Fastness Properties of Ink Jet Prints on Coated Papers

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Abstract

In order to produce color ink jet prints with good optical and fastness properties, the use of coated special papers is generally essential. However, the high cost of these media limits their use in home and networked office printing environments and in industrial printing. For this reason, coated papers intended for conventional printing would be of great interest also as ink jet print media. So far, there is no general understanding of their usability in ink jet printing in terms of their optical and fastness properties. This study examines the optical and fastness properties of ink jet prints on coated papers. Three paper sets were used in this study. Reference set consisted of commercial matte-coated ink jet papers. The effects of polymer system and pigment composition on ink jet print quality were studied by means of two pilot paper sets, which had conventional kaolin as the main coating pigment.

Generally, the light fastness levels obtained with pilot papers were quite good or in some cases even better than those obtained with commercial papers, but this was found to be dependent on the type of colorant. On the other hand, poor water fastness due to the low cohesion of the coating was the weak point of the studied pilot papers. Within the studied commercial and pigment set papers, the differences between fastness values could not be clearly related to structural properties or the composition of the coating. Instead, within the polymer set, differences in light and water fastness could be explained by differences in the composition of the coatings.

Introduction

Ink jet technology is becoming more common in small-scale color printing and in low-cost variable data printing applications, such as direct mail advertising. To achieve high print quality, the use of coated papers is essential. Of currently available ink jet grades, matte-coated papers are the most suitable option for these applications because of their lower cost compared to photo-quality ink jet papers. Matte ink jet coatings typically consist of amorphous silica pigments, a PVA binder (polyvinyl alcohol) and a cationic polymer additive such as quaternary amine. Technically, this kind of coating works well in ink jet printing, since it is hydrophilic, highly porous and able to fix the anionic ink jet colorants. However, the problem is its high cost, which makes large-scale printing uneconomical. Lower-cost coated grades such as conventional printing papers would therefore be an interesting option also as an ink jet printing medium.[1-4]

In conventional printing papers, typical coating color consists of kaolin and one or two secondary pigments such as calcium carbonate to increase ink absorption and brightness, and latex, such as SB latex (styrene-butadiene latex), as a binder.[5] The downside of kaolin-based coatings with respect to ink jet printing is their small pore volume and surface area, which would enhance rapid drying of ink jet inks. The use of precipitated calcium carbonate and surface-enhanced aluminosilicate (SEAS) as a replacement for silica pigments has been recently suggested as a means to obtain a coating which would combine the good properties of silica and conventional kaolin coatings.[2]

This study attempts to provide a general understanding on the suitability of conventionally coated papers for ink jet printing. Optical and fastness properties are of particular interest here. In this study, the effects of the polymer system and pigment composition on ink jet print quality are studied. To explore the usability of conventional printing papers in ink jet printing, conventional kaolin was selected as the main pigment for the model coatings.

Literature Background

Ink Properties Affecting Print Fastness

Several factors in the ink formulation influence the fastness properties of an ink jet print. It is well known that pigmented inks, because of their crystalline structure, have better light and water fastness than dye-based inks. It has been found that the fastness properties of dye-based inks can be considerably improved by controlled dye aggregation in the ink-receiving layer. Substituents of the colorant molecule should on the one hand impart maximum solubility in an aqueous solution, but on the other, they should not interfere with dye-aggregation, once the colorant is in its solid state[6]. There are two common ways to implement controlled dye-aggregation, namely pH switching and zwitterionic mechanisms. In the pH switching mechanism carboxy groups of the colorant molecule solubilize it in slightly alkaline ink, but protonate on paper with a slightly lower pH, resulting in an insoluble, water-resistant form. The formation of zwitterions due to protonation of the basic piperazine group is instantaneous and leads to a print which is virtually insoluble in water.[7] Organic ink solvents have also been reported to influence the aggregation behavior of the dyes.[6]

