

PAPER I

**Inkjet print quality: the role of
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CaCO₃ coatings**

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Inkjet Print Quality: The Role of Polyvinyl Alcohol in Speciality CaCO₃ Coatings

T. LAMMINMÄKI, J.P. KETTLE, P. PUUKKO, P.A.C. GANE
and C. RIDGWAY

The aim of this work is to clarify the controlling role of polyvinyl alcohol (PVOH) as a binder in the formation of coating and pore structure and how it affects the high-speed inkjet image quality formation. The results show that the pigment type and the binder amount have a large interactive effect on pore structure formation. The studied PVOH can transfer into the intra-particle pores of pigments, and the swelling of PVOH closes up the pores which have diameters of ~30 nm, but this depends on the amount of binder used. The optical properties of the whole paper, not just the coating, are the most important regarding print density, but the properties of the coating layer itself have a dominant effect when considering the ink bleeding.

L'objectif de cet ouvrage est de clarifier le rôle de régulateur que joue l'alcool polyvinylique (PVOH) comme liant dans la formation du couchage et la structure des pores, et de démontrer comment elle affecte la qualité de la formation de l'image à jet d'encre à haute vitesse. Les résultats démontrent que la sorte de pigment et la quantité de liant ont un impact interactif important sur la formation de la structure des pores. L'alcool polyvinylique étudié peut se transférer à l'intérieur des pores de pigments intra-particulaires, et son gonflement resserre les pores ayant un diamètre de ~30 nm. Cependant, ceci dépend toujours de la quantité de liant utilisée. Les propriétés optiques du papier entier, et non seulement le couchage, sont les facteurs les plus importants en ce qui a trait à la densité d'impression, mais les propriétés de la couche de couchage ont un impact dominant relativement aux bavures de l'encre.

INTRODUCTION

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 surface of paper [1]. There is an urgent need to develop the coating layer properties based on the mechanisms which control these properties

in inkjet printing, and the interaction of pigment and typical inkjet paper coating formulation binders, in determining coating pore structure, is an area that has received insufficient attention in this respect.

The absorption speed and volume of the ink diluent/solvent challenge the capacity of the paper surface to generate acceptable inkjet print quality. The water-solvent should absorb very rapidly into the paper. The applied ink droplets should not mix together on the surface or intermingle in the structure of the sheet. Ink droplet setting is a phenomenon that happens on a millisecond scale, but the final ink drying can take hours [2]. The amount of applied solvent can be very high, so the paper needs a high porosity to get all of the water-solvent into the paper structure. Even in emerging systems where the volume of diluent is strictly controlled, the rate of absorption still plays a decisive role.

The absorption volume and speed is commonly explained adopting the Lucas-Washburn equation. According to Lucas-

Washburn's equilibrium equation, the volume of liquid in a capillary should be greater, the larger the radius, at a given time. On the other hand, the practical studies have shown that smaller radius capillaries initially fill faster than larger capillaries. Ink sets faster on a fine pore structure coating layer than on a highly porous, large pore containing coated paper. This disagrees with the model of Lucas-Washburn. Clearly, there is a distinction between fine and large pores and furthermore, there are effects occurring on the short timescale on the surface and in the pore network as well as in a single and several interconnected capillaries that Lucas-Washburn does not capture [3-5].

Ridgway et al. [3] further studied the Lucas-Washburn equation. They showed that there are a number of more detailed descriptions of flow entry effects into capillaries, such as the energy loss equation of Szekely [5]. Bosanquet [6] added the inertial wetting term associated with an accelerating fluid. A solution of the equation of Bosanquet for short times is proposed by Schoelkopf et al. [7],

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T. Lamminmäki, J. Kettle and
P. Puukko
VTT Tech. Res. Centre Finland
P.O. Box 1000
FIN-02044 VTT, Finland
(taina.lamminmaki@vtt.fi)
P.A.C. Gane
TKK, Vuorimiehentie 2,
FIN-01250 Espoo, FINLAND,
and OMYA Development AG
CH-4665 Oftringen
Switzerland
C. Ridgway
OMYA Development AG
CH-4665 Oftringen
Switzerland

which showed that liquid penetration distance by absorption into the finest capillaries over short timescales has a direct proportionality to the time elapsed. When inertia dominates, the finest pores will absorb further and faster. Furthermore, if we consider a network of such fine pores, remembering that a fine pore in coatings is typically equally as short as its diameter is wide, then in combination with enough reservoir volume between them, we can visualize a preferred pathway effectively by-passing the larger pores or at least limiting the access to them. This has been constructed by Ridgway et al. [8] using the Pore-Cor visualization (Pore-Cor and Pore-Comp are a software network model and a sample compression model, respectively, developed at the University of Plymouth, Plymouth, UK). In this pathway, the velocity of absorption is high, and so the passage into the porous medium is defined by the combination of pore sizes within the inertial wetting regime (nanopores) and the connecting reservoir structure consisting of larger pores which fill more slowly. Therefore, we can assume that small pores are needed for quick inkjet ink penetration at the moment of droplet setting and large pores are needed for the storage of all the solvents into the structure. The connectivity relation between these is crucial if the maximum absorption rate for large volumes is to be maintained.

In coating colours, we have, besides the pigments with their particle packing characteristics and internal pore structure, if present, the binder. By changing binder amount or binder type we can influence the inkjet ink penetration. Primarily, the binder amount should be sufficient enough to ensure that the coating colour has adequate adhesion to the paper surface and cohesion so that dusting problems are minimal. The surface strength is not needed at such high levels as in traditional off-set printing, but nonetheless dust generation is critical, as it could lead to blockage or damage of the inkjet nozzles, and so diminish the print quality and reduce the lifetime of expensive print engine components. In coating colours for inkjet papers, polyvinyl alcohol (PVOH) is

a very commonly used binder, and it has a high capability to bind pigments. It is also a very hydrophilic binder, and exhibits swelling on contact with water [9-11]. Pinto et al. [11] showed in their study that ink diffusion is unrestrained by PVOH, and the colorant concentration profile is uniform in a PVOH layer as shown by time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis. Lately, the binder type has been shown to have an effect on the inkjet ink print density and bleeding development, Nilsson [12] and Svanholm [13]. However, the binder swelling tendency in the inkjet print quality formation of Versamark VX5000e has not been studied so widely.

The aim of this work is to clarify:

- the role of PVOH as a swelling binder in the porous CaCO₃ coating layer structure,
- the role of porosity and pore diameters in the inkjet ink setting process, and
- how the PVOH coatings work in the print quality formation of dye-based inks in high-speed inkjet printing.

MATERIALS AND METHODS

Coating Compositions and Coating Trials

A range of calcium carbonate-based pigments provided by Omya AG, Oftringen, Switzerland and one CaCO₃ pigment from Minerals Technology Europe, Zaventem, Netherlands were used. The main idea behind this pigment selection was to vary the mean particle diameter and specific surface area of the pigments (Table 1). The binder in the coating colours was polyvinyl alcohol (PVOH, Mowiol 40-88 provided by Clariant International AG, Muttenz, Switzerland). The selected PVOH had a degree of hydrolysis 87.7 ± 1.0% and a molecular weight of 204 000 g·mol⁻¹ [14].

