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Influence of Paper on Colorimetric Properties of an Ink Jet Print

Marjeta Černič
Pulp and Paper Institute Ljubljana, Bogišičeva 8, 1000 Ljubljana, Slovenia
E-mail: meta.cernic@icp-lj.si

Sabina Bračko
Faculty of Natural Sciences and Engineering, University of Ljubljana, Snežniška 5, 1000 Ljubljana, Slovenia

Abstract. *Paper for ink jet printing has to obtain optimal printing runnability, printability, and printing quality. Therefore, it must have some specific properties that ensure optimal drying time, mechanical stability of a print, and its light and water resistance. The paper surface should enable the printing ink to be dried as fast as possible. The aim of the applied research was to determine how an ink jet color print on paper changes with time immediately after printing, and how long it takes for the color print to stabilize. Color differences* ΔE^*_{ab} *were measured that appeared on print after a certain amount of time with regards to values attained immediately after printing. The influence of paper on colorimetric properties and optical density of a print was analyzed by measuring some structural, surface, and sorption properties. The values attained show that the paper surface should enable wetting and ink penetration in paper structure. The biggest changes in colorimetric properties of the print became visible during 1 h after printing; however, color print finally stabilizes only after 96 h. Research results confirmed the importance of paper sorption properties for obtaining high-quality ink jet color prints.* © *2007 Society for Imaging Science and Technology.*
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INTRODUCTION

The important parameters for producing a quality print are the properties of inks, printers, and paper. Quality paper should enable images of high contrasts and excellent reproduction of lively colors and sharp outlines. In order to achieve these properties, a print needs to be dried carefully since droplets should not spread on the surface. To obtain proper print quality, it is important to have a thorough knowledge of paper characteristics and ink properties. The properties of a print under particular printing conditions in conventional printing techniques are well defined by a number of standards. Although producers of ink jet printers refer to certain recommendations for inks and paper, proper standards have not been developed or published yet.[1–5]

Paper for ink jet printing must have some specific properties that ensure optimal drying time, mechanical stability of a print, and its resistance to light and water.[6–9] The paper surface should enable the printing ink to be dried as fast as possible by absorption, adsorption, and evaporation, which depend on sorptive properties of paper and climatic conditions in a certain space.[10–12] According to the ink structure the ink jet printer can be divided into two categories, i.e., water-based ink jet and phase change ink jet, which is generally more substrate independent. Immediately after the water-based ink contacts the paper, all the interactions between ink droplet and paper take place. At the same time, the ink drying process begins and progresses until the ink is immobilized on the paper. The way the ink dries on the paper can be very critical to the quality of the final printed image, because the deformation of the print image, such as feathering, wicking, paper expansion, and bleed-through, all take place before the ink is immobilized.[13–15]

The ink drying process involves three major routes that govern the quality of print image that describes Fig. 1: evaporation of ink carrier (water or solvent), XY-direction spreading (ink traveling on paper surface), and Z-direction penetration (ink absorbed into paper). The ink that dries quickly through evaporation generally offers less time for ink spread and results in sharp and less deformed image. Feathering and wicking of the printed image are generally results of extensive XY-direction spreading. Bleed-through, as well as the optical density of the image, is strongly affected by the depth of Z-direction penetration. The speed of ink traveling through each route is generally different and depends on the ink formulation as well as the chemical and physical structures of paper. This is why we can see differences in print quality on different papers, and different inks offer different print quality on the same paper. In most cases, the rate of evaporation is much slower than the rate of XY-spreading and Z-penetration, which become the primary actions that contribute to the final shape of the printed image.[15] The ideal "Case B" for the ink to dry on the paper (Fig. 1) is to control carefully the rate of both XY-spreading and Z-penetration via adjusting the chemical and physical compositions of the paper. If both XY-spreading and Z-penetration take place in a desired way, the printed image should be able to expand proportionally to the original print out from the printing head. The resolution as well as the optical density of the print image will be retained and the feathering and wicking, as well as the bleed-trough problems, should be reduced.[16,17]

