

## Fastness Properties of Ink Jet Prints on Coated Papers—Part 2: Effect of Coating Polymer System on Water Fastness

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The use of coated ink jet papers consisting of components typical for conventional printing papers would be advantageous in small scale applications for economical reasons. This study attempted to gain an understanding of the mechanisms affecting the water fastness of ink jet prints on conventionally coated papers. The effect of the polymer system of the coating was of particular interest. This was studied with FTIR and Raman spectroscopy using dye based model inks and kaolin coated pilot papers with known compositions. The data on water fastness were consistent with the hypotheses of the study. The results indicated that the water fastness of the studied ink jet prints was improved when the impermeability of the coating or its ability to fix the colorants with ionic bonds increased. With hydrophilic coatings, the structural properties of the coatings were of minor importance due to the dissolution of the binder. Rather, the ability of the coating to fix the colorants with ionic bonds proved to be critical. With hydrophobic coatings the structural properties of the coatings had more relevance. In this case, water fastness was improved with decreases in the porosity and wettability of the coating.

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### Introduction

The purpose of this article is to obtain general understanding on the effect of the coating polymer system on the water fastness of ink jet prints on conventionally coated papers. Part 1<sup>1</sup> of this series addressed the effects of the coating polymer system on the light fastness of ink jet prints on conventionally coated papers.

Two of the most critical elements with regard to water fastness are ink formulation and recording media. Typical ink jet dyes have significant water solubility and if there are no strong binding forces holding the dye to the receiver medium, the dye will dissolve when the image comes into contact with water or moisture.<sup>2</sup> It is a well-known fact that pigmented inks, because of their crystalline structure, have better water fastness than dye based inks. Also, the use of water insoluble dyes in conjunction with water soluble polymers in ink jet inks has been suggested as a means of improving water fastness.<sup>3</sup> The fastness properties of dye based inks can, nevertheless, be considerably improved by utilizing the controlled dye aggregation in the ink receiving layer.<sup>4</sup> This can be affected both by the chemical structure of the colorant<sup>5</sup> and by the properties of organic ink solvents.<sup>4</sup>

The nature of coating components is important in controlling the fastness properties as it determines the

chemical and physical environment of the colorant in the print.<sup>4</sup> In addition to the attachment of the dye to the coating, the cohesion of the coating itself (or solubility of the coating components) is a critical factor.<sup>6,7</sup> Water fastness can be improved by using modified pigments such as cationized calcined kaolin clay<sup>8</sup> or cationic PCC<sup>9</sup> in the coating. Further, the use of water insoluble amino group-containing fine particles as pigments has been suggested.<sup>10</sup>

The polymer system of the coating is perhaps the most significant factor affecting the fastness properties of an ink jet print. This is partly due to the possibility of stabilizing and immobilizing the colorant both physically and chemically with the polymers, and partly due to their major influence on the cohesion of the coating. Preeminently 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 receptive coating is needed to give both a good image and water resistance.<sup>6,7</sup> Efforts to enhance water fastness have often also employed dye mordants such as cationic polymers. For example, poly-DADMAC is commonly used due to its ability to form ionic complexes with anionic dyes.<sup>2,11–13</sup> The use of hardening agents that are capable of cross-linking hydrophilic binders has also been reported.<sup>14</sup> Moreover, the use of cationic latexes as a means of improving the water fastness of ink jet prints has been suggested.<sup>2,15</sup>

This study is an extended version of a conference paper<sup>16</sup> presented at IS&T's NIP17 conference. The article is structured as follows. Firstly, the hypotheses of the study are presented. Materials and methods used in this study are described in the experimental part, which is

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**TABLE I. Suggested Water Fastness Mechanisms of Ink Jet Prints on Conventionally Coated Papers**

Influencing factor	Water fastness mechanism
Porosity	Protective layer
Roughness	
Wettability	
Dye distribution in z-direction	
Ionic interactions	Chemical stabilization
Dye distribution in z-direction	

followed by results and discussion, and finally the conclusions are presented.

