Ink -Media Interaction: Aggregation Of Color Pigments By Salt With Different Valency And Impact On Print Quality

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Abstract

We previously reported on the effect of surface properties on inkjet print quality and print functionality. Printing can furthermore be used to effectively functionalize paper surfaces or to modify surface properties of paper for subsequent inkjet printing. Migration of molecules and particles from the paper surface may cause destabilization of the pigment dispersion and result in aggregation of pigments, as shown previously for different concentrations of calcium chloride at the surface of uncoated paper. In this work, utilizing standardized methods such as inkjet printing, ink draw down and print density measurements, it is shown that surface functionalisation using di- and trivalent salts may effectively destabilize a pigment dispersion, causing aggregation of pigments which in turn has a major impact on the print quality.

Introduction

Inkjet printing is a digital non-impact liquid deposition method which gives the possibility to place, with high accuracy, ink droplets with volumes down to approximately 1 pl onto a substrate. Commercial high speed inkjet printing is furthermore a relatively new technology and has not yet reached its full potential, and it follows that inkjet printing in many ways is a promising technology for both traditional color printing [1] and for the developing field of printed electronics [2]. In color printing, the colorants in the inkjet ink may be dyes or pigments [3]. The colorants are dissolved in the carrier liquid and separated from each other in the inkjet chamber before printing typically by electrostatic forces and by steric hindrance. In the inkjet printing process, as the inkjet droplet impinges on the paper, the carrier liquid should vanish quickly from the paper surface through evaporation or absorption to inhibit color-to-color bleeding in multicolor printing. The colorants should furthermore quickly adhere to the uppermost paper surface layer to ensure that the colorants avoid following the advancing liquid front down into the paper. This is typically accomplished by cationic polymers at the paper surface in the case of anionic dyes, and can be accomplished by adding for example salt to the paper surface in the case of waterborne pigmented inks [4]. The stability of nano particles in solution is frequently described by the DLVO theory for which the screening of the electrostatic forces between nano particles depends on the ion valency and on the ion concentration [5]. It was proposed that the ionic substances at a paper surface may diffuse up into the ink as the inkjet droplet impinges upon the paper surface, thereby influencing the colloidal stability of the nano particle pigments in the carrier liquid [6].

In recent work we studied the effect of the concentration of calcium chloride at the paper surface and showed that flocculation of nano particle pigments may occur at the paper surface to yield an increase in the color gamut volume, the print density and the edge definition, resulting in an improved detail reproduction of the printouts [7,8]. The main purpose of this work was to study how paper treated with salt of different valency can cause aggregation of nano particle pigments and thereby improve the print density and the color gamut volume.

Materials and Methods

The starting material was mill-produced base paper (i.e. paper not subjected to surface sizing treatment). The base paper was surface treated with water containing 0.5-3 weight-% (w-%) of different salts, using laboratory bar coating equipment. Aqueous solutions of sodium chloride (NaCl), potassium chloride (KCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), and aluminum chloride ($AlCl_3$) were prepared and applied onto the paper surface using a hand-held bar coater (KCC202). In the preparation of the salt solutions, the anhydration/hydration form of the salt was considered in order to ensure the salt concentrations stated here. The samples are listed in *Table 1*, where the concentration is given in (g salt /100 g water)*100%.

Table 1. Samples of surface treated base paper.

Sample	Salt	Concentration [%]
1	NaCl	1
2	NaCl	2
3	NaCl	3
4	KCl	1
5	KCl	2
6	KCl	3
7	$CaCl_2$	1
8	$CaCl_2$	2
9	$CaCl_2$	3
10	$MgCl_2$	0.5
11	$MgCl_2$	1
12	$MgCl_2$	2
13	$MgCl_2$	3
14	$AlCl_3$	0.5
15	$AlCl_3$	1
16	$AlCl_3$	2
17	$AlCl_3$	3

Caution was taken to apply the same amount of liquid and pressure on the different paper samples in the coating process, as well as to coat all the paper samples at the same bar coater velocity. The coating process was performed utilizing the skills of highly experienced personnel at MoRe Research, Sweden. After the coating procedure, the samples were dried for 45 s utilizing an infrared dryer. An exception was the 3% $AlCl_3$ sample, which was dried for 20 s only, due to a slight discoloration.