Media Properties Affecting Print Fastness

The nature of coating components determines the chemical and physical properties of the colorant in the print and is thus important in controlling the fastness properties of the print[6]. According to Khoultchaev et al.[8], the presence of pigment in the coating formula generally increases the UV resistance of the coating. The type of pigment affects the pH of the coating, which has been shown to have an influence on light fastness. In general, proton-donating compounds have been found to favor the hydrazo form (=N-NH-) of certain azo dyes, whereas proton-accepting compounds favor the azo form[9]. Inorganic oxides, such as SiO_2 and TiO_2 tend to produce acidic surface layers, whereas the use of $CaCO_3$ produces a more basic surface. Al_2O_3, on the other hand, produces a coating with more neutral pH due to its amphoteric nature[10]. If water fastness is considered, both the cohesion of the coating itself and the attachment of the dye to the coating can have an effect[8]. Therefore, the solubility of the pigments has to be taken into account when selecting the formulation of an ink jet coating.

The binder system of the coating is perhaps the most significant factor affecting the fastness properties of an ink jet print, since polymers can stabilize and immobilize the colorant both physically and chemically and since they have an effect on the cohesion of the coating.[8,11] Porous ink jet photo papers usually contain a protecting surface coating or polymer layer, which literally protects the chromophore from detrimental UV light and oxygen.[12,13] Materials with a high proportion of hydroxyl functionality, like PVA and cellulose derivatives, have been found to promote light stability, since they act as free radical quenchers[11]. Also, an increase in the hydrogen bonding capability of the host polymer has been found to reduce the fading of certain azo dyes.[14] Polymers containing alkyl groups and ethylcellulose have also been found to enhance light stability of certain yellow pigment.[15] On the other hand, polymers containing UV light absorbers and polymers containing styrene destabilize the azo colorants,[15] which is the case also for coating layers containing PVP and polycationic systems.[10,11] Wang et al. suggested that the poor light fastness of nitrogen-containing polymers such as PVP, may be due to the fact that nitrogen-containing dyes aggregate less when in contact with this kind of polymers.[16] Since most ink jet media use water-soluble polymers as a binder to absorb ink vehicles, the receptive coatings will swell and be washed away when in contact with water for extended periods of time. Therefore, a careful balance between hydrophilic and -phobic components in the receptive coating is needed to give both good image and water resistance.[8,11]

Additives are commonly used to improve the fastness properties of ink jet prints. Several studies[4,13,17] have shown that cationic additives such as poly-DADMAC markedly improve the water fastness of ink jet prints by forming an ionic complex with anionic dyes. However, they have been found to decrease the light fastness of some anionic dyes[17]. This effect has been explained by the location of the colorant in the cationic coating - as the dye is fixed at the surface of the substrate it is more vulnerable to UV light and thus to photo-decomposition[12]. The light fastness of the print can be enhanced somewhat by adding antioxidants or transitional metal salts to the coatings to decrease dye oxidation and stabilize the dyes with complex formation[10,16].

Experimental

Paper Samples

The reference set consisted of six commercial matte-coated ink jet papers. The binder composition was analyzed with a FTIR spectrometer and iodine test. All the samples contained PVA, and most of them also polyvinyl acetate or styrene-butadiene latex. The pigment composition of the paper surface was analyzed by EDS analysis, and according to the results, all the studied samples contained silica, with the exception of one paper, which contained Mg- and Al-based pigments.

In the first pilot paper set, the properties of the coatings were altered by means of variations in the polymer system, which caused changes in the absorption properties and net charge of the coating, see Table 1. The absorption properties of the coating were varied using different types and amounts of binders (5-20 pph hydrophilic polyvinyl alcohol PVA or hydrophobic styrene acrylate latex SA). The net charge of the coatings and thus the propensity to bind anionic dyes was varied using either 1 pph anionic carboxymethyl cellulose (CMC) or 3 pph cationic poly-diallyl dimethyl ammonium chloride (poly-DADMAC) as dispersant. In anionic coatings A1-A9, the coating pigment was kaolin, which was pre-dispersed with polyacrylate. In color A8, oxidized starch was used as an additional dispersant. In color A9, weakly cationic styrene acrylate latex was used as a binder and weakly cationic starch as an additional dispersant. However, the net charge of the color A9 was anionic. In cationic colors A10 and A11 dry SPS kaolin was used. The pH of colors A1-A9 was 8 and of colors A10-A11, 5. The base paper was surface-sized copy paper with a grammage 80 g/m^2. The amount of coating is 10 g/m^2 and the papers are uncalendered.