### Hypotheses of the Study

This study deals with the effects of the coating polymer system on the water fastness of soluble dyes on kaolin coated papers. Therefore the influence of paper properties and dye-polymer interactions are of particular interest. The mechanisms that are expected to be dominant in the build-up of water fastness, as suggested by the literature, are summarized in Table I. Also included are the factors that are presumed to have relevance to water fastness mechanisms.

The first hypothesis is that the coating is capable of acting as a protective layer against water. According to the presumption, dissolution of the colorants is inhibited because of the reduced penetration of water into the coating. In particular, the porosity and the wettability of the coating are expected to be the major influencing structural factors. These can be affected by alterations in the polymer system, more specifically by changes in the amounts and types of the coating polymers.

Secondly, it is hypothesized that the coating components are capable of chemically stabilizing the colorant of the ink. Particularly, the presence of ionic interactions between the dyes and the coating components is presumed to promote water fastness.

## Experimental

### Materials

The study focuses on the effects of the coating polymer system on the water fastness of ink jet prints on kaolin coated papers. This was studied using a pilot paper set and model inks with known composition. Further details concerning the coatings and model inks are given in the Experimental section of Part 1.<sup>1</sup>

### Characterization of the Coated Papers

Coated papers were analyzed to determine their roughness, porosity, and wettability. Roughness and porosity measurement methods are described in Part 1<sup>1</sup> of this study. The contact angle with distilled water is used as a measure for wettability in this work.

The contact angle measurements were accomplished using a sessile drop method, where a water droplet with a nominal volume 1  $\mu$ l is dropped onto a paper surface with a burette. The behavior of the droplet is recorded with a video camera. The calculation of the contact angle  $\theta$  is accomplished with a PC from the side-view image of the droplet using the SCAN-P 18:66 standard method. The maximum height of the droplet ( $h$ ) and the diameter of the contact surface ( $a$ ) are determined once the droplet is in contact solely with the paper surface. The droplet was allowed to be freely in contact with the paper for 1 second prior to the determination of  $h$  and  $a$ .

**TABLE II. Data on Contact Angles of Unprinted Papers and Water Fastness Values of the Ink Jet Prints**

Sample	Contact angle [° deg.]	Water fastness $\Delta E^*$		
		AR 249	DY 86	DV 107
A1	46.8	62.81	46.09	28.96
A2	45.7	67.09	47.39	36.04
A3	59.5	70.20	50.99	40.68
A4	41.3	55.23	39.22	26.43
A5	55.7	52.78	39.64	25.94
A6	63.1	50.57	35.38	17.93
A7	71.1	43.50	30.62	18.72
A8	61.1	57.99	42.51	19.66
A9	80.0	52.01	45.22	18.02
A10	36.2	18.12	21.53	10.06
A11	55.1	21.19	25.03	14.65

In SCAN-P 18:66 standard method, the droplet is assumed to be a spherical segment. However, with a non-ideal surface like paper this presumption is not completely valid due to the chemical heterogeneity and structural irregularities of the paper surface, the penetration of water into the paper and possible effects of swelling. Based on the measurement data (Part 1<sup>1</sup>), roughness and porosity are presumed to be reasonably constant in the size-scale of the droplet used in this method. Therefore, these factors, nevertheless, are omitted and the samples are considered to be comparable with each other.

### Water Fastness Test

To examine the effect of the coating polymer system on the water fastness of ink jet prints, sets of printed samples were prepared as described in the Experimental section of Part 1<sup>1</sup> of this study. The water fastness of the prints was measured by immersing the printed samples into deionized water for 5 minutes without agitation, and allowing the immersed prints to dry for at least 5 hours at room temperature. Analogous methods have also been used in other studies.<sup>6,11,12</sup> The test conditions of the immersion method are rather severe, and therefore the results might not necessarily reflect the real conditions of print use. The advantage of this method, nevertheless, is that it enables an even exposure of the printed area to water. Color difference  $\Delta E^*$  was used as a measure of water fastness, and it was measured as is described in Part 1<sup>1</sup> of this study.

