are found in Papers II-IV. The key parameters of the calculated PLS models are compiled into Table 3, and the resulting PLS weight plots for the anionic, weakly cationic and cationic coating groups are presented in Figures 9-11, respectively.

*Table 3. PLS models for water fastness of dye-based ink jet inks on anionic, weakly cationic and cationic model coatings.  $R^2XCum$ ,  $R^2YCum$  and  $Q^2Cum$  denote the explained cumulative variation of X- and Y-variables, and the predicted cumulative variation, respectively.*

Coating system	PC	$R^2XCum$	Eigenvalue	$R^2YCum$	$Q^2Cum$
<b>Anionic</b>	<b>1</b>	0.381	3.05	0.731	0.374
	<b>2</b>	<b>0.870</b>	3.91	<b>0.752</b>	<b>0.320</b>
<b>Weakly cationic</b>	<b>1</b>	0.491	3.44	0.382	-0.0297
	<b>2</b>	<b>0.824</b>	2.33	<b>0.821</b>	<b>0.165</b>
<b>Cationic</b>	<b>1</b>	0.446	3.57	0.452	0.275
	<b>2</b>	<b>0.826</b>	3.04	<b>0.511</b>	<b>0.202</b>

All three PLS models presented in Table 3 consist of two principal components (PC). The eigenvalue of the third component was smaller than 1 in every case, so they were neglected from the discussion. The key parameters of the PLS models imply that the explained variation of water fastness variables ( $R^2YCum$ ) is clearly larger with anionic (75.2%) and weakly cationic coatings (82.1%) than with cationic coatings (51.1%). Furthermore, the predicted data variation ( $Q^2Cum$ ) is low, particularly for weakly cationic and cationic coatings (16.5% and 20.2%, respectively).

The PLS weight plot presented in Figure 9 illustrates the effect of the physical properties of the coating on the water fastness of dye-based ink jet inks on anionic model coatings (Paper III). The weight plot indicates that the studied paper-related variables have similar effects on both dye-based model inks, the most influential variables being  $\theta_a$  micro roughness and average pore diameter. The contact angle (wettability) of the coating, Bendtsen roughness,  $R_a$  micro roughness and total pore area have a moderate effect, whereas Bendtsen air permeability and the polarity of the coating appear to be rather irrelevant. Generally speaking, the model suggests that the water fastness of the DY86 2p20 and DV107 model inks improves as the roughness ( $\theta_a$ ,  $R_a$  and Bendtsen roughness) and average pore diameter of the coating decrease, and as the total pore area and contact angle of the coating increase. This is in accordance with the hypothesis.

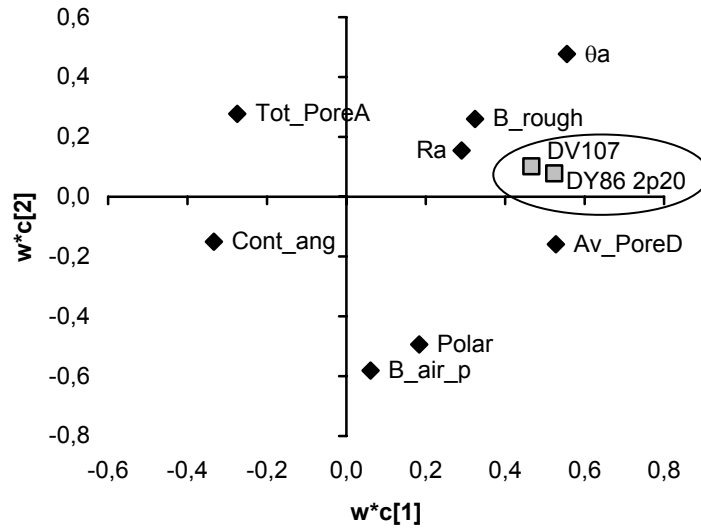


Figure 9. PLS model depicting the effect of the physical properties of the coating on the water fastness of dye-based ink jet inks on anionic model coatings.

Figure 10 presents the PLS weight plot for the water fastness of dye-based ink jet inks on weakly cationic model coatings (Papers III and IV). In contrast to the anionic coatings, the studied paper-related variables have somewhat different effects on the water fastness of the two model inks. The model suggests that the water fastness of DY86 2p20 ink improves as  $\theta_a$  micro roughness decreases and as the contact angle increases (wettability decreases). An increase in average pore diameter, and decreases in total pore area and  $R_a$  roughness have moderate effects, whereas the influence of the other variables is negligible. With DV107 ink, the most influential factors are the porosity parameters (Bendtsen air permeability, total pore area, average pore diameter). Bendtsen and  $R_a$  roughnesses have a moderate impact, whereas the influences of  $\theta_a$  roughness, contact angle and polarity are small. The model suggests that the water fastness of DV107 ink improves as the porosity and roughness of the coating decrease. Hence, the results for the weakly cationic coatings are partly in agreement with the hypothesis.

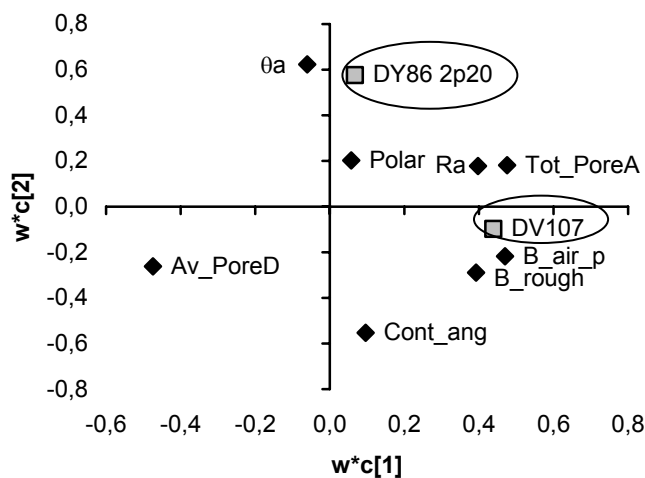


Figure 10. PLS model depicting the effect of the physical properties of the coating on the water fastness of dye-based ink jet inks on weakly cationic model coatings.



Figure 11 presents the PLS weight plot for the water fastness of the two dye-based model inks on cationic model coatings (Papers III and IV). The results imply that with DY86 2p20 ink, the surface chemical properties are the most influential factors for water fastness, whereas the roles of roughness and porosity are smaller. The model suggests that the water fastness of the DY86 2p20 ink improves as the contact angle,  $\theta_a$  micro roughness and total pore area of the coating decrease, and as the polarity and average pore diameter increase. With DV107 ink, the significance of the physical properties of the coating is quite small, except that an increase in Bendtsen air permeability is favorable for water fastness. The model also suggests that increased coating roughness has a small beneficial effect. Consequently, the results are contradictory to the hypothesis.

