Migration processes in four-color inkjet printing

Optimization and analysis

The development of digital printing technologies is driven by the increasing demands toward authenticity, personalization and customization[1]. In particular, inkjet printing is engineered meanwhile to the industrial scale and is known to be a fast and low cost procedure. However, the quality of four-color printing on uncoated but surface sized papers has to be improved.

Introduction

The quality of inkjet printing dependents on printing technology, ink properties, and paper characteristics[2]. The ink properties are mainly defined by viscosity, surface tension, and colorants[3,4]. Print quality on the paper is influenced by surface topography, porosity, surface energy, whiteness and chemical properties. The paper surface can be tailored by composition and application of sizing agents or calendering processes.

Surface sizing with starch enables the accessibility of ions by a swelling layer and promotes the fixation of inkjet colorants on the paper surface as well as the separation of ink vehicle. Salts composed of multivalent metal ions such as calcium chloride perform the aggregation of ink pigments[5]. In addition, cationic polymers are often applied to bind colorants electrostatically on the paper surface. PolyDADMAC, e.g., lead to low wicking, low bleeding, high dot quality of the print result[1] and increased water fastness[6]. Moreover, PolyDADMAC causes a decreased polar component of the surface energy[1], which has a positive effect on printability.

Migration processes of ink or paper components are key issues of print characterization. The ink penetration depth could be determined by cross-section analysis[7], delamination method[8], confocal laser scanning microscopy[9,10,11,12], and spectral reflectance based on the Kubelka-Munk theory[13]. However, the distinction between penetration of colorant (pigment) and ink vehicle in context with the migration of fixation salts could provide new insights about mechanisms occurring in the paper. Thus, a targeted development of inkjet papers will be enabled.

In context with this work, we critically evaluated the phenomenon of the migration of yellow in four-color inkjet printing. The general assumption is that the colors printed first, usually in the order black, cyan, and magenta, are consuming the fixation salts. Thus, the penetration of the color printed as the last one, mostly yellow, is explained by deficiency of salt. However, we calculated the consumption of fixation agent from the charge balance based on titration

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Pictures: PTS

Keyence microscope VHX-900F

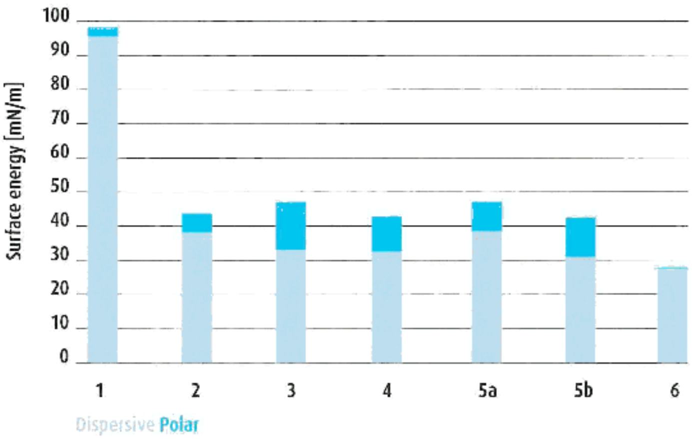


Figure 1: Surface energy parameters of papers 1-6 according to OWRK (calculation based on values of Rabel).

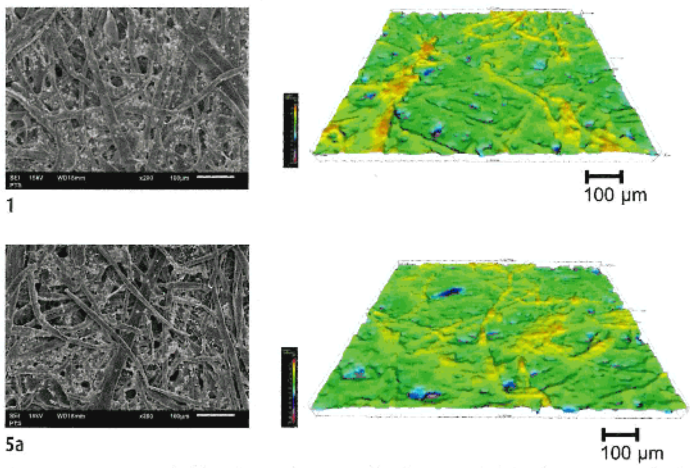


Figure 2: SEM images (left) and optical topographical images (right) of base paper 1 (top) and surface sized paper 5a (bottom).

experiments of ink pigments assuming 300 % total ink coverage. The amount of negative charges resulting from ink pigments is approximately 1 mmol/m². The pick-up of multivalent salts such as calcium chloride is at least one magnitude higher than theoretically required, e. g. 11 mmol/m² positive charges for 0.6 g $CaCl_2$/m². Thus, it could be assumed that migration of yellow ink is not only related to a lack of fixation agent.