### Spectroscopic Measurements

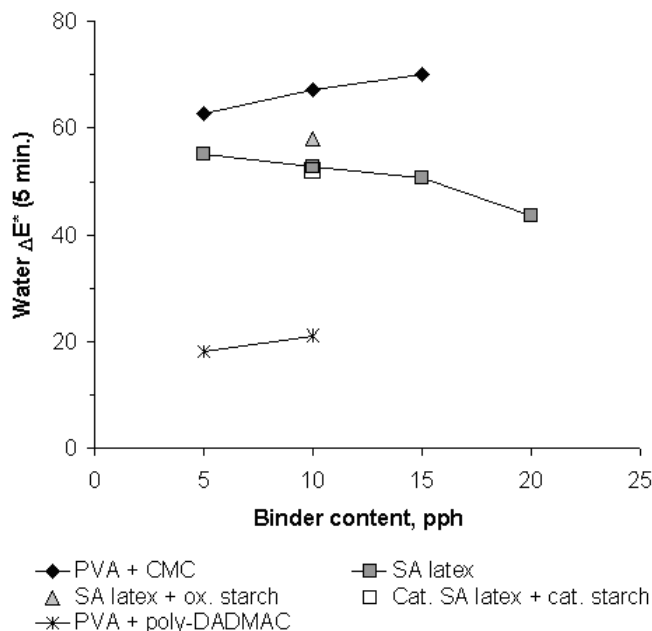
FTIR and Raman spectra from unprinted and printed samples were recorded to get more information on the chemical composition of the samples and conceivable paper-ink interactions affecting the fastness properties. The methods are presented at length in Part 1<sup>1</sup> of this study.

## Results and Discussion

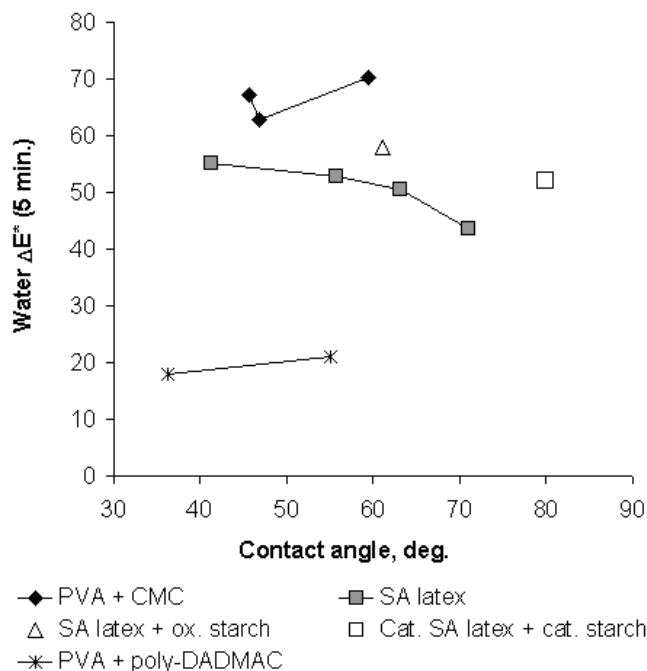
### Effect of Physical Properties of the Coating

Measured contact angles and water fastness values are presented in Table II. (Roughness and porosity data on these papers are given in Table III of Part 1<sup>1</sup> of this study).

