Fastness Properties of Ink Jet Prints on Modified Conventional Coatings

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Abstract

In order to produce color ink jet prints with good fastness properties, the use of special coated papers is generally essential. The use of modified conventional coating pigments has been suggested as a means to obtain a coating that combines the good properties of silica-based ink jet coatings and conventional coatings. This study examines light and water fastness of dye-based ink jet prints on coated papers containing modified conventional pigments. The properties of the coatings were altered by using different ratios of coating pigments, and the types of binder and dispersant. Inks with known composition were used for test printings. The fastness properties of the prints were analyzed both conventionally and with FTIR and Raman spectroscopy.

This study indicates that light and water fastness of ink jet prints is amended distinctly when the modified coating pigments are used instead of pigments intended for conventional printing papers. However, mechanisms that govern the build-up of light and water fastness of the studied dye-based inks depended also on the polymer system of the coating. The data suggest that on cationic PVA + p-DADMAC coatings primarily the chemical paper-ink interactions contribute to fastness properties, whereas on weakly cationic latex-starch coatings structural paper properties have relevance as well.

Introduction

Ink jet coatings based on silica pigments, a PVA-binder (polyvinyl alcohol) and a cationic polymer additive are currently the state-of-the-art for coated ink jet papers. This kind of coating works very well in ink jet printing, since it is hydrophilic, highly porous and able to fix the anionic ink jet colorants. However, because of their high cost and relatively poor printability in other printing processes their usability is rather limited in combinations of ink jet and conventional printing processes. Hence lower-cost coated grades consisting of same components as conventional printing papers would be an interesting option also as ink jet printing medium.[1-4]

Generally the liquid ink jet inks dry excessively slowly on conventional printing papers because of their inadequate absorption capacity. This deteriorates print quality severely. Various approaches have been presented to obtain a coating that would combine the good absorption properties of silica grades and the lower-cost of conventional printing papers. For example, the use of precipitated calcium carbonate (PCC) and surface-enhanced aluminosilicate (SEAS) as a replacement for silica pigments has been suggested,[1] as well as the modification of traditional offset coating formulations with bentonite and PVP-copolymer.[5] Also the use of cationic starch in ink jet coatings along with conventional pigments has been suggested.[4]

In order to achieve proper long-term ink jet print quality with these novel coatings, the knowledge on the underlying mechanisms of the fastness properties is essential. Previously, the effects of coating polymer system on fastness properties of ink jet prints on conventional kaolin-coatings has been investigated.[6,7] The objective of the present study is to examine light and water fastness of ink jet prints on coatings consisting of modified coating pigments.

Experimental

Model Coatings

The sample set consisted of twelve model coatings, whose absorption properties had been varied by modifying the pigment ratio and the type of coating polymer system, see Table 1. The coating pigments were modified PCC and kaolin pigments designed specially for ink jet coatings. Two polymer systems were used: 1) PVA-binder combined with p-DADMAC dispersant and 2) weakly cationic styrene acrylate latex binder combined with weakly cationic starch dispersant. The binder content was 10 pph in both cases. Surface sized copy paper with grammage 80 gm^{-2} was used as a base paper. The coating was accomplished with CLC laboratory coater.

The coated papers were analyzed to determine their roughness, porosity and contact angle. Roughness was measured with a Mitutoyo 401 profilometer and the porosity characteristics were determined both with the SCAN-P 60:87 standard test method (Bendtsen air permeability) and with mercury porosimetry. Contact angles with water were measured with an in-house test set-up based on the use of a video camera and PC.

Table 1. Compositions of the Model Coatings

Paper	PCC:kaolin	Binder	Dispersant
1	100:0 (pph)	PVA 10 pph	p-DADMAC 3 pph
2	80:20		
3	60:40		
4	40:60		
5	20:80		
6	0:100		
7	100:0	Weakly cationic SA latex 10 pph	Weakly cationic starch 4 pph
8	80:20		
9	60:40		
10	40:60		
11	20:80		
12	0:100		

Model Inks

Four model inks with different organic co-solvent were prepared for the study. The model ink formulation was the following: 4 wt.% dye, 10-20 wt.% organic co-solvent and 76-86 wt.% distilled water. The colorant was yellow anionic azo colorant CI Direct Yellow 86 (DY 86) in all cases. Three organic co-solvents were used: 2-pyrrolidone (marked as 2-p in the figures), diethylene glycol (DEG) and tetraethylene glycol (TEG). The model inks were analyzed to determine their pH (Schott pH meter), surface tension (Sigma 70 computer-controlled automatic surface tension meter based on the ring method) and viscosity (Bohlin VOR rheometer). The pH-values of the model inks ranged between 7.47 - 7.96, surface tensions between 52.1 - 58.5 mN/m and viscosities between 2.41 - 2.77 mPas.