Surface sizing and -characterization

Formulations based on starch solutions containing calcium chloride or PolyDADMAC were applied on a base paper by bar coating (Table 1, 1–6) or roll coating (5b). The pick-up was in the range of about 2 to 4 g/m² in order to yield a thin layer, which can be penetrated easily by the ink vehicle. Spectrophotometric measurements revealed that the paper samples retained their degree of whiteness of about 90 %.

Table 1: Surface sizing of base paper with starch-based formulations.

Sample	Starch [%]	$CaCl_2$ [%]	PolyDADMAC [%]	Pick-up [g/m²]
1 Base paper	-	-	-	-
2	10	0	0	2.6-2.7
3	10	2	0	2.3-3.8
4	10	10	0	2.7-4.3
5a-b	6	6	3	3.6-4.7
6 Benchmark	-	-	-	-

A key parameter of the paper surface is an appropriate surface energy to allow the wetting by ink but to avoid an excessive spreading. Figure 1 shows a decrease of the surface energy from approx. 100 mN/m (base paper) to about 40 mN/m as a result of the sizing. The lower surface energy including a slight polar component limits the spreading and the adsorption of ink drops and thus, the print quality is improved[2]. Scanning electron microscopy (SEM) as well as optical topographical imaging[14]. Figure 2 indicate a thin film on the paper surface with a very similar topography compared to the base paper. The fibers seem to be enclosed by a thin polymer layer. The sized paper is still porous and able to absorb the ink vehicle quickly.

Dynamic ink penetration

Figure 3 shows the ink penetration time into paper samples. 20 pL droplets were dispensed from a piezo capillary and filmed with a high speed camera. The penetration time is still small for all paper samples although there is a starch layer on the fibers.

Pigment migration

Coatings for an improved fixation of ink colorants on the paper surface reduce the penetration of pigments or dyes, which has a positive effect on color reproduction in general. Figure 4 shows a net diagram illustrating the influence of surface sizing on the penetration depth of ink pigments. The values are based on single colors and a dense pattern of KCMY. The untreated base paper contained no fixation agent and in particular, the colors yellow and magenta were deeply penetrating into the paper (up to >100 µm). The sizing with starch lead to less pronounced migration since the ink pigments were embedded in the polymer network and a proper separation of the ink vehicle was performed. An increasing amount of calcium chloride to the sizing formulation could decrease the penetration depth. Multivalent metal ions induce the aggregation of ink pigments and a precipitation of the particles on the surface occurs[5]. However, the fixation of colors could be improved further by the addition the cationic polymer PolyDADMAC. The penetration depth of the ink pigments decreased to 20 µm. Pigments that are partially soluble in the ink vehicle, especially yellow[15], could be fixed by complexation. Moreover, PolyDADMAC is known to increase the viscosity of the ink and reduces the penetration into the paper[16]. The optimized surface sizing applying starch, calcium chloride, and PolyDADMAC lead to less pigment migration into the paper compared to a benchmark paper with so-called ColorLok technology.