An example on the effects of the coating polymer system on water fastness is presented in Fig. 1. This illustration represents the general behavior observed for all the model inks. It is evident that with the anionic PVA coatings an increase in the binder content deteriorates



**Figure 1.** Effects of binder type and amount on the water fastness of acid dye AR 249.

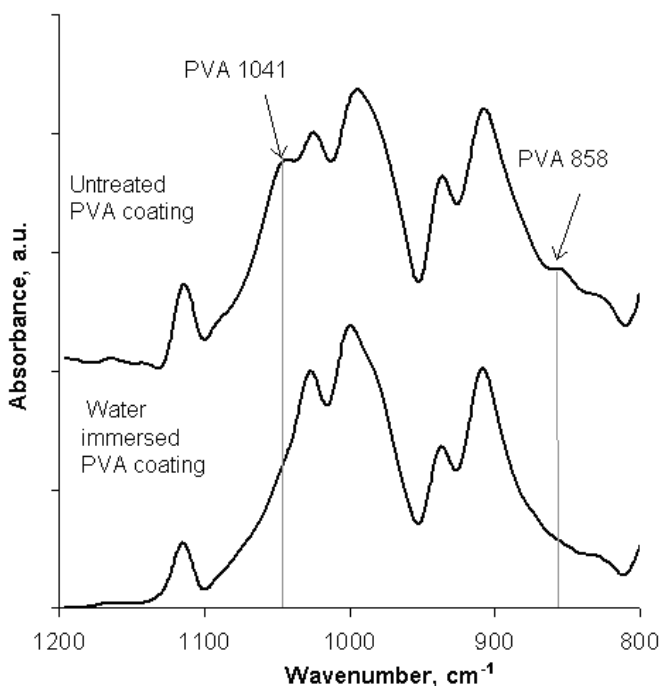


**Figure 2.** Effect of wettability of the coating on water fastness of acid dye AR 249.

water fastness, whereas with the SA latex coating an opposite behavior can be observed. The ranking of the coating types was generally analogous with every colorant. The anionic PVA-CMC coatings have the lowest water fastness, whereas the cationic PVA-poly-DADMAC coatings produce the highest water fastness. The role of starch was not completely unambiguous. The differences between the colorant types were consistent; the highest water fastness was always obtained with DV 107, whereas the AR 249 had the strongest tendency to dissolve.

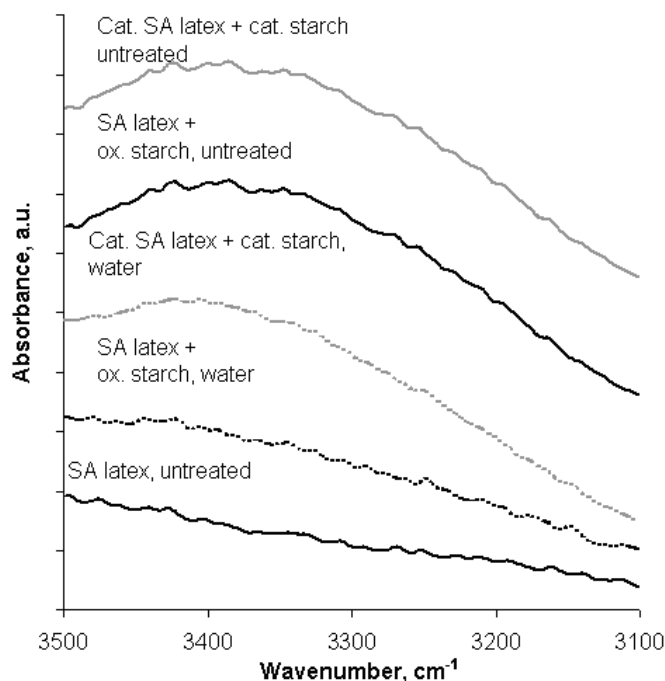
According to the hypotheses of this study, water fastness is improved as the porosity and wettability of the coating decrease. The data on wettability presented in Table II suggest that the contact angles of the coatings measured with water increase as the binder content increases, independent of the binder type. Therefore the wettability of the coating decreases, which in turn should predict an improvement in the water fastness of the prints. However, as the example in Fig. 2 indicates, this is true only for the anionic SA latex coatings. Instead, the water fastness of PVA coatings deteriorates rather than improves as the wettability of the coating decreases. This behavior is common for all the model inks.