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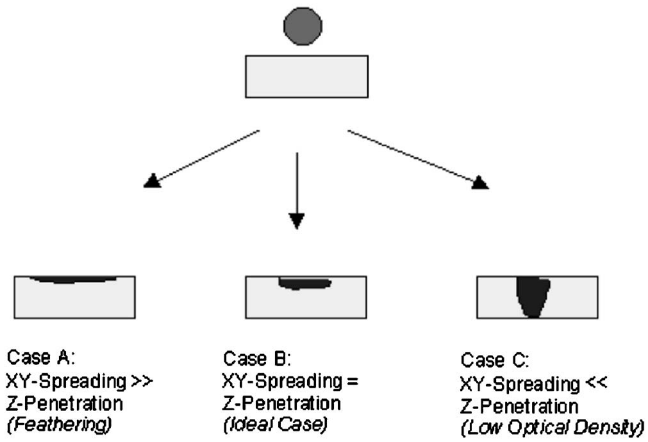

Figure 1. Three cases of drying mechanisms of water-based ink-jet drop on a plain paper.[15]

EXPERIMENTAL

The goal of this research study was to investigate how the sorption properties of paper affect both the XY-spreading and Z-penetration during the ink drying process. Therefore, the changes in colorimetric properties that occur on prints were observed in a defined time interval. In addition, it was important to define the amount of time after which the measured values are stabilized. The influence of paper on colorimetric properties and optical density of a print was analyzed by measuring structural, surface, and sorption properties.[18–20]

Materials and Methods

Paper Properties

Three paper grades for ink jet printing weighing 80 g/m^2 made by different producers were used. Paper samples 1 and 2 (MOTIF™ office paper and Rotokop Radeče, respectively) were of regular quality whereas sample 3 (Epson ink jet paper) was lightly surface coated and thus intended for high quality prints such as photographs. A comparative analysis of physical-chemical and surface properties was conducted in order to determine the influence of paper structure on the change of colorimetric properties of an inkjet print. Samples 1, 2, and 3 were tested under standard climate conditions (ISO 187). The following analyses were performed on the basis of standard or nonstandard testing methods:

- Basic physical properties: grammage (ISO 536), thickness, specific volume (ISO 535), ash content (ISO 2144)
- Paper homogeneity: formation index—Kalmes M/K 3-D (Pulp and Paper Institute method).
- Surface properties: Bekk smoothness (ISO 5626), Gurley porosity (ISO 5636-5).
- Sorption properties: Cobb 60 water absorption (ISO 535), contact angle (TAPPI 458) and surface tension—DAT 1100 (Fibro System AB).

The results of tested properties of papers 1, 2, and 3 are shown in Table I and Fig. 2.

Table I. Paper properties.

Properties	Paper 1	Paper 2	Paper 3
Grammage, g/m^2	80.7	79.1	85.0
Specific volume, cm^3/g	1.26	1.29	1.27
Formation index, M/K 3-D,	49.3	36.6	51.9
Ash content, %			
• 500 °C	24.1	19.3	11.0
• 900 °C	14.0	11.4	10.0
Smoothness, Bekk, s			
• Top side A	14	19	12
• Bottom side B	16	20	16
Porosity, Gurley, s	11	23	36
Water absorptivity, Cobb 60, g/m^2			
• Top side A	24	20	37
• Bottom side B	23	21	29
Contact angle, FibroDat, 2 s/50 s, °			
• Top side A	94/85	107/102	11/0
• Bottom side B	91/91	97/85	105/84
Surface tension, FibroDat, side A, mN/m			
• Total	96	98	70
• Dispersion part	92	90	24
• Polar part	4	8	46

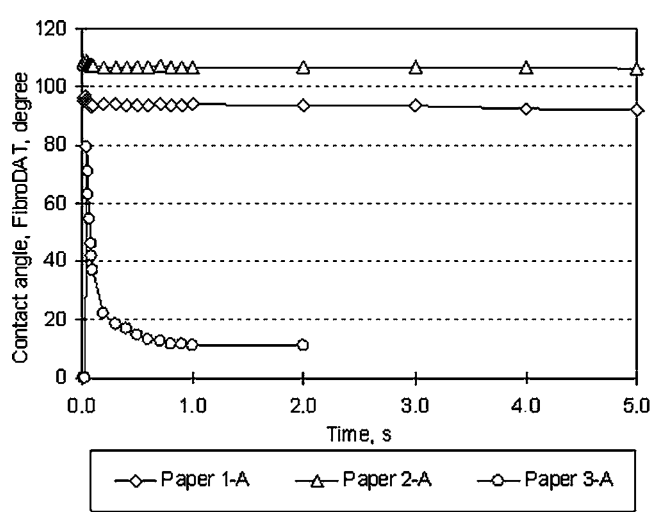

Figure 2. Contact angle for papers 1, 2, and 3 in dependence of time.