The study was started by looking at the properties of pure pigments. Pigment cakes and 100 g·m⁻² coating layers on glass plates were produced from a range of formulations. The cakes were made with Teflon moulds,

drying them at 23°C. The glass plates were coated with an Erichsen film applicator (Model 288, Hemer, Germany) using blades with a fixed gap height between 100 and 500 µm. All the pigments had been dispersed by the pigment manufacturers themselves.

The pigment properties are shown in Table 1. The choice of pigments was made to illustrate the effects of particle size and internal pore structure, including raw material sources from ground calcium carbonate (GCC), subsequently modified to generate high surface area and internal pores (MCC), and precipitated calcium carbonate (PCC). The pigment diameters were determined by sedimentation (Sedigraph 1500, Micromeritics, Norcross, GA, USA) or by laser light scattering (NanoSight, Amesbury, UK) and the values given are quoted from the specifications of the manufacturers. The pH and zeta-potential (AcoustoSizer II, Colloidal Dynamics/Agilent Technologies, Espoo, Finland) were determined in the coating colour, which in this case contained 10 pph PVOH (based on 100 pph by weight pigment). We note that all but one of the pigments exhibit a cationic slurry property, being designed to adsorb anionic ink dye so as to prevent strike through and to maximize print density by concentrating the colorant near the coating surface. Coulombic interaction also acts to maintain water fastness of the ink.

The liquid uptake capacity of the porous structures was measured with Si-oil absorption. During the oil absorption, the pigment cake was left for one hour in Si-oil, and the weight of cake before and after Si-oil saturation was measured. The available porosity for oil absorption is determined at normal air pressure and is defined as absorbed Si-oil volume in the coating cake, divided by the sum of the coating layer volume without oil, plus the absorbed Si-oil volume.

The pore volume and pore size distribution was measured with mercury porosimetry (Micromeritics AutoPore IV), adopting the Pore-Comp correction to account for penetrometer expansion, mercury compression and compression of the sample skeletal

TABLE I
PIGMENT PROPERTIES

Properties	Ground calcium carbonate - GCC	Modified calcium carbonate - "MCC large"	Modified calcium carbonate - "MCC small"	Precipitated calcium carbonate - "PCC large"	Precipitated calcium carbonate - "PCC small"
Weight median pigment particle diameter, µm (<i>d</i> _{50%})	0.65	2.70	1.30	2.70	Small 0.02-0.03 Av. 0.25 *)
Specific surface area, m ² g ⁻¹ (BET, ISO 9277)	10.7	46.2	27.0	63.7	73.9
Zeta-potential, mV (AcoustoSizer II)	-9	13.1	13.6	1.6	-0.6
Registered trade name	HYDROCARB 90	OMYAJET B6606	OMYAJET C3301	OMYAJET B5260	JetCoat 30
*) NanoSight (results had two peaks: small at 20-30 nm and average at 0.25 µm)					

Pigment/Binder	Colour 1	Colour 2	Colour 3	Colour 4
"PCC large"	100	100	100	
"PCC small"				100
PVOH	7	12	30	7

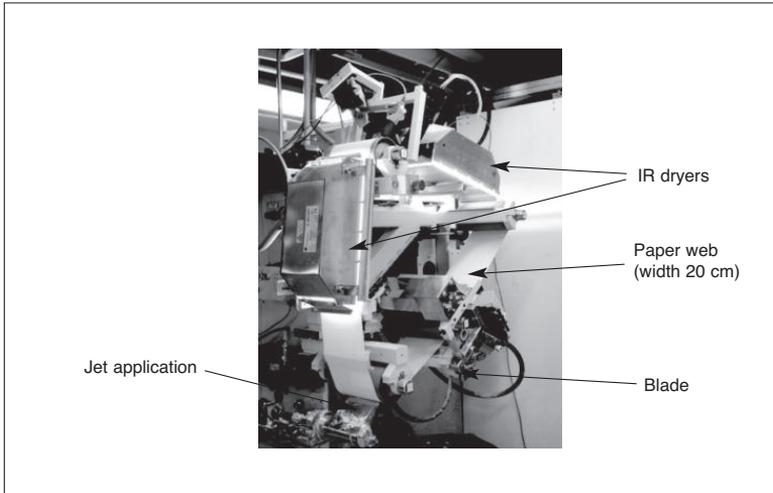
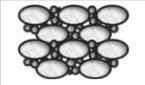
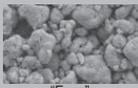
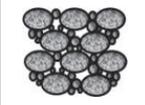


Fig. 1. Image of KCL SAUKKO [16].

Pigment	Air permeance, $\mu\text{m. (Pa.s)}^{-1}$	Porosity (coating cakes), %	Structure of pigment	Illustrated coating layer structure
GCC	0.1	17.7	 Rhombohedral	
"MCC large"	1.3	46.2	 "Roses"	
"MCC small"	0.7	31.9	 "Roses"	
"PCC large"	1.8	48.9	 "Eggs"	
"PCC small"	2.3	32.9	 Spherical	

material, expressed as the elastic bulk modulus, according to Gane et al. [15]. The coatings, with their different binder amounts were analyzed up to 140 Pa (low pressure port) and 440 Pa (high pressure port), respectively. The coated glass plates were analyzed by the thin layer chromatography method (TLC), putting the plate into the eluent (equivalent to either the ink diluent alone or the whole ink, depending on volume or chromatographic separation analysis). The distance of eluent movement during time was measured. The optical properties of the coating layer were studied as a function of eluent uptake and distance, e.g., opacity according to ISO 2471:2008. Behind the coated glass plate a stock of blotting boards (fully bleached) was used as backing.

The KCL pilot coater was used to apply coatings on a larger scale to traditional base paper, which was chosen to be a commercial base sheet for a coated fine paper, $53 \text{ g}\cdot\text{m}^{-2}$. The base paper was first pre-coated so that the top coating of main interest was prevented from penetrating into the base paper. The pre-coating of $7 \text{ g}\cdot\text{m}^{-2}$ was applied with a film coater on both sides of the paper, and the actual studied coating layer of $8 \text{ g}\cdot\text{m}^{-2}$ with short dwell application (blade). The pre-coating had 100 pph of GCC (Hydrocarb 60), 12 pph styrene-butadiene latex and 0.6 pph carboxymethylcellulose. The recipes of the top coating are introduced in Table 2. The coating speed was $1800 \text{ m}\cdot\text{min}^{-1}$ and the final moisture content of the coated web was 5 wt%.