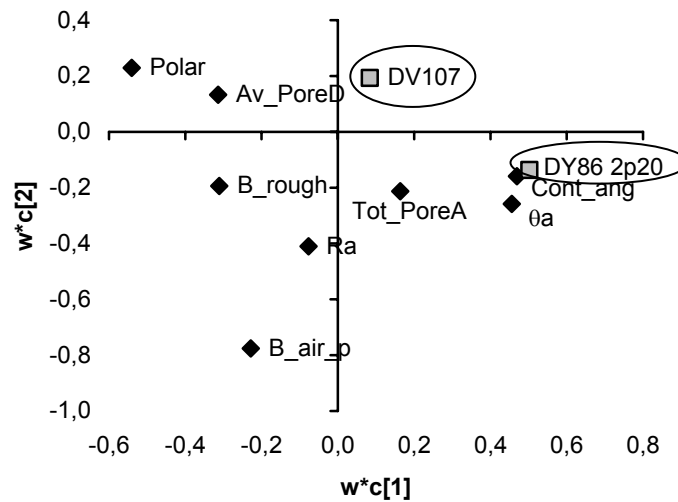


Figure 11. PLS model depicting the effect of the physical properties of the coating on the water fastness of dye-based ink jet ink on cationic model coatings.

### 5.3.3 Chemical paper-ink interactions

Chemical paper-ink interactions were presumed to contribute to the water fastness of ink jet prints as well. The results of this thesis suggest that the water fastness of the dye-based model inks is largely determined by the mode of attachment of the colorant to the coating, and by the cohesion of the coating itself (Papers III and IV). On anionic coatings, evidence was found that hydrogen bonding would be a prevailing mechanism for the attachment of the colorant to the coating (Paper III). Meanwhile, the FTIR spectroscopic data obtained from the cationic model coatings gave indications of ionic bonding between the colorant and the coating (Paper IV). An example of this is presented in Figure 12. The upper curve represents the FTIR spectrum of the dried DY86 colorant (Figure 2), whereas the lower curve stands for the PCA loading values of printed DY86 DEG ink. The FTIR bands marked to the spectra represent the sulphonate groups ( $\text{Ar-SO}_3^-$ ) of the colorant. It is evident that in the colorant spectrum measured from the printed sample, these bands have shifted to lower wavenumbers. This might signify weakening of the bonds of the sulphonate group owing to its ionic interaction with the cationic groups of the coating.

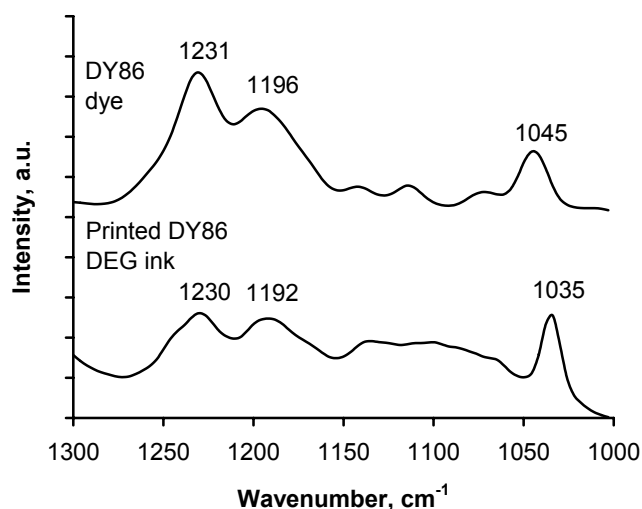


Figure 12. FTIR-DTGS spectrum of the dried direct dye DY 86 and the PCA loading values of printed DY86 DEG ink.

With regard to the cohesion of the coating layers, FTIR measurements suggested that the hydrophilic polymers used in the model coatings, PVA and starch, dissolve during water immersion (Papers III and IV). This behavior was particularly pronounced on coatings containing large amounts of PVA binder (Paper III). As an example of this, a PCA loading plot calculated from the FTIR-ATR spectra measured from the PVA-poly-DADMAC coatings printed with DY86 inks (Paper IV) is presented in Figure 13. The plot depicts the difference between untreated and water-immersed prints, and demonstrates that they differ in terms of the contributions related to PVA, poly-DADMAC and the DY86 colorant. The spectral changes suggest at least partial dissolution of PVA from the coating during exposure to water, whereas the dye and poly-DADMAC are still retained in the coating.

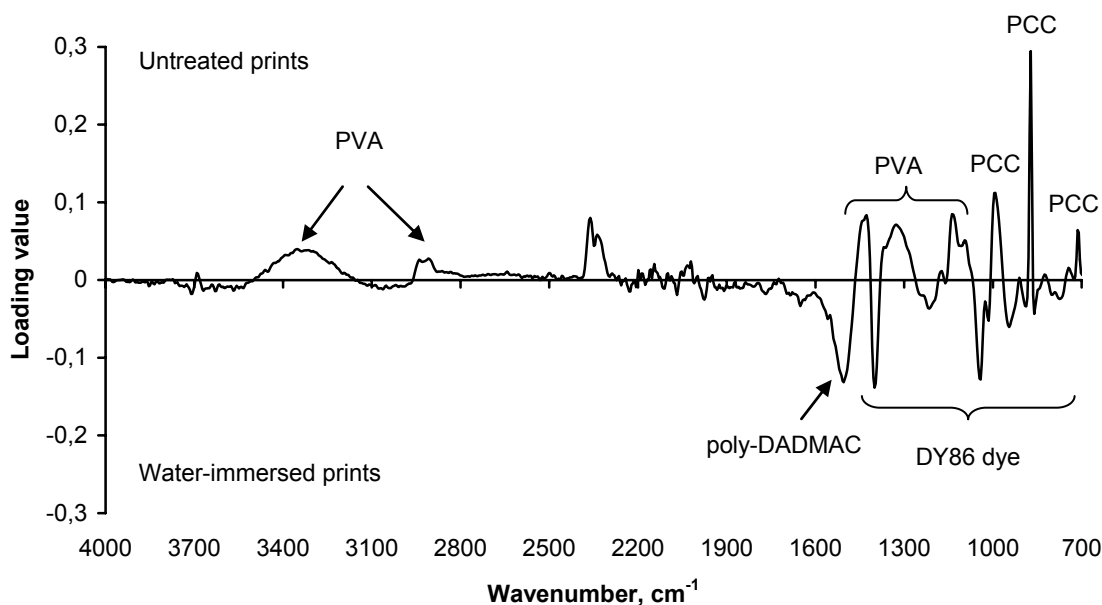


Figure 13. PCA loading values of untreated and water-immersed prints (all DY 86 inks, all PVA-poly-DADMAC coatings).