The Monitoring of Colorimetric Properties of Prints

The 3×3 cm color testing chart with CMYK color fields of 100% and 50% color application intensity was created by means of the Adobe Photoshop™ image software. Color and black cartridges (Epson color ink for the Epson Stylus-Color™ 900 printers for 1400 dpi resolution with A4, PHOTO, and color print settings) were used for printing. The $L^*a^*b^*$ values of color print samples on individual paper grade were measured according to the ISO 13656 standard[21] by means of the spectrophotometer Spectrolino (Gretag Macbeth, D50/2° lighting, 45°/0 measurement geometry, a 4 mm measuring aperture, on black basis) in defined time intervals in order to determine how long it does take for the color to dry and thus for its colorimetric properties to stabilize. The measurements were divided into two groups: first, color differences were monitored in shorter time intervals after 3, 6 10, 15, 20, 30, 60, 90, and 120 min. In the second case, color differences were measured after longer periods, that is, after 1, 2, 3, 4, and 7 days. Measurements were conducted at constant temperature of 21 °C ± 2 °C and relative humidity of 32% ± 2%. Between each measurement, samples were kept in the dark. The tested values were compared with results obtained immediately after printing.

The calculated color difference ΔE^*_{ab} was monitored and inserted into diagrams separately for each paper sample and each CMYK color.[22,23] Color differences ΔE^*_{ab} for CMYK color samples are represented in Figs. 3 and 4.

Colorimetric Properties of Dry Prints

Optical density of the color print is usually the only parameter, which is measured during the printing process.[24] Optical density of a dry print (D) was measured by the densitometer RD 918 (Gretag Macbeth), 7 days after printing. The results are presented in Fig. 5. Figure 6 represents the color differences ΔE^*_{ab} between the dry prints (7 days after printing) and the prints immediately after printing.

Cross-Section of Color Prints

Qualitative microscopic analysis of color print cross sections was made by cryoscopic microtome at −25 V and minutely examined, under an optical microscope at a magnification of 160×. The results for black print are presented in Fig. 7.

RESULTS AND DISCUSSION

Characterization of Paper Substrates

Table I summarizes the mean values of basis structural, surface, and sorptive properties of papers 1, 2, and 3. A visual analysis of paper samples proved papers 1 and 2 to be natural and surface nontreated—they are not visibly two sided. However, paper 3 is surface pigmented on the topside whereas the bottom side is similar to the other two samples.

By all paper samples 10% to 14% *ash content* has been obtained. The high values of ash content at 500 °C are due to calcium carbonate being used as paper filler in all samples except sample 3, which is filled by clay or other pigments on silicate basis proven by a very small change in ash content at different temperatures. The topside of paper 3 is very white, whereas the bottom side is slightly yellow. Two-sidedness is thus apparent.

Paper homogeneity or *formation* is defined by transmission of light through paper, which can be either satisfactory or unsatisfactory depending on the appearance of the surface in transmitted light.[25] The test was conducted on an M/K 3-D analyzer as transmission of light through an A4 paper sheet. Homogeneity of paper on the basis of relative weight deviation of a certain spot in comparison to average weight is defined by means of measuring both the size of distributed flocks and empty spots, as well as by measuring formation using the FI-formation index. Growing deviations in relative weight decrease the level of formation index and thus the quality of homogeneity. Based on practical experience, the minimum values of FI should be around 30 in black and white printing and more than 50 in color printing.[6,8,13]

Since all paper samples achieved *Bekk smoothness* values in the range of 12 to 20 s they could be classified as machine calendered papers, which are not appropriate for products of high printing quality. Slight two-sidedness was observed with all paper samples.

The results of testing *air porosity* by Gurley show slight differences between the papers 1, 2, and 3. A very high porosity was achieved by paper 1 (11 s) whereas paper 2 obtained a slightly lower porosity value (23 s). All values obtained correspond to requirements for printing runnability in electrophotographic printing and are most probably appropriate for satisfactory runnability in ink jet printing as well.[10,11]

All paper samples obtained *surface absorptivity of water* by Cobb-60 values of 20 g/m^2 or higher, which point to a lower quality of sizing (Table I). The values are appropriate for offset printing but not for electrophotography, which requires a nonabsorbent surface with Cobb values lower than 20 g/m^2. According to practical experience, the obtained values are most probably appropriate for ink jet printing. A considerable deviation was observed in paper 3, which exhibited high absorptivity on the top, pigmented side (Cobb values is 35 g/m^2—denoting low-quality sized paper) and a slightly lower level of absorptivity on the bottom side.

