

PAPER II

## **The role of binder type in determining inkjet print quality**

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# The role of binder type in determining inkjet print quality

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**KEYWORDS:** Binder, Absorption, Polyvinyl alcohol, Styrene acrylate latex, Porosity, Permeability, Capillarity, Ink penetration

**SUMMARY:** There is an increasing trend for the use of aqueous-based inkjet inks in high-speed commercial printing and this challenges the hydrophilic and absorptive properties of the paper surface. The aim of this work is to clarify the role of polyvinyl alcohol (soluble polymer) and styrene acrylate latex (suspension polymer) as binder in the formation of the coating structure for the purpose of inkjet printing. The coating layer properties were studied in combination with a chosen speciality calcium carbonate pigment. The inkjet image quality was assessed on coated papers. The role of diffusion of colorant as well as vehicle absorption was studied using dye-based inks. Among the other traditional paper surface characterization methods, the surfaces were analyzed with the Clara device, which shows how the external pressure affects the inkjet ink penetration into the coated paper structure by measurement of capacitance changes during ink penetration through the paper. The method indicates that inkjet ink penetration depth and speed depends on binder type. The chemical nature of binders affects the ink movement. The polyvinyl alcohol concentrates within the fine pores of the structure and absorbs water in its polymer matrix, and is seen simultaneously to adsorb ink dye, whereas the styrene acrylate acts effectively as a hard sphere, affecting the packing structure of the coating forming a more permeable coating layer. Therefore, structural as well as chemical differences of coating layers determine the final inkjet print quality.

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There is often reported a high expectation for growth in the field of inkjet printing. Growth is predicted across the range of print formats, including both traditional offset markets as well as for small print runs and for variable information printing. The use of aqueous-based inkjet inks challenges many aspects of a paper coating surface, including its structure and absorptivity. The water of

the ink should absorb rapidly into the porous structure. At the same time, the spread of the ink on the surface should be controlled so that the absorption front moves mainly in the thickness direction of the paper whilst providing sufficient spread for continuity of the image without the onset of colour bleeding. There is an urgent need to develop the coating layer properties further based on the mechanisms which control these properties in inkjet prints.

Traditionally, the best inkjet print quality is achieved with coated papers which contain silica pigments. The most common binder is polyvinyl alcohol (PVOH). This choice is dictated because it is one of the few binders that produce sufficient surface strength of the coating layer for fine high specific surface area pigments (Miller et al. 1996). Modified PVOH has also been used: carboxylic-, acryl amide-, sulfonic-, cationic- and silicone-modified PVOH. The use of other types of pigments in the inkjet area has been accompanied by the introduction of some other binders such as polyvinyl pyrrolidone, polyacrylic acid, polyacrylamide, methylcellulose, cellulose derivatives, gelatin, polyvinyl acetate latex, vinyl acetate ethylene and cationic starch (Lavery, Provost 1997, Khoultaev, Grazyk 1999, Morea-Swift, Jones 2000, Glittenberg, Voigt 2001, Yip et al. 2003, Malla, Devisetti 2005). The attributes of PVOH include its non-ionic, hydrophilic nature, its ability to cross-link whilst being plasticizable. It is both shear and temperature stable and provides strong binding strength (Miller et al. 1996, Pinto, Nicholasm 1997). The binding strength of PVOH depends on the degree of polymerization; high peel strength being achieved with a high degree of polymerization (Hara 2005).

Svanholm et al. (2006) and Svanholm (2007) studied silica pigments with PVOH binder coated on fine papers. It was shown that the silica pigments with large internal pore diameters require more binder than pigments with smaller pores to get the dye colorants to remain on top of the coating. It was reported that PVOH can form a film at the upper surface of the coating and assist colorant fixing. A partially hydrolyzed and higher molecular weight PVOH gave the best colour gamut and the sharpest line edges, and also sufficient binding strength. Cawthorne et al. (2003) found that the partially hydrolyzed PVOH produced a lower roughness of the coating layer than did a fully hydrolyzed PVOH. There are fewer hydrogen bond interactions between

silica pigment and the partially hydrolyzed PVOH. At the coating drying stage, there exists, therefore, less shrinkage, which is often responsible for increased coating surface roughness. More recently, the binder type has been shown to have an effect on the inkjet ink print density and bleeding development, (Nilsson, Fogden 2008). However, the behaviour of inkjet inks in relation to binders under the influence of external pressure, representing the surface tension of the inkjet droplets, has not been studied so widely.

Vikman and Vuorinen (2004a) studied light fastness of an inkjet printed surface containing PCC, kaolin, and their blends. The binders were PVOH and cationic starch together with cationic styrene acrylate latex. With dye-based inks, the significance of structural properties of the coating layer regarding the light fastness decreased when the strength of the chemical paper-ink interaction increased. The dyes benefit from a dense coating structure, whereas a coarse structure of the coating appears to be advantageous for the pigment-based inks. However, this kind of coating structural connection to water fastness was not detected as the single controlling factor, rather the surface adsorption via Coulombic interaction was key for water fastness in the case of dye-based ink (Vikman 2004b).

Heilmann and Lindqvist (2000) studied water-based inks in the area of continuous inkjet. The studied surfaces consisted of sized uncoated paper, a coated paper, and one, surface swelling, superabsorber-based glossy paper. They applied a single droplet of ink on each of the surfaces and measured the droplet penetration from the top side and in the cross direction. The droplets reached the final dot size on the silica coated paper in the first 50 ms, whilst on the surface sized paper it took as long as 500 ms. Coating with swelling binder/absorber displayed a little faster ink levelling time than the non-swelling coating. The non-swelling coating reached the final dot size within the first 100 ms.

