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The effect of binders and modified precipitated calcium carbonate on ink absorption behavior in a multilayered coating layer

Mielonen Katriina, Laukala Teija, Backfolk Kaj, LUT School of Energy Systems, Group of Packaging Technology, P.O.Box 20, FI-53851 Lappeenranta Finland

Abstract

The effect of binders and modified precipitated calcium carbonate on ink absorption behavior and print quality in multilayered coating layers was studied. Also the effect of the number of multilayer was investigated, the target being on determining the role of the deposited hydrophilic binder layer. The coating layers of anionic NaCMC and cationic PCC were alternately spray-coated onto the substrate. It was found that a small amount of binder in the outer coating layer improved the print quality, whereas thicker binder layers closed the pores and reduced the print quality. The effect of the first hydrophilic pre-coating layer on ink spreading and absorption in the three-structure coating was relatively small although better than the reference which was free from a pre-coating.

Introduction

Print quality is dependent on the ink-substrate interaction and substrate permeability or absorption behavior in order to provide good print quality and an adequate ink drying and ink adhesion. [1, 2]. For dye-based inks, anionic dye colorants naturally interact with cationic chemicals in the coatings. Cationic additives are usually used in coating formulations to improve the print quality and to fix the colorant molecules. A proper colorant fixation produces high optical density, brighter color and sharper lines, low bleeding and low print through and high rub and wet resistance [3, 4]. In coatings suitable for water based inkjet inks, different components used to increase the ink fixation and ink hold-out have been tested such as precipitated calcium carbonate (PCC) [5] and extenders such as nanopigments [6, 7] or porous absorbents.

The challenge, however, is to find an optimal nanostructure coating having high ability to absorb colorants, while the said coating still showing good surface strength properties. The use of higher amounts of nanoparticle binders in combinations with nano- or micro-size pigments might lead to liquid repelling effect causing intercolor bleeding and reduced dye fixation. Previous works have shown that by tuning the surface chemical properties and nanoscale surface properties by deposition small amounts of chemicals, a significant improvement on ink substrate interaction can be obtained and hence print quality or ink adhesion is improved [8].

In this paper, we have investigated the effect of layered structure based on binder-pigment-binder thin coatings on ink absorption behavior. The effect of first pre-coating binder layer as an absorbent layer was determined. The layered structures comprised a middle layer of a highly cationic precipitated calcium carbonate (PCC) free from binder. Different amounts of top coating, i.e. hydrophilic binder layer was also evaluated. NaCMC was used as the hydrophilic binder, whereas a synthetized PCC was developed to provide fixing sites for the colorants.

Methodology

The base substrate used in this study was 290 g/m^2 uncoated paperboard that was surface treated with spray coater (Spalas Coating System, Nanotrons, USA). Targeted coat weight for NaCMC layers was 1g/m^2 and for the precipitated calcium carbonate (PCC) layer 3g/m^2.

PCC were synthetized via carbonation of calcium hydroxide with CO_2 in the presence of a cationic functional chemical (PDADMAC, Catiofast® BP, BASF). The chemical and precipitation conditions were chosen to adjust and control both PCC morphology and the surface chemistry. The ζ-potential for the PCC suspension was +31.7 mV (Malvern Zetasizer Nano ZS). PCC was diluted in a 0.01M NaCl solution and after dilution, pH was set to 9.1. Scanning electron microscope (SEM, Hitachi SU3500 with Hitachi SE detector) images were captured to analyze the shape and size of PCC particles. SEM images revealed that PCC particles consisted of cigar-shaped particles (Figure 1) and aggregates formed of the nanoparticles..

A hydrophilic NaCMC binder (sodium carboxymethyl cellulose, Finnfix® 5, CP Kelco, Finland) was used to create an absorbent pre-coating, while the PCC particles, substantially free from binders, were deposited on the pre-coating layer in order to clarify the role of nanostructure and charge on the solvent uptake and dye absorption. The intermediate coating comprising PCC was thus free from binder and therefore top coating comprising NaCMC was sprayed onto the coating to provide particle adhesion. The amount of top adhesive layer varied from one to five layers. Same test series was thus made without the first pre-coating layer to reveal the effect of first binder layer on print quality.

Pre-coating layer and PCC coating layers were dried before applying the last binder layers, which were applied as a wet-on-wet principle without intermediate drying between each layer. NaCMC was diluted in tap water to a solids content of 5 wt-% and the solid content of PCC was 14.7 wt-%. The Brookfield viscosity (100 rpm, spindle number 5) determined for the NaCMC was 133 cP and for the PCC 20 cP.