The *dynamic wetting interaction* between a liquid and a paper surface can reveal problems affecting printing, sizing, or coating.[13–15] Dynamic contact angle and spreading rate of ink drops were measured from side images of the drop profile, which was monitored as a function of time with a DAT 1100 instrument (Fibro Systems AB), with a time resolution of 20 ms. The measurements of *FibroDat contact angle* (Fig. 2) led to a similar conclusion as measurements of Cobb values. After 2 s, the measured contact angles of samples 1 and 2 are 90° and 105°, respectively, which denote higher hydrophobicity. After 50 s, these values lowered by 5° to 10°. The topside of paper 3 achieved total water absorption within 2 s. Its surface is thus completely water absorbent, which is probably caused by a specialty pigment coated surface, which enables optimal absorption of inks in ink jet printing. The results of surface absorptivity show that paper

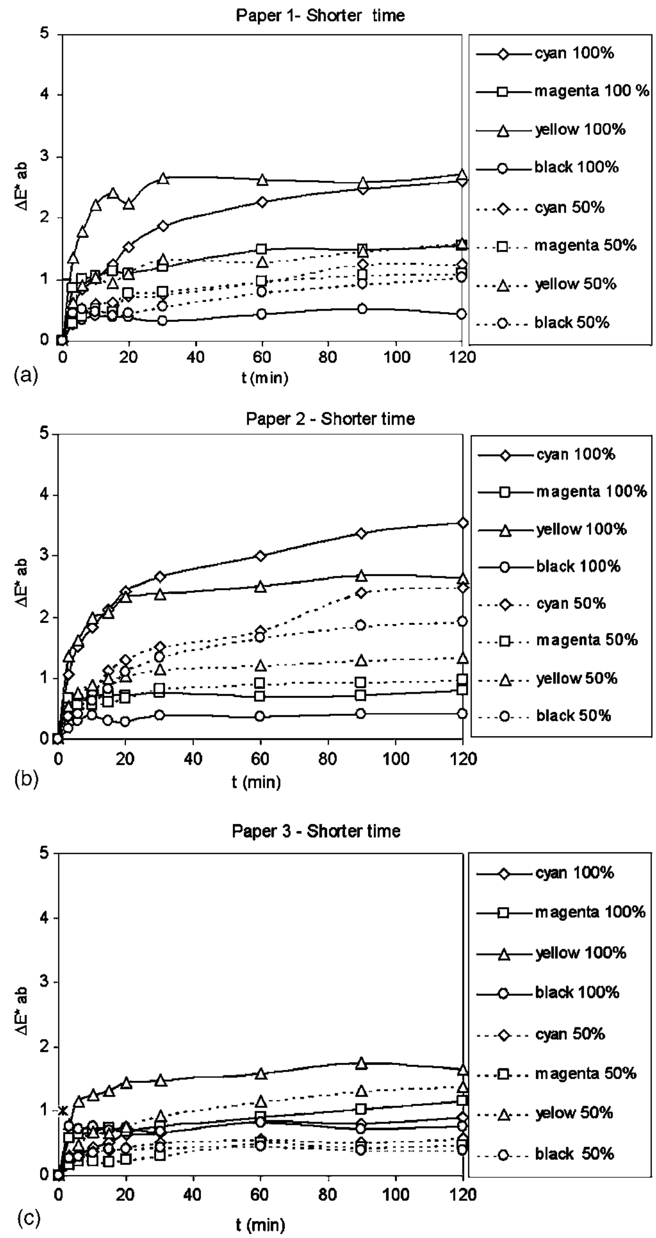

Figure 3. Color difference ΔE^*_{ab} of CMYK prints on papers 1, 2, and 3, up to 120 min after printing.