The role of latices in inkjet coatings has not been studied in much detail. In offset coatings, Rousu et al. (2005), amongst others, showed that the properties of latex affect the ink setting. Low glass transition temperature and gel content of latex, together with oil-matched solubility index through monomer composition, increase ink setting rate. However, the latex particle size can affect the packing of the coating layer, and, through that, modifies the setting speed. Moreover, Rousu et al. (2000 and 2005) showed that the latex type influences the degree of chromatographic separation of the oils from the offset ink within the coating structure. Even a small amount of latex affected the

separation process. The reason behind this can be found from the polar/non-polar nature of the latex polymer. The diffusion phenomenon and associated binder swelling, acts to preferentially absorb certain oils and further decreases the diameter of pore capillaries. Hydrophilic binders, for example polyvinyl alcohol, have higher swelling tendency than latices in water. Donigian et al. (1998) noticed similar behaviour in their study. Adding PVOH in the coating generally slows down the movement of water in the case of dye-based inks.

The aim of this work is

- to clarify the role of styrene acrylate latex versus polyvinyl alcohol binder in the formation of the coating structure in terms of inkjet printing, and
- to find out how the dye-based inkjet ink movement within the coated paper structure during absorption depends on the binder properties.

## Materials and Methods

### Coating compositions and coating trials

An inkjet speciality precipitated calcium carbonate coating pigment (OMYAJET B5260, provided by Omya AG<sup>1</sup>) was used as the sole pigment. The pigment diameter (weight median,  $d_{50}$  with Sedigraph 5100) was 2.70  $\mu\text{m}$ , specific surface area 63.7  $\text{m}^2\text{g}^{-1}$  (BET, ISO 9277) and zeta-potential of the slurry 1.6 mV. The binders were polyvinyl alcohol (PVOH, provided by Clariant International Ltd.<sup>2</sup>) and styrene acrylate latex (SA, provided by Ciba Specialty Chemicals<sup>3</sup>). PVOH had a degree of hydrolysis of  $87.7\pm 1.0\%$ , molecular weight of 204 000  $\text{g}\cdot\text{mol}^{-1}$  and density 1.26  $\text{g}\cdot\text{cm}^{-3}$  (20°C). SA latex had a particle size of 180 nm, glass transition temperature of -20°C and density of the dispersion 1.03  $\text{g}\cdot\text{cm}^{-3}$ . In SA-containing coating colours, the virtually non-ionic nature of the PCC slurry was first changed to anionic by adding sodium polyacrylate (Polysalz S<sup>4</sup>), having a molecular weight of 4 000  $\text{g}\cdot\text{mol}^{-1}$ . The chemical structures of PVOH and the compounds which form the SA latex are introduced in *Fig 1*.

The coated papers were produced on the KCL pilot coater<sup>5</sup>. The base paper, 53  $\text{g}\cdot\text{m}^{-2}$ , was a commercial fine paper designed for a coated fine paper grade. The base paper was first pre-coated so that the top coating could not penetrate into the base paper, and so it is ideal for isolating the coating effects.

<sup>1</sup> Omya AG, Postfach 32, CH-4665 Oftringen, Switzerland

<sup>2</sup> Clariant International AG, Rothausstrasse 61, CH-4132 Muttenz 1, Switzerland

<sup>3</sup> Ciba Specialty Chemicals, Klybeckstrasse 141, CH-4002 Basel, Switzerland

<sup>4</sup> BASF Aktiengesellschaft, Paper Chemicals, 67056 Ludwigshafen, Germany.

<sup>5</sup> Oy Keskuslaboratorio – Centrallaboratorium AB, Tekniikantie 2, FIN-02150 Espoo, Finland

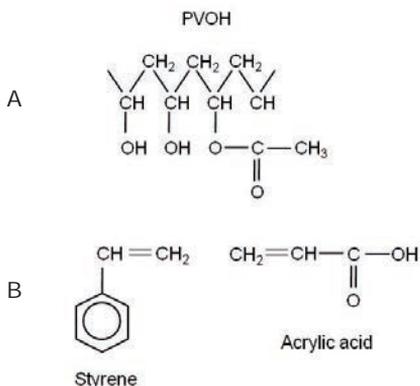


Fig 1. The chemical structure of polyvinyl alcohol and the components of styrene acrylate latex.

A pre-coating of  $7 \text{ g}\cdot\text{m}^{-2}$  was applied with a film coater ( $1\,000 \text{ m}\cdot\text{min}^{-1}$ ) on both sides of the base paper, and the final top coating layer of  $8 \text{ g}\cdot\text{m}^{-2}$  was applied with a short dwell application (blade) using a coating speed of  $700 \text{ m}\cdot\text{min}^{-1}$ . The pre-coat had 100 pph of ground calcium carbonate with a narrow particle size distribution of  $60 \text{ wt}\% < 1 \mu\text{m}$  (Covercarb 60<sup>1</sup>), 12 pph styrene-butadiene latex (DL966<sup>6</sup>) and 0.6 pph carboxymethylcellulose (Finnfix 10<sup>7</sup>). The recipes of the top coats are summarized in Table 1. The final moisture content of the web for each coating point was 5%.

The degree to which inkjet ink penetrated into the coated paper structure was studied with the Clara device (Fig 2) (Salerma 1998, Lamminmäki 2009b). The measuring principle of Clara is based on the fact that the resistivity of a dry surface is very high whereas a moistened surface conducts electricity more readily.

### Analysis of the coated papers

The coated papers were analyzed using the methods outlined in Table 2.

Table 1. The top coating colours in pilot trials. \* AcoustoSizer II

Component / pph	Coating colour					
	7 pph PVOH	12 pph PVOH	30 pph PVOH	7 pph SA	12 pph SA	30 pph SA
Inkjet PCC	100	100	100	100	100	100
PVOH	7	12	30			
SA				7	12	30
Polysalz S				6	6	6
<b>Measurement</b>						
Solids content, %	25.1	24.3	22.2	28.1	31.0	30.9
Zeta-potential*, mV	2.4	2.1	2.6	-37	-33	-33
pH	8.4	8.5	8.4	8.5	8.2	7.9

<sup>6</sup> DL966: styrene butadiene latex supplied by Dow Suomi Oy, Urho Kekkonenkatu 7 B, PL 117, 00101 Helsinki, Finland

<sup>7</sup> Finnfix is a trademark of Noviant Oy, Malminkatu 34, 00100 Helsinki, Finland

Table 2. Used measuring methods.