Interactions between the coating components may also influence the cohesion of the coating and eventually the water fastness of the printed image. With weakly cationic latex-starch coatings (Paper IV), the water fastness of the dye-based model inks was found to be better on coatings containing large amounts of modified kaolin than on PCC-rich coatings. Moreover, the dyes proved to be at least partially attached to a component that dissolves during water treatment, viz. polymers. The FTIR spectra measured from the coating pigments and unprinted coatings gave indications of variable interactions between the coating polymers and pigments, see Figure 14.

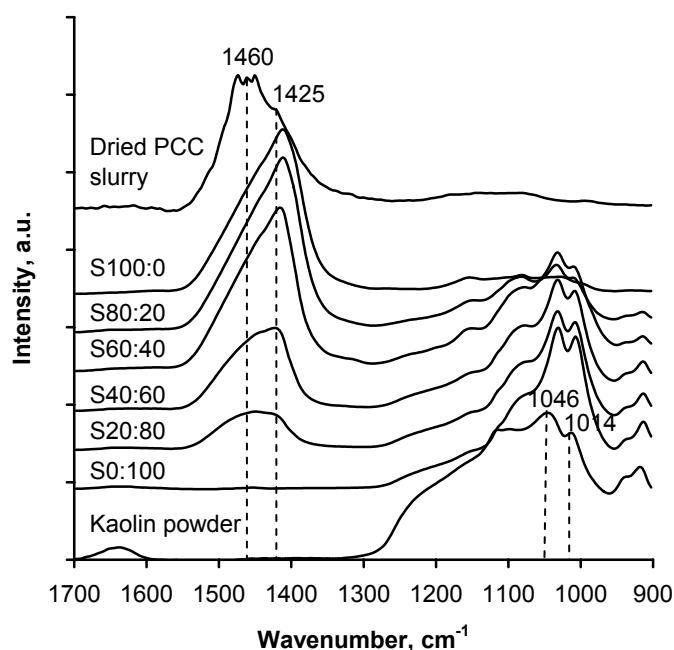


Figure 14. FTIR spectra of kaolin powder, untreated latex-starch coatings, and dried PCC slurry. The spectra are vertically shifted for clarity.

It is evident that the positions of the major FTIR bands of PCC and kaolin in Figure 14 are dependent on the PCC:kaolin ratio of the coating. In the spectrum of the dried PCC slurry, the bands at 1460 and 1425  $\text{cm}^{-1}$  represent the carbonate group  $\text{CO}_3^{2-}$  (Colthup et al. 1990). In the case of latex-starch coating containing PCC as a sole pigment (S100:0), their positions are lowered to 1443 and 1412  $\text{cm}^{-1}$ , which supposedly indicates interaction of PCC with the coating polymers. As the proportion of kaolin increases in the coating, the PCC bands shift gradually towards a higher wavenumber range, implying diminished interaction of PCC with the coating polymers. Corresponding shifts of certain kaolin bands can be observed as well. These observations suggest that kaolin and PCC compete for the coating polymers to some extent. Furthermore, the large wavenumber shifts of the FTIR bands of kaolin imply that the weakly cationic polymers used in this study tend to interact more strongly with the colors containing large amounts of kaolin, perhaps because of the more anionic nature of the pigments at higher pH levels (Paper IV). This could reduce the dissolution of starch and dye from the coating and thereby enhance the water fastness of the anionic, dye-based colorant.

## 5.4 Mechanisms influencing light fastness of ink jet prints

### 5.4.1 Effect of coating composition

As with water fastness, a PCA analysis was conducted for the light fastness values of DY86 2p20 and DV107 inks on the model coatings (Table 2) to evaluate the effect of the coating composition on photofading. The results represent the general behavior observed. The score plot illustrating the influence of the model coating composition on light fastness is presented in Figure 15. The data on the physical properties of the coatings and the calculated light fastness values can be found in Papers II-V.

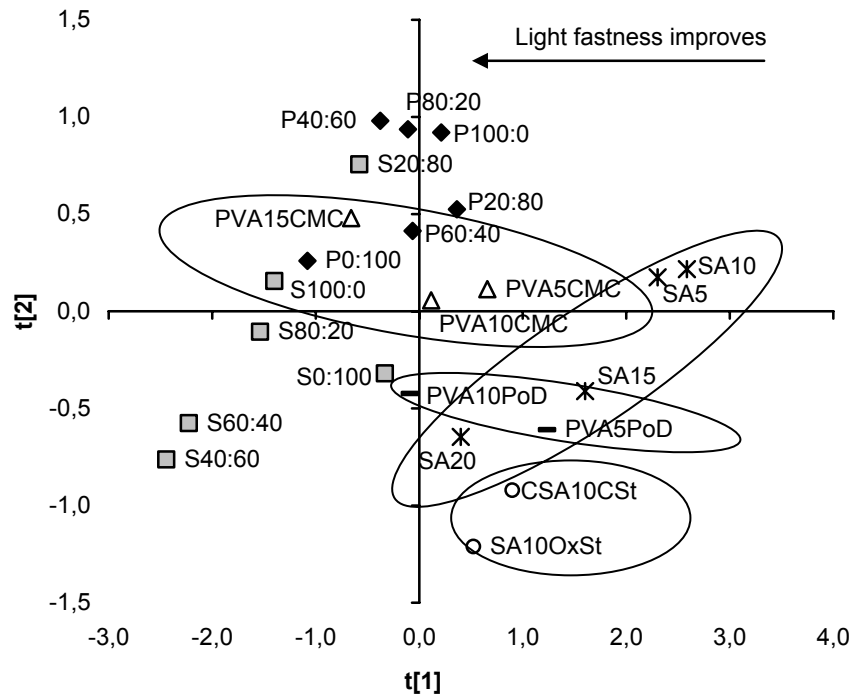


Figure 15. Grouping of the coating compositions as a function of light fastness values. Keys to the abbreviations denoting the observations are listed in Table 2.