Hence, contact angle measurements do not seem to predict the water fastness of ink jet prints on these coating very well. The contradiction between the contact angle and the water fastness data in the case of PVA can partly be explained by the tendency of PVA to dissolve from the coating during water immersion. In the contact angle measurement the water droplet, which comes into contact with the coating, is very small (volume ca. 1  $\mu$ l). Therefore, it is not markedly able to dissolve PVA from the coating. Instead, in the water fastness test the print is immersed completely into water, which results in the dissolution of PVA. This is illustrated in Fig. 3, which presents FTIR-ATR spectra measured from an untreated and a water immersed



**Figure 3.** FTIR-ATR spectra of PVA coating printed with AR 249 before and after water immersion. The spectra have been shifted vertically for clarity.

print on an anionic PVA coating. The bands at wavenumbers 1041  $\text{cm}^{-1}$  and 858  $\text{cm}^{-1}$  originate from PVA,<sup>17</sup> and as is evident, they decrease as a result of water immersion. This indicates that PVA has dissolved at least partly from the coating. Increasing the PVA content impairs the situation further. Also, visual inspection of the water immersed samples showed that both on anionic and cationic PVA coatings the dyes had

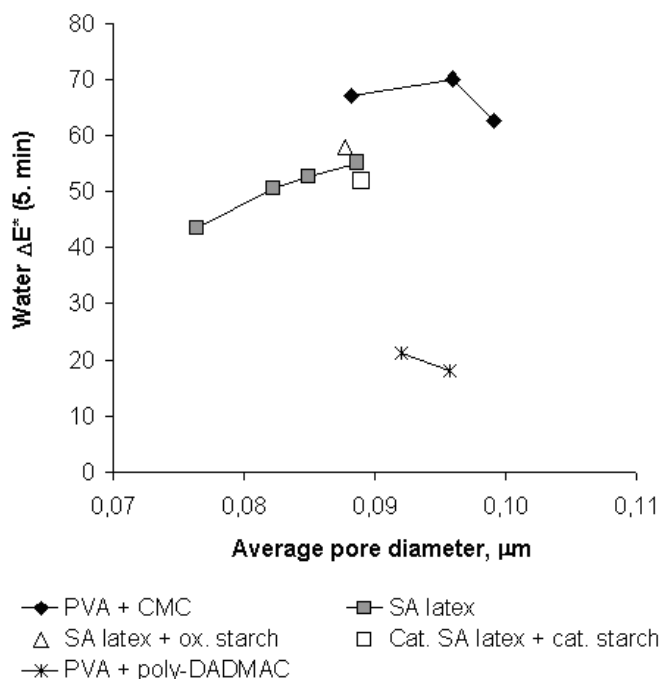


**Figure 4.** FTIR-ATR spectra of starch containing latex coatings before and after water immersion. The spectra are vertically shifted for clarity.

spread extensively, if not completely dissolved from the coating.

The dissolution of the coating polymers can also be observed for starch-latex coatings. Figure 4 illustrates the effect of water immersion on unprinted starch-latex coatings by means of FTIR-ATR spectra. This graph presents the stretching region of hydrogen bonded OH groups of starch-latex coatings before and after water immersion, along with an untreated anionic latex coating. The spectra were scaled to the kaolin band at wavenumber  $3684\text{ cm}^{-1}$ . As is evident, the plain SA latex coating does not contain hydrogen bonded OH groups. The use of starches and weakly cationic latex in the coating, on the other hand, introduces hydrogen bonded OH groups into the coating. The FTIR-ATR spectra show that the amount of hydrogen bonded OH groups has diminished in the starch coatings as a result of water immersion, indicating that these polymers are prone to dissolution. This in turn deteriorates the water fastness of the AR 249 and the DY 86 dyes. Conversely, the water fastness of the DV 107 prints is improved when starches are used. This implies that in the case of the DV 107 prints there are some special chemical colorant-coating interactions prevailing.