Property	Method	Notice
Thickness and apparent bulk density	ISO 12625-3:05	
Coat weight with ash content	ISO 1762:01	
Permeability	Air permeance	Parker Print Surf using 20 kPa measuring pressure
Contact angle of water	Droplet	Fibro 1100 DAT with 2 $\mu\text{l}$ drop, apparent contact angle after 0.5 s
Ink absorption time	VTT internal	DIGAT (Lamminmäki et al. 2007), cyan dye-based ink (used in Versamark® VX5000e, applied ink amount $8 \text{ gm}^{-2}$ )
Cumulative porosity of coating	Mercury intrusion porosimetry (Åbo Akademi <sup>8</sup> )	Pascal porosimeter <sup>9</sup> using 140 Pa (low pressure port) and 440 Pa (high pressure port)

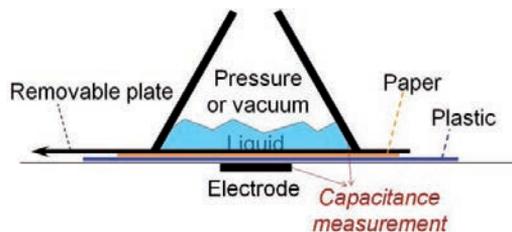
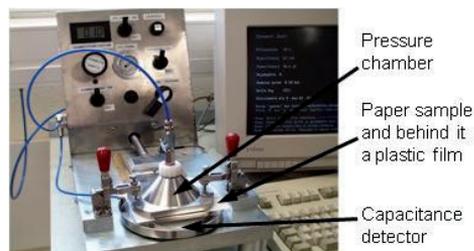


Fig 2. The structure of Clara.

The liquid forms a conducting material whose movement affects the capacitance between the liquid chamber and the electrode under the studied sample. The chamber can be pressurized from an under pressure of -0.5 bar to an over pressure of +5 bar. The measuring area is  $6.8 \text{ cm}^2$ . In the measurement, cyan ink, as used in Versamark® VX5000e<sup>10</sup>, was applied at an amount of 5 ml. The measurements were made after equilibration under a relative humidity of 50% RH and 23°C temperature. The result is expressed as a curve of capacitance change during time as the liquid penetrates through

<sup>8</sup> Åbo Akademi, Porthaninkatu 3-5, FI-20500 Turku, Finland

<sup>9</sup> Ing. Prager Elektronik HandelsGmbH, Traunstrasse 21, A - 2120 Wolkersdorf, Austria

<sup>10</sup> Easman Kodak Company, 343 State Street, Rochester, NY 14650, USA

the sample in the  $z$ -direction. The resulting curve is an average of five parallel measurements.

The maximum value of capacitance is about 190 pF, and this value depends on the capacitance of the plastic film backing the sample. When the capacitance reaches this maximum value, it is interpreted that the ink has penetrated through the whole paper structure.

Fig 3 shows some examples of the resulting curves. We can assume that the contact of liquid with a porous hydrophilic substrate goes in the following order (Oliver 1982):

1. When there is no external pressure: All the absorption is by capillary wetting force in coating pores fine enough to exert a Laplace pressure drop. In pores larger than those exerting significant wetting force, the movement is followed by thin layer wall wetting and diffusion.
2. When pressure is applied:
  - a. If the pressure is small compared to the capillary pressure in the fine pores, then liquid starts to be forced into the larger pores under Poiseuille flow whilst capillary pressure filling continues as above.
  - b. If the pressure is higher than the capillary force, or all the pores are filled, then the action is by permeation flow according to Darcy's law in saturated structures.

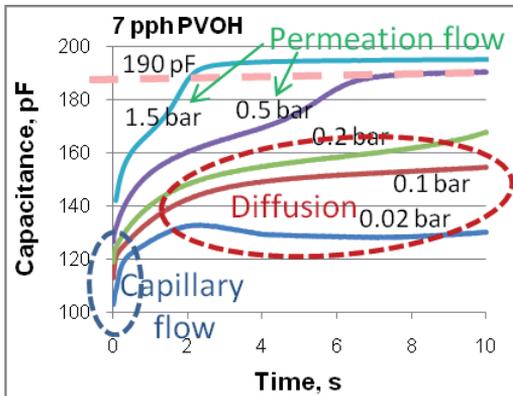


Fig 3. Result curves of Clara at five different external pressures. The used liquid was cyan dye-based ink (used in Kodak Versamark® VX5000e).

The bimodal behaviour of each curve illustrates the competition between the initial capillary wetting and the permeable flow characteristic once capillaries/pores are filled.

Paper thickness,  $d_{\text{paper}}$ , in the  $z$ -direction can be divided into the dry,  $d_{\text{dry}}(t)$ , and wet,  $d_{\text{wet}}(t)$ , parts during the measurement.

$$d_{\text{paper}} = d_{\text{dry}}(t) + d_{\text{wet}}(t) \quad [1]$$

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

$$1/C_{\text{tot}} = 1/C(t) + 1/C_{\text{pl}} \quad [2]$$

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

$$C(t) = A\epsilon/d_{\text{dry}}(t) \Rightarrow d_{\text{dry}}(t) = A\epsilon/C(t) \quad [3]$$

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

The thickness of the wet part of the paper, which we estimate to be the penetration depth of the water front, can be calculated by combining equations 1, 2 and 3:

$$d_{\text{wet}}(t) = d_{\text{paper}} - A\epsilon/C(t) = d_{\text{paper}} - A\epsilon(1/C_{\text{tot}} - 1/C_{\text{pl}}) \quad [4]$$