The role of pigment properties alone in the inkjet ink setting process was also studied, so as to subsequently identify the interactive roles of pigment and binder combined. In this case the coating was applied with a semi-pilot coater, KCL SAUKKO (Fig. 1), using jet application and blade. The coating was dried with two infra red dryers. The speed of the web was $900 \text{ m}\cdot\text{min}^{-1}$. The same base paper was used as in the pilot coating. Based on the pilot-trials the binder amount was selected to be 10 pph of PVOH (Mowiol 40-88) to represent commercially acceptable strength and anti-dusting properties. The structural illustrations of produced coatings are given in Table 3. The target coating layer amount of $10 \text{ g}\cdot\text{m}^{-2}$ was not achieved in one single coating layer. The low solids content and the low viscosity of the coating colours limited the applied coating layer thickness, and therefore we had to apply the same coating colour twice.

The air permeance of coated papers was measured with Parker-Print Surf measurement using 20 kPa pressure. The opacity was measured according to the standard ISO2471:2008 and light scattering coefficient ISO 9416. The surface strength of coated papers was studied with an IGT device using ISO 3783 with medium viscosity oil. The absorption time of dye was measured with DIGAT that has been introduced and described in detail in the literature [17]. The ink was anionic dye-based

ink (from a Versamark VX5000e) and the applied ink amount was 8 g·m⁻². The surface structure of the coating layer was imaged with the scanning electronic microscope (SEM).

Inkjet Printed Surfaces

Inkjet printing was carried out on a Versamark VX5000e, which produces inkjet droplets by the continuous stream inkjet method. The inks were dye-base and the main diluent/solvent was water. The surface tensions of the inks were observed to fall in the small range of 51-55 mN·m⁻¹ (25°C), depending on dye colour, and the viscosity was 1-2 mPa·s. Printing speed was 100 m·min⁻¹ and the drying drum and hot air dryer were set to a temperature of 80°C (when studying pigment type to emphasise absorption criteria) and 100°C (when studying the range of binder amount to provide runnability at the highest binder level).

The print density of the printed surface was measured with GretagMacbeth D196. Both a camera and scanner systems were utilized to analyze the bleeding, in terms of distance from the formal colour boundary. The parallel reporting from the two systems was also a part of the development of the scanner method. In the camera system, a picture was taken with an imaging camera from a solid printed line used to define the bleeding boundary, and a grey level profile across the line was constructed. The normal edge width for the given print was measured as the distance between two points A and B. Point A was defined as the point at which the surface across the line image was 10% brighter than the darkest region in the line and B, 10% darker than a given background. The black surface had grey value zero and white 254. Each unprinted paper was adjusted to the value 170. The normal edge width described the bleeding distance of inks. The smaller the number, the sharper is the printed line. In the scanner system, an Epson Perfection V700 Photo was used, with a resolution of 2400 dpi. The grey level profile of the line was again measured with an image analysis program using a similar definition of the points A and B, but now A was 15% brighter than the darkest region and B, 15% darker than a background. The grey levels were adjusted as in the previous camera system. The differences in the optics caused some differences in the results between these methods. Mottling was analyzed with a scanner system. The printed surface was scanned with an Epson Expression 1680 Pro scanner using a resolution of 300 dpi. The scanned figure was handled with a wavelet transform (PapEye program). The ink colorant penetration was studied by embedding the printed surface in LRWhite resin (Electron Microscopy Sciences, Hatfield, PA, USA). The embedded sample was placed in a refrigerator to reduce smearing of the dye. The cross-sections were then imaged in a light microscope (Zeiss Axioscope 2 plus).

RESULTS

PVOH and Porosity Formation of the Coating Layer

The intrinsic structure of the coating layer, without the influence of the base paper, was studied using the coating cake material. At this point, we have to remember that the structure of the coating cake, formed by drying a relatively large volume of coating colour, could be expected to be somewhat different to that of the structure of a thinly applied coating layer on a paper surface, where the coating process variables affect the forming structure, including differences in shrinkage behaviour. This issue has been resolved to some extent by the development of a pigment tablet formation device at Omya AG [7], however this was not used in this work as the PVOH binder is soluble, and filtration might have led to an unwanted depletion of binder. In this current work, however, we saw that the differences were in fact minimal between the measurements on the

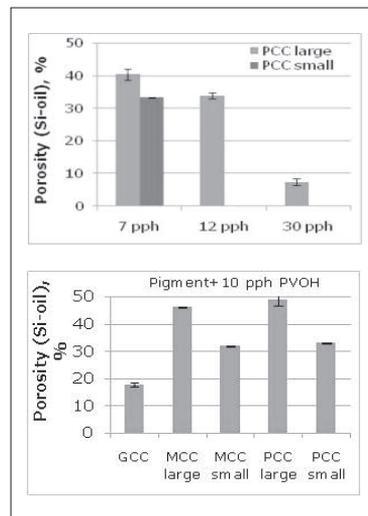


Fig. 2. Absorption capacity of pigment cakes as a function of PVOH binder level, measured by the Si-oil absorption method.

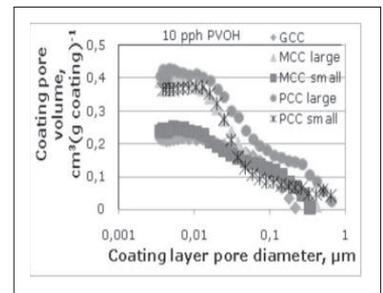


Fig. 3. The cumulative pore volume distributed as a function of pore size, as measured using mercury porosimetry.

coated papers and the coating cakes.

The absorption capacity of the coating cakes was analyzed with Si-oil absorption (Fig. 2). As expected, increasing the binder amount reduced the level of porosity as measured by this technique. At the binder level 10 pph, the porosities of fine particulate "MCC small" and "PCC small" pigments were found to be on the same level. The highest porosities were produced by the large particle size coatings. This illustrates the likely particle packing characteristics.

The porosities of the coating layers were also calculated from mercury porosimetry results, when the base paper effect and the amount of coating layer are taken into account, following the method of Ridgway et al. [18]. The cumulative intruded pore volumes of the coating layers are illustrated in Fig. 3. The "PCC large" coating produced again the greatest pore volume, and it had more large size pores. The lowest porosities were seen for GCC and "MCC small".

The results of Si-oil porosity and mercury porosimeter measurements correlate very well (Fig. 4). The slight differences can be analyzed in respect to the high pressures used in the mercury measurement. At the final stages of mercury intrusion, the pressures are sufficiently high to compress any elastic components present as part of the skeletal structure of the porous material. Polymers, in particular

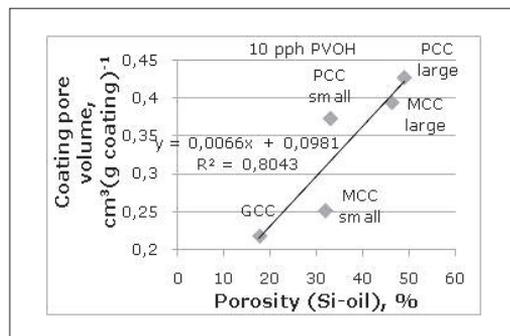


Fig. 4. Correlation between the results of Si-oil porosity and mercury porosimeter.

binder, undergo such compressive effects. The result is an absence of hysteresis between the intrusion and extrusion curves as a function of pressure increase and decrease, respectively. The gradient of this elastic region can be determined and related to a bulk modulus expressing the volume compressibility of the material, Gane et al. [15]. The bulk modulus of the paper coating, based on "PCC large" with 10 pph PVOH, was 30.6×10^3 MPa and based on "PCC small", also with 10 pph PVOH, was 22.0×10^3 MPa. This means that the "PCC large" paper can resist pressure on the skeletal components more so than "PCC small" paper. This reflects the distribution of polymer in respect to the pigment particle packing and the pore sizes present. The finer pigment, with its higher surface area, will necessarily present more polymer species and amount, including dispersant, to the coating colour.

