The effect of drying behavior of coatings containing pigment and $CaCl_2$ on inkjet print quality

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Abstract

The effect of drying behavior of coatings containing starch, synthetic silicate pigment and $CaCl_2$ on inkjet print quality was studied. It is known, that print quality is dependent on the ink-substrate interaction, absorption behavior of the substrate and colloidal stability behavior of the ink at the substrate interface. One efficient way of improving the fixation of anionic inkjet pigment colorants is by controlling the electrostatic interaction and colloidal stability by using e.g. divalent or multivalent metal salts. In this study, we have investigated the effect of end moisture content of coating containing hydroxypropylated-starch, synthetic silicate and divalent metal salt ($CaCl_2$) on inkjet print quality of pigment-based ink. It was seen that significant differences in print density could be obtained when using different drying strategies. The obtained effects on substrate-ink interactions were ascribed to changes in coating structure and migration of $CaCl_2$ and better film forming caused by the more intense drying process.

Introduction

Print quality is dependent on the ink-substrate interaction, absorption behavior of the substrate and colloidal properties of the ink. In order to provide good print quality and ink adhesion at high speeds, the interfacial conditions at the interface needs to be optimized. [1, 2]. It is known that coating e.g. with starch or clays can improve print quality [3, 4, 5], whereas coatings can be further modified with nanopigments or cationic mordants in order to improve fixation of colorants.

An efficient way of improving the fixation of anionic inkjet pigment colorants is by controlling the electrostatic interaction and colloidal stability by using e.g. divalent or multivalent metal salts [1, 6, 7]. The effects of using divalent salts can be further enhanced when using a tailored pigment surface modification as demonstrated by Yu and von Gottberg [8]. Oko et al. [9] reported a series of aggregation and sedimentation experiments prepared with commercial pigment-based inks, generic ink formulations and various specific ingredients, and they found differences in response to the presence of $MgCl_2$ or $CaCl_2$. Aggregation and sedimentation of inkjet inks are thus linked to particle aggregation, which affect the distribution behavior of colorant pigments. Commercial implementation of the similar recipe has been presented [10] based on divalent cationic salt ions resulting in fast ink setting and increased optical densities. [11]

Usually divalent salt is added during size press application that brings salt near paper surface [12], which help to capture inkjet drops when they land on the paper. Our previous works have shown that by tuning the surface chemical properties in coating by deposition of chemicals e.g. starch and synthetic silicate, a significant improvement on ink substrate interaction could be obtained [13]. In this study, the aim was to determine the effect of drying strategies of modified inkjet coatings containing small amounts of divalent salt together with hydroxypropylated starch and synthetic silicate on print quality of pigment based inks.

Methodology

The base substrate used in this study was a solid bleached sulphate paperboard 190 g/m^2 that was coated using a pilot coater (KCL, Finland). Drying was made with a combination of IR-drying and air float drying. A dispersed synthetic silicate (Laponite RDS, Rockwood Additives Ltd, UK, 15 parts) was used in combination with cooked potato-based, low-viscous, low-anionic hydroxypropylated starch (Solcoat P55 Solam GmbH, Germany, 85 parts). When 5 part divalent metal salt ($CaCl_2$) was added, the amount of silicate was reduced to 10 parts. Targeted coat weight was 8 g/m^2 and the end moisture content of the coated samples containing $CaCl_2$ were adjusted to be 6.7%, 4.5% and 2.5 wt%.

The coated paperboards were characterized with contact angle measurements (Attension Theta optical tensiometer, Biolin Scientific, Sweden). Contact angles were measured for distilled water (γ=72.8 mN/m), for 99 % diiodomethane CH_2I_2 (DIM, Alfa Aesar, γ=50.8 mN/m) and for 99.8 % ethylene glycol 1,2-ethanediol (EG, VWR Prolabo, γ=48.0 mN/m) The droplet volume was 0.8 µl. Contact angle was recorded immediately after the drop was released from the needle and when surface spreading and absorption started. The change of the contact angle was measured from initial contact to 10 seconds or complete wetting.