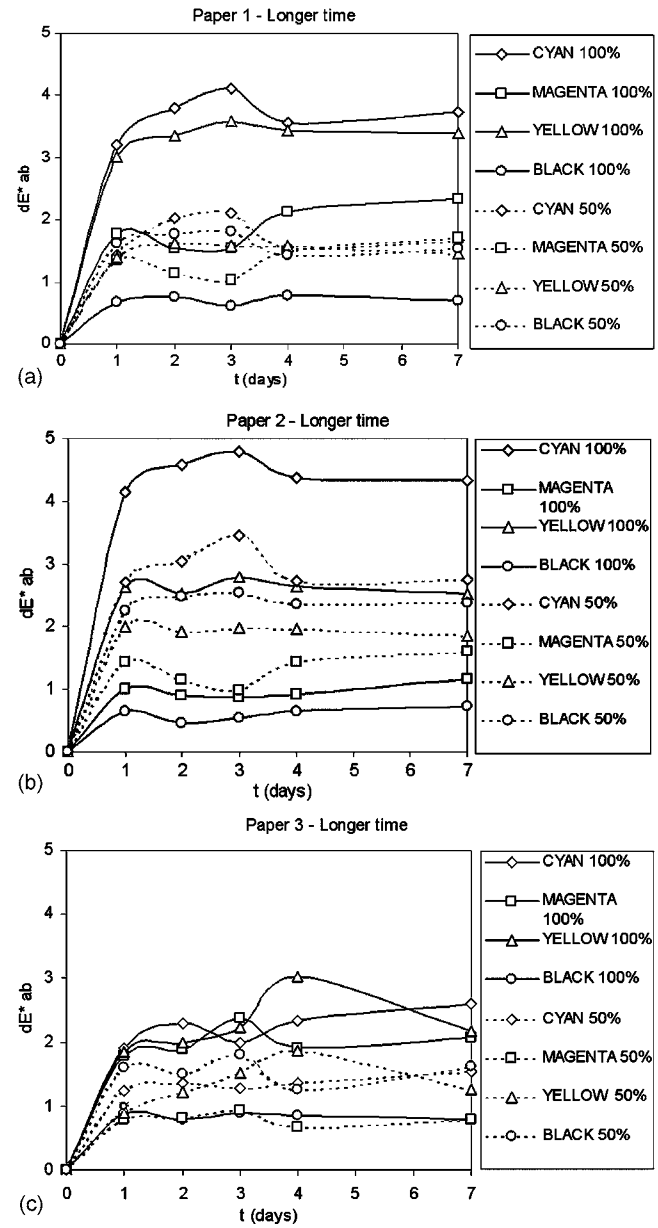

Figure 4. Color difference ΔE^*_{ab} of CMYK prints on papers 1, 2, and 3, up to 7 days after printing.

3 is not appropriate for offset and electrophotographic printing.

The *drying phenomena* of water-based ink on paper can be influenced by several parameters of paper, such as type of fiber, filler distribution, sheet formation, coating, and degree of surface sizing. Each of these parameters has a different degree of impact on the ink drying phenomena. Very important for ink jet printing is the surface tension of paper, which influences the wetting of the surface with liquid ink and affects two processes that occur simultaneously when an ink droplet hits the paper surface: spreading and/or penetration of the droplet.[16,17,26] The liquid wets (spreading) the surface of a solid substance if its surface tension γ_L is lower than the surface tension γ_S of the solid. Liquid surface tensions are directly measured, whereas solid surface tensions are commonly derived from contact angle measurements using semi-empirical equations, thus producing values that depend on the choice of contact angle test liquids and interpretative equations.[27,28] Surface and interfacial tensions γ are related to the contact angle θ by the Young equation,[26]

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta, \tag{1}$$

where the subscript SV, SL, and LV refer to the solid/vapor and solid/liquid surfaces and the liquid/vapor interface, respectively. Surface tension is calculated on the basis of measuring the contact angles of two or three liquids of different polarities or surface charge.[17] When the surface tensions of two liquids are known and the contact angle measured with