The surface treated paperboards were characterized with contact angle measurements by using an 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), for 99.8 % ethylene glycol 1,2-ethanediol (EG, VWR Prolabo, γ=48.0 mN/m) and for dye-based ink (Memjet M101 black ink). The droplet volume was 0.8 µl. Contact angle was recorded immediately after the drop was released from 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.

Multilayer treated samples were additionally printed with desktop inkjet printer (Lomond Evojet, Memjet) using dye-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.

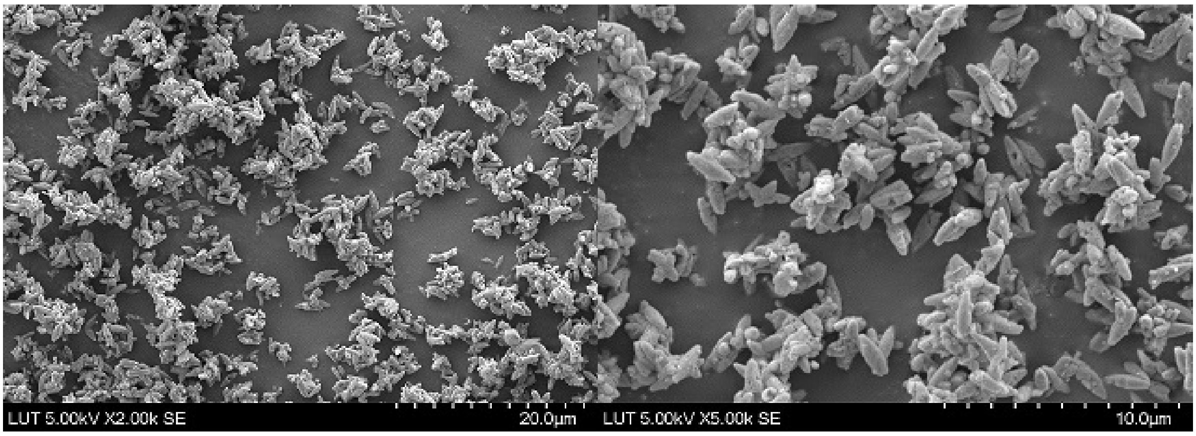

***Figure 1**. Scanning electron microscope (SEM) images for the cationic PCC particles.*

Results

Surface characterization

Contact angles were determined to characterize the wetting properties of surface treated papers. Contact angles were measured for distilled water, EG, DIM and black dye-based ink. Result only for the black ink is presented here (Figures 2a and 2b) where cationic PCC-layer is indicated by C and anionic NaCMC-layer is indicated by A. On the uncoated reference sample, the contact angle for the ink was approximately 103° and did not changed during the 10 s measurement.

Contact angle determined of the black dye ink revealed fast spreading and absorption of the ink when the outer surface was treated from one to three times with NaCMC. On these surfaces contact angle decreased from 17° to 7° during 1 s measurement on ACA treated papers. When the surface was treated four or five times with NaCMC, ink spreading and absorption were reduced and contact angle on these surfaces (ACA4 and ACA5) was slightly higher (25°-30°), probably because NaCMC as a binder closed the surface. There were no significant differences of contact angle results of ink between the samples with and without pre-coating.

Print quality

Print densities of the 100% black and magenta prints were measured from the surface treated samples. Figure 3 shows that the print density of the black print increased with increasing number of outer NaCMC layers. It can be seen that without pre-coating, print density is higher than with pre-coating, and that three layers of NaCMC on the top of the surface is enough to obtain optimal print density. On these surfaces, cationic PCC layer in the middle provides enough fixation sites for the dye colorants.

For the magenta prints, print density slightly increased when the number of outer NaCMC-layer increased and optimal print density was achieved after two outer layers of NaCMC. No significant effect on print density of magenta prints between the samples with and without pre-coating was seen.