The pressure exerted by inkjet ink droplets in a high speed inkjet press are clearly less than 1.5 bar. If we assume that the droplet size is 15 pl, as quoted by Kodak for the Versamark<sup>10</sup> technology, the speed of impingement of the droplet onto the paper surface is 15 m·s<sup>-1</sup> and ink density 1 000 kg·m<sup>-3</sup>, the pressure that we estimate, by utilizing the common pressure, density and speed formula, of the droplet hitting the paper surface is a little under 0.1 bar. The measured capacitance values of Clara remain in this pressure area under the maximum value of 190 pF after 10 s measuring time at 0.1 bar pressure (Fig 3). This indicates that the studied ink did not penetrate through the whole paper, and so the ink front is still within the paper structure. If we assume that the maximum capacitance value is achieved in the thickness  $d_{\text{paper}}$ , then the penetration depth and speed turn out to be too high compared with the calculated pressure penetration. This finding fits well with the work of Schoelkopf, Gane et al. (2000), which showed that absorption proceeds by a preferred pathway network of pores depending on pore entry criteria, including inertia retarding the filling of larger pores. Such a preferred pathway network results in the wetting front being non-uniform and liquid can reach deep into the structure leaving a proportion of unfilled pores.

### Printing trials

The coated papers were printed with the Kodak Versamark® VX5000e<sup>5</sup> inkjet printing unit, which works with a continuous stream inkjet principle. The inks are dye-based inks and the main diluent/solvent is water. The surface tensions of the inks were measured as 51-55 mN·m<sup>-1</sup> (25°C), depending on dye colour, and the viscosity 1-2 mPa·s. The printing speed was 100 m·min<sup>-1</sup> and the drying drum and hot air dryer had a temperature of 80°C.

The inkjet colorant penetration depth was characterised in respect to print density and print-through. The print density was measured with GretagMacbeth D196<sup>11</sup>. In the analysis of print-through, a scanner system with image analysis (MATLAB based PTA program) was utilised. The scanner system adopted an Epson Perfection V700 Photo scanner with resolution of 300 dpi. In the print-through evaluation, the studied area was taken from the reverse side of a printed area, with the reference area in all cases being unprinted. The show-through was measured from the printed area upon which was placed an unprinted sample of the same coated paper. The strike-through was then calculated by subtracting the show-through from the print-through. The colour difference was reported as Delta E94, which followed the CIE 1994 colour difference equation. This takes better account of the different colours of the printed surface than conventional  $\Delta E^*$  (Mäkinen et al. 2005 and 2007). In the study of bleeding (mixing of the inks at their interface), a scanner system was used. The scanning was made again with the Epson Perfection V700 Photo scanner, with a chosen resolution of 2 400 dpi. The grey level profile of the printed line was measured with an image analysis program using a definition of the points A and B. Point A was 15% brighter than the darkest region and B 15% darker than a background. The black surface had grey value set to zero, and white a value of 254. Each unprinted paper was adjusted to the value 170. The normal edge width described the bleeding distance of inks.

Table 3. Properties of coated papers.

Coating	Coat weight / g·m <sup>-2</sup>	Bulk thickness / μm	Apparent bulk density / kg·m <sup>-3</sup>	Cumulative pore volume / cm <sup>3</sup> g <sup>-1</sup>	Contact angle (water) / ° (STDEV / %)
Base paper	-	85.8±0.6	777±5	0.620	N/A
Pre-coating	7.4±0.6	90.3±0.6	906±6	0.439	91.8 (2.0)
7 pph PVOH	8.2±0.2	97.3±0.5	928±4	0.507	50.2 (4.0)
12 pph PVOH	8.3±0.1	95.6±0.3	937±3	0.441	62.4 (2.0)
30 pph PVOH	8.8±0.3	97.2±0.4	922±4	0.500	86.7 (2.0)
7 pph SA	8.5±0.5	97.6±0.5	929±5	0.483	93.6 (1.0)
12 pph SA	9.7±0.5	97.9±0.8	937±7	N/A	109.0 (3.0)
30 pph SA	6.6±0.3	94.2±0.7	937±7	0.464	114.0 (3.0)

<sup>11</sup> Gretag-Macbeth AG, Althardstrasse 70, CH-8105 Regensdorf, Switzerland

The ink colorant penetration depth was illustrated by embedding the printed surface in LR white resin<sup>12</sup> (with refrigerator) and taking a cross-section image with a light microscope (Zeiss Axioskope 2 plus).

The colorant fixing properties were studied by testing the water fastness. The printed single-colour 70% half-tone dot areas were immersed into de-ionised (23°C) water for 5 min. After that the samples were left hanging to dry in dark conditions at 23°C temperature and 50% RH moisture content overnight (at least 17 h). Similar methods have been used in other studies (Ryu 1999, Khoultchaev 2001, Vikman 2004a). The colour change  $\Delta E^*$  was measured with a GretagMacbeth SpectroEye<sup>7</sup> spectrophotometer. The spectrophotometer used a configuration of 2° measuring angle, D65 illuminant, UV-filter on and the coated unprinted paper defined as a white area. CIELab\* values were measured before and after the water-treatment.  $\Delta E^*$  was calculated following the standard equation of SCAN-P 89:03.

## Results

### Coated paper properties

Table 3 shows the results of coat weight, bulk, thickness, density, cumulative pore volume of coated papers and contact angle of water. Fig 4 illustrates how binder amount increase decreased the air permeance results of the whole paper.

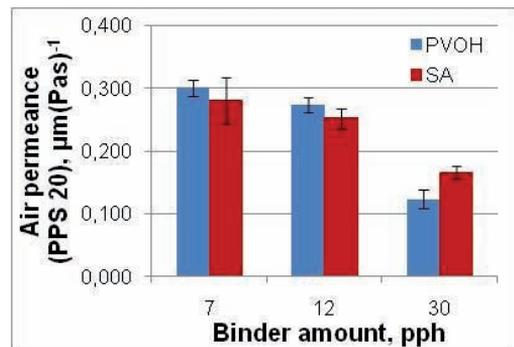


Fig 4. The air permeance of studied layer structures.