The tendency of PVA to dissolve during the immersion test seems to refute the hypothesis that decreased porosity should improve water fastness. The porosity data in Table III of Part 1<sup>1</sup> and the water fastness data in Table II of this article suggest that this postulate is true only for SA latex coatings. In contrast, the water fastness of PVA coatings deteriorates along with decreasing porosity, as is presented in Fig. 5. The data is only shown for AR 249 to better illustrate the differences between the coatings. However, this is the general behavior observed for all the model inks. Thus, it appears that in the case of water insoluble coatings, the decrease in the porosity of the coating improves water fastness



**Figure 5.** The relation between average pore diameter of the coating and water fastness of acid dye AR 249.

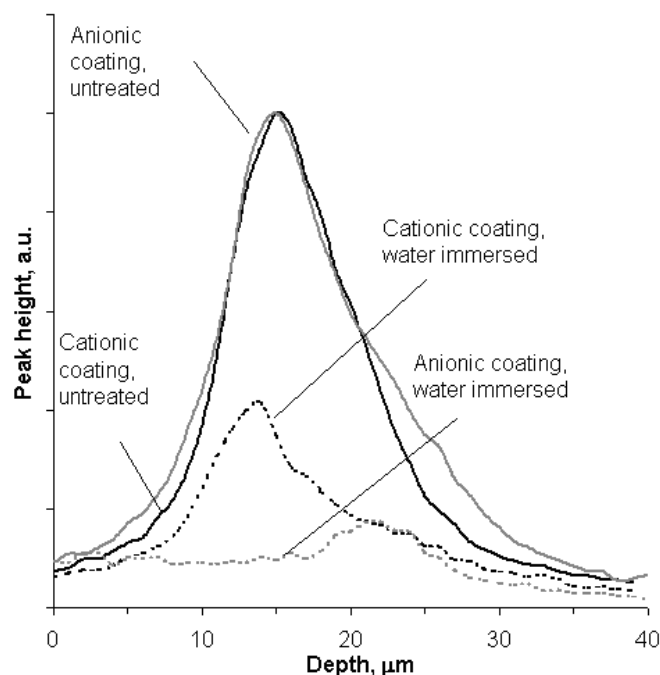
somewhat, whereas with water soluble coatings it does not seem to have much relevance.

#### Effect of Chemical Paper-Ink Interactions

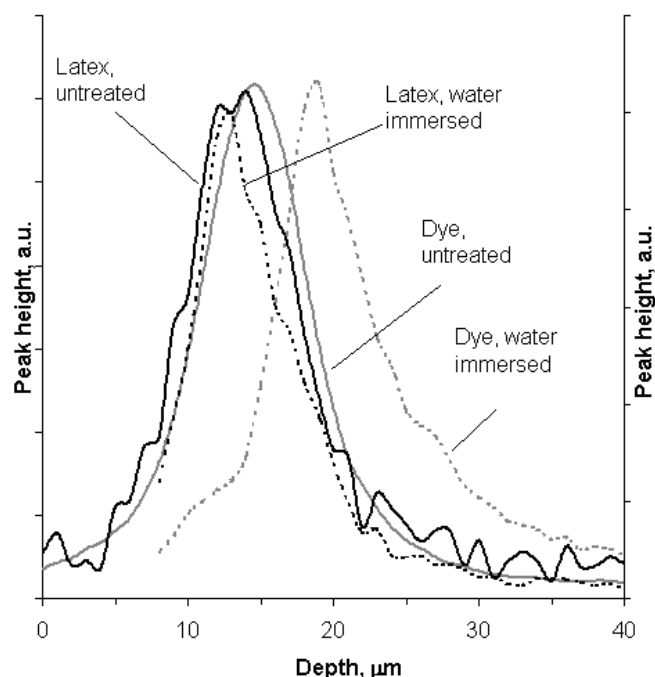
According to the second hypothesis of this study, the presence of ionic interactions between the dyes and the coating components should promote water fastness. The data presented in Fig. 1 and in Table II show that with all the colorants in this study, the lowest water fastness is always obtained with coatings containing PVA and CMC. The use of cationic poly-DADMAC as a dispersant, instead of anionic CMC, improves water fastness considerably. In the Part 1<sup>1</sup> FTIR-ATR measurements from the unprinted and printed samples led to the suggestion that on anionic PVA coatings the dyes are mostly attached to the binder with hydrogen bonds, whereas on cationic coatings their tendency to do so is weaker. This implies that on cationic PVA coatings the dyes are attached mainly with ionic bonds to poly-DADMAC. This is also in accordance with the literature.<sup>2,11–13</sup> The difference between anionic and cationic PVA coatings can also be seen from the Raman depth profiles in Fig. 6, which presents the effect of water immersion on the distribution of anionic dye printed on anionic and cationic PVA coatings. The depth profiles show that on the cationic coating there is more colorant left after water immersion, and the dye distribution is concentrated on the surface of the coating compared to the anionic PVA coating, where the center of the dye distribution has shifted almost ten micrometers deeper into the coating.