Fastness Tests

To examine the fastness properties of ink jet prints on coated papers, sets of printed samples were prepared using the model coatings. Solid yellow areas were printed with an Epson Stylus Photo 890 ink jet printer using model inks. 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 with a Minolta CM-1000 spectrophotometer from the prints before and after exposure to light or water. The printed areas were quite uneven particularly in the case of TEG and 2-pyrrolidone inks, which has inevitably caused variation to the measured optical properties. To compensate for this, several parallel measurements were taken from each test point.

Light fastness tests were accomplished by exposing the prints to artificial sunlight for 100 hours with a Suntest CPS+ xenon arc lamp equipped with optical filter system, which cuts off the wavelengths below 310 nm. Test chamber settings were 615 Wm^{-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 runs, the test chamber temperature CST remained fairly constant, whereas the BST ranged from 44°C to 56°C. This may have caused some variation in the results. Water fastness 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.

Spectroscopic Measurements

FTIR and Raman-spectroscopic measurements were accomplished to gain more information on the paper-ink interactions affecting light and water fastness. FTIR-ATR spectra were measured with a Bio-Rad FTS 6000 spectrometer using a germanium micro-ATR crystal and sampling resolution 8 cm^{-1}. Raman 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

Light Fastness on PVA + p-DADMAC coatings

Light fastness of the printed samples on PVA + p-DADMAC coatings (Papers 1-6) after 100 h light exposure is presented in Fig. 1 as a function of PCC:kaolin pigment ratio of the coating. The type and the amount of ink co-solvent are shown in the legend. Figure 1 shows that on PVA + p-DADMAC coatings the PCC:kaolin pigment ratio does not appear to have marked effect on light fastness. However, the previous study[6] showed that light fastness of yellow ink jet prints on coating consisting of conventional kaolin and an identical PVA + p-DADMAC polymer system with the present study, was ΔE* = 21.39 when the DY 86 2-p 20% ink was used. Thus it appears that the use of modified PCC and kaolin pigments instead of conventional kaolin improves light fastness only subtly.

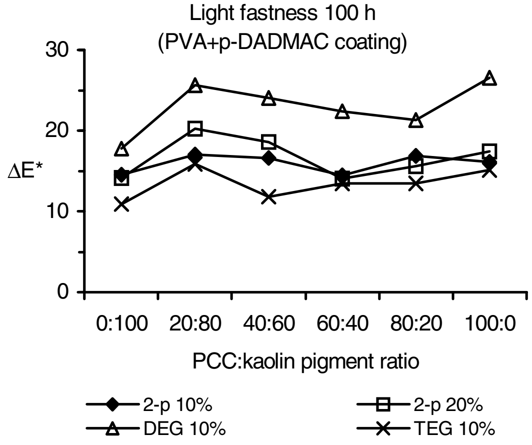

Figure 1. Light fastness of anionic ink jet inks on cationic PCC-kaolin coatings. Coating polymer system: PVA-poly-DADMAC. Large ΔE denotes poor light fastness.

On the basis of the previous study,[6] structural paper properties were expected to contribute to light fastness. In particular, decrease in porosity of the coating was presumed to be beneficial to the photo-stability of the prints.

However, distinct trends between porosity or roughness of the coating and light fastness of the prints could not be found from the present data. This suggests that the major factor influencing the photo-stability of these prints is the chemical stabilization of the dye by the coating components. Materials with a high proportion of hydroxyl functionality, like PVA, have been found to promote light stability due to their capability to act as free radical quenchers.[8] Indication of the favorable impact of PVA-binder was also observed in the previous study.[6]

Light Fastness on Latex-Starch Coatings

Light fastness of ink jet prints on latex-starch coatings (Papers 7-12) after 100 h light exposure as a function of PCC:kaolin pigment ratio is presented in Fig. 2. The type and the amount of ink co-solvent are shown in the legend. Light fastness of these coatings appears to be roughly in the same range with PVA+p-DADMAC coatings. According to the results of the previous study,[6] light fastness of yellow ink jet prints consisting of conventional kaolin and an identical latex-starch polymer system was ΔE* = 30.56 when ink DY 86 2-p 20% was used. Thus, the use of modified PCC and kaolin pigments improves light fastness compared to coatings consisting of conventional kaolin.