The pigment cakes made from "MCC small" and "PCC small" with binder had very similar Si-oil absorption volume capacities, as seen in Fig. 4, but exhibited very different porosity values when analyzed with the mercury porosimeter. This lets us deduce, that binder tends to blank off the entry to, or connectivity between, pores. Thus, the oil cannot access all the pore volume, whereas the intruding mercury can break through the pore-blanking binder films. This effect is confirmed by the equivalence between the two methods for the pigment cakes without PVOH, in which both techniques access the same pore volumes (Fig. 5).

Traditionally, taking the first derivative of the cumulative mercury intrusion curves

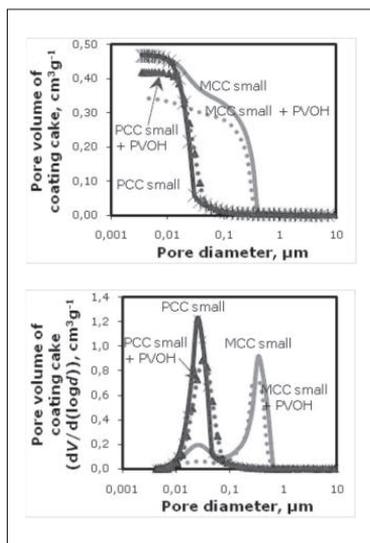


Fig. 5. Cumulative pore volume and pore size distribution curves of "MCC small" and "PCC small".

provides a pore size distribution. This description, although limited to an equivalent bundle of capillaries, and thus ignoring pore shielding effects, is nonetheless useful for comparison purposes between topologically different structures, Gane et al. [19]. We see that the PCC coating structure has only ultrafine pores in the 20-60 nm range (Fig. 5). In contrast, the MCC coatings have both large- and small-size pores, indicating that the MCC structures have both intra- and inter-particle pores. The addition of 10 pph PVOH decreases the pore volume of the MCC coating structure more than that of PCC. The peak of intra-particle pores of the MCC pigment decreases most markedly, clearly indicating that PVOH has filled intra-particle pores.

Effect of Pigment Properties on Internal Liquid Transport

The thin layer chromatography method was used to analyze the eluent movement through the pore networks of the pure pigment packing structures. Long-time passage of liquid through a porous network is defined by the surface wetting force resisted inversely by the permeability of the structure. The greater the permeability and the more the occurrence of fine pore structure surrounding that permeable pathway, the greater will be the transport length in a given time. The longest water/ethanol eluent transport distance through the structure was achieved with the most porous pigments (Fig. 6). The "MCC large" and "PCC large" pigments have very similar size and amount of intra-pigment pores, but MCC has smaller inter-particle pores and so less large pores to contribute to permeability, as Fig. 12 later shows. The GCC and "MCC small" coatings have quite similar capability to transport eluent. The distances are short because of the lack of permeability. The "PCC small" pigment unexpectedly transfers the liquid further in the structure than the other pigments. This would not be expected when looking purely at the fine pore structure, but the sample structures made from the "PCC

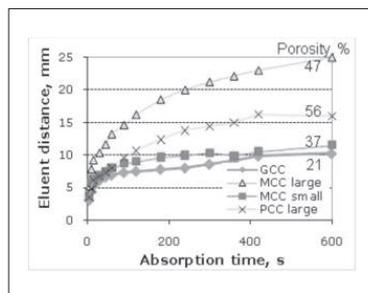


Fig. 6. Water/ethanol eluent (50%/50%) transfer over time in the thin layer pigment chromatography layers formed on glass plates without binder.

small" pigment had a multitude of cracks, which contribute to the permeable transfer of eluent effectively in the pigment layer. This effect is not one of intrinsic particle packing, but the response to shrinkage as the layer forms. These cracks are seen as essential if this pigment is to work in transporting liquid. The results indicate that pigments with higher pore volume transfer liquid more effectively than the lower pore volume structures depending on permeability.

Coating Layer Structure on Paper Surface

Role of Binder

The higher binder amount increased the surface strength of the coated papers (Fig. 7).

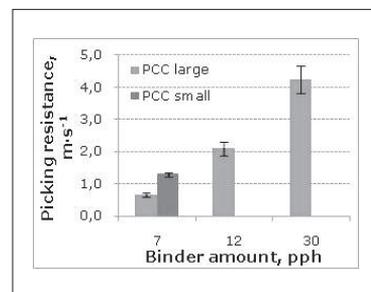


Fig. 7. Surface strength of coated papers measured with the IGT pick test method.

At a binder amount of 7 pph, the "PCC small" had a slightly higher surface strength than "PCC large". Once again, this is due to the difference in interior structure permeability determining the level of binder depletion likely to occur when applied to an absorbent substrate. The surface strength of $2 \text{ m}\cdot\text{s}^{-1}$, defined as the speed at which the tack oil begins to induce pick from the coated paper in the test nip, is considered high enough to ensure attachment of the coating to the paper substrate and to prevent dusting during the inkjet printing.

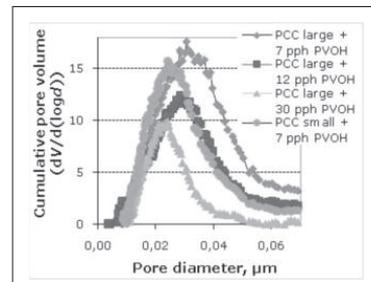


Fig. 8. The first derivative of the cumulative mercury intrusion curves (Pascal porosimeter) illustrating the effect of the binder level.

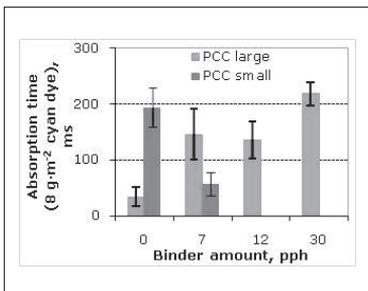


Fig. 9. Effect of binder amount on absorption time (DIGAT) for PCC coatings on glass plate.

Figure 8 shows how the binder amount increase decreases most of all the volume associated with the 30-50 nm size pores within the pore diameter area 0-0.1 μm , primarily responsible for the capillary driven absorption.

The absorption speed into the thin layer coatings on glass using the DIGAT apparatus became slower as the binder amount increased (Fig. 9). It was based on surface strength versus ink absorption speed results, that the PVOH amount of 10 pph was selected for our studies of different CaCO_3 pigments.