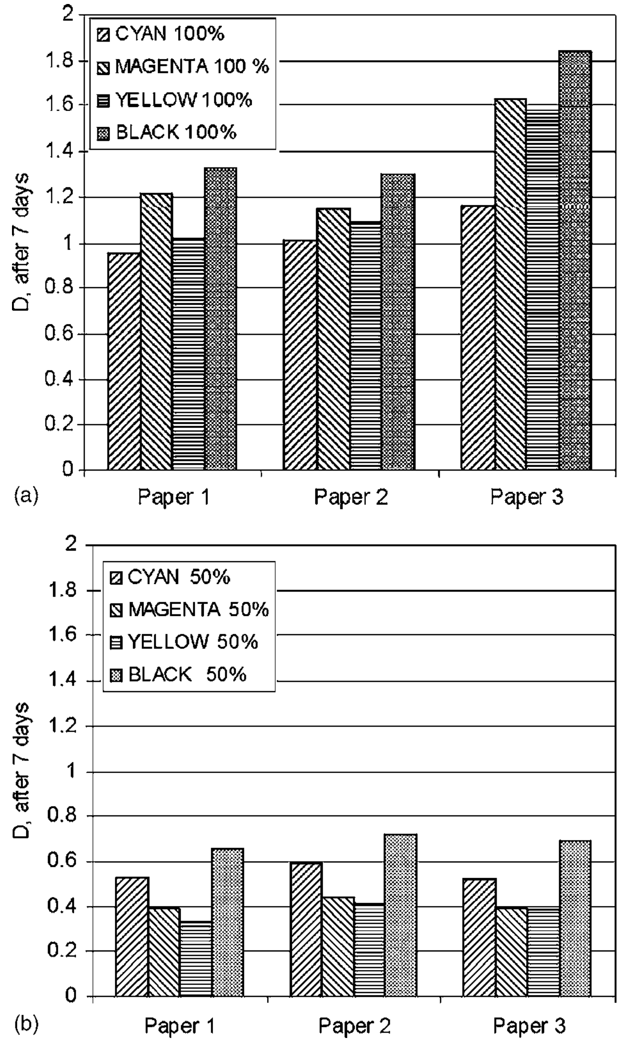

Figure 5. Optical density (D) of 100% and 50% CMYK prints (on papers 1, 2, and 3). Measurements were made 7 days after printing.

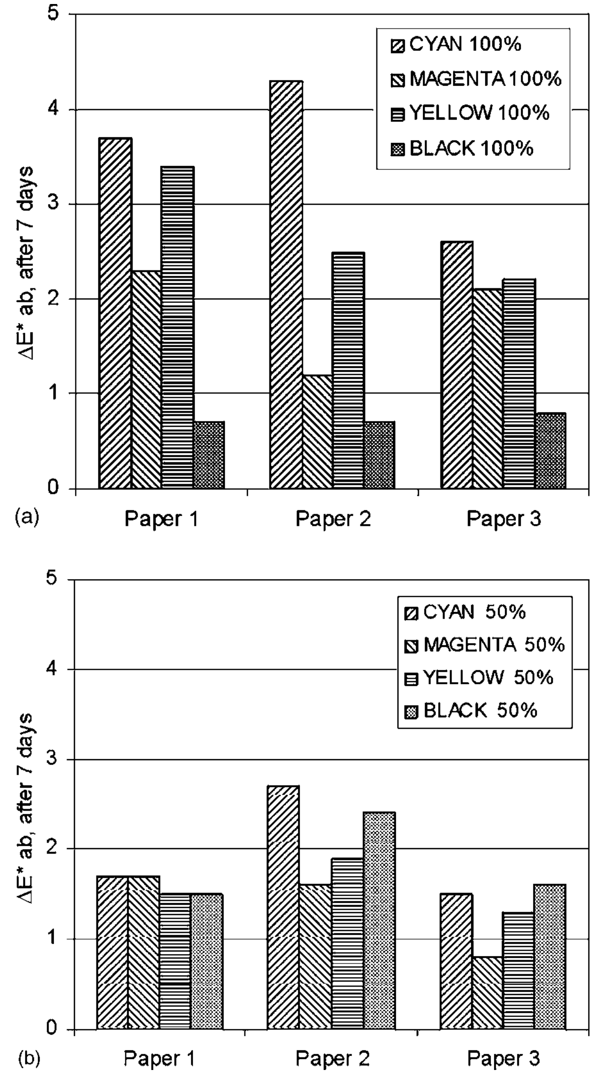

Figure 6. Color differences ΔE^*_{ab} between the CMYK prints immediately after printing and 7 days of drying.