Table 1. Polymer compositions of the first pilot paper set.

Color	Binder	Dispersant	Net-charge
A1-A3	PVA	CMC	Anionic
A4-A7	Anionic SA	-	Anionic
A8	Anionic SA	Oxidized starch	Anionic
A9	Weakly cat. SA	Weakly cat. starch	Anionic
A10-A11	PVA	Poly-DADMAC	Cationic

In the second pilot paper set, the types of coating pigments and their ratios were varied as shown in Table 2. The set consisted of five double-coated papers and their precoated base paper. The pre-coating pigment was $CaCO_3$. In the double-coated papers, the second coating layer consisted of two different pigments, namely kaolin and secondary pigment A or B, which are intended to increase the bulk of the coating. All colors contained 12 pph of styrene-butadiene latex as a binder, 1 pph of CMC as a co-binder and 0.3 pph of glyoxal as an insolubilizer. The pH of coating colors containing pigment A was 8.5 and that of colors containing pigment B, 7.5.

Table 2. Pigment compositions of the second pilot paper set.

Color	Kaolin, %	Pigment A, %	Pigment B, %
B1	70	30	0
B2	50	50	0
B3	30	70	0
B4	30	0	70
B5	70	0	30

The coated papers were analyzed to determine their roughness, Bendtsen air permeability, surface energy and contact angle. Roughness was measured with a Mitutoyo 401 profilometer, Bendtsen air permeability with the SCAN-P 60:87 standard test method, and surface energy and contact angle with an in-house test set-up based on the use of a video camera and PC. In surface energy measurements, glycerol was used as a polar liquid and hexadecane as non-polar liquid. Contact angles were measured with water. Bendtsen air permeabilities of the pigment coating set were practically immeasurable because of the dense nature of the coating structure. For this reason, the porosity characteristics were determined with mercury porosimetry.

Model Inks

Three azo colorants with different chemical properties were chosen for this study. Magenta azo colorant CI Acid Red 249 (AR 249) represents acid dyes, yellow anionic azo colorant CI Direct Yellow 86 (DY 86) belongs to the class of direct dyes and magenta colorant CI Direct Violet 107 (DV 107) is a modified direct azo dye with enhanced fastness properties. The model ink formulation was the following: 4 wt-% dye, 20 wt-% 2-pyrrolidone and up to 100 wt-% distilled water. The model inks were analyzed to determine their pH and surface tension, Table 3, using a Schott pH meter and the Sigma 70 computer-controlled automatic surface tension meter, which is based on the ring method.

Table 3. Measured model ink properties.

Property	AR 249	DY 86	DV 107
pH-value	7.1	7.5	8.1
Surface tension, mN/m	41.5	56.8	58.1

Methods

To examine the fastness properties of ink jet prints on coated papers, sets of printed samples were prepared using the coating color composition as a variable. Solid yellow or magenta areas were printed with an Olivetti JP 960 ink jet printer using model inks. Density and L*a*b*-values for all the ink-paper combinations were measured with a Macbeth RD-918 densitometer and a Minolta CM-1000 spectrophotometer, respectively, prior to the fastness tests.