The binder amount had very minimal effect on print density in the case of the "PCC large" structures (Fig. 10). However, the pigment change from "PCC large" to "PCC small" at a binder amount of 7 pph clearly increased the print density. Therefore, at these binder levels and at these short absorption times, the binder swelling is unlikely to close the larger pores. The "PCC large" structure determines the colorant transport on this case.

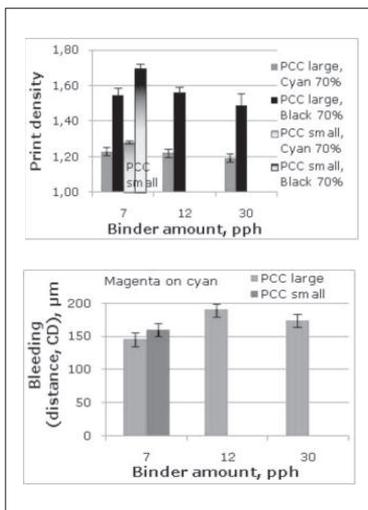


Fig. 10. Print density (measured from 70% halftone dot field) and bleeding distance of dye-based ink printed on PCC surfaces as a function of PVOH content.

A higher amount of binder generated a significant increase in the amount of bleeding. The coatings with 12 pph and 30 pph of PVOH produced the widest bleeding distance (Fig. 10). Interestingly, the bleeding did not increase indefinitely as the binder amount increased, but rather plateaued, showing the loss of pore volume is likely to be countered by the swelling nature of the PVOH in its ability to absorb and hold liquid once sufficient PVOH is present. The other explanation can be in the ink amount. The ink amount could be so low in

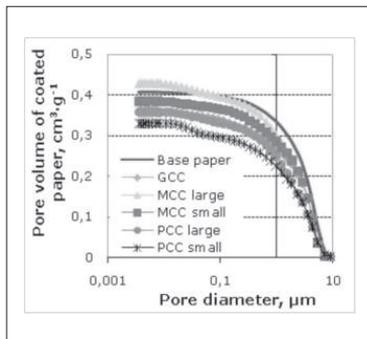


Fig. 11. The cumulative mercury intruded pore volume of coated papers. All coatings had 10 pph of PVOH.

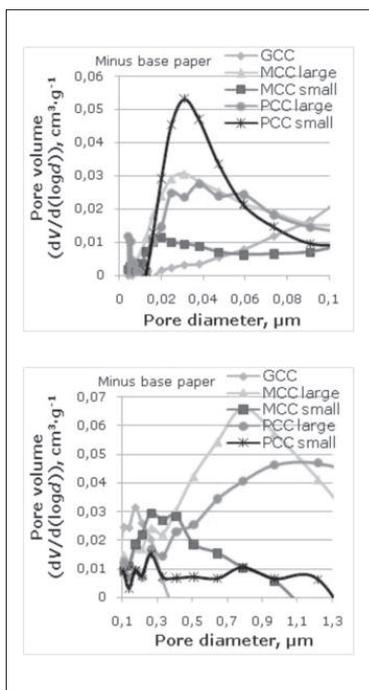


Fig. 12. The pore size distribution curves from mercury porosimetry of studied coated papers. The base paper values have subtracted from the results. The coatings have 10 pph PVOH.

the printing that the absorption time of 220 ms can still be short enough to prevent the onset of bleeding. The effect of time delays will be discussed later.

Effect of Pigment Variables

Figure 11 shows the cumulative pore volume intrusion by mercury of the coated papers which had been produced with five different pigments. The coating layers have partly penetrated into the base paper structure. All of the coated papers have lower pore volume results in the area of 1-10 μm than the base paper before coating.

The pore size distributions of the studied coatings are illustrated in Fig. 12. Generally, the pore size distributions of the coatings on paper reflected the main features of those of the cakes and of the thin layer chromatographic slides. "MCC large", "PCC large" and "PCC small" coatings have small pores, 20-40 nm in diameter, whereas GCC and "MCC small" had clearly less of such small pores. The coatings with the two large 2.7 μm diameter pigments ("MCC large" and "PCC large") had the same amount of small-scale pores. The GCC coating

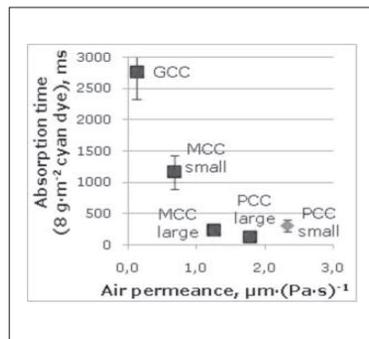


Fig. 13. Effect of air permeance on absorption speed (DIGAT).

had mainly 0.1-0.3 μm diameter pores and "PCC large" had the largest diameter pores, 1.0-1.3 μm . "MCC large" and "PCC large" had both small and large-scale pores. "PCC small" coating had mainly only small-scale pores.

The absorption speed into the coated papers was quickest with "PCC large", with the three pigments "MCC large", "PCC large" and "PCC small" all absorbing within the high speed range. The slowest absorption was, as to be expected, with GCC (Fig. 13). The relative requirements of capillarity and permeability are well reflected in these data. The capillarity is provided by the ultrafine pores and the liquid transfer by the permeability of the coating layer, Ridgway and Gane [20].

The highest print density (Fig. 14) was achieved with the coating structure on paper derived from "PCC small", and the lowest

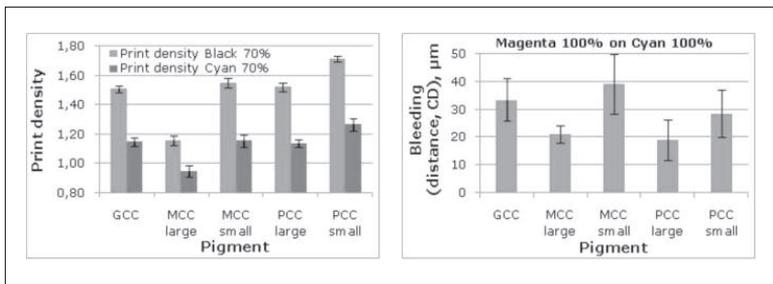


Fig. 14. Effect of coating pigment type on print density and bleeding (distance, measured with camera system) of dyes.

from "MCC large". At the same time, "MCC large" and "PCC large" coatings produced the lowest bleeding values.

DISCUSSION

Role of PVOH Swelling

We can assume, on the basis of mercury porosimetry results, that PVOH binder can go into or cap (film over the entry) intra- as well as the connecting pores, and exists around the larger inter-particle pores as Boisvert et al. [21] and Wedin et al. [22] assumed in their studies. At sufficiently high levels, any interaction of the binder with the liquid phase of the ink becomes important, not only in the structural modification of pore volume but in the diffusion of liquid through the polymer network, effecting swelling in the case of PVOH.