Fig 5 shows that the pores of the pre-coating layer are located in the area of 100-550 nm. The first derivative curves (Laplace equivalent pore size distribution, ignoring pore shielding) of PVOH and SA coatings, where the derivative results of pre-coated paper have been subtracted, are illustrated in Fig 5 (right side). PVOH coatings displayed more of the smaller diameter pores than in the case of the SA latex coatings. At the binder amount of 30 pph,

<sup>12</sup> Electron Microscopy Sciences, P.O. Box 550, 1560 Industry Road, Hatfield, PA-19440, USA

the PVOH coating had less pores within the 35-85  $\mu\text{m}$  diameter region than the SA coating. These results indicate a pore filling behaviour of the PVOH.

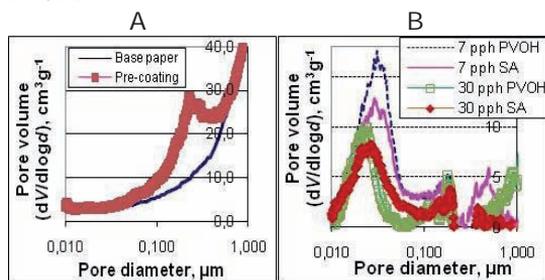


Fig 5. The first derivative of cumulative mercury intrusion curves of base paper and pre-coated paper (left side) and PVOH and SA coated papers (right side). A refers to substrate and B the pore size distributions of the coatings with the substrate and pre-coat subtracted.

### Ink absorption time

The ink absorption time into the top coating layer was measured with the DIGAT (Lamminmäki et al. 2007), which records the glossmeter voltage change as a result of the applied inkjet ink layer during time. The absorption time is the time between 10% of maximum voltage and 10% of saturation voltage value. It was seen (Fig 6) that the 7 pph binder coatings had the quickest absorption, and that there was very little difference between the values for the 12 pph and 30 pph binder containing top coatings. There was only a slight difference between the ink absorption values for the two types of binder used.

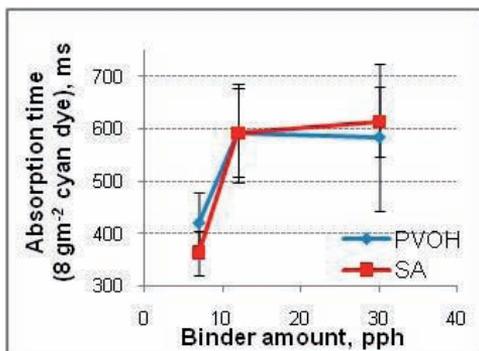


Fig 6. Absorption time of inkjet ink into coatings with different amount of binder. Absorption time was measured with DIGAT device using 8  $\text{g}\cdot\text{m}^{-2}$  cyan dye-based ink (used in Versamark® VX5000e press).

### Absorption properties of whole paper structure at 1.5 bar

The capacitance results at 1.5 bar (Fig 7) show that ink movement through the paper is dependent on the amount of binder present, i.e. the coating which had more binder had a slower capacitance change. Measurement at this pressure represents most strongly the permeability of the coating. The relative change from capillarity to permeability can

be distinguished by the bimodal nature of the curve. Clearly, the highest binder levels dampened the capillary effect as the curve becomes monotonic. For the ink to penetrate through the structure with PVOH coatings took from 2.5 s to 11 s, and with SA coatings took from 0.9 s to 3 s. The fastest ink penetration speed was reached with 7 pph binder and ink penetrated more quickly through the SA coating papers than through the PVOH papers.

Fig 8 illustrates how penetration speed of cyan dye developed through the studied papers at the external pressure of 1.5 bar. In the discussion part, we shall come back to these figures and their interpretation.

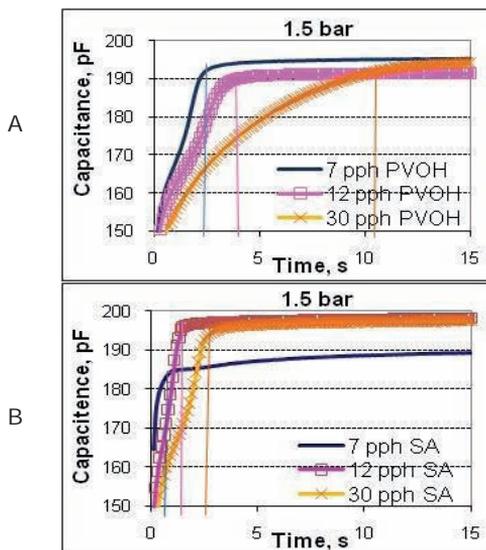


Fig 7. Cyan dye-based ink penetration through the coated papers at the external pressure of 1.5 bar, as measured with the Clara device: A – refers to PVOH and B – to SA latex, respectively.

### Absorption properties of coated paper at 0.1 bar

Fig 9 shows how the studied dye penetrates through PVOH and SA-containing coatings at 0.1 bar external pressure, i.e. within a pressure regime caused by inkjet droplets and their impingement. At the lowest binder amount, 7 pph, the used cyan ink penetrates more rapidly in the SA latex coating than in the PVOH coating. The slope of the curve in the beginning of the measurement is larger with the SA coating than with PVOH. When the binder amount is increased, the curves of PVOH and SA coatings come closer to each other.

We see that the bimodal nature of the curves is far less at the lower pressure, supporting the dominance in this case of capillary pressure. Only in the case of the low level of latex do we see an indication of bimodality, and this supports the likelihood of there being greater permeability in this case, such that even at low pressure some external pressure driven Poiseuille flow can be established.