Light fastness tests were accomplished by exposing the prints to artificial sunlight for 6, 12, 24, 48, 72 and 100 hours with a Suntest CPS+ xenon arc lamp. Test chamber settings were 615 W/m^2 for irradiance and 40°C for black standard temperature BST. Relative humidity and temperature of the measurement room were set to 35% and 24°C, respectively. According to the data on test chamber conditions gathered during the light exposure run, the test chamber temperature CST remained fairly constant, but the BST tended to rise towards the end of the runs. However, the standard deviations of the chamber and black standard temperatures were mostly clearly below 1°C. Water fastness values of the prints were measured by immersing the printed samples into de-ionized water for 5 minutes and allowing the immersed prints to dry for at least 5 hours at room temperature. Rub fastness was left outside of this study, since according to the preliminary tests, rub fastness of all the studied ink-paper combinations was generally very good and no differences between them could be discerned. Color difference $\Delta E=(\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})^{1/2}$ is used as a measure of light and water fastness and to calculate it, L*a*b* values were measured from the prints again after light exposure and water immersion.

FTIR and Raman-spectroscopic measurements were used to gain more information on the paper-ink interactions affecting the fastness properties of these samples. FTIR-ATR spectra were measured with a Bio-Rad FTS 6000 spectrometer using a germanium micro-ATR crystal and sampling resolution of 8 cm^{-1}. Depth profiling of the prints was accomplished with a dispersive Kaiser Raman Hololab series 5000 spectrometer using 785 nm laser wavelength, a 100x-immersion objective, a sampling resolution of 1 cm^{-1} and a depth profiling step of 1 μm. With kaolin-containing coatings, fluorescence complicated Raman measurements and interpretation of the spectra.

Results and Discussion

Optical and Fastness Properties

Fig. 1 shows a comparison of solid area densities and density deviations of the printed samples before the fastness tests. With all the studied model inks, the use of commercial ink jet papers yielded clearly bigger solid area densities and their density deviation was smaller compared to the pilot papers. Variation of the polymer system of the kaolin-based coating yielded slightly bigger densities than variation of the pigment composition. The density deviations presented in Fig. 1 and visual inspection of the samples show that there is a lot of variation in the solid area densities of the pilot paper sets, especially in the pigment set. This can be related to the slow ink absorption into the coating. Contact angle measurements with water showed that the commercial papers were able to absorb water markedly more quickly than pilot papers. The complete absorption of a water droplet took about 20 s with the commercial papers, whereas with the pilot papers it took, even in the best case, about 7 min. In the pigment set, also the dense structure of the coating, which was evident from the air permeability measurements, may have caused extra variation in solid area densities.

Based on the measurements of the paper properties, the commercial papers are rougher, more porous, polar and their surface energy is larger compared to the studied pilot papers. Also, the studied commercial papers generally have more variation between the samples in these properties than the samples of pilot paper sets. None of the studied paper properties can adequately explain the differences in densities between these groups. The observed differences seem to be more related to the composition of the coatings rather than to their structure.

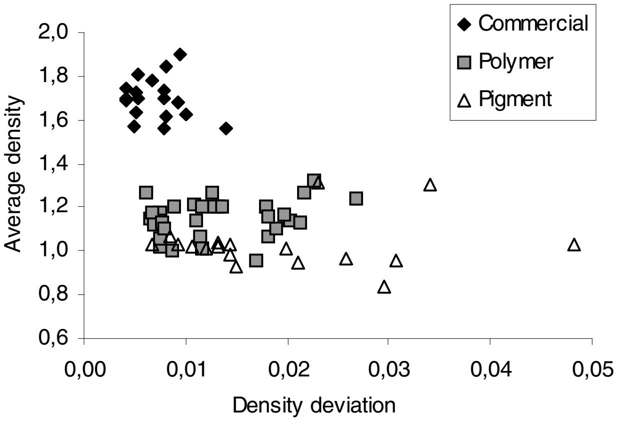

Figure 1. Average solid area densities and standard deviations for various ink-paper combinations.