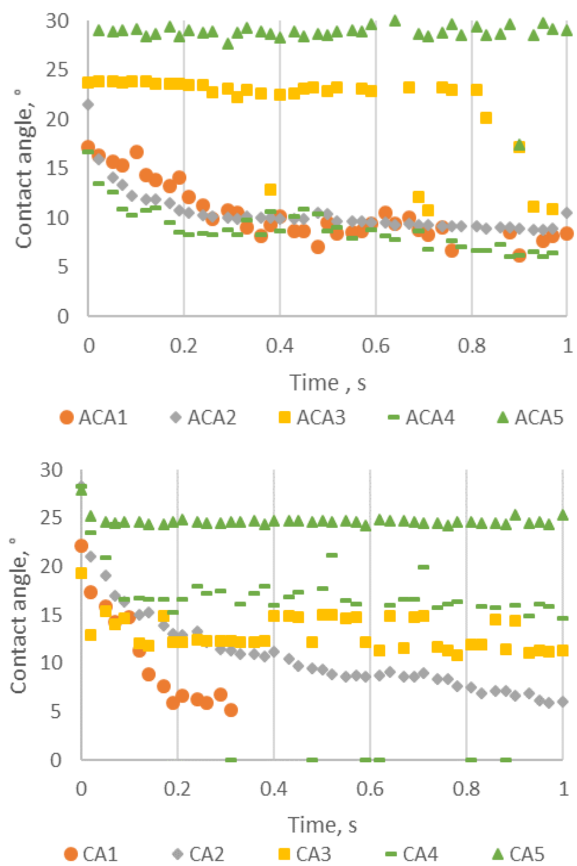

***Figure 2a and 2b.** Contact angle results for the black ink on the surfaces with (a) and without (b) pre-coating.*

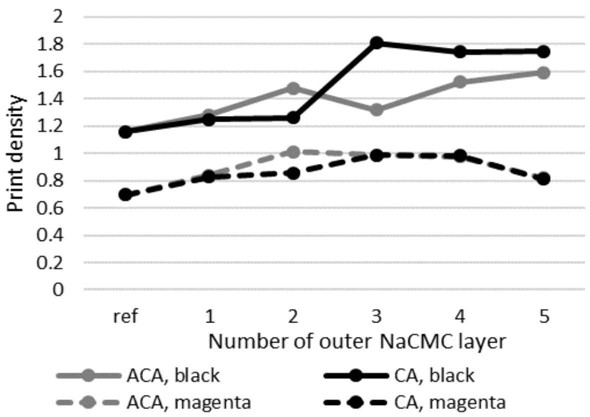

Figure 3*. Print densities for the black and magenta prints.*

The ink wicking and bleeding were measured and results are presented in Table 1. The effect of amount of the binder for wicking and bleeding behavior is obvious. Lowest wicking and bleeding values were achieved when the outer layer of the coating surface is treated only once or twice with NaCMC. The results showed that when the number of the outer NaCMC layer was increased, bleeding and wicking a more pronounced. These results were supported by photomicrographs seen in Figure 4.

CLSM images (Figure 5) revealed the effect of the PCC coating on the ink absorption behavior. The PCC suspension deposited onto the substrate, despite some uneven coverage, lead to quite significant differences in the vertical and lateral ink spreading behavior. A different ink absorption behavior was seen on the outer coating layers compared to the PCC layer (middle layer). In areas with less amounts of cationic PCC, the ink was able to penetrate deeper and hence a higher lateral fluorescence intensity was seen.

CLSM images revealed also that when the outer layer was treated five times with NaCMC, the surface became uneven, which was ascribed to the high amount of water in NaCMC solution causing reorganization and depletion of hydrophilic polymer solution during spray coating.

Table 1. Wicking and bleeding for the black and red lines as raggedness values.

Number of outer NaCMC layer	With pre-coating			
	Wicking, raggedness, µm		Bleeding, raggedness, µm	
	Black	Red	Black	Red
ref	25	18	44	45
1	1.9	2.1	2.2	2.5
2	2.0	2.7	2.2	2.7
3	3.5	4.0	3.0	5.0
4	8.8	6.9	11.0	12.0
5	6.5	8.3	11.0	13.0
Number of outer NaCMC layer	**Without pre-coating**			
	Wicking, raggedness, µm		**Bleeding, raggedness, µm**	
	Black	**Red**	**Black**	**Red**
1	1.9	2.3	2.2	3.0
2	2.4	2.3	2.2	2.5
3	5.8	3.7	4.4	8.1
4	5.6	6.3	6.4	7.0
5	6.4	5.7	7.4	11.0