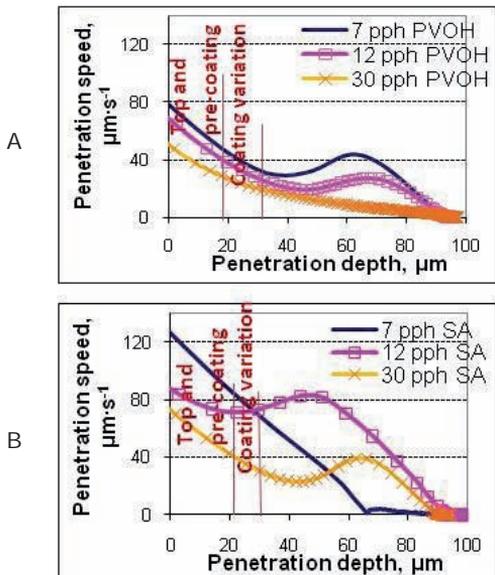


Fig 8. Cyan dye-based ink penetration speed through the paper structures having PVOH and SA coatings at external pressure 1.5 bar. The coating variation refers here to the thickness differences of the coating layer : A – refers to PVOH and B – to SA latex, respectively.

**Print quality**

The black ink produced higher print densities than cyan ink (Fig 10). There were observed to be a couple of black print density results on the SA latex coatings that were on a somewhat higher level than the other results, but otherwise print densities were very close to each other. The strike-through was lower with PVOH coatings than with SA, again supporting the greater permeability of the latex-containing coatings.

The highest bleeding tendency was exhibited by the SA coatings with binder amounts of 12 pph and 30 pph, respectively (Fig 11). The finding that applying a high level of binder does not prevent strike-through illustrates the role of base paper as coating pore volume becomes limited. Although the increased binder level leads to a semi-sealing of the coating layer to permeation, the excess liquid volume must proceed into the body of the paper. It is then the transmission of liquid through the base paper, by fibre wall wicking, for example, that leads to the appearance of ink on the reverse side of the sheet.

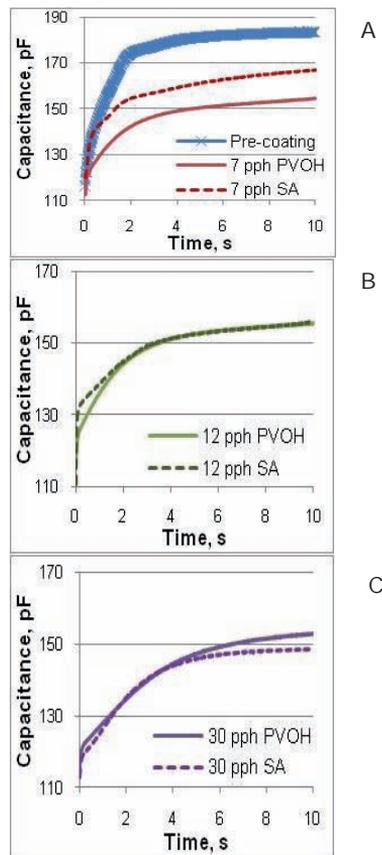


Fig 9. The effect of binder type and binder amount on the results of Clara. Measured with Versamark® cyan ink using 0.10 bar external pressure: A, B, and C refer to 7, 12 and 30 pph binder levels, respectively.

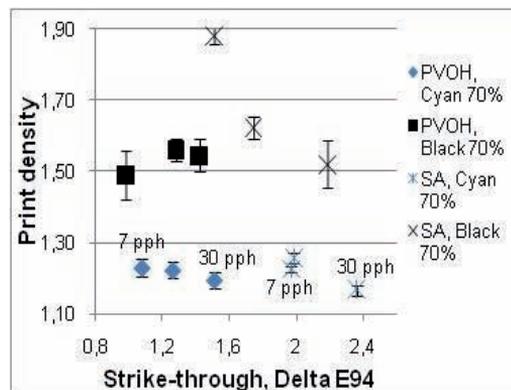


Fig 10. Print density against strike-through of dye-based ink printed surfaces. Printed with Versamark® VX5000e.

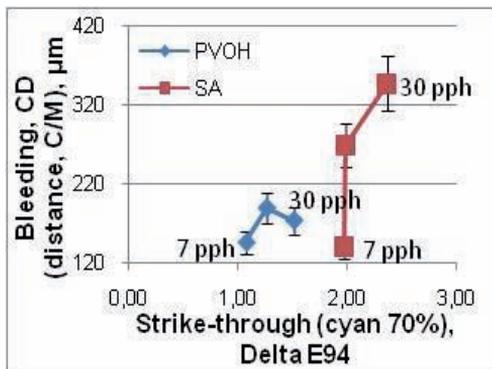


Fig 11. The bleeding (distance, CD - against printing direction, C/M - magenta line on cyan preprinted surface) against strike-through of studied coated papers.

In the water fastness properties, Fig 12, the PVOH and SA-containing coatings showed a totally different nature. The colorant had become fixed in the case of the PVOH coatings faster (lower  $\Delta E^*$ ) than in the SA coatings. The colour changes in black surfaces were minimal. However, cyan, magenta and yellow ink had clearly poorer fixing to the SA coatings than to the PVOH coatings.

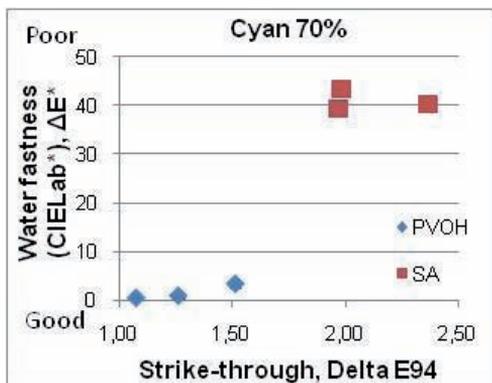


Fig 12. The water fastness of cyan dye-based ink printed surfaces. Printed with Versamark® VX5000e.