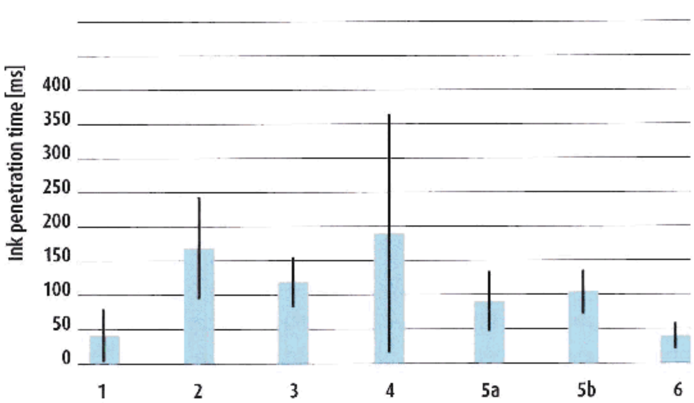
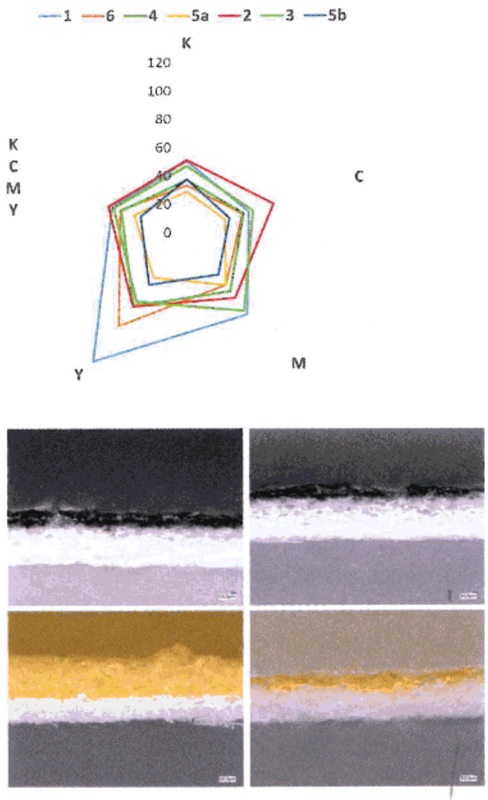


Figure 3: Ink penetration time of 20 pL-droplets into papers 1-6.



1 5a

Figure 4: Ink penetration depths in µm of single and mixed colors of KCMY in papers 1-6 (top) and exemplary images of cross sections recorded by a digital microscope (bottom).

Color gamut

Interestingly, deviations in the color gamut were found, i.e. there was a difference between the CIELAB coordinates of mixed colors (Figure 5). The sizing with starch caused a red shift of CY (green) areas. This effect was boosted by increased amounts of calcium chloride. The value a decreased from -50.8 (untreated base paper 1) to -41.0 (Starch/$CaCl_2$ 10/10, 4). Moreover, the value b decreased (blue shift) from 32.0 to 19.4 for areas of MY (red). The deviation of CIELAB coordinates could be compensated by the addition of polyDADMAC. The values are in the range of a surface sized sample containing starch with less calcium chloride (10/2), i.e. a=-42.9 (CY) and b=26.5 (MY). A deviation of 2 units of one or more CIELAB coordinates is visible by inexpertly eye.

Migration of salt

Another interesting aspect is the migration of fixation agents, since a lack of calcium chloride on the paper surface may lead to pigment migration. Chloride ions were visualized in the paper samples by means of SEM-EDX mapping (Figure 6). An image (b) of a cross-section from surface sized and partially printed paper shows still a uniform chloride containing layer near to the surface. The border of blank and printed area is marked in the background. Thus, no salt migration in the z-direction by the ink vehicle was observed. The drying of the ink at the paper surface probably leads to an accumulation of the fixation agents at the interface rather than to a distribution over the entire cross-section.

To verify these results two reference samples were prepared. On one hand, an image was recorded showing the margin of surface sized and untreated paper (c). There is a clear contrast between chloride containing (yellow) and blank paper surface. On the other hand, migration of salt was performed on purpose by a 10 µL drop of water sucked through the paper by vacuum (d). A dark spot indicates that migration of chloride ions could be detected by this method in general.