We made a theoretical calculation about the binder swelling effect within the pores. Firstly, we assumed that the binder forms a uniform layer on the pore wall (Fig. 16A) and the thickness of this layer depends on the specific surface area of the pigment (thicker binder film at lower specific surface). The geometry of the pore is also assumed to be simple, as that the binder forms a uniform

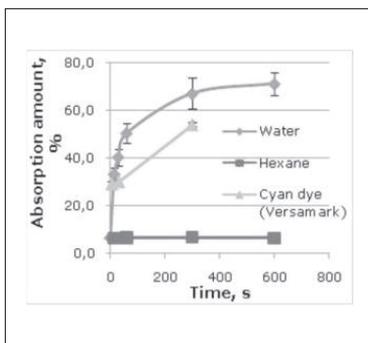


Fig 15. Absorption amount of PVOH films as a function of time. Assuming that the specific gravity of water = 1 and PVOH = 1.26. The swelling factor is given by absorption amount. Absorption amount = $100 \cdot (\text{mass of liquid absorbed into the film} / \text{mass of dry binder})$.

layer on the interior surface of a circular equivalent capillary. In this way, we can calculate how the pore entrance area changes during the binder swelling process.

PVOH is a hydrophilic binder [10,11]. Figure 15 illustrates how a PVOH film (200–250 μm) absorbs water but not non-polar hexane as a function of time. The PVOH film exhibited a 29.2% swelling when exposed to cyan dye-based ink (Versamark VX5000e) after 5 s, and this value has been used in our calculations.

The results of the calculation are illustrated in Fig. 16. The pore volume and amount of binder represent what is to be found in 1 g of coating structure, as taken from mercury porosimetry and the coating formulation, respectively. The first line on the left is the pore area when the structure has been formed from pigments alone. The addition of 10 pph binder into the coating results in pore diameters being reduced by the absorbed layer of PVOH by an amount of 13 nm when the PVOH is dry - this being twice the absorbed thickness to describe diameter loss in a cylindrical pore. The closing point of pore diameter increases to 24 nm when the binder swelling found to be 29.2 % occurs on contact with inkjet ink. This can lead to complete blocking of the finest pores, reduction in pore size in general and loss of connectivity in the structure when the binder is concentrated at pore nodes. The higher the amount of binder the thicker the binder film is, and thus the effect of swelling also increases. It seems that the swelling affects most or nearly all of the intra-particle pores. This means that these pores are effectively acting purely via a binder-swelling liquid uptake mechanism.

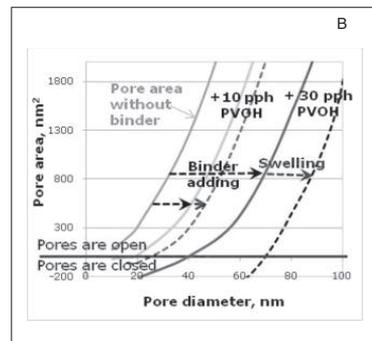
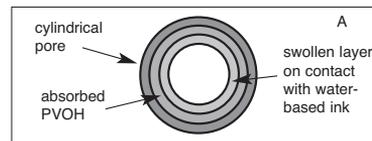


Fig. 16. The theoretical calculation of PVOH swelling effects. The coating amount was 1 g and density of PVOH 1.26 $\text{g}\cdot\text{cm}^{-3}$. The swelling of PVOH film was 29.2 % after 5 s (cyan dye). Specific surface area of pigment $10 \text{ m}^2\cdot\text{g}^{-1}$.

So in theory, the binder swelling can affect the absorption speed of inkjet inks through the closing up of small pores. Table 4 shows the extent of the time delays that exist in the inkjet printing machine. At $100 \text{ m}\cdot\text{min}^{-1}$, the delay between the first inkjet nozzles to the beginning of drying is 2.6 s, and to the end of drying, 3.8 s. The 5 s time considered in binder swelling is within this same timescale. The effect of swelling diminishes when liquid has less time to affect the binder and therefore we can assume that swelling has a smaller role at higher printing speeds, but it will not totally disappear. Thus, diffusion into polymer networks can occur within the timescale of inkjet printing, even at high speeds.

How Does PVOH Work with Different Types of Calcium Carbonates?

From the optical point of view, "PCC small" pigment particles are so fine that they cannot scatter light effectively and in that sense, the pigment is optically inactive (Fig. 17). According to the theory of Kubelka-Munk [23], those particles which have a diameter of

TABLE IV
TIME DELAYS IN THE VERSAMARK VX5000E PRINTING PRESS

	Speed 15 $\text{m}\cdot\text{min}^{-1}$	Speed 100 $\text{m}\cdot\text{min}^{-1}$
Cyan to yellow (CMKY)	5 s	0.8 s
Yellow to drying beginning	12 s	1.8 s
Drying beginning to end	8 s	1.2 s
SUMMARY	25 s	3.8 s

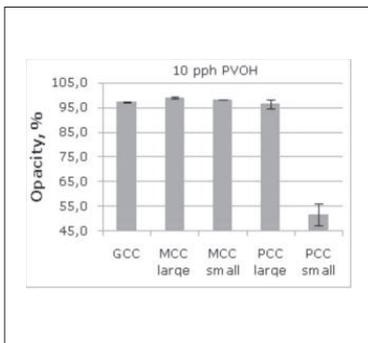


Fig. 17. Opacity of coating layers on the glass plate (100 g-m⁻²).

the order of the wavelength of light (0.1-1 μm) affect strongly the light scattering. The opacity and light scattering coefficient of the "PCC small" coating layer remains lower because the pigment size is so small, 20-30 nm. The results agree with other previous results [24,25]. The other pigments had quite similar opacities on glass plates.

The optical properties of the whole coated paper dominate the print density formation. The "PCC small" is virtually optically inert (Fig. 18), whereas the other pigments strongly affect the light scattering and therefore the level of print density. The correlation between the pore volume of the whole paper and print density was in the range of -0.904 – -0.949, whereas correlation between the pore volume of the coating layer alone and print density was as low as -0.050 – -0.217. Therefore, the whole paper structure plays a role in generating the print density, not only the coating layer. This of course depends on the nature of the base paper, but if optically interactive it will contribute to the background light white noise and so reduce print density, especially of penetrated dye-based inks.

If we consider the case of pigment-based inks found in many new high-speed inkjet devices, the finer intra-particle pores will selectively exclude the ink pigments, in a

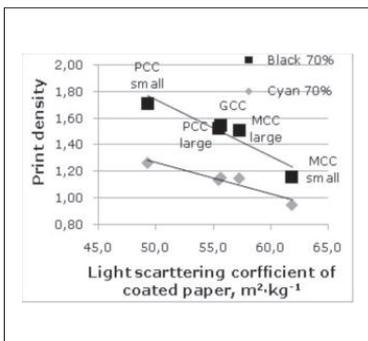


Fig. 18. Effect of light scattering coefficient on print density. Correlation: black -0.943 and cyan -0.950.

