

Light Fastness of Ink Jet Prints on Modified Conventional Coatings

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Summary

Production of color ink jet prints with excellent fastness properties generally requires the use of special coated papers. The use of modified conventional coating pigments has been suggested as a means to obtain a coating that would combine the good properties of silica-based ink jet coatings and conventional coatings. This study examined the light fastness of ink jet prints on modified conventional coatings using traditional measurements of physical paper properties and print quality, vibrational spectroscopy and multivariate data analysis methods. The properties of the coatings were altered by using different ratios of coating pigments and different types coating polymers. Experimental inks with a known composition were used for test printings.

The results indicated that the effect of the PCC:kaolin ratio of the coating on light fastness is dependent on the ink-coating combination. With dye-based inks, the role of the structural properties of the coating decreased with an increase in the strength of the chemical paper-ink interactions. In general, the light fastness of pigmented ink was clearly better than that of dye-based inks. Furthermore, the dye-based inks seemed to benefit from a dense coating structure, provided that they had penetrated into the coating layer, whereas a coarse structure of the coating appeared to be advantageous for the pigmented inks. The role of chemical paper-ink interactions was found to be rather complex. However, some evidence of a partial degradation of the colorant molecule was obtained. The effect of the coating composition on photo-fading remained ambiguous, but the interactions between the colorant and the coating polymers nevertheless seem to play an important role.

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 in coated ink jet papers. This kind of coating is well applicable to ink jet printing, owing to its hydrophilic nature, high porosity and ability to fix the anionic ink jet colorants (Bugner 2002; Chapman and Michos 2000; Glittenberg et al. 2002; Lunde 1999; Ryu et al. 1999; Yoldas 1998). For economic reasons, coatings based on modified conventional pigments tailored for ink jet printing, such as PCC or kaolin, have recently been developed to replace silica grades (Glittenberg et al. 2002; Lunde 1999; Jopson 2001). So far, only a few studies related to the fastness properties of ink jet prints on such coatings have been completed. However, knowledge of the underlying mechanisms of fastness properties is essential in looking for good long-term ink jet print quality.

In an earlier study (Vikman 2003 a), the light fastness of ink jet prints on conventional kaolin coatings was investigated, with special focus on the effect of the coating polymer system. The results indicated that the light fastness of the studied dye-based model inks could be explained with reference to both the structural and chemical properties of the coating. In another study (Vikman 2002), modified conventional coating pigments were in most cases found to improve the light fastness of model ink jet inks compared to conventional kaolin coatings (Vikman 2003 a). The improvement in light fastness was 1.0 – 18.3 ΔE^* units, depending on the coating and ink compositions.

The objective of the present study was to further examine the role of chemical and physical paper-ink interactions for the development of the light fastness of ink jet prints on coatings consisting of coating pigments tailored specifically for ink jet printing. This was studied using experimental coatings and inks, and vibrational spectroscopic methods.

Experimental

Materials

The focus of the experimental work was on examining the influence of the pigment composition of the coating on light fastness. This was studied using a pilot paper set and model inks with known compositions. The structure of the coating layer, absorption properties and net-charge were altered by varying the pigment and polymer composition of the coating colors (Table 1). The PCC and kaolin pigments used in the model coatings were specifically tailored for ink jet printing. Two soluble azo colorants with different chemical properties (DY

86, DV 107) and one pigment dispersion (PY 83) were chosen for the inks. The model ink formulations and the data on model ink properties are shown in Table 2. A detailed description of the model coatings and inks is included in the previous paper (Vikman and Vuorinen 2004).

Methods

Coated papers were analyzed to determine their porosity, roughness and surface chemical properties using the methods described in earlier papers (Vikman 2003 a; Vikman 2003 b). Bendtsen air permeability and average pore diameter were used as porosity parameters. Macro roughness of the coating was depicted with Bendtsen roughness, and micro roughness with a profilometric roughness parameter θ_a (theta angle). θ_a micro roughness is the angle of inclination of the roughness profile measured from the paper surface. Polarity was measured with the sessile-drop method (Vikman 2003 b) using hexadecane and glycerol as test liquids. It was calculated as the ratio of the polar force component of the surface energy of the paper to the total surface energy, which is the sum of polar and dispersion force components of the surface energy. The inks were analyzed to determine their pH, surface tension and viscosity (Vikman and Vuorinen 2004).