## Discussion

### Ink penetration through the coated paper, at 1.5 bar

The Clara results of coated papers at 1.5 bar external pressure (Fig 8) show that the form of penetration speed curves in coating layers is very similar for the PVOH-containing coatings, and this continues until a depth of 32  $\mu\text{m}$ . The thickness of top-coating is about 10  $\mu\text{m}$  and pre-coating about 7  $\mu\text{m}$ . This means that ink penetration has continued very similarly within the coating layers dominated by the external pressure. The rate at the higher pressure level is determined more strongly by permeability, and thus the rate is determined by the layer of least permeability, i.e. the top-coating.

In our earlier study it was noticed (Lamminmäki et al. 2009) that the used PVOH can go into the intra-particle pores (pore diameter of 20-60 nm) of speciality porous coating pigments. The pore intrusion derivative curve (Fig 5) shows that most of the pore diameters of pre-coating are between 100 nm and 550 nm. Therefore, it is possible that the PVOH contained in the top-coating colour has also penetrated into the pre-coating layer. Secondly, the PVOH can dissolve in the inkjet ink water vehicle and be transported in part from the coating, as Fig 13 shows, and so it can affect ink properties during the penetration process. Thus, there can be several aspects which can affect the inkjet ink movement in the coating layer. However, the lack of permeation change tells us that the top coat dominates the permeation property, since larger pores below it simply act to maintain the flow rate under pressure rather than speeding it up. Therefore, even though PVOH can in effect be somewhat mobile, the effect is not strong enough to be observed here.

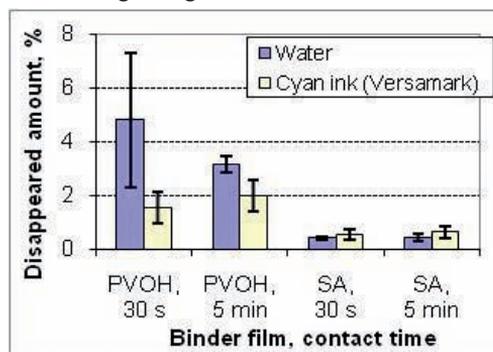


Fig 13. The dissolving of binder films in de-ionized water and cyan dye-based ink - film thickness 200-250  $\mu\text{m}$ . In the binder film absorption measurement, the PVOH film was put in the test liquid for duration of either 30 s or 5 min. After that the liquid was weighted and put into the oven to evaporation. The result is the relative change of liquid (before and after drying).

Moreover, the hydroxyl groups of PVOH can bind ink solvent (water) within the porous coating layer, and this process causes swelling and closing of the smallest coating pores (Lamminmäki et al. 2009). It has been shown previously that a PVOH film (200-250  $\mu\text{m}$ ) absorbed Versamark® VX5000e cyan ink up to 29.2% of its volume after 5 s (Lamminmäki et al. 2009). At the same time, SA latex film (200-250  $\mu\text{m}$ ) absorbed only 1.0% of its own volume of the same cyan ink. Therefore, we can assume that the swelling of SA latex affects less in the SA coatings.

The Clara results indicate that ink penetrates under pressure quicker in SA coatings than in the PVOH coatings. PVOH-containing coating has the lower permeability when compared with the SA latex bound coating (Fig 14). In addition, the PVOH binder swells under diffusion by ink vehicle,

whereas SA binder cannot. Therefore ink becomes held longer in the PVOH-containing coating before it continues travelling further under capillary action, or is retarded by reduced pore connectivity as a result of the swelling under permeation. Thus, there must also be a concentration difference of ink at a certain moment between PVOH and SA bound coatings. We may also assume that the latex part of the top-coating cannot transfer into the pre-coating structure to the same extent as PVOH might during the coating process, because the mean diameter of latex particles (180 nm) is partially too large to flow into the pores of the pre-coating (100-500 nm). Furthermore, once the topcoat is immobilized this flow cannot happen within the topcoat either. Therefore, the top- and pre-coating layers of latex coatings are probably more separately defined than those in the case of PVOH bound coatings. The role of diffusion in these binders will be studied more closely in our forthcoming work.

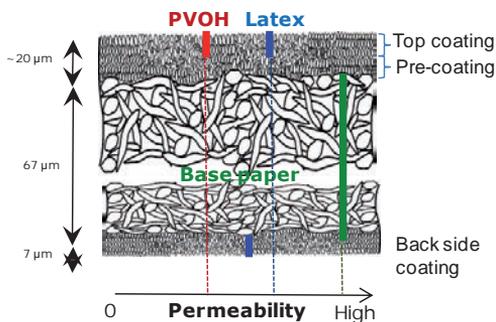


Fig 14. Binder type effect on permeability under external pressure (1.5 bar) through the studied coatings with PVOH and SA latex. Red line describes the permeability level in PVOH coated papers and blue line is the permeability in SA latex coatings. Green is the permeability of base paper.

#### Ink transportation at small external pressure, 0.1 bar

At lower pressure, 0.1 bar, corresponding to that of an inkjet ink droplet impingement at the paper surface, the ink moves slower into the coating structure than at 1.5 bar. The ink penetration is controlled more strongly by capillary absorption, and again more slowly in the PVOH coating than in the SA coating, supporting the supposition that PVOH absorbs ink water, swells and causes the closing of the small pores. Moreover, this means that at a certain moment the ink concentration in the pre-coating is lower because the ink stays longer in the top-coating. This can influence the ink spreading behaviour in and on the top-coating.