The first principal component PC1 of the PCA score plot presented in Figure 15 represents the changes in light fastness values of ink jet prints, with the light fastness of the observations improving as a function of decreasing score value  $t[1]$ . It is evident that the grouping of the coating sets is much more disorganized than with water fastness, and the trends within the groups are rather ambiguous. Some general remarks can nevertheless be made based on the score plot. On the average, the light fastness of ink jet prints is better on coatings containing modified PCC and kaolin tailored for ink jet coatings than on conventional SPS kaolin coatings. The highest light fastness values of the two dye-based model inks are typically obtained with weakly cationic latex-starch coatings (S0:100...S100:0), particularly for the coatings containing large amounts of PCC. However, the trend is not entirely unequivocal. The light fastness on weakly cationic latex-starch coatings with SPS kaolin (CSA10CSt) is clearly lower than on coatings containing modified PCC and kaolin and a similar polymer system. The lowest light fastness values are obtained with anionic latex coatings (SA5...SA20) containing small amounts of binder. An increase in the latex content, or addition of oxidized starch, improves the photopermanence of the two model inks considered here.

The grouping of the PVA coatings with regard to light fastness is not completely unambiguous either, as Figure 15 illustrates. The light fastness on cationic PVA-poly-DADMAC coatings with modified pigments and on anionic PVA-CMC coatings containing SPS kaolin is generally in the same range. In contrast, the light fastness on cationic PVA-poly-DADMAC coatings with SPS kaolin is somewhat lower, particularly at low binder contents. The score plot also indicates that on PVA coatings containing SPS kaolin as a coating pigment, light fastness improves with an increase in the binder content of the coating, irrespective of the type of polymer system.

#### 5.4.2 Physical properties of the coating layer

As the PCA score plot in Figure 15 implied, the contribution of the coating composition to light fastness is very intricate. The effect of the physical properties of the coating on light fastness was examined with separate PLS models for PVA and SA latex coating sets, because the presumable stabilization or destabilization mechanisms of the colorants against light fading are likely to be different with these types. The coating-related variables (X variables) are the same as in the PLS analyses of water fastness data, and the light fastness variables (Y variables) are the corresponding color difference values of the DY86 2p20 and DV107 model inks. The data on the physical properties of the coatings and the calculated light fastness values are found in Papers II-V. The key parameters of the calculated PLS models for both coating sets are compiled into Table 4, and the corresponding PLS weight plots are presented in Figures 16 and 17.

*Table 4. PLS models for light fastness of dye-based ink jet inks on PVA and SA latex model coatings.  $R^2XCum$ ,  $R^2YCum$  and  $Q^2Cum$  denote the explained cumulative variation of X- and Y-variables, and the cumulative predicted variation, respectively.*

Coating system	PC	$R^2XCum$	Eigenvalue	$R^2YCum$	$Q^2Cum$
PVA coatings	1	0.525	4.2	0.285	0.145
	2	<b>0.795</b>	2.16	<b>0.413</b>	<b>0.0593</b>
SA latex coatings	1	0.45	3.6	0.715	0.671
	2	<b>0.667</b>	1.73	<b>0.785</b>	<b>0.662</b>

The data presented in Table 4 indicates that the two-component PLS model for the PVA coatings explains 41.3% of the variation in the light fastness values and predicts only 5.93% of their variation. In contrast, the corresponding values for the SA latex coatings are clearly better, 78.5% and 66.2%. In the SA latex model, the eigenvalue of PC3 was larger than 1, but the component was nonetheless neglected owing to its small contribution to the explained and predicted variations of the light fastness values.

The PLS weight plot presented in Figure 16 depicts the effect of the physical paper properties of the PVA model coatings on the light fastness of DY86 2p20 and DV107 inks. The first principal component PC1 separates the two observations, indicating that the physical properties of the coatings have different influences on their light fastness. The model suggests that with DY86 2p20 ink, light fastness improves as the  $\theta_a$  micro-roughness of the coating surface decreases, and as polarity and Bendtsen roughness increase. Moreover, the model suggests that an increase in porosity would be advantageous, its role nevertheless being rather small. This is contradictory to the hypotheses. In contrast, the model indicates that the light fastness of the DV107 ink increases as the wettability of the coating decreases (contact angle increases), and as polarity and Bendtsen air permeability decrease. The roles of roughness,

pore diameter and pore area are small or even negligible. Hence, the data on the light fastness of DV107 ink is partly consistent with the hypotheses.

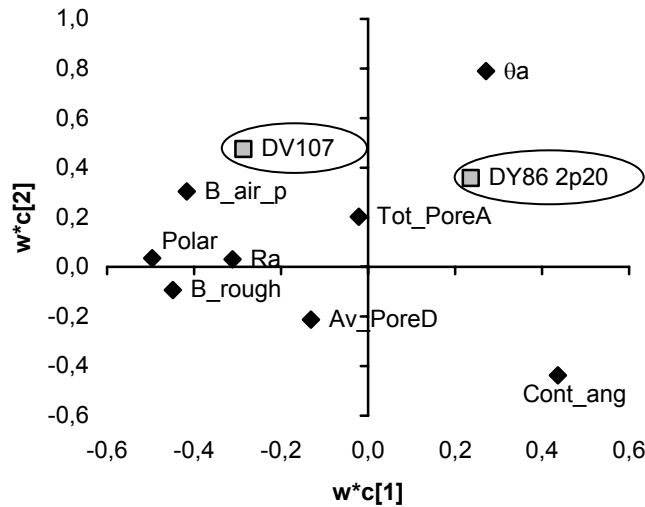


Figure 16. PLS model depicting the effect of the physical properties of the coating on the light fastness of dye-based ink jet inks on PVA model coatings.

Figure 17 presents the PLS weight plot for the light fastness of dye-based ink jet inks on SA latex coatings. Both light fastness observations are located in the same quarter of the plot, indicating that the studied paper-related variables have similar influences on them. Accordingly, for both inks, the most influential factors are the contact angle and Bendtsen roughness of the coating, whereas the roles of porosity and polarity are small. In the case of DV107,  $R_a$  roughness has a rather strong effect as well. In general terms, increases in contact angle (decrease in wettability) and roughness are beneficial. Thus, the data is partly consistent with the hypotheses.