The test chart for inkjet printing experiments was created in Adobe Photoshop and Adobe InDesign CS3. All colors were defined in RGB coordinates. The test chart, which is shown in *figure 1,* contained 11x7 color patches of cyan, magenta, yellow, black, red, green and blue color with tone values ranging from 0 to 100%.   .

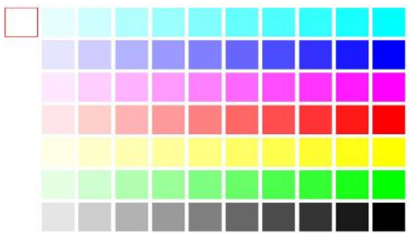

Figure 1. *Test chart for determining color gamut volume.*

Printouts were made using a HP Officejet Pro 8000 desktop printer with pigmented, water-based inkjet ink.

The spectral reflectance of the inkjet printed samples was measured using a spectrophotometer (Spectrolino) in the 45°/0° geometry with D65 illumination and 10° standard observer angle. From the CIE L*a*b* values the color gamut volume was calculated using own written software.

Ink draw down measurements were performed on the paper samples treated with salt solution. Approximately 0.2 ml of pigmented water based ink allocated along a 6 cm line was spread out over the paper sample using a hand-held Mayer rod #8. The print density was subsequently determined by measurement of the CIE Y-value using an Elrepho d/0 (L&W) instrument with UVX illumination and with paper white as background.

Results & Discussion

The print density data on samples 1-17 after ink draw down treatment are depicted in Figure 2. Surface treatment using the monovalent salts sodium chloride and potassium chloride did obviously not bring any major improvements to the print density in the concentration regime studied here. On the other hand, the divalent salts calcium chloride and magnesium chloride, as well as the trivalent salt aluminum chloride, exhibited a major impact on the print density as shown in Figure 2. In the case of the di- and trivalent salts, there was a clear improvement in the print density when increasing the concentration of salt from 0.5 w-% to 1 w-% ($MgCl_2$ and $AlCl_3$) and when increasing the concentration of salt from 1 w-% to 2 w-% ($CaCl_2$, $MgCl_2$ and $AlCl_3$). The data do furthermore indicate a tendency of the print density to level out in the concentration regime between 2 w-% and 3 w-%, although the print density is still higher for the higher concentration for all three salt concentrations.

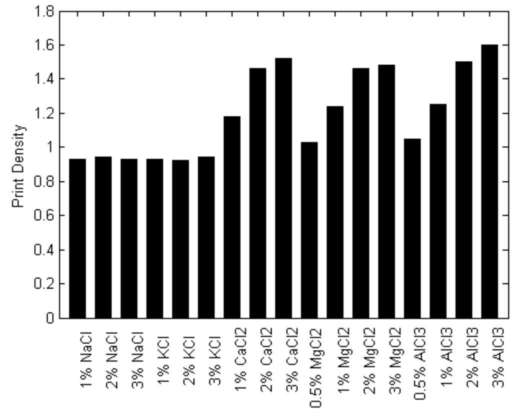

Figure 2. Print density on samples 1-17 after ink draw down treatment.

Figure 3 shows the color gamut volume for samples 1-17 after inkjet printing. The samples subjected to surface treatment with solutions containing the monovalent salts sodium chloride and potassium chloride exhibited a minor increase in the print density as the concentration of salt in the aqueous solution was raised from 1 w-% to 3 w-%. The data in Figure 3 do moreover show that the divalent salt magnesium chloride and the trivalent salt aluminum chloride had a major effect on the color gamut volume in the lower concentration regimes studied here. From previous studies [7,8] we know that the same holds for calcium chloride, although the surface treatment in that particular study was not directly equivalent to the surface treatment discussed here. It can however be concluded that an increase in the salt content beyond 1 w-% does not increase the color gamut volume of the printouts for the di- and trivalent salts. The color gamut volume does clearly level out at concentrations above 1 w-% of $CaCl_2$, $MgCl_2$ and $AlCl_3$.