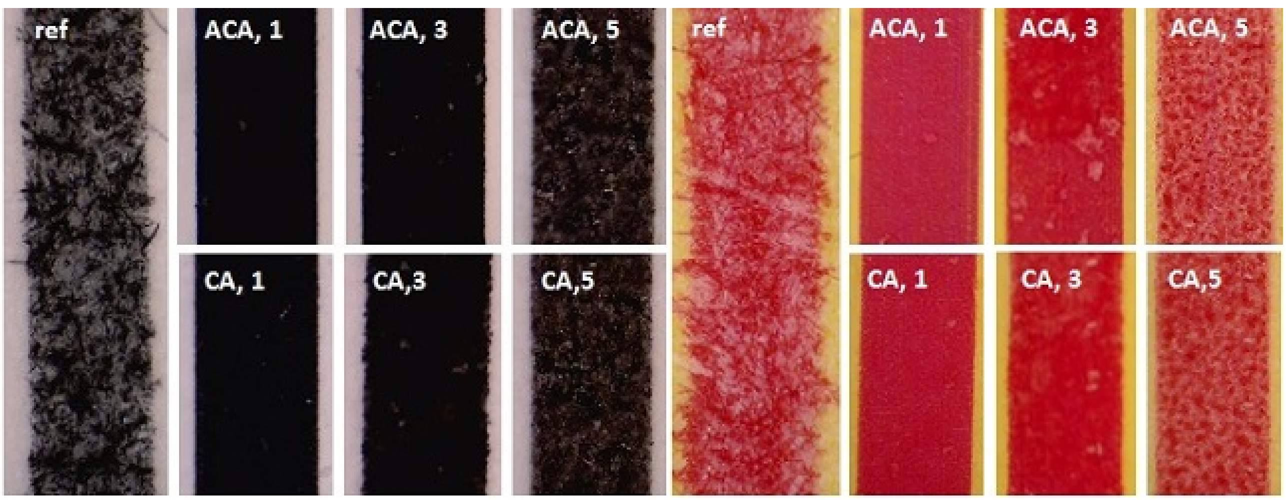

Figure 4*. Photomicrographs of the vertical wicking of black ink and vertical bleeding of red in contact with yellow ink. Paper surfaces were treated with and without pre-coating with one, three and five outer NaCMC layer.*