Figure 2 shows a comparison of light and water fastness between the commercial and pilot paper sets. In general, water fastness of ink jet prints on commercial papers was clearly better than that of the pilot papers, independent of the colorant. On the other hand, the light fastness level achieved with the pilot papers was in some cases even better than that of commercial papers. As expected, the best light fastness was achieved with all sample sets using modified direct dye DV 107. With DV 107, the differences in light fastness values between the sample sets were small. On the other hand, when acid dye AR 249 or direct dye DY 86 was used, more variation in light fastness occurred between the sample sets, and none of the sample sets was clearly better or worse than the others. Within the studied commercial and pigment set papers, the differences between fastness values can not be clearly related to structural properties or the composition of the coating. This holds true especially for commercial papers. Prevailing interactions between the studied dyes and the coating pigments affecting the fastness properties of the print need to be clarified further. Instead, within the polymer set, differences in light and water fastness can be explained by differences in the composition of the coatings.

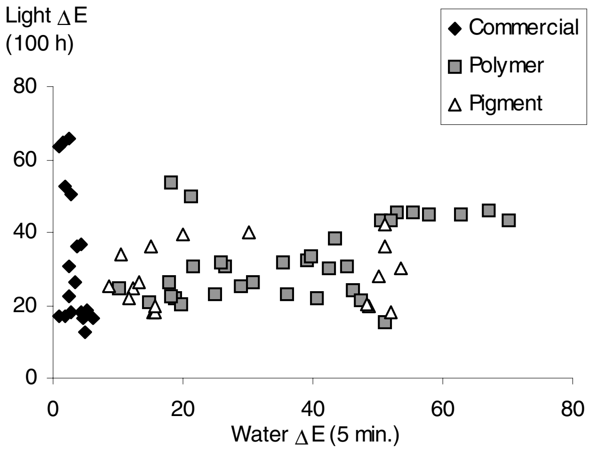

Figure 2. Comparison of fastness properties between commercial and pilot paper sets.

Effect of Coating Polymer System on Light Fastness

The results of the light fastness tests show that an increase in the amount of binder improves light fastness independent of the binder or the type of dispersant, as seen from the example in Fig. 3. There is a slight increase in color difference ΔE if the amount of styrene acrylate latex is increased from 5 to 10 pph, but after that, ΔE starts to get smaller, so light fastness is improved.

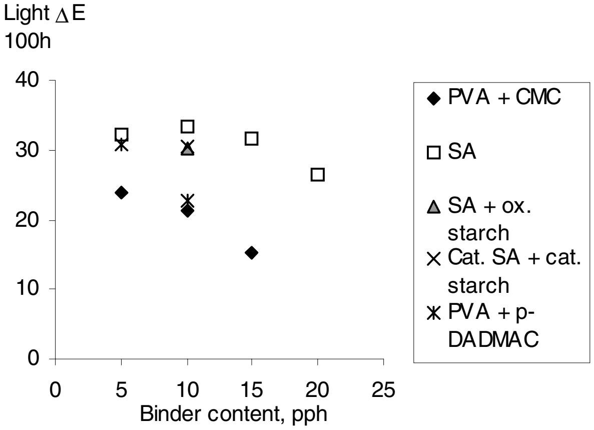

Figure 3. Effect of binder type and amount to light fastness

On the basis of the literature,[11-14] PVA could act as an oxygen barrier and also as a stabilizing agent for the azo dyes due to the formation of hydrogen bonds. On the other hand, small amounts (10 pph or less) of styrene acrylate could destabilize the azo dyes due to the presence of styrene,[15] which is seen as larger ΔE compared to anionic PVA coating. As the amount of SA latex increases, light fastness begins to improve, which would indicate that the barrier effect of the polymers dominates. An example on the effect of PVA amount on the light fastness of an anionic azo dye is shown in the Raman depth profile of Fig. 4. At PVA contents of 5 pph, light exposure of the print results in the decomposition of the dye especially from the surface layers of the coating. This is seen as a shift of dye maximum deeper into the coating. As the amount of PVA is increased from 5 to 15 pph, more dye remains in the surface layers after light exposure, although the total amount of dye in the print is decreased.