To examine the effect of the pigment composition of the coating on the light fastness of ink jet prints, printed samples were prepared (Vikman and Vuorinen 2004) and tested for light fastness (Vikman 2003 a) in compliance with the procedures described in the earlier papers. In the light fastness test, the data on test chamber conditions indicated that the chamber temperature CST remained fairly constant throughout the exposure periods, whereas the black standard temperature BST rose somewhat above the set-up value. This may have caused some variation in the results. The color difference ΔE^* calculated as an average of ten CIEL*a*b* measurements was used as a measure of light fastness. It should be noted that the model ink compositions were not optimized for the printer's performance, but rather selected to simplify the analysis of paper-ink interactions. Consequently, they do not necessarily represent the behavior of typical commercial inks. Moreover, the printed areas were extensively striped, instead of the ink being evenly spread over the paper surface, which may have caused further variation in the measured print quality parameters. The ΔE^* values of the unprinted coatings were negligible compared to the printed areas.

To get information on the chemical composition of the samples and conceivable paper-ink interactions affecting light fastness, FTIR-ATR and UV Resonance Raman (UVRRS) spectra

were recorded from unprinted and printed samples. The FTIR method is described at length in the previous paper (Vikman and Vuorinen 2004). The UVR spectroscopy used in this study was a Renishaw 1000 UV, equipped with a Leica microscope and an Innova 300C FreDTM frequency doubled Ar⁺ laser. A CCD camera was used for detecting the scattered light. The laser was operated at a wavelength of 244 nm using an objective with 15x magnification and a resolution of 7 cm⁻¹. The spectrometer was calibrated with diamond and Teflon samples prior to the measurements. Printed samples were rotated during the measurement to prevent burning of the samples. It should be noted that the FTIR spectra of the printed samples contained several overlapping bands originating from the coating components and the dye. Moreover, the analysis of the UVR data was complicated by fluorescence originating from the kaolin-coated samples. These factors have undoubtedly caused some variation in the results.

The measurement data were analyzed using projection methods, principal component analysis (PCA) and projections to latent structures (PLS). A detailed description of the methods and their mathematical background can be found in the literature (Eriksson et al. 2001).

Results

Effect of Physical Properties of the Coatings on Light Fastness

Effect of the PCC:kaolin ratio. Measured paper properties and calculated light fastness values for the model inks are presented in Table 3. The light fastness of the printed samples after 100 h exposure on PVA-poly-DADMAC and weakly cationic latex-starch coatings is presented as a function of the PCC:kaolin ratio in Figs. 1 and 2, respectively. It is evident that the PCC:kaolin pigment ratio and the ink composition both affect light fastness, depending on the ink-coating combination. Fig.1 shows that on PVA-poly-DADMAC coatings, there is no distinct correlation between the light fastness of the dye-based model inks and the PCC:kaolin pigment ratio. In contrast, on weakly cationic latex-starch coatings (Fig. 2), a clear improvement in light fastness of the dye-based model inks is obtained as the proportion of PCC is increased from 0 to 40 pph. With larger PCC amounts, no major change can be observed. However, with both types of coating, the light fastness seems to be dependent on the ink composition. The modified direct dye DV107 generally gives lower light fastness than the direct dye DY86 ink with the same carrier phase composition. Moreover, TEG as a co-solvent gives better light fastness than 2-p and DEG. The best light fastness is obtained with the pigmented ink PY83 with both coating sets. For the PVA-poly-DADMAC coatings, an

increase in the amount of PCC is beneficial, whereas the light fastness of PY83 on latex-starch coatings does not seem to be dependent on the PCC:kaolin ratio.

PLS analyses. The effect of the physical properties of the coating on light fastness was studied by PLS analysis. Six paper-related variables were selected for the analyses: Bendtsen air permeability (B_{air_p}), average pore diameter (Av_PoreD), Bendtsen roughness (B_rough), θ_a micro roughness (θ_a), polarity (Polar) and pH value of the coating color (Color_pH). The analysis was performed for PVA-poly-DADMAC and latex-starch coating sets separately, because the model containing all the data was found to explain mainly the differences between polymer systems, not between light fastness values. Consequently, as the models are based on small sample sets, they should not be used for predictive purposes. The results of the PLS analyses are presented in Table 4. The analysis of the results is based on two components, since the eigenvalue of the third principal component PC3 is smaller than 1 in both models.

The two-component PLS model for the PVA-poly-DADMAC coatings explains altogether 82.3 % of the variation in physical properties of the coating (R^2X Cum), 74.1 % of the variation in light fastness values (R^2Y Cum), and predicts 29.6 % of their variation (Q^2 Cum). A weight plot depicting the effect of the physical paper properties on the light fastness of ink jet prints on the PVA-poly-DADMAC coating is presented in Fig. 3. The PC1 and PC2 explain 43.8% and 30.3% of the variation in the light fastness values, and separate the studied experimental inks roughly into three groups. This indicates that the studied physical properties of the coating contribute in different ways to the light fastnesses of these colorant types. The model suggests that the most important variables affecting the light fastness of the dye-based model inks on PVA-poly-DADMAC coatings would be the θ_a micro roughness and polarity of the coating. In particular, light fastness improves as θ_a micro roughness decreases (the surface of the coating becomes smoother), and as polarity decreases. On the other hand, the light fastness of the pigmented ink PY83 seems to be more dependent on the factors related to porosity and macro roughness, with an increase in Bendtsen roughness and Bendtsen air permeability, and a decrease in average pore diameter being particularly beneficial. In addition, the model suggests that a decrease in the pH of the coating color is advantageous. This is quite likely explained by the increased amount of PCC in the coating color (Table 1).