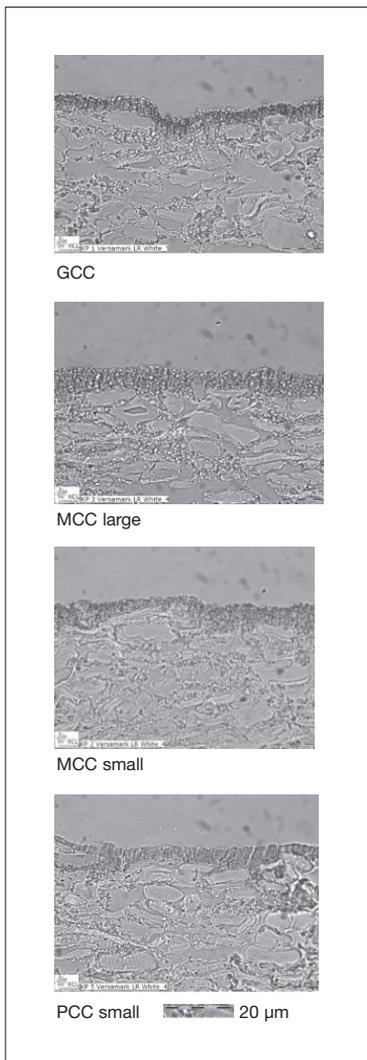


Fig. 19. Cross-section dye-base ink printed surfaces.

such a way that the colorant will be more concentrated in the remaining permeable structure between the particles, i.e., in the inter-particle pores. Therefore, depending on the amount of PVOH present, and whether it fills just the intra-particle pores or also the inter-particle pores, we can expect either a greater transfer of ink pigment into the underlying base paper or a better ink pigment holdout, respectively, i.e., to achieve good ink pigment holdout, the permeability has to be reduced. The ink pigments form a filter cake in the more closed case and this leads to reduced permeability. Therefore, the properties of the whole paper structure will have either a major or minor role in determining print density depending on the level of permeability.

In these experiments, where speciality

coating was applied to a pre-coated paper, the colorants stay in the coating layers and do not penetrate into the base paper (Fig. 19). However, it seems that the colorant is quite uniformly distributed in the coating layer including "MCC large". Even the cationic nature of the "MCC large" pigment did not fix the colorants in a manner that was visibly differently from the anionic pre-coat GCC. This suggests that either (i) the surface area is insufficient to trap all the colorant, (ii) the ink does not encounter the cationic nature of the pigment, or (iii) the coating is too permeable to provide surface contact for all the colorant as it flows through the structure. There is some slight detectable concentration gradient for the finer pigments, and this reflects the reduced internal pore network permeability.

The cross-section in Fig. 20 is of a PVOH film absorbed with cyan ink. It shows that ink colorants have penetrated significantly into the binder film after 30 s absorption time, but not completely. Therefore, the colorants can be expected to diffuse into the PVOH layer together with the water. The result is in good agreement with the observations of Oka et al. [26] and Svanholm et al. [27]. In a coating structure, colorants are distributed quite uniformly through the coating layer. This could be an indication that PVOH has covered the pigments and colorants are predominantly

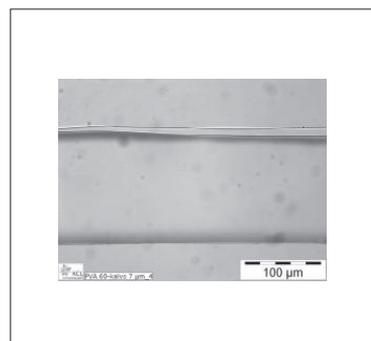


Fig. 20. Cross-section figure of cyan dye-based ink into PVOH film. About 200 μm thick film had sunk into the cyan ink during 30 s time.

in the PVOH. Therefore, the pigment type or charge has very minimal effect on colorant location when PVOH is used as binder.

The bleeding distance (Fig. 21), however, seems to be dependent on the pore volume of the coating layer, but not the pore volume of the whole paper. This confirms the lack of transfer of ink to the base paper for these coating layer configurations. Table 5 shows all the porosity related aspects of coating layer correlate well with bleeding. In addition, the increase of surface energy decreases the bleeding distance. If we consider comparing the results of bleeding measured with dye-

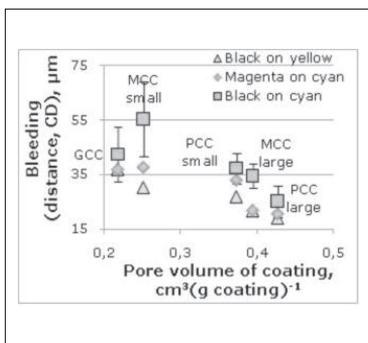


Fig. 21. Bleeding of the studied coated surfaces. Bleeding measured with high-resolution camera.

based inks versus pigment-based inks, the bleeding distances for pigment-based ink can often be considered to be less, because the filter cake formation effect of ink pigments prevents sub-surface lateral spread. However, we must recall that this depends strongly on the permeability characteristics of the coating and and, hence, interaction with the base paper.

The large porosity "MCC large" and "PCC large" coatings had fine pores of similar amounts and sizes, but in the large-size area of the bimodal distribution (inter-particle pores), the "PCC large" has ~1.2 μm diameter pores whereas the "MCC large" has smaller inter-particle pores at 0.8 μm. The larger pores of PCC allow ink to penetrate more quickly into the coating structure and therefore the bleeding formed is less. In addition, the binder swelling influences more strongly in the MCC pigment coating than in the PCC. The thickness of binder layer is higher on the MCC coating because the specific surface area of pigment is lower.

The PVOH swelling phenomenon should have a strong effect on GCC and "MCC small" coatings, which have less of the ultrafine 20-60 nm diameter pores than the other pigments. As the "MCC small" does have some more of the smaller pores than GCC, so the swelling should affect mostly these pores, rendering them ineffective. The bleeding values are indeed quite similar.

Comparing the "MCC small" and "PCC small" coatings, the porosities are quite similar, but "PCC small" has more of the finest pores. The "MCC small" coating absorbs ink clearly slower than "PCC small". The binder swelling closes up pores during the ink absorption process. It seems that in our medium porosity area, the coating with smaller pores give less bleeding. This illustrates that the bleeding effect is surface absorption rapidity defined.

One aspect that we have not yet discussed is the web drying on the high-speed inkjet press. This accelerates the inkjet drying process and so affects the degree of ink penetration. However, we propose that a more important aspect of current dryers is in the web behaviour in and after the dryer when the rolled printed paper becomes unwound and exposed to the new environment. The print quality of the paper should remain high after the opening of its printed reel. Furthermore, if the ink has been insufficiently dried before the rewinding state, the ink can transfer onto the back side of the paper and the set-off problem can be expected to become more obvious.