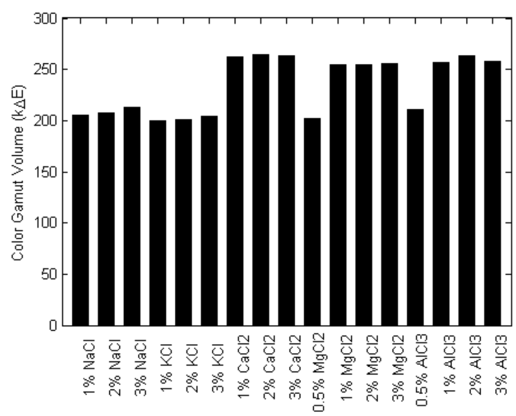

Figure 3. Color gamut volume of inkjet printouts on samples 1-17.

The print density data in Figure 2 may at first appear to be inconsistent with the color gamut volume data in Figure 3 in that adding of di- and trivalent salts to the surface treatment solution has an effect on the print density all the way up to salt concentrations of 3 w-% and possibly beyond (Figure 2), whereas the color gamut volume of the printouts levels out already at, or below, 1 w-% (Figure 3). A plausible explanation to the differences may have to do with the differences in the amount of ink applied to the paper surfaces in the two experiments. In the ink draw down treatment the paper surface is flooded with ink and one may expect the nano particle pigments in the ink to be in excess at salt concentrations corresponding to 1 w-% of salt. An increase in the amount of salt at the paper surface would then lead to a continued breaking-up of the colloidal stability of the nano particle pigments in the ink, and consequently increase the print density. In the inkjet printing process, on the other hand, a relatively small amount of ink is applied onto the paper substrate, and one may argue that the salt does effectively break up the colloidal stability of the nano particle pigments in the ink already at 1 w-% of salt. An increase in the amount of salt would therefore not increase the color gamut volume.

The results in this study can to a large extent be discussed in terms of the DLVO theory. It can be assumed that the colloidal stability of the nano particles in the ink dispersion is maintained by electrostatic interactions between nano particles having the same surface charge. The introduction of salt into the colloidal solution results in a screening of the repulsive electrostatic forces between the nano particle pigments. The data presented here do moreover indicate that the diffusion of salt is sufficiently fast to destabilize the ink dispersion within the time frame for ink absorption and evaporation during inkjet printing

Conclusion

Base paper was surface treated with aqueous salt solutions containing mono-, di-, and trivalent salts and subsequently subjected to ink draw down treatment or inkjet printing using aqueous, pigmented ink. Monovalent salts at the paper surface resulted in no or only a minor increase in the print density and in the color gamut volume, whereas the di- and trivalent salts did effectively increase the print density and the color gamut volume. The ink draw down treated samples did exhibit an increase in the print density with increasing concentration of salt. This was explained by the large amount of ink applied onto the paper surface in the ink draw down experiment.

Acknowledgements

The authors gratefully acknowledge financial support from VINNOVA (The Swedish Governmental Agency for Innovation Systems), the Knowledge and Competence (KK) Foundation, and the Kempe Foundations (projects NextJet – Next Generation Substrates for Inkjet Printing 2007-12, and Ink-Media Interaction in printing technology: a nanoscopic approach, 2012-13). JÖ gratefully acknowledges financial support from the Swedish Graphic Companies Federation (GFF) for participation at the NIP-conference.

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Author Biography

Jonas Örtegren received a PhD in Polymer Technology from the Royal Institute of Technology in Stockholm, Sweden, in 2001. He thereafter joined the Max-Planck-Institute for Colloids and Interfaces in Potsdam, Germany, where he developed nonlinear optical methods to study the dynamics at the liquid-air interface, and thereafter the Norwegian University of Science and Technology in Trondheim, Norway, where he studied optics of soft matter. He came to Digital Printing Center (DPC) in northern Sweden in 2005 and has until recently worked on building up of the academic research at DPC. Since 2012 he is an associate Professor in Materials Science at the Mid Sweden University.