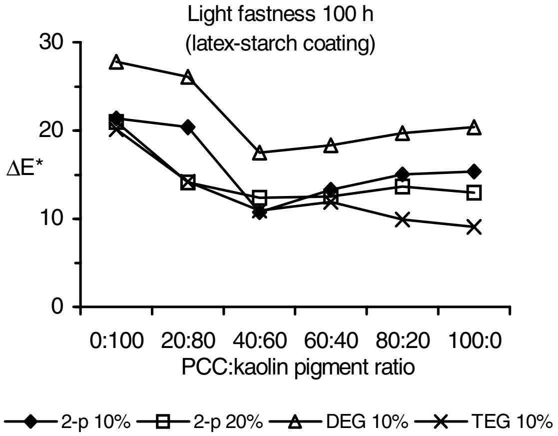

Figure 2. Light fastness of anionic ink jet inks on cationic PCC-kaolin coatings. Coating polymer system: weakly cationic SA-latex + weakly cationic starch. Large ΔE denotes poor light fastness.

The results presented in Fig. 2 imply that light fastness is improved as the proportion of PCC is increased in the coating. However, as the amount of PCC exceeds 40 pph, light fastness does not change markedly anymore or it even slightly deteriorates. Improved light fastness due to increased PCC:kaolin ratio can be partly explained with physical properties of the coatings. According to that data increases in the coating layer porosity and in the surface roughness improve light fastness. However, increase in the average pore diameter of the coating layer result in decreased light fastness. This behavior could be interpreted in such a way that penetration of the ink into the coating layer is enhanced when coating has small pores but large total pore area. Hence, inside the coating the dye molecules would be more effectively protected from exposing light. However, relations with the measured structural paper properties are not completely unambiguous. It is likely that light fastness of these dye-based inks is dependent on specific interactions with kaolin and PCC.

Effect of Ink Co-solvent on Light Fastness

The co-solvent composition of the ink on the other hand appears to have slight impact on light fastness on both PVA and latex coatings, see Figs. 1 and 2. In both cases the use of DEG as an organic co-solvent produces the lowest light fastness, whereas the TEG and 2-pyrrolidone inks seem to be somewhat more stable. In the case of latex-starch coatings, this can partly be explained with the differences in the ink penetration into the coatings, see Fig. 3. Lucas-Washburn equation[9] predicts that the depth of fluid penetration into porous matrix is increased as surface tension of the penetrating fluid is increased and viscosity decreased. The data on ink properties suggest that light fastness is improved as surface tension of the inks increase (the TEG and 2-pyrrolidone inks have higher surface tension than the DEG-ink). In contrast, meaningful correlations between ink viscosity and light fastness cannot be found. Figure 3 implies that the TEG and 2-pyrrolidone inks have penetrated more extensively into the latex coating than the DEG ink. This is likely to enhance the protection of the colorant against light exposure. It has to be nevertheless emphasized that the printed surfaces were uneven especially in the case of the TEG and 2-pyrrolidone inks, which has likely caused some uncertainty to the results.

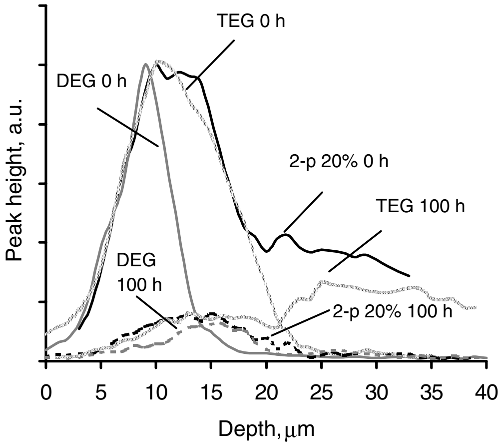

Figure 3. Effects of the type and amount of ink co-solvent and light exposure on the distribution of anionic colorant DY 86 on latex-starch coatings.

Ink solvent composition has inevitably an influence also on the chemical state of the colorant in the print and thus on its photo-stability. It has been found[10] that increased aggregation of the colorant as a result of increased hydrophobic nature of the ink solvent is beneficial for light fastness of ink jet prints. Therefore, photo-stability of DEG inks should be higher than that of TEG ink. However as

Figs. 1 and 2 indicate, the present results are completely opposite. Thus, further investigations are needed to clarify the effects of ink solvent composition on light fastness.