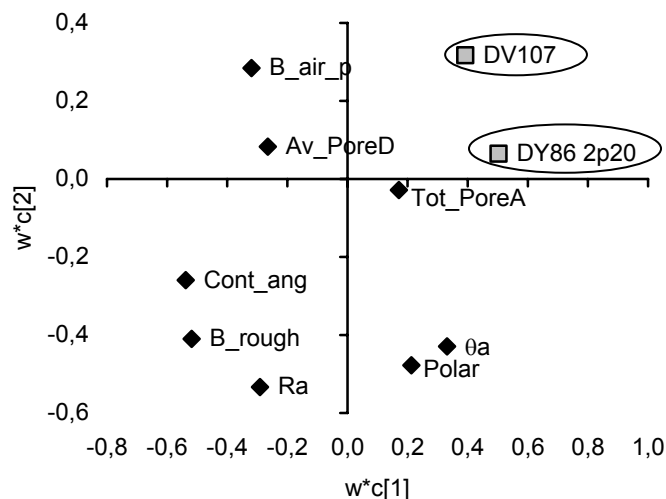


Figure 17. PLS model depicting the effect of the physical properties of the coating on light fastness of dye-based ink jet inks on SA latex model coatings.

### 5.4.3 Chemical paper-ink interactions

Light exposure of the printed samples was found to cause differences in their FTIR and Raman spectra, indicating that the amount of colorant was reduced (Papers II, V and VI). Furthermore, some evidence of alterations in the chemical structure of the samples could also be obtained. Examples of the results representing the common behavior of both PVA-poly-DADMAC and SA latex-starch coatings are presented in Figures 18 and 19. The graphs are PCA loading plots calculated from the FTIR-ATR and UV resonance Raman spectra measured from the unexposed and light-exposed prints.

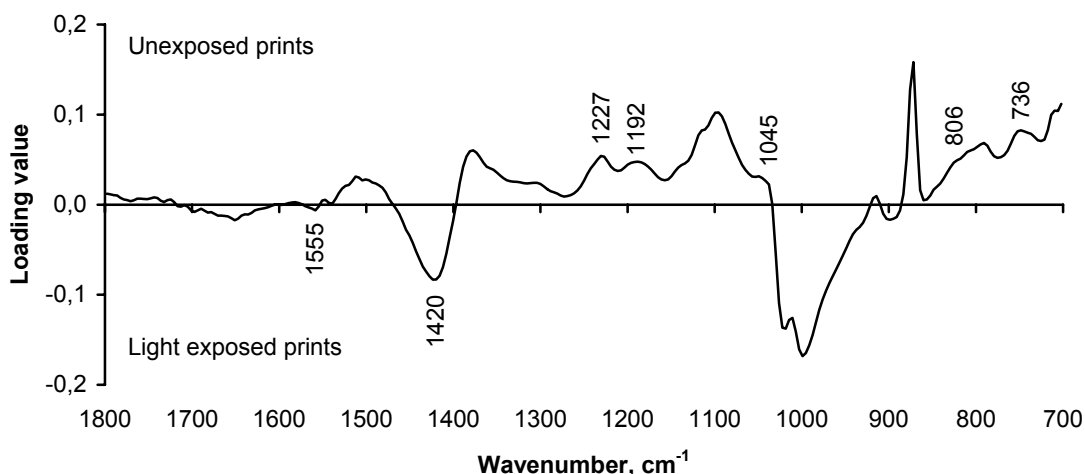


Figure 18. Loading values of untreated and light-exposed prints (FTIR-ATR spectra, DY86 deg ink, modified conventional coatings with PVA-poly-DADMAC polymer system).

The positive loadings in Figure 18 representing the unexposed prints can be associated with PCC, kaolin, PVA binder and the DY86 colorant (Paper V). The colorant bands at 1227, 1192 and 1045  $\text{cm}^{-1}$  likely originate from the sulphonate group, respectively, whereas the bands at 806 and 736  $\text{cm}^{-1}$  represent the benzene ring of the colorant (Colthup et al. 1990, Lin-Vien et al. 1991). Meanwhile, the negative contributions at 1555  $\text{cm}^{-1}$  at 1420  $\text{cm}^{-1}$  representing the light-exposed prints may conceivably be assigned with the triazine group of the DY86 colorant (Colthup et al. 1990, Lin-Vien et al. 1991, Larkin et al. 1999). Thus, contributions originating from the colorant appear at both sides of the loading plot, which would indicate partial degradation of the colorant as a result of light exposure.

Further evidence on the degradation of the DY86 colorant was obtained from the UV resonance Raman data seen in Figure 19. The positive loadings of the PCA curve could primarily be associated with the DY86 colorant, PVA binder and PCC pigment. In particular, the contributions at 1609  $\text{cm}^{-1}$  supposedly correspond to the benzene ring, and the bands at 1571  $\text{cm}^{-1}$  and 1357  $\text{cm}^{-1}$  to the naphthalene units (Dollish et al. 1974, Trotter 1977, Colthup et al. 1990, Lin-Vien et al. 1991). Added to this, the Kerr gated resonance Raman spectroscopic measurements (Paper VI) implied that particularly the azo bonds of the DY86 colorant would degrade as a result of exposure to light. Thus, the spectroscopic data suggest that the aromatic, sulphonate and azo groups of the colorant would be particularly prone to light fading, whereas the triazine would be more stable.

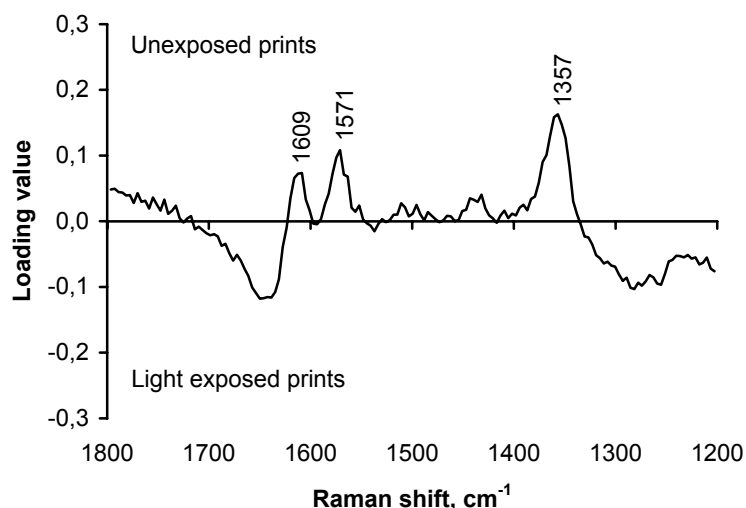


Figure 19. Loading values of untreated and light-exposed prints (UVRRS spectra, all DY86 inks, P0:100 and P100:0 coatings)

The possible stabilization mechanisms of the colorant and evaluation of which coating components might contribute to the photodegradation of the studied colorants proved to be a very complex matter. The results presented in Paper II implied that the improvement in the light fastness of the dye-based model inks would be related to the amount of hydrogen bonding between the dye and the coating. The observed behavior is illustrated in Figure 20 by means of FTIR-ATR spectra measured from unprinted and printed PVA coatings.