The chemical composition of the coated surfaces were evaluated by X-ray Photoelectron Spectroscopy, XPS, using a state-of-the-art electron spectrometer (Axis Ultra by Kratos Analytical), monochromatic Al Kα X-rays and effective neutralization. The depth of analysis of the method was less than 10 nm. The elemental surface composition was determined from low resolution survey scans, while high resolution measurements of carbon C 1s and oxygen O 1s regions were utilized for a more detailed evaluation of the carbon compounds. CasaXPS software was utilized and, for the carbon regions, a specific four-component fitting routine tailored for cellulosic specimens was used [14]. An in-situ reference sample of pure cellulose was measured with each sample batch.

Coated samples were additionally printed with desktop inkjet printer (HP OfficeJet Pro 8000 Enterprise) using pigment-based inks. Print quality was assessed by measuring print density with X-rite SpectroEye spectrophotometer in the 100% tone value areas for the black and magenta colors.

Wicking was measured from the raggedness of the black and red printed lines on the base paper, and bleeding was measured from the raggedness of the black and red lines printed on white with a yellow boundary using digital pocket microscope (DPM 100, Fibro System AB). Additionally confocal laser scanning microscope, (CLSM, Zeiss LSM 710, Carl Zeiss Ltd. Germany) images were captured from the printed surfaces.

Results

Surface characterization

Contact angles were determined to characterize the wetting properties of the coated papers. Contact angles were measured for distilled water, EG and DIM, but results for distilled water are only presented here in more detail.

On the uncoated reference sample, the contact angle for the water was approximately 114º and did not changed during the 5 s contact time. Contact angles determined for the coated samples, however, decreased approximately 20° during 5 s measurements, see Figure 1. Lowest contact angle value was obtained for surface coated with starch and synthetic silicate. The addition of $CaCl_2$ seems to initially increase the contact of water indicating temporarily a more hydrophobic surface. The results shows further that drying to and lower the end moisture content gives a surface with higher contact angle of water thus indicating a more water repelling character at least prior longer contact times with water. Droplet volumes for the coated samples did not change during the measurement suggesting that decrease of contact angle is more dominated by spreading than absorption.

Samples for the XPS analysis spectra are shown in Figure 2 and surface atomic concentrations in Table 1. The major element in all analyses were carbon and oxygen but also minor elements were found, namely calcium, chlorine, sodium, magnesium and nitrogen, which could be used in a compound identification. Calcium and chlorine were present only for the surfaces coated with silicate pigment or silicate together with $CaCl_2$. The content of Ca- and Cl-ions in the coating containing only silicate was small (0.1% both), which confirms that Ca- and Cl-ions in silcate+$CaCl_2$ samples in different end moistures originates from the divalent salt added to coatings. The lower the end moisture content i.e. more effective drying is used, the higher the content of Ca- and Cl- ions is on the surface.

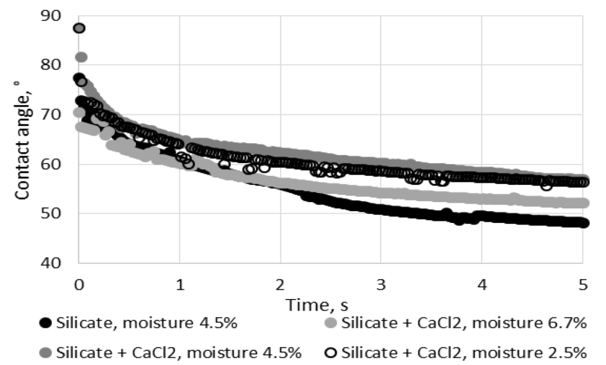

Figure 1. *Contact angle for water. Contact angle for the reference sample is 114° after 5 s contact time.*