As is evident from the water fastness results presented in Fig. 1 and Table II, anionic styrene acrylate latex improves water fastness compared to the anionic PVA-CMC coatings. A further improvement is achieved with increased latex amounts. This could be explained by the more hydrophobic nature of the coating, as the use of anionic styrene acrylate latex makes the coating non-





**Figure 6.** Dye distribution on PVA coatings before and after water immersion. Black lines denote cationic coatings, gray lines anionic coatings and dotted lines water immersed samples.



**Figure 7.** Ink penetration into anionic styrene acrylate latex coating. Black lines denote latex, gray lines denote dye, and dotted lines denote water immersed samples.

swellable and more hydrophobic compared to the PVA coatings. This is illustrated in Fig. 7, which presents the Raman depth profiles measured from prints on latex coatings before and after water immersion. As can be seen, the dye has initially penetrated into the anionic latex coating. After the water immersion, the dye has partly dissolved and the mass center of the dye distribution has shifted a few micrometers deeper into the coating. The distribution of the latex, on the other hand, has not markedly changed either in the amount or in the placement. This indicates that anionic styrene acrylate latex does not considerably dissolve during the water immersion test. Therefore, the presumption that the hydrophobic coating is able to form a protective layer against water seems to hold true.

## Conclusions

The goal of this study was to gain a general understanding of the underlying mechanisms of the water fastness of ink jet prints on coated papers made up of the same components as conventional printing papers. The effect of the polymer system of the coating on water fastness achieved with soluble ink jet dyes was of particular interest. This was studied using model inks with known compositions and a set of pilot papers, which had conventional kaolin as the main pigment and the composition of the polymer system as a variable. The main methods were FTIR and Raman spectroscopy. The results of this study are exploitable in the development of low cost coated ink jet media.

The data on water fastness were consistent with the hypotheses of the study. The coating was assumed to be able to form a protective layer against water due to decreases in the porosity and wettability of the coating as a function of increasing binder content. This presumption held true for coatings containing water insoluble

binder (styrene-acrylate latex). However, if water soluble PVA was used as a binder, the opposite behavior was observed.

The second hypothesis concerned the chemical stabilization of the colorant of the ink. The presence of ionic bonds between the colorant and the coating proved to be beneficial for water fastness, as was presumed. Moreover, chemical interactions between colorant and coating had larger influence on water fastness than the physical properties of the coating.

The results of this study thus give indication that the water fastness of dye based ink jet prints on coated papers comprising the same components as conventional printing papers is governed by the same mechanisms that have been suggested for special ink jet papers. ▲

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