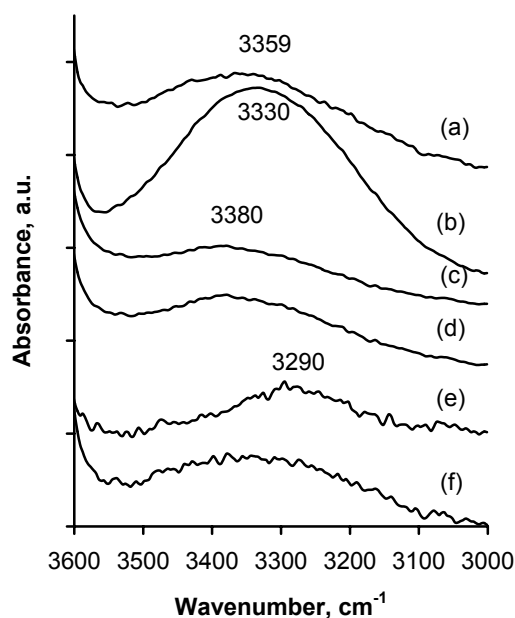


Figure 20. FTIR-ATR spectra of (a) unprinted and unexposed coating with 5 pph PVA; (b) unprinted and unexposed coating with 15 pph PVA; (c) printed and unexposed coating with 5 pph PVA; (d) printed and unexposed coating with 15 pph PVA; (e) printed and light-exposed coating with 5 pph PVA; (f) printed and light-exposed coating with 15 pph PVA. The spectra have been shifted vertically for clarity.



In Figure 20, distinct changes in the 3600-3000  $\text{cm}^{-1}$  wavenumber region representing the hydrogen-bonded hydroxyl (OH) groups can be observed as a function of the binder content of the coating. In the spectra of unprinted and unexposed coatings with 5 pph PVA content (spectrum a) and with 15 pph PVA content (b), the main OH absorptions are positioned at 3359  $\text{cm}^{-1}$  and 3330  $\text{cm}^{-1}$ , respectively. As a result of printing, the center point is shifted to the higher wavenumber (3380  $\text{cm}^{-1}$ ) with both binder contents (spectra c and d). This might suggest the presence of colorant-polymer interaction, viz. hydrogen bonding (Slark and Hadgett 1999). After 100 hours of light exposure, the OH band of the 5 pph PVA coating (spectrum e) has shifted to a smaller wavenumber (3290  $\text{cm}^{-1}$ ), indicating a decreased amount of hydrogen bonding. Meanwhile, the OH band of the light-exposed and printed 15 pph PVA coating (spectrum f) resembles that of the corresponding unexposed print (spectrum d).

Light exposure may also cause changes to the nature of the coating compounds, which may even result in destabilization of the colorant. Some evidence on this kind of behavior could be found with anionic SA latex coatings containing SPS kaolin. Figure 21 shows the C-H stretching region of the FTIR-ATR spectra of unprinted SA latex coatings with 10 pph binder content. Bands at the wavenumbers 3062 and 3030  $\text{cm}^{-1}$  correspond to the aromatic CH groups in the latex's styrene moiety, whereas the bands at 2930 and 2855  $\text{cm}^{-1}$  can be assigned to the  $\text{CH}_2$  groups (Lin-Vien et al. 1991). As a result of light exposure (spectrum b), the intensities of the bands originating from the aromatic groups decrease, but the bands representing the aliphatic  $\text{CH}_2$  groups become more prominent. Similar indications could be seen with coatings containing modified and kaolin (Paper V) as well. Moreover, the Raman depth profiles indicated a decrease in the styrene content with this kind of coatings (Paper II).

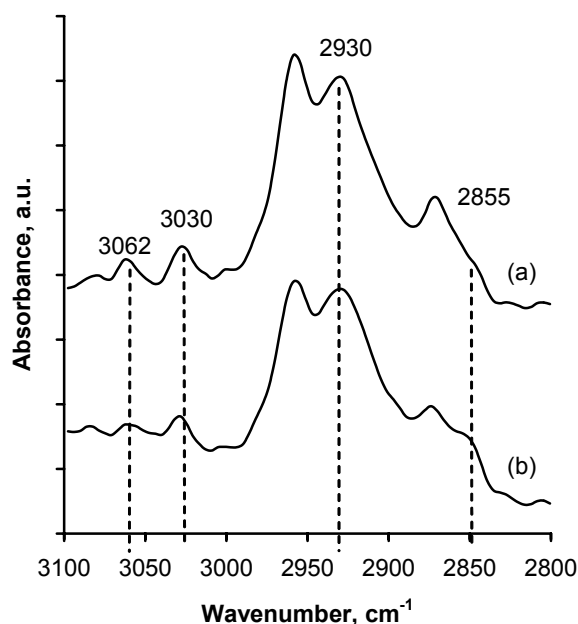


Figure 21. Effect of light exposure on the FTIR-ATR spectra of unprinted SA latex coatings. Spectrum (a) unexposed coating, 10 pph SA and (b) light-exposed coating, 10 pph SA. The spectra have been vertically shifted for clarity.

## 6 DISCUSSION

The results presented in the earlier chapters showed that the light and water fastness of ink jet prints depend markedly on both the coating composition and the type of ink. The depth profiling results indicated that the penetration of dye-based colorants into the coating is much more extensive than that of pigmented ink. This is consistent with the literature (Bugner 2002), according to which dye-based colorants generally tend to penetrate into the coating layer with the carrier phase, whereas pigment particles form a filter cake on top of the pigment coating. The physical properties and the chemical composition of the coating layer thus inevitably influence the environment of the dye-based colorant. Consequently, the effect of the coating composition on fastness properties can be explained with reference to both the physical and the chemical properties of the coating, as was hypothesized.

In general, the studied pigmented ink proved to have superior permanence towards both water and light exposure compared to the dye-based inks. This is in accordance with the literature (Kuramoto 1996), according to which the stability of the pigmented inks can be explained by the crystalline structure of the colorant particles. The results indicated that unlike in the case of dye-based inks, the chemical nature and internal structure of the coating layer did not play a decisive role with pigmented inks. This likely follows from the location of the colorant in the coating. As the it is layered primarily to the top of the coating, the properties of the coating surface are presumably dominating physical factors for print permanence (Papers IV and V).

### 6.1 Water fastness

Table 5 summarizes the findings related to mechanisms influencing the water fastness of the dye-based model inks.