these liquids, one can solve for the solid's surface free energy components by writing an equation pair using either geometric or harmonic mean equations; note that the acceptable combinations of contact angles with a liquid pair are such that the increase in contact angles decreases the surface tension and polar component.[26–28] The surface tension was determined on the basis of the contact angle measurements for water and formamide. The total surface tension has been resolved into the dispersion part (van der Waals) and the polar part, using the geometric mean method equation:[26]

$$\gamma_i(1+\cos\theta_i) = 2[(\alpha_i \gamma_s^{\mathrm{disp}}) + (\beta_i \gamma_s^{\mathrm{pol}})]^{1/2} \quad (i = 1,2,\ldots), \qquad (2)$$

where the first component, γ_s^{disp}, is due to the dispersion forces and the second, γ_s^{pol}, to the hydrogen bond and electrostatic forces. The subscript i is used to number the test liquids. The parameters α and β for test liquids are known and are given in Table II. During research, the contact angles of water ($\gamma_W = 72.8$ mN/m) and formamide ($\gamma_F = 58.0$ mN/m) were measured after 2 s, and the surface tension on the topside of papers was calculated. Figure 2 represents the contact angle values after 2, 3, 4, or 5 s. The calculated values of total surface tension and its disperse and polar part are presented in Table I.[26] Paper samples 1 and 2 obtained high contact angle values, denoting that their surfaces are less absorbent for water. The quality wetting with the totally absorbent surface was already obtained with paper 3 with more polar surface tension after 2 s, in comparison with papers 1 and 2, which exhibited very low polar component of total surface tension. Sorption in those two papers is caused only by the dispersion component of the liquid surface tension.

The Monitoring of Colorimetric Properties of Prints

Colorimetric properties of a print represent an important criterion of print quality.[4,5,11,13,17] Since measured values change with time, standards for offset printing recommend spectrophotometric tests on prints dried 72 h after printing.[18,19] An appropriate standard for ink jet printing has

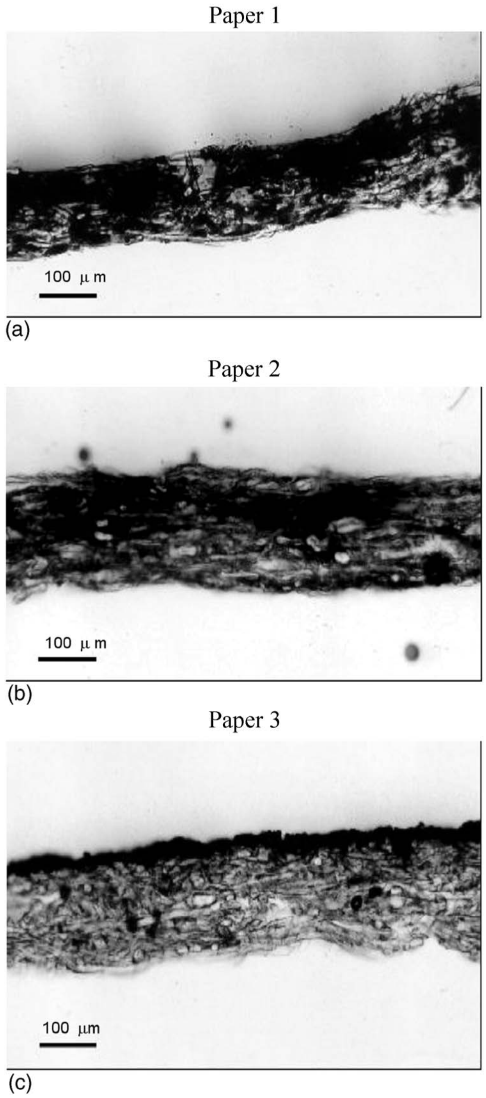

Figure 7. Cross-section structure of black (K) prints on papers 1, 2, and 3 (magnification 160×).

not been developed yet. Monitoring of the color difference ΔE^*_{ab} that appears on prints after a certain time due to ink drying proved the interdependence of ink drying speed and paper properties. In addition, differences among inks of different colors occur. Therefore, each paper was tested to evaluate the time necessary for the colorimetric properties of a print to stabilize. It was presumed that the appearance of a print does not change if the color difference amounts to 0.2 unit or less. The color difference ΔE^*_{ab} was calculated according to Eq. (3):[23]

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}, \qquad (3)$$

where $\Delta L^* = L^*(t) - L^*(0)$, $\Delta a^* = a^*(t) - a^*(0)$, and $\Delta b^* = b^*(t) - b^*(0)$ are the differences calculated for monitoring ink color of the print dried for time t (t) and the original (0) color print, where $t=0$. Individual color prints on paper samples were tested in order to determine the shortest period necessary for a color to dry. After brief monitoring (Fig. 3), the results proved that cyan (C) and yellow (Y) inks need more time to dry than other colors.

Table II. Surface tension components for the test liquids water and formamide, mN/m.