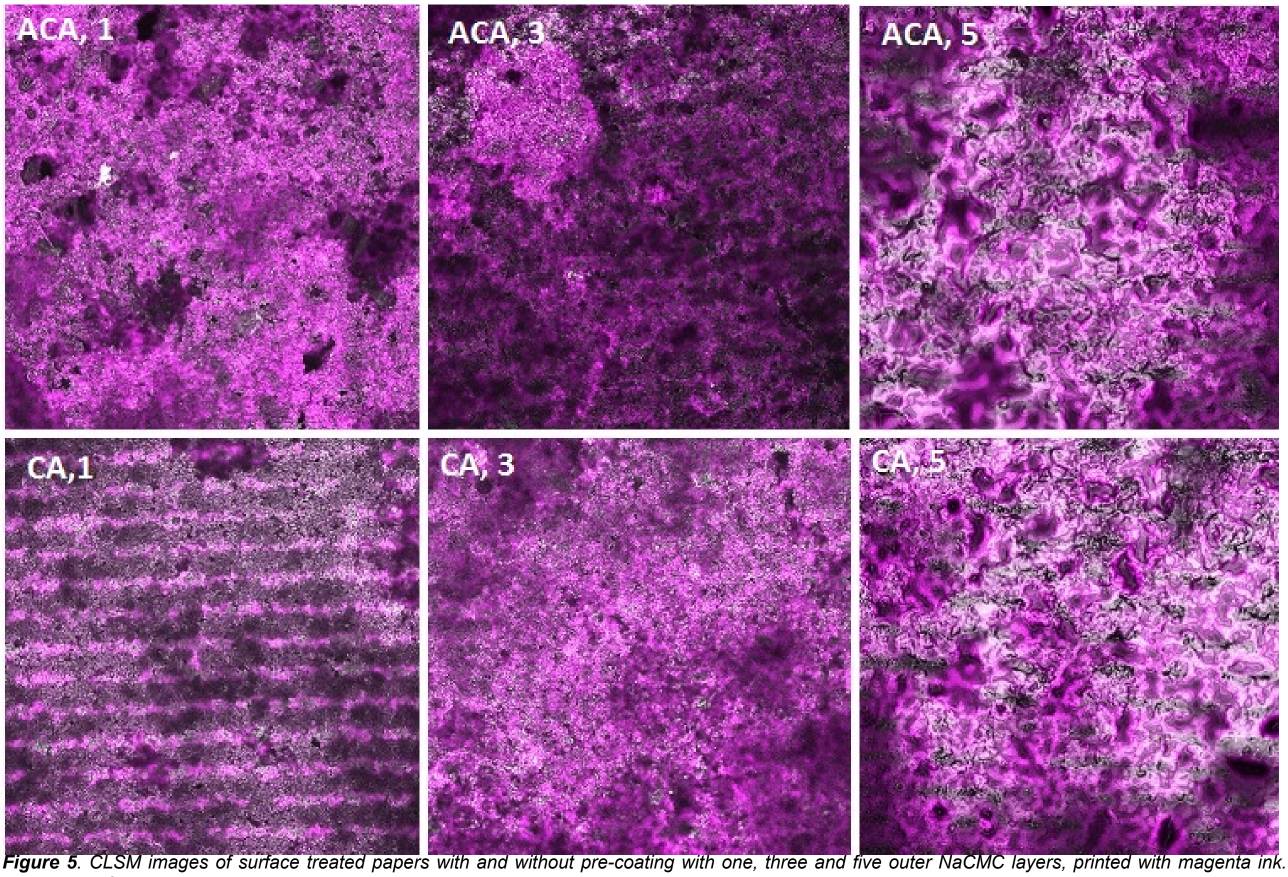

***Figure 5**. CLSM images of surface treated papers with and without pre-coating with one, three and five outer NaCMC layers, printed with magenta ink. Resolution of the one image is 420 µm x 420 µm.*

Summary

The effect of binders and modified precipitated calcium carbonate on ink absorption behavior in a multilayered coating layer was studied. The effect of the number of outer binder layer was determined as well as the effect of pre-coating. It was found that when the number of the outer binder layer increased, the surface became more closed and ink absorption become slower although contact angle was relatively low. It was further demonstrated that two layers of outer NaCMC layers provided sufficient hydrophilicity and permeability to promote good print quality. For this structure, only small wicking and bleeding and line raggedness was observed confirming optimal ink-substrate interaction behavior.

References

[1] Malla, P. B. and Devisetti, S. (2005). Novel kaolin pigment for high solids ink jet coating. Paper technology, 46(8), pp.17–27.

[2] Lundberg, A., Örtegren, J., Norberg, O. and Wågberg, K. (2010). Improved Print quality by Surface fixation of Pigments. In: NIP & Digital Fabrication Conference. Society for Imaging Science and Technology, Austin, Texas, USA, pp. 251–255.

[3] Kettle, J., Lamminmäki, T. and Gane, P. (2010). A review of modified surfaces for high speed inkjet coating, Surface and Coating Technology, 204(12–13), pp. 2103–2109.

[4] Jonckherree, E. and Mabire, F. (2003). Improving the waterfastness of high quality matt and glossy ink-jet printing papers. Paper technology, 44(6), pp. 38-44.

[5] Donigian, Douglas W., et al. "Ink-jet dye fixation and coating pigments." Tappi journal 82.8 (1999).

[6] Storbeck, W., Dietrich, D. and Schneider, R. (2005). Fixation of Pigmented Black Ink on Matte Coated Ink-Jet Substrates. In: NIP25 and Digital Fabrication Conference, Society for Imaging Science and Technology, Baltimore, Maryland, USA, pp. 306–311.

[7] Lamminmäki, T., Kenttä, E., Rautkoski, H., Bachér, J., Teir, S., Kettle, J. and Sarlin, J. (2013). New Silica Coating Pigment for Inkjet Papers from Mining Industry Sidestreams. Journal of Surface Engineered Materials and Advanced Technology, 3(3), pp. 224–234.

[8] Mielonen K., Ovaska S-S., Johansson, L-S., Österberg, M. and Backfolk, K., (2016) Three-layered polyelectrolyte structures as inkjet receptive coatings: Part 1. Interaction with dye-based ink, Journal of Imaging Science and Technology 60(3) pp. 30501-1-30501-9(9).

Author Biography

D. Sc. Katriina Mielonen is a post-graduate researcher and a member of the Packaging Technology research group in Lappeenranta University of Technology, LUT School of Energy Systems. She finished her PhD within the group of Prof. Backfolk with the focus on inkjet printing, surface treatment and printing in packaging technology. She continued her work with Prof. Backfolk as a post-doctoral researcher.