*Table 5. Summary of the factors influencing the water fastness of anionic, dye-based model inks.*

Contributing factor	Anionic coatings	Weakly cationic coatings	Cationic coatings
<b>Physical properties of the coating</b>	<ul style="list-style-type: none"> <li>Moderate to strong contribution to water fastness</li> <li>Effects in accordance with the hypothesis</li> </ul>	<ul style="list-style-type: none"> <li>Moderate contribution to water fastness</li> <li>Effects in accordance with the hypothesis, but depend on the colorant type</li> </ul>	<ul style="list-style-type: none"> <li>Negligible contribution to water fastness</li> <li>Effects contradictory to the hypothesis</li> </ul>
<b>Chemical paper-ink interactions</b>	<ul style="list-style-type: none"> <li>Prevailing mechanism hydrogen bonding</li> <li>Cohesion of the coating critical</li> </ul>	<ul style="list-style-type: none"> <li>Prevailing mechanisms ionic and hydrogen bonding</li> <li>Cohesion of the coating may have influence</li> </ul>	<ul style="list-style-type: none"> <li>Prevailing mechanism ionic bonding</li> <li>Cohesion of the coating not critical</li> </ul>

The hypothesis that the coating would be able to form a protective layer against colorant dissolution was found to hold true for anionic and partly for weakly cationic coatings. In contrast, the influence of physical paper properties on water fastness was virtually negligible for the cationic coatings. This suggests that the stronger the chemical paper-ink interactions, the less relevant the physical properties of the coating. Another conceivable explanation for

the deviations from the hypothesis could be the apparent differences in the physical properties of the coating sets due to the pigment types (conventional SPS kaolin vs. modified PCC and kaolin). In many cases, the water fastness of the studied model inks was better on coatings containing modified pigments than on SPS kaolin coatings, even though the trends in the physical properties were contradictory to what was envisioned based on the hypotheses. In addition, the porosity and wettability of the coating were expected to be the most influential physical factors, but the results of PLS analyses emphasized the role of roughness instead. Within the original coating sets, however, (Papers III and IV), the hypothesis regarding the physical paper properties proved to hold true rather well. Furthermore, the distinctions in the inherent fastness of the various colorant types included in this study may also have caused anomalies from the hypothesis.

Apparently, the strength of the chemical paper-ink interactions is a very significant factor contributing to the water fastness of dye-based ink jet ink. The colorants used in this study were primarily anionic, except for the DV107, whose exact chemical composition is not known. These colorants are presumably attached to anionic coatings with hydrogen bonding, whereas in the case of cationic coatings, ionic bonding is the prevalent chemical paper-ink interaction mechanism. Furthermore, despite the evident dissolution of PVA binder as a result of water immersion, the water fastness of all the studied dye-based model inks on cationic PVA-poly-DADMAC coatings proved to be very good (Papers III and IV). This is also consistent with the literature (Niemöller and Becker 1997, Shaw-Klein 1998, Ryu et al. 1999, Wexler 2001). However, the results indicated that on anionic coatings the dissolution of the PVA binder severely impaired water fastness, and an increase in the binder content aggravated the situation further (Paper III). The apparent reason for this is that the amount of unbound polymer in the coating has increased (Tang et al. 1999). Obviously, the hydrogen bonding of the colorant as a sole binding mechanism is not adequate to fix the colorant to the coating.

On weakly cationic latex-starch coatings, both hydrogen and ionic bonding are likely to be the prevailing chemical paper-ink interaction mechanisms. In addition, the cohesion of the coating, or the tendency of the hydrophilic coating polymer (starch) to dissolve as a result of water immersion, was also found to contribute. The results indicated that the dye is primarily attached to the polymer matrix of the coating. Therefore, its water fastness can be presumed to be dependent on both dye-polymer and polymer-coating pigment interactions. According to the results, water fastness was better on kaolin-rich coatings than on PCC-rich ones (Paper IV), which was assumed to originate from the stronger interaction between weakly cationic starch and kaolin than between starch and PCC particles. This is supported by the literature, according to which both cationic and amphoteric starches adsorb strongly on kaolin particles (Wang et al. 1996), whereas the interaction between cationic starch and calcium carbonate weakens as the density of cationic surface sites increases as a result of  $\text{CaCl}_2$  addition (Hedborg and Lindström 1993).

## 6.2 Light fastness

The observations related to the light fastness of the dye-based model inks are summarized in the following table.

*Table 6. Summary of the factors influencing the light fastness of dye-based model inks.*

<b>Contributing factor</b>	<b>PVA coatings</b>	<b>SA latex coatings</b>
<b>Physical properties of the coating</b>	<ul style="list-style-type: none"> <li>• Small contribution</li> <li>• Mostly contradictory to the hypothesis</li> </ul>	<ul style="list-style-type: none"> <li>• Moderate contribution</li> <li>• Mostly in accordance with the hypothesis</li> </ul>
<b>Chemical paper-ink interactions</b>	<ul style="list-style-type: none"> <li>• Partial degradation of the colorant</li> <li>• Hydrogen bonding beneficial</li> <li>• Ionic bonding possibly detrimental</li> </ul>	<ul style="list-style-type: none"> <li>• Partial degradation of the colorant</li> <li>• Hydrogen bonding beneficial</li> <li>• The degree of hydrogen bonding depends on the degree of ionic interactions</li> <li>• Chemical changes of styrene may be detrimental</li> </ul>

The spectroscopic measurements implied that the DY86 colorant would undergo a partial degradation as a result of light exposure on both PVA and SA latex coatings. The Raman data of the light-exposed samples suggested that particularly the azo group and the aromatic rings would be vulnerable to light fading. These findings are in accordance with the literature (Griffiths and Hawkins 1972, Griffiths and Hawkins 1977, Kuramoto 1996), which suggests that the aromatic structures and the azo bond of the azo colorants decompose at least partly in the photooxidation reaction. On the other hand, the FTIR-ATR measurements implied that the sulphonate groups of the colorant would be susceptible to light fading, whereas the triazine ring of the colorant would be more stable. In fact, the s-triazine structure is known to be resistant to light fading. Moreover, a study (Hu et al. 2003) on the photocatalytic oxidation of anionic, triazine-containing azo dyes in waste waters has shown that the substituents attached to the naphthalene group of a dye molecule will hydroxylate easier than those linked to the triazine group. The DY86 colorant used in this study corresponds to this kind of colorant.