In the SA coating, the ink moves faster in the coating layer, similarly as seen before at the higher pressure. Some action of permeability can now be expected even at low pressure. This is effectively a drainage effect superposed on the capillary effect. At the pressure 0.1 bar, it is possible to notice

changing points of the capacitance slope as measured in the 7 pph SA-containing coated papers. The first changing point of the capacitance curve located at a time of 0.3 s (Fig 9), on the basis of both 0.1 bar and 1.5 bar results, is when the capillary force filled pores are starting to become saturated and the remaining larger pores fill under the low but present external pressure. This changes the mechanism from capillary wetting to permeation. This continues through the wetting of the base paper as the rate of base paper penetration is controlled by the permeability of the coating layer. If we now consider the absorption time of 0.36 s for the 7 pph SA-containing coating, as measured by DIGAT, we can conclude that the ink has already penetrated through the coating layers at the moment when the gloss of the ink layer disappears. The PVOH bound coating does not display this kind of clear changing point of penetration speed at any of the studied binder amounts. The reason behind this considered to be the same as at 1.5 bar external pressure, i.e. the absorption by a swelling of the PVOH.

The addition of binder amount, up to 12 pph and 30 pph, decreases the porosity and permeability of the coating layers. At a binder amount of 12 pph, the SA-containing coating absorbs the ink still more rapidly than PVOH. However, deeper in the paper the ink moves very similarly regardless of binder type. The ink goes through the SA coating quicker than through the PVOH coating, but stays longer in the interface of base paper and pre-coating, where the pore size increases. At the binder amount of 30 pph, the capacitance values are pretty much same. Initial wetting of the base paper at low external pressure is therefore assumed to be the rate controlling factor and is predominantly diffusion limited.

#### Ink movement effect on print quality

On the basis of the Clara capacitance results we can expect that the SA bound coatings with higher ink penetration speed produce lower print density and higher print-through because the colorants can move deeper into the coated paper structure. As Fig 10 shows, the strike-through is higher with SA papers than with PVOH papers. The cross-section figures (Fig 15) show how the cyan colorants have been transported eventually to the base paper from the SA bound coated surface, whereas the colorants are held within the coating layer containing PVOH.

On the other hand, SA bound coatings will display both hydrophilicity, due to the latex stabilising surfactants and carboxylation, and a certain hydrophobic nature associated with the underlying polymer matrix. Previous workers predicted less ink droplet spreading (Bahr 2000) due to

hydrophobicity. The results here indicate that neither the latex nor the quick ink movement in the paper structure prevent the colorants from spreading on the SA coatings. One explanation for this can be the surfactants that have been used in latex production. They could aid lateral transport of colorants on the top part of the coating, although the penetration speed of the ink is quick enough to prevent the existence of inter-colour bleeding. A further consideration is that the larger pored latex bound coatings evidence less “capture” of the wetting front compared to the internal diffusion responding PVOH. We see that this could be related either to the reduced permeability of PVOH coatings and/or the slight cationicity of the PVOH itself since the coating pigment is itself had z-potential of 1.6 mV. If the SA latex bound coating would contain additional chemical components that could fix the colorants of the ink, and arrest lateral spread, then SA or any other latex type might have a better possibility to work functionally in inkjet coatings.

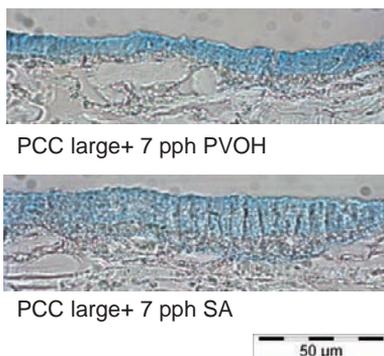


Fig 15. Cross-section micrographs of coatings comparing the cases with 7 pph of PVOH and SA, respectively. Printed with Versamark® VX5000e.

The water fastness results (*Fig 12*) show that the colorants, other than black, have reduced capability to withstand the water treatment and remain less within the printed SA bound coatings than within the PVOH coatings. *Fig 16* shows how cyan ink that was applied directly to a film of the binder alone has attached to the PVOH film but not to a corresponding SA latex film. We see therefore, that the PVOH has a positive action by direct adsorption of dye.



Fig 16. Colorant fixing to PVOH and lack of fixing to SA latex films after 30 s absorption time.

In the case of PVOH coatings, the longer ink residence time in the coating layer, has not become reflected as a larger bleeding tendency (*Fig 11*). It seems that the ink vehicle diffusion in the PVOH layer has happened so quickly that the colorants have no time to transfer in the *xy*-direction on the top of the coating. The colorants stay adsorbed to the PVOH binder and no print-through problems occur.

## Conclusions

The inkjet ink penetration speed depends on the used binder type in the coating layer and the level of external pressure, if applied. The PVOH binder can allow diffusion of the inkjet liquid phase, and swells under the influence of the ink. This acts to close the nano-size pores and therefore slows down the ink penetration speed in the coating structure. Moreover, PVOH dissolves and this may have an effect on the ink properties and binder transport during the penetration process.

It is also possible that PVOH binder can move into a pre-coating or base paper structure during the coating process and close up some of the smallest pores there too. The results show, that ink penetration speed depends on both capillarity and permeability. The capillary wetting force is most active in the finer pores, and once these become saturated then permeability is the controlling factor for further imbibition, this latter being even more dominant when external pressure is applied. The structure of SA latex bound coatings allow the ink penetration into the paper structure to occur faster than in PVOH bound coatings, since the SA-containing coatings are effectively more permeable.

The ink seems to stay initially on the top of the studied coatings displaying a quite similar delay before it penetrates into the coated papers, but the ink penetration speed in the coating layer is higher in SA bound coatings, especially under external pressure. This indicates that the ink diffusion in the PVOH binder happens as quickly as the ink flow in the SA-containing coating. The quicker ink penetration speed (as measured by the capacitive method, Clara) in the SA bound coating structure causes colorant transportation to the top part of base paper, and therefore print-through problems occur. The SA latex can neither bind ink colorant nor prevent bleeding compared with the inter-diffusion action of the ink liquid phase in the PVOH. The structural as well as chemical differences of coating layers determine the final inkjet print quality formation.

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