Water Fastness on PVA + p-DADMAC Coatings

Water fastness of ink jet prints on PVA + p-DADMAC coatings (Papers 1-6) as a function of PCC:kaolin pigment ratio is presented in Fig. 4. According to the previous study,[7] water fastness of ink jet prints on coating consisting of conventional kaolin and an identical polymer system (PVA, p-DADMAC) was ΔE* = 25.03 when the DY 86 2-p 20% ink was used Thus, a marked improvement in water fastness is achieved using modified PCC and kaolin pigments in ink jet coatings.

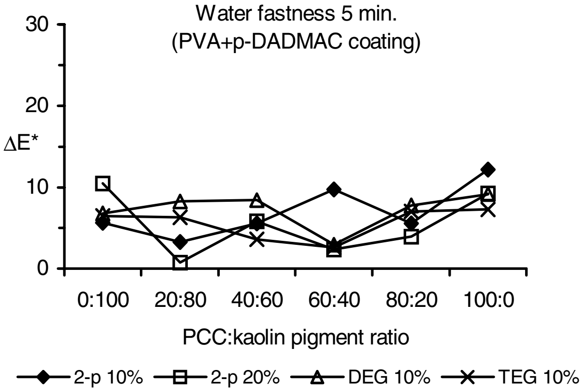

Figure 4. Water fastness of anionic ink jet inks on cationic PCC-kaolin coatings. Coating polymer system: PVA-poly-DADMAC. Large ΔE denotes poor water fastness.

It is evident that neither the amount of PCC:kaolin ratio nor the ink co-solvent type has a marked influence on water fastness on PVA + p-DADMAC coatings. Various paper properties were correlated with the water fastness data, and as in the case of light fastness, straightforward relations could not be found for this sample set. Contact angle measurements indicated that PVA + p-DADMAC coatings are highly wettable, for their contact angles vary between 7.2°-38.0°. Thus, one possible explanation for the poor correlation between structural paper properties and water fastness could be the tendency of PVA-binder to dissolve from the coating during the water immersion. This is illustrated in Fig. 5, which presents the FTIR-ATR spectra of dry PVA-binder and DY 86 2-p 20% print on PVA-p-DADMAC coating before and after water immersion.

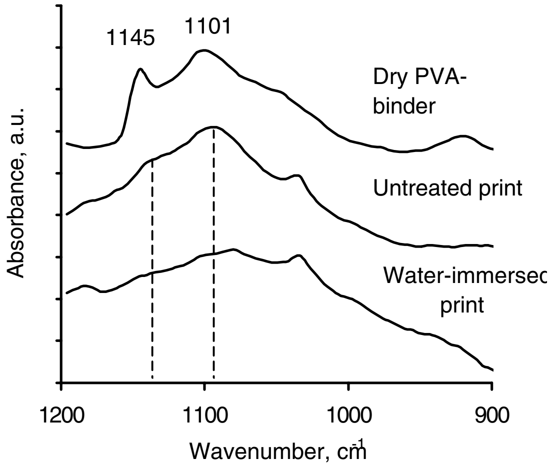

Figure 5. FTIR-ATR spectra of dry PVA-binder and PVA-p-DADMAC coating printed with Y1 2-p 20% ink before and after water immersion. The spectra have been shifted vertically for clarity.

The bands at wavenumbers 1145 cm^{-1} and 1101 cm^{-1} in the FTIR-ATR spectrum of an untreated print originate from PVA-binder.[11] As is evident, they decrease as a result of water immersion, which implies that PVA-binder has dissolved at least partly from the coating. This kind of behavior was already noticed in the previous study.[7] It is likely that the anionic dye molecules are primarily attached to cationic coating with ionic bonds that strongly resist dye dissolution.[3] Therefore, water fastness of the studied prints is very good even though the PVA-binder tends to dissolve. It hence appears that on the PVA + p-DADMAC coatings mainly the chemical interactions between the ink and coating components to contribute to water fastness.

Water Fastness on Latex-Starch Coatings

Figure 6 depicts the effects of PCC:kaolin pigment ratio and ink solvent composition on water fastness of ink jet prints on weakly cationic latex-starch coatings (Papers 7-12). It is evident that water fastness on latex-starch coatings is clearly worse than on PVA + p-DADMAC coatings (Fig. 3), in spite of their hydrophobic nature (contact angles in the range of 93.3°-107.8°). The use of modified PCC and kaolin pigments nevertheless clearly improves water fastness compared to conventional kaolin, for previous results[7] suggest that water fastness of ink jet prints on coated papers consisting of conventional kaolin and an identical latex-starch polymer system was ΔE* = 45.22 when the ink DY 86 2-p 20% was used.