The results of this study indicated that the contribution of the coating composition to light fastness is very intricate even within coating groups. Some general remarks on the possible stabilization or destabilization mechanisms of the colorants can nevertheless be made. The PLS analysis indicated that the significance of the physical paper properties for light fastness was more pronounced with SA latex coatings than with PVA coatings. However, the results did not come up with the expectations very well, for the roles of porosity and polarity were smaller than presupposed, whereas the contribution of roughness was surprisingly emphasized. As in the case of the water fastness data, one possible explanation for this could be the differences in the physical properties of the coatings containing SPS kaolin vs. modified PCC and kaolin. With SPS kaolin coatings, the protective layer theory held true for all colorant-coating combinations (Paper II), but with coatings containing modified PCC and kaolin (Paper V), the contribution of the physical properties depended strongly on the ink-coating combination in question. In addition to the variables included into the PLS models, the pH value of the coating has been reported to have an influence on the light fastness of dye-based colorants (Wnek et al. 2002). In particular, precipitation of anionic colorants onto acidic media should enhance light fastness owing to the aggregation of the colorants. Nevertheless, in this study manifest correlations between the pH value of the coating and light

fastness could not be found; the differences in pH values between the coating types may not be large enough to cause clear distinctions between the samples.

The intricacy of the light fastness results might be also be related to the decisive role of chemical paper-ink interactions in photopermanence. The results presented in Paper II implied that the improvement in the light fastness of the dye-based model inks would be related to the amount of hydrogen bonding between the dye and the coating. This is in agreement with the literature (Clifton and Nugent 2000, Wnek et al. 2002). On the other hand, the anionic DY86 dye was suggested to form ionic bonds with the cationic or weakly cationic coatings (Papers III and IV). Furthermore, with weakly cationic latex-starch coatings, the water and light fastness values proved to correlate negatively (Papers IV and V), suggesting that increased attractive interaction between colorant and coating would result in decreased light fastness. Thus, it would seem reasonable to presume that chemical stabilization of the colorant and thereby light fastness would be affected by the way of colorant's attachment to the coating. These ideas are supported by the literature, according to which cationic compounds like PVP and poly-DADMAC destabilize azo colorants (Yuan et al. 1997, Lavery et al. 1998, Shaw-Klein 1998). It has also been proposed that the aggregating tendency of dyes is reduced if they get into contact with nitrogen-containing polymers (Wang et al. 1999). Both the poly-DADMAC and cationic starch used in the model coatings of the present study contain quaternary ammonium groups (Papers II and V). Consequently, ionic paper-ink interactions might reduce the tendency of the DY86 colorant to form hydrogen bonds with the surrounding media, viz. the binder, and also its capability to form colorant-colorant aggregates, thereby causing the light fastness of the print to deteriorate.

Another possible factor contributing to the light fastness of the dye-based colorants could be light-induced changes in the coating compounds. For example, polymers containing UV light absorbers as substituents, such as styrene, may destabilize some azo dyes (Wing-sum Kwan 1999). Moreover, UV light has proven to be responsible for changes in the aromatic structures of uncoated papers made from mechanical pulps (Forsskåhl et al. 1995). Typical photosensitizers in pulp and paper include entities containing aromatic and conjugated carbonyl groups, and double bond structures (Forsskåhl 2000). Indeed, this study gave some evidence of light-induced changes in SA latex coatings. Moreover, the light fastness of dye-based model inks was generally found to be lower on SA latex coatings than on PVA coatings with similar pigment composition (Papers II and V).

## 7 CONCLUSIONS

The goal of this study was to gain a general understanding of the mechanisms contributing to the light and water fastness of ink jet prints. The effects of the physical properties of the coating and chemical paper-ink interactions were of particular interest. These were studied using model inks and coatings with known compositions, utilizing FTIR and Raman spectroscopy as the main analytical methods. The results can be utilized in developing low-cost, coated ink jet media.

In the first part of this thesis, the applicability of FTIR and Raman spectroscopic techniques to the ink jet studies was evaluated. Light- and immersion-induced changes in the location of the colorant and in the chemical interactions between colorant and paper could be detected with both methods. FTIR-ATR, confocal NIR-Raman, UV Resonance Raman and Kerr gated Resonance Raman spectroscopy proved to be particularly suitable for analyzing paper-ink interactions in ink jet prints.

The second part of this thesis focused on studying the effects of the physical properties of the model coatings and chemical paper-ink interactions on the permanence of ink jet prints. The results indicated that the light and water fastness of ink jet prints generally depend markedly on both the coating composition and the type of ink. Superior print permanence was obtained with pigmented ink on modified conventional coatings, and in this case, both the physical properties of the coating and chemical paper-ink interactions were found to play only a small role. With dye-based inks, improvements in light and water fastness could in most cases be obtained by using modified conventional coatings instead of conventional kaolin coatings.

The water fastness of anionic dye-based inks was found to be strongly dependent on the chemical interactions between the coating components and the colorants. In general, the hypothesis that the coating would be able to physically protect the colorant from water immersion was found to hold true for anionic coatings, whereas for cationic coatings the results were contradictory to the hypothesis. This anomaly was explained by the decisive role of the ionic bonding between the anionic colorant and the cationic coating. Moreover, the cohesion of the coating itself and the interactions between the coating components may well influence water fastness by affecting the type of chemical groups available for the colorant to interact with.

The light fastness of anionic dye-based model inks proved to be much more intricate phenomenon than the water fastness, and unequivocal trends were rather difficult to find. The contribution of the physical properties of the coating was found to rely strongly on the ink-coating combination in question. This emphasizes the relevance of the chemical paper-ink interactions to light fastness. With conventional coatings, the light fastness data was in rather good agreement with the hypotheses, whereas on modified conventional coatings, common trends were difficult to find. When examining the effects of chemical paper-ink interactions, there were some indications of the degradation of the anionic azo colorant molecule used in the model inks, but the role of the coating composition in this context still remained unclear. However, the interactions between the colorant and the coating polymers, particularly hydrogen bonding, apparently are important. Furthermore, exposure to light may also induce changes in the chemical composition of the coating polymers, which possibly contribute as well. Detailed clarification of the photodegradation mechanism of the studied colorants and the effect of various coating components on this requires more specific studies with model compounds.

To conclude, the results of this thesis indicate that both the physical properties of the coatings and chemical paper-ink interactions affect the light and water fastness of ink jet prints. The chemical paper-ink interactions play a dominant role, whereas the significance of the physical paper properties depends on the types of ink and the coating. The type of colorant proved to have a major impact on print permanence, but the results also indicated that fastness properties can be influenced to some extent by choosing the right coating ingredients. As the pigment composition primarily contributes to the structural properties of the coating, the polymer composition of the coating is likely to be a dominant factor for the fastness properties of ink jet prints.

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