Liquid	γ-Total	γ-Dispersion part	γ-Polar part
Water	72.80	21.80	51.00
Formamide	58.00	39.00	19.00

Figures 3 and 4 show that color differences of the prints increase with time. We tried to estimate the time necessary for the drying process to be completed so the prints would stabilize and their color would remain thereafter unchanged. As shown, the results depend strongly of the paper and ink characteristics. The longer time of drying was found for the cyan (C) ink, which required at least 4 to 7 days, regardless of paper. Magenta (M) ink needed 7 days to stabilize on papers 1, 2, and 3; however, no major color differences were observed after 4 days. For yellow (Y) inks, it was found that the changes of color could be observed as long as 7 days on paper 3. Surprisingly, yellow ink seems to stabilize after only 3 days on papers 1 and 2. As for black (K) prints, the results have shown that the samples with 100% coverage stabilize within one day as no evident color difference was observed later. This, however, was not the case with the 50% prints; they required more time to stabilize. This is obvious especially on paper 1.

According to the results, the biggest changes in colorimetric properties of the prints occur in the first 60 min after printing. A suitable drying period of ink for ink jet printing can be estimated on the basis of the average time needed for the samples to stabilize and dry. The color of prints was on average changing for 4 or even 5 days. Therefore it can be assumed that the drying process has not been completed before 96 (or even 120) hours after printing. According to the ISO 2834 standard covering offset printing, samples should be dried in air and dry after 72 h. In comparison with this standard's requirements, our results show that the drying process of an ink jet printing ink takes at least 1 day longer. In addition, the results of monitoring the drying process for a longer period show that the highest optical density was achieved on paper 3, but, at the same time, most of the color prints on paper 3 were stabilized only after 7 days. Therefore, we can assume that paper 3, absorbing the highest amount of ink, takes longer to dry.

Colorimetric Properties of Dry Prints

The results of the *optical density* measurements for 100% and 50% CMYK coloration are presented in Fig. 5. For comparison, the final color differences ΔE^*_{ab} after 7 days for CMYK color prints with 50% and 100% coloration are shown in Fig. 6. Considerable deviations among samples were noted; we presumed that the optical density value, D, of prints should be at least 1.0 at 100% coloration and 0.5 at 50% coloration. For 100% coloration, all colors except cyan exceeded the optical density value of 1.0. The lowest value was therefore obtained by cyan (C), slightly higher values by magenta (M) and yellow (Y) colors, and the highest by black (K). Comparision of optical density of prints and the observed color differences after 7 days shows that highest optical density is obtained for samples with the smallest color difference and vice versa. Main deviations were seen in the cyan print on paper 2. Paper 3 yields higher optical densities than the other papers. Such results were probably caused by the composition of the specialty coating on this paper that enables total bonding, absorption, and adsorption of the ink onto coating pigment particles.

From Fig. 6 it can be seen that the extent of color differences that were observed on prints during the drying period depends on paper as well as ink characteristics and is connected with their structure and chemical composition, i.e., with the process of binding of certain colorant onto the paper surface.

Cross Sections of Color Prints on Paper

Figure 7 represents cross sections for black prints. It can be seen that the ink is adsorbed onto the surface coating of paper 3, whereas papers 1 and 2 have no such capability and therefore the ink is absorbed into the whole cross sectional structure of the papers. That causes a decrease in print quality expressed by lower values of optical density as well as bigger color differences after drying and confirms the results of measured D and ΔE^*_{ab} shown in Figs. 5 and 6.

CONCLUSIONS

On the basis of comparative analysis of prints on selected papers it can be concluded that the sorptive properties of paper surface are of key importance for the quality of an ink jet print. Optimal values of sorption and water penetration have to be provided by the paper surface in order to achieve optimal bonding and adsorption of ink onto pigment particles or fibers. In addition, optimal surface tension of paper has to be achieved with regards to the surface tension of ink.

On all paper samples, the most evident changes in their colorimetric properties occur during the first 60 min after printing.

Prints are for the most part stabilized after 4 to 5 days, depending on color, i.e., composition of the ink. Due to ongoing changes in color, colorimetric measurements are recommended not sooner than 96 h after printing.

Paper 3 with a special pigment coating produced the best results with respect to the quality of color prints and their optical density. Color differences between the prints on this paper were lower. The color changes of prints on this paper during the process of drying were considerably lower than the changes observed for the color prints on the other two papers, in spite of the fact that the time necessary for stabilization of the ink and to obtain the final color was found to be larger than for prints on papers 1 and 2.

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