Effect of Binder Amount

"PCC large" and "PCC small" pigments were studied more closely by using different PVOH amounts. All the print density results are very near each other (Fig. 22). The cross-section images from printed papers (Fig. 23)

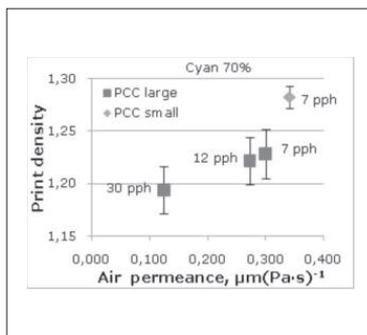


Fig. 22. Connections between print density and air permeance as a function of PVOH amount.

indicate that the colorants of ink distribute within the coating layer at 7 pph PVOH and at these coat weights do not penetrate into the base paper. At 30 pph PVOH in the coating, colorants are concentrated more in the top layer of the coating. However, there are places where the colorants have moved into the base paper due to the cracks in the coating, and this

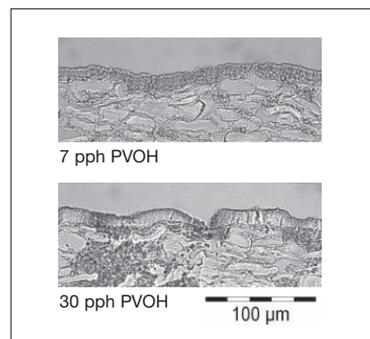


Fig. 23. Cross-section images of coatings containing different amounts of PVOH, that have been printed with cyan dyes.

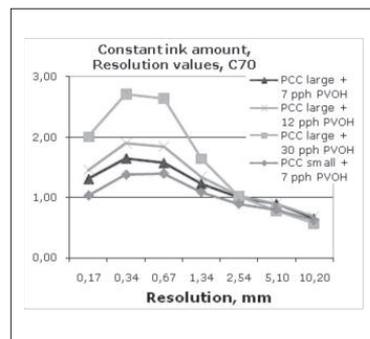


Fig. 24. Mottling of cyan ink (70% halftone dot area) printed surfaces.

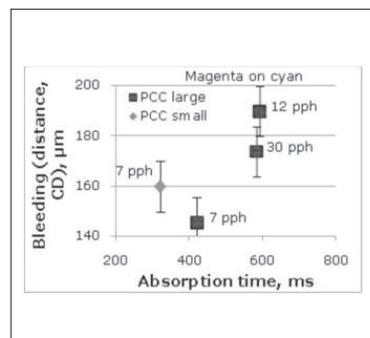


Fig. 25. Bleeding distance against absorption time. Measurement by scanner system and absorption time with DIGAT (8 g·m⁻² cyan dye).

Paper property	Bleeding distance		
	Magenta on cyan	Black on cyan	Black on yellow
Pore volume of coating layer	-0.898	-0.951	-0.943
Ink absorption speed (cyan)	0.653	0.745	0.994
Air permeance	-0.575	-0.786	-0.883
Surface energy of coated paper*	-0.653	-0.724	-0.978
Pore volume of whole paper	-0.210	0.063	-0.104

*Surface energy as defined by the sessile drop model, albeit a gross approximation for absorbent surfaces.

decreases the print density as well as increases the small scale mottling values (Fig 24). The results of light scattering (S-coefficient 52.9-54.1 m²kg⁻¹) from all the papers are very near each other. Therefore, knowing that the pigments have very different light scattering, the whole paper properties are dominant in this respect.

Again, the bleeding distance depends on the fine pore coating properties. Therefore, not unsurprisingly, the least bleeding distance is reached with the lowest binder content coating (Fig. 25). The higher binder amount increases the bleeding.

Figure 26 shows that absorption time gets longer when binder amount increases from 7 pph to 12 pph. However, the 30 pph of binder is on the same level as 12 pph. These results are similar to those of Nilsson et al. [12]. When the binder amount is lower the ink moves into the coating layer mainly by

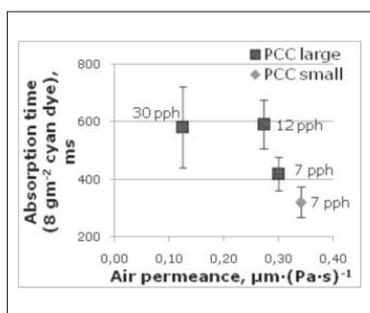


Fig. 26. Effect of PVOH amount in relation to air permeance and absorption time of cyan dye.

capillary flow. At 30 pph binder amount, smaller capillaries are already closed and the dominating liquid transfer mechanism is diffusion in the binder layer, as Gane et al. [28] indicate for their case of swelling polyacrylate dispersant covering the pigment surface. However, once a PVOH threshold amount is reached, specific for each pigment, this diffusion dominates and so provides a constant absorption speed from that binder level

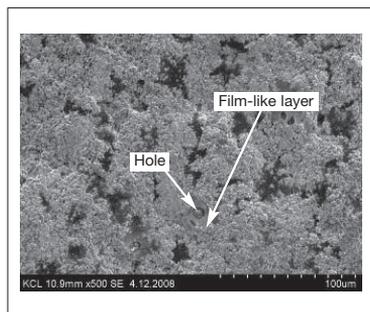


Fig. 27. Topographic image (SEM) of 30 pph PVOH "PCC large" pigment coating.

upwards (Fig. 26). The threshold point for the influence of binder swelling within these coatings should be expected at a binder amount of 12 pph.

Another significant problem with the 30 pph coating is the coating layer distribution. The SEM image (Fig. 27) shows that the 30 pph PVOH coating layer is not very uniform and there are places where the binder has formed film-like layers which exhibit significant clumping. As a result, holes distributed across the film-like layer can also be seen.

Although, the increase of PVOH amount closes up the coating structure, at higher amounts of PVOH the shrinkage associated with the soluble binder formulation causes an uneven coating layer structure and this is reflected in a deterioration of print quality.

CONCLUSIONS

The major controlling parameters for liquid ink absorption into porous inkjet coating structures are confirmed to be capillarity and permeability in relation to the fine pores and the larger interconnected pores, respectively. A quick absorption of ink can be reached even with medium porosity coating structures, provided the coating has a lot of nano-size pores. In the case of porous pigment particles, such as modified or structured calcium carbonate, the fine pores are associated with intraparticle pores and the larger pores are defined by the particle packing.

The role of PVOH binder is shown to be complex both in relation to pore structure modification and its affect on liquid uptake by diffusion. PVOH swells during the diffusion process. Although the volume of liquid imbibition related to PVOH swelling can be small at low binder levels, it acts to dominate the ink interaction with the pigment surface and the fine pore structure as binder levels increase, even at those levels required to prevent dusting. It seems that the colorants of dye-based inks locate more uniformly in the coating structure because PVOH covers the pigment surfaces and masks any surface cationicity of the pigment. The dye follows the aqueous liquid as it diffuses into the surface layer of PVOH. The impact of diffusion processes is even seen at high printing speeds, though the shorter the time to reach dryers, if present, the less is the volume of liquid involved. The swelling affects especially the accessibility to the intra-pigment pores of porous pigments.

The coating layer properties have a connection to print quality via the ink absorption speed and volume capacity. An ink absorption that is too slow at the coating surface means that the colorants have more time to mix together and bleeding problems are more visible. The surface energy of the coating layer also affects the colorant movement.

The optical properties of the whole coated paper dominate the achievable print density. This is because inkjet coating

pigments are generally designed to have low scattering potential and so the base paper, if optically active, has a strong show through effect through the coating layer.

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