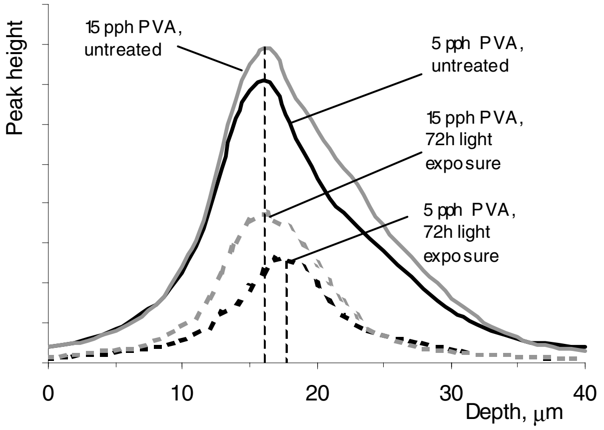

Figure 4. Dye distribution on PVA coatings before and after light exposure. Dotted lines denote light-exposed samples.

A comparison of anionic and cationic PVA coatings (Fig. 3) reveals that light fastness is slightly better with anionic (PVA-CMC) coatings, especially at low binder contents (5 pph). This could be explained by the fact that a cationic coating is more porous than an anionic one, so the colorant could be more prone to the effects of oxygen.

The addition of oxidized or weakly cationic starch to latex coating generally improves light fastness. The effect is small with acid dye AR 249 or direct dye DY 86, but more pronounced with modified direct dye DV 107. With oxidized starch, the dye is probably stabilized more effectively due to the introduction of hydroxyl and a few carboxylic acid groups into the coating. However, further investigations are still needed to establish the exact stabilization mechanisms.

Effect of Coating Polymer System on Water Fastness

An example of the results of the water fastness tests is shown in Fig. 5. If coatings containing different binder-dispersant-combinations are compared, it can be seen that the poorest water fastness is obtained with coatings containing PVA and CMC. This holds true for all the model inks studied here. The use of cationic poly-DADMAC instead of anionic CMC as a dispersing agent considerably improves water fastness of prints on PVA coatings, especially at low binder contents (5 pph). This is probably due to the increase in the amount of cationic binding sites in the coating. FTIR-ATR spectra measured from the prints before and after water immersion showed that PVA had dissolved at least partly from the coating. Thus, on anionic PVA coatings dyes seem to be mostly attached to the binder, probably with hydrogen bonds. Instead, the cationic dispersant is able to fix the anionic dyes even though PVA dissolves. Water fastness is further impaired irrespective of the type of dispersant, if the amount of PVA is increased in the coating.

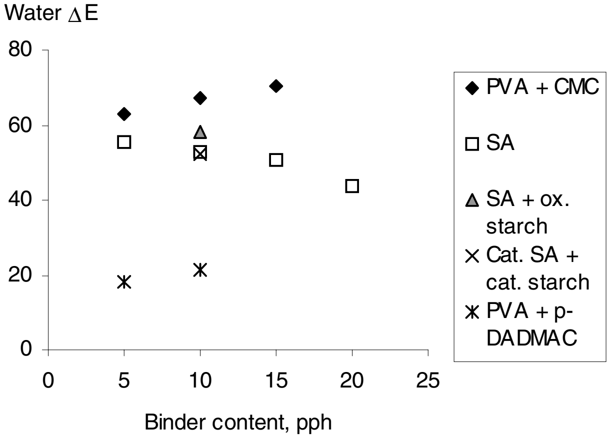

Figure 5. Effects of binder type and amount to the water fastness of ink jet prints.

Visual inspection of the water-immersed samples showed that on anionic PVA coatings printed areas had lightened considerably and dyes had spread somewhat on unprinted areas. On cationic PVA coatings, however, despite of extensive spreading, dyes had been retained on the sheet. This can be seen also from the Raman depth profile in Fig. 6, which presents the effect of water immersion to the distribution of anionic dye printed on anionic or cationic PVA coatings. On the cationic coating there is more colorant left after water immersion and the dye distribution is emphasized on the surface of the coating compared to the anionic PVA coating.