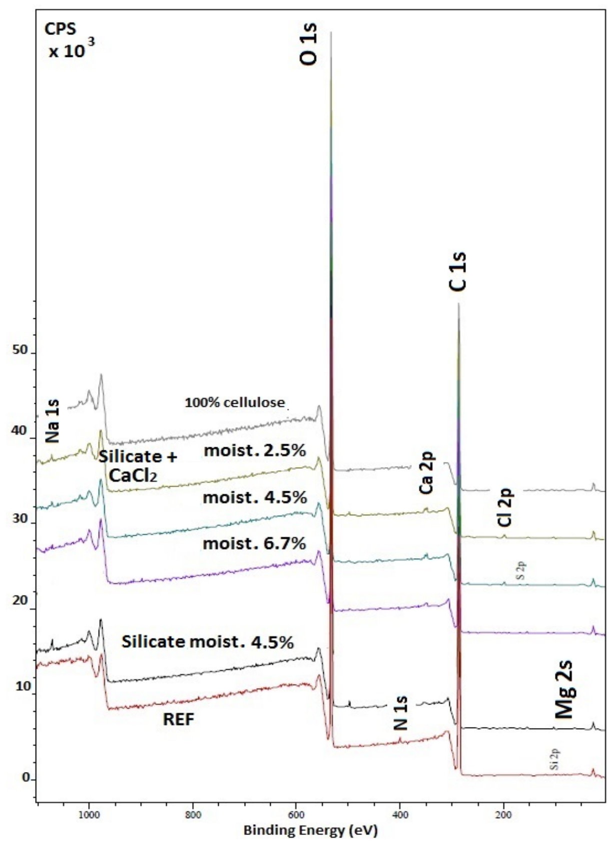

Figure 2. *XPS wide spectra of the reference and coated samples.*

Table 1. Surface atomic compositions as percentage for reference and coated samples.

Test point	C 1s	O 1s	Si 2p	Ca 2p	Cl 2p	Mg 2s	N 1s	Na 1s	S 2p
Ref	72.5	26.9	0.2				0.3	0.1	
Silicate, moisture 4.5%	61.3	37	0.8	0.1	0.1	0.3	0.1	0.2	0.1
Silicate + $CaCl_2$, moisture 6.7%	63	35.3	0.6	0.3	0.3	0.3	0	0.1	0.1
Silicate + $CaCl_2$, moisture 4.5%	63.4	34.6	0.4	0.5	0.5	0.2	0.1	0.2	0.1
Silicate + $CaCl_2$, moisture 2.5%	63	35	0.4	0.5	0.6	0.2	0	0.2	0.1

Print quality

Figure 3 shows the effect of drying behaviour of the coatings on print density (black pigment ink 100% tone area). Print densities are presented in correlation with surface atomic concentration as a sum of the Ca- and Cl-ions, measured by X-Ray photoelectron spectroscopy. The $CaCl_2$ on the surface of the paperboard increases the print density (from 1.8 to 2.4) for samples dried to end moisture content of 4.5%. Decrease in end moisture content from 6.7% to 2.5% leads to significant increase in print quality (from 2.1 to 2.5). The lower the end moisture content, the more $CaCl_2$ were found on the top of the substrate. This lead to a more efficient ink pigment particle precipitation on the surface of the coating layer, while the anionic surface coating allowed fast ink vehicle removal into the paper. This is probably caused by the joint effect of booming $CaCl_2$ and better film forming of synthetic silicate caused by the more intense drying process.

Z-stack confocal laser scanning microscope images (Figure 4) support this assumption. By optimizing the coating structure through drying, it is possible to control and adjust ink-substrate interaction enabling a controlled ink setting which explains the increased print densities on these surfaces. $CaCl_2$ is migrated during drying to the top of the coating layer and can then more efficiently capture ink particles. Print density for magenta prints were 0.9 for reference sample and 1.0 for all coated sample so the effect of coating were not so obvious in that case.

Horizontal and vertical wicking and bleeding for black and red lines are presented in table 2. For the reference sample, horizontal wicking for the red line (23.9 µm) and bleeding for the black (55.5 µm) and red (32.5 µm) lines were remarkably high compared to coated samples where highest value were 15 µm. For most of the samples, raggedness was between 6 - 9 µm confirming that silicate in the coatings reduced lateral ink spreading well.

Addition of $CaCl_2$ did not affect the wicking or bleeding in end moisture content 4.5%, but when the end moisture content decreased from 6.7% to 2.5% also bleeding and wicking decreased being in good level. Interestingly, horizontal wicking of black was lower in the reference sample than in samples containing silicate or silicate and $CaCl_2$. No significant differences between the raggedness values for horizontal and vertical lines could be noticed.