Conclusion

In this work we optimized the surface sizing of paper regarding pigment migration in four-color inkjet printing. It turned out that a high penetration of yellow is not only related to the amount of fixation agent but rather to the kind of pigment fixation system. The surface sizing with starch and calcium chloride lead to ordinary results in the range of benchmark paper provided with ColorLok technology. Fixation of colors that are partially soluble in the ink vehicle, in particular yellow, can be improved further by the addition of polyDADMAC. Utilization of the cationic polymer instead of excessive amounts of calcium chloride has also the advantage that a proper color gamut of the print result could be achieved. The migration of fixation agent was measured by SEM-EDX mapping of chloride ions. Surprisingly, a migration of salt arising from the printing process was not observed. In addition, we could not detect any lack of fixatives on the paper surface, which would explain a migration of yellow and thus lead to incorrect color rendering. However, the inkjet paper was optimized by varying the fixative composition. The

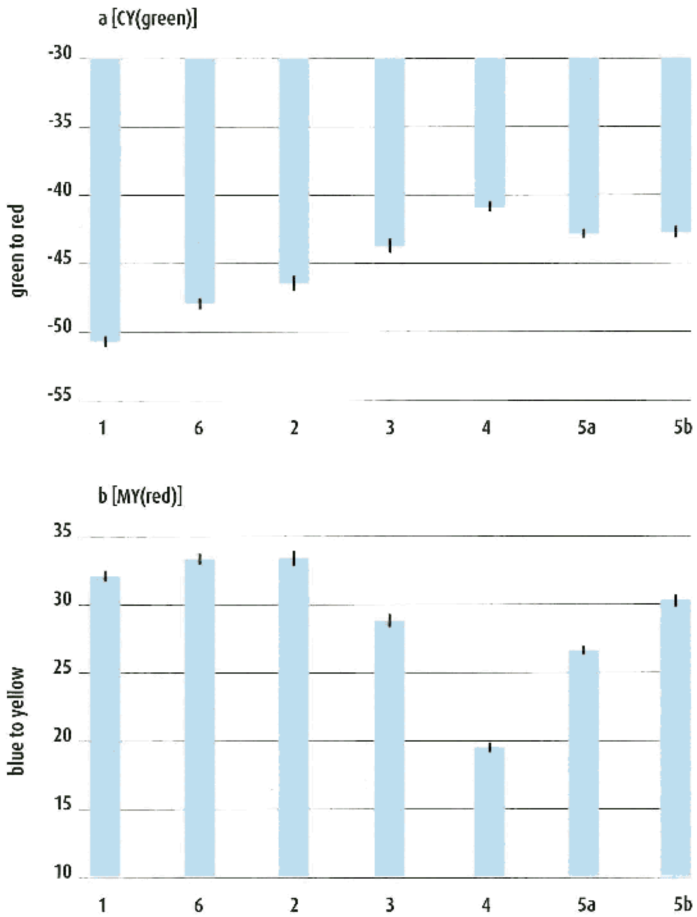


Figure 5: CIELAB coordinates a (CY) and b (MY) of inkjet prints on papers 1–6.

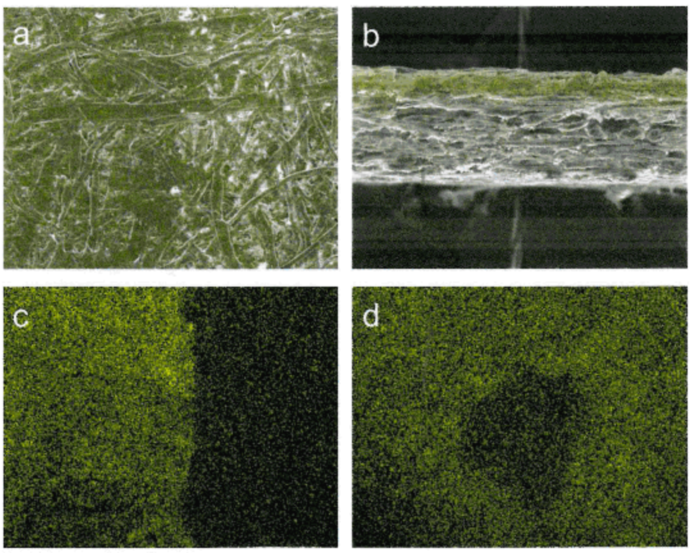


Figure 6: SEM-EDX mapping of chloride ions arising from surface sizing of base paper with starch and calcium chloride. a: View on the surface sized area; b: cross-section with border of printed and blank areas; c: margin of surface sized (left) and untreated paper (right); d: spot with lower chloride concentration arising from a drop of water sucked through the paper on purpose.

work was supported by digital microscopy and SEM-EDX of printed paper cross sections. In this context, these techniques proved to be powerful tools for the development of inkjet papers.

Acknowledgment

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