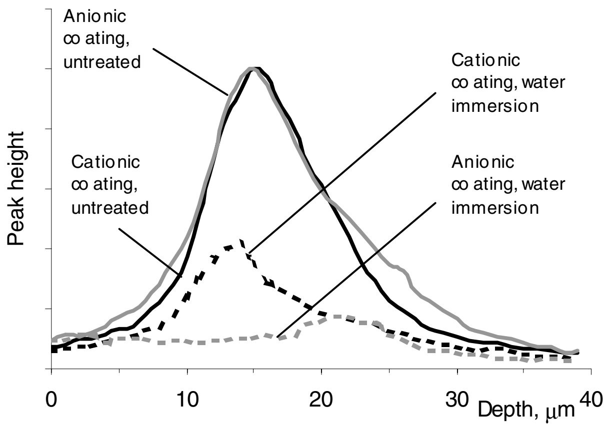

Figure 6. Dye distribution on PVA coatings before and after water immersion. Dotted lines denote water-immersed samples.

The use of anionic styrene acrylate latex makes the coating non-swellable and rather hydrophobic. As can be seen from Fig. 7, anionic styrene acrylate latex improves water fastness compared to anionic PVA coatings. A further improvement is achieved with increased latex amounts. Apparently, this can be explained by the more hydrophobic nature of the coating, which lets the dye dissolve only from the surface of the coating. However, aqueous inks penetrate into the coating with the help of the co-solvent, 2-pyrrolidone, as shown in the Raman depth profiles of Fig. 7.

The effects of oxidized and weakly cationic starches as dispersants in latex coatings are not unambiguous. With anionic dyes (Acid Red 249 and Direct Yellow 86), both starches slightly impaired water fastness, which can probably be attributed to the more hydrophilic nature of the coating. On the other hand, with Direct Violet 107 the use of starches improved water fastness.

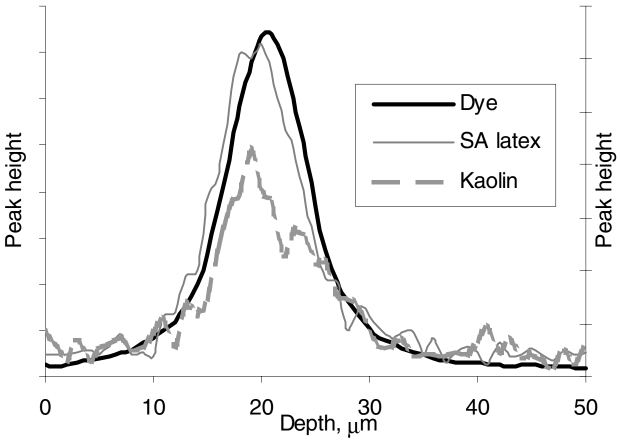

Figure 7. Ink penetration into styrene acrylate latex coating.

Conclusions

The goal of this study was to gain general understanding on the applicability of conventionally coated papers for ink jet printing. In particular, optical and fastness properties were of interest. Reference paper set consisted of commercial matte-coated ink jet papers. The effects of polymer system and pigment composition on ink jet print quality were studied by means of two pilot paper sets, which had conventional kaolin as the main coating pigment.

Generally, the light fastness levels obtained with the pilot papers were found to be quite good or in some cases even better than those obtained with the commercial papers. However, this was found to be dependent on the colorant type. On the other hand, water fastness seemed to be the weak point of the pilot papers. Low cohesion of the coating due to the highly water-soluble coating components was found to impair water fastness. This may limit the use of conventional printing papers in ink jet printing. Within the studied commercial and pigment set papers, the differences between fastness values could not be clearly related to structural properties or the composition of the coating. Instead, within the polymer set, differences in light and water fastness could be explained by differences in the composition of the coatings. Further investigations are still needed to establish the exact stabilization mechanisms.

In future studies, the focus will be on the effects of ink composition and modified conventional pigments on ink jet print quality.

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Biography

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