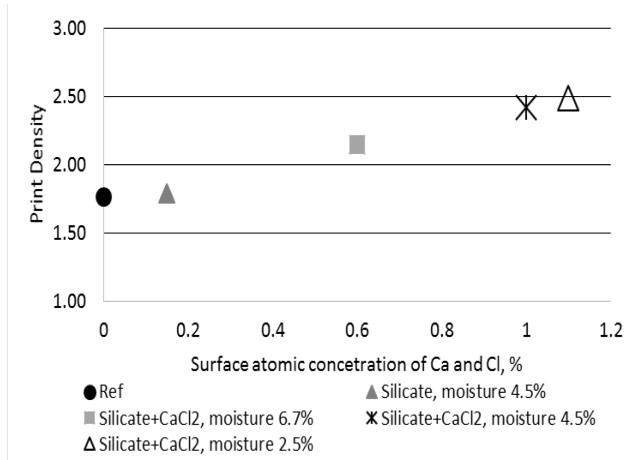

Figure 3. *Print density of the black pigment-based ink as a function of surface atomic concentration as a sum of Ca and Cl.*

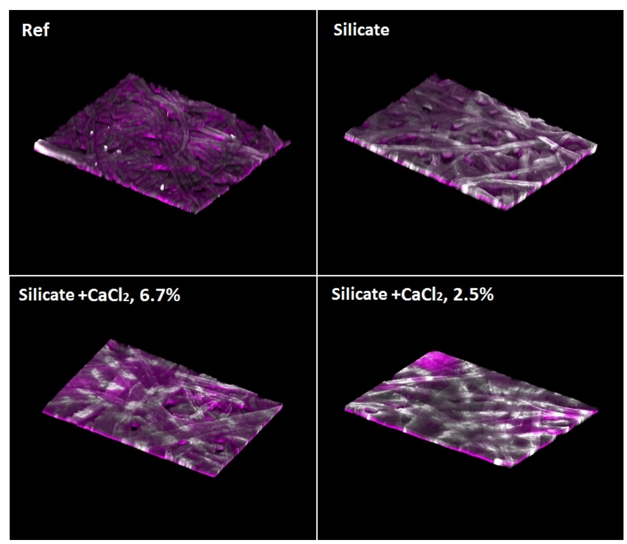

Figure 4. *Z-stack CLSM images of the Ref and coated samples. Resolution of the one image is 424.3 µm x 424.3 µm.*

Table 2. Horizontal and vertical wicking and bleeding for the black and red lines as raggedness values.

Test point	Horizontal line wicking, raggedness, µm		Horizontal line bleeding, raggedness, µm	
	Black	Red	Black	Red
Ref	6.3	23.9	55.5	32.5
Silicate, moisture 4.5%	7.4	6.1	9.5	13.5
Silicate + $CaCl_2$, moisture 6.7%	10.6	7.3	11.3	15
Silicate + $CaCl_2$, moisture 4.5%	8.9	6	8.2	9.2
Silicate+ $CaCl_2$, moisture 2.5%	8	5.8	8	8.3
Test point	**Vertical line wicking, raggedness, µm**		**Vertical line bleeding, raggedness, µm**	
	Black	**Red**	**Black**	**Red**
Ref	9.8	27.6	51.8	35.8
Silicate, moisture 4.5%	11.3	9.7	12.5	13.9
Silicate + $CaCl_2$, moisture 6.7%	15.1	10.9	15.5	21.1
Silicate + $CaCl_2$, moisture 4.5%	12.2	9.1	12.4	11.5
Silicate+ $CaCl_2$, moisture 2.5%	11.5	9	11.9	10.1

Summary

The effect of end moisture (drying strategies) on coatings containing hydroxyproylated starch, synthetic silicate and divalent metal salt on inkjet print quality were determined. It was found that the effect of drying strategy was remarkable on inkjet print quality e.g. print density and bleeding and wicking. The migration of divalent salt during drying increases when more effective drying is used and end moisture content of coated samples is lower. It was further demonstrated that the effect of $CaCl_2$ in coatings contained synthetic silicate on print quality is not significant but by optimizing the drying conditions in the end of the coating, remarkably good print density can be achieved.

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