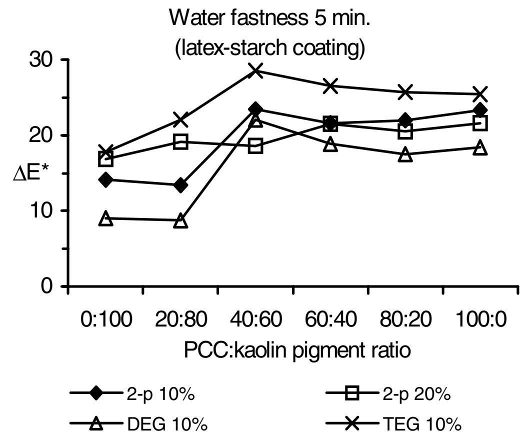

Figure 6. Water fastness of anionic ink jet inks on cationic PCC-kaolin coatings. Coating polymer system: weakly cationic SA-latex + weakly cationic starch. Large ΔE denotes poor water fastness

Figure 6 shows that on latex-starch coatings an increase in the PCC:kaolin ratio results in deteriorated water fastness. This is the most distinct as the amount of PCC is increased from 0 to 40 pph, whereas at higher PCC amounts water fastness is leveled out or even slightly improved. This behavior suggests the presence of two affecting mechanisms and can partly be related to the differences in the structural properties of the coatings. Figure 7 presents water fastness as a function of wettability of the coating, depicted by its contact angle with water.

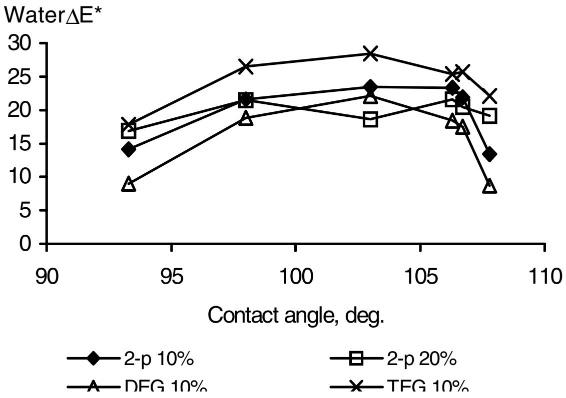

Figure 7. Relation between water contact angle and water fastness of ink jet prints on cationic PCC-kaolin coatings. Coating polymer system: cationic SA latex + cationic starch coatings. Large ΔE denotes poor water fastness

The data suggest that in the contact angle region 93-103°, water fastness is generally deteriorated even though the wettability of the coating decreases. According to the measurements on paper properties, at lower wettability region the structural factors appear to contribute to water fastness. In particular, decreasing porosity and roughness of the coating improve water fastness somewhat. This could be explained by hindered penetration of water into the coating because of the denser coating structure. However, Fig. 7 also implies that as wettability of the coating increases further (contact angle region 103-108°), water fastness begins to improve. The data alludes that at this region the porosity of the coating does not have much relevance anymore. Instead, the surface chemical properties are postulated to be in control. However, decreasing roughness of the coating appears to improve water fastness be somewhat, possibly because of the reduced contact area between the exposing water and the coating surface.

As in the case of light fastness, the effects of ink solvent composition on water fastness are not completely manifest. Earlier study[12] indicated that water fastness is improved as the glycol co-solvent becomes more hydrophobic (DEG → TEG). However, the present data indicates a completely opposite behavior. Meaningful correlations between the measured ink properties and the water fastness values could not be found. Thus, further experiments are needed to clarify the impact of ink co-solvents on water fastness.

Conclusions

Results of this study indicate that marked improvement in light and water fastness of ink jet prints is obtained with the use of modified coating pigments compared to coatings consisting of conventional kaolin. This holds true especially for water fastness. Different mechanisms seem to govern the build-up of fastness properties of the studied dye-based inks on PVA + p-DADMAC and latex-starch coatings. The data on light and water fastness suggest that on cationic PVA + p-DADMAC coatings chemical paper-ink interactions primarily contribute to fastness properties, whereas on weakly cationic latex-starch coatings structural paper properties have relevance as well. However, more extensive understanding of the mechanisms behind light and water fastness of ink jet inks on the studied coatings requires further investigations. The next step is to examine the possible paper-ink interactions in more detail using model compounds and spectroscopic methods.

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Biography

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