The PLS model for the weakly cationic SA latex-starch coatings (Fig. 4) explains 94.7 % of the variation in physical properties of the coating, 72.0 % of the variation in light fastness values, and predicts 45.6 % of their variation. In this case, the model separates the model inks

into three groups. If the light fastness of DY86 TEG ink is considered, the properties depicting the structure of the coating seem to have the greatest relevance. The model suggests that a decrease in average pore diameter, and increases in Bendtsen air permeability and Bendtsen roughness would be especially beneficial. For the other dye-based inks, light fastness appears to be related more to the polarity and θ_a micro roughness of the coating, with photo-permanence improving with an increase in polarity and θ_a micro roughness. Finally, the model suggests that the light fastness of the pigmented ink PY83 is governed mainly by the polarity of the coating, along with Bendtsen roughness and average pore diameter. In other words, decreased polarity and Bendtsen roughness, and increased pore size appear to be beneficial.

Effect of Chemical Paper-Ink Interactions on Light Fastness

To obtain information on the effects of chemical paper-ink interactions on possible light-induced changes in the prints, FTIR-ATR and UVRRS measurements, and PCA analyses were carried out. The focus was on the DY86 colorant, since its chemical structure is known.

PVA-poly-DADMAC coatings. In the FTIR-ATR loading plot (Fig. 5) the positive contributions representing the unexposed prints can be assigned primarily to the DY86 colorant, PCC and kaolin pigments (Colthup et al. 1990; Lin-Vien et al. 1991), and PVA polymer (Krimm et al. 1956; Cooney et al. 1994). The bands at 1227, 1192 and 1045 cm^{-1} can conceivably be assigned to the sulphonate group, and the bands at 806 and 736 cm^{-1} to the benzene ring of the colorant (Colthup et al. 1990; Lin-Vien et al. 1991). The positive contributions in the UVRRS loading plot (Fig. 6) represent the DY86 colorant, PVA binder and PCC pigment. The band at 1609 cm^{-1} corresponds supposedly to the benzene ring, and the bands at 1571 cm^{-1} and 1357 cm^{-1} to the naphthalene units of the dye (Trotter 1977; Dollish et al. 1974; Colthup et al. 1990; Lin-Vien et al. 1991). The negative loadings in both the FTIR-ATR (Fig. 5) and UVRRS (Fig. 6) loading plots represent the light-exposed prints. The origin of these contributions is not completely evident. Basically the observed negative loadings could originate either from some photo-degradation product of the DY86 colorant or coating components. The most common photo-degradation mechanism of azo dyes in the presence of light, moisture, and oxygen is generally thought to be oxidation (Kuramoto 1996; Wnek et al. 2002). Considering the suggested photo-oxidation mechanism of the 4-arylaazo-1-naphthols (Griffiths and Hawkins 1972; Griffiths and Hawkins 1977; Kuramoto 1996), formation of 2-methyl-p-benzoquinone as the photo-oxidation product of DY86 colorant might theoretically

be possible. However, the observed negative loadings in Figs. 5 and 6 do not seem to clearly represent either 2-methyl-p-benzoquinone or any of the coating compounds used for the model coatings. Meanwhile, the negative FTIR contributions (Fig. 5) at 1555 cm^{-1} and 1420 cm^{-1} might possibly be associated with the triazine ring of the DY86 colorant, respectively (Larkin et al. 1999; Lin-Vien et al. 1991; Colthup et al. 1990).

Weakly Cationic SA Latex-Starch Coatings. The positive contributions of the FTIR-ATR loading plot (Fig. 7) originate primarily from DY86 colorant, PCC and kaolin pigments (Colthup et al. 1990; Lin-Vien et al. 1991), and the SA latex (Jang and Beom-Seok 2000; Mathakiya et al. 2001). Again, the bands at 1231 , 1196 and 817 cm^{-1} represent the dye, and they may be associated with the sulphonate groups and the benzene ring, respectively (Colthup et al. 1990; Lin-Vien et al. 1991). Similarly, the positive contributions of the UVRR loading plot (Fig. 8) can be assigned for the most part to the DY86 colorant. As in the case of PVA-poly-DADMAC coatings, the contributions at 1609 , 1563 and 1357 cm^{-1} purportedly represent the benzene and naphthalene units, respectively (Trotter 1977; Lin-Vien et al. 1991; Dollish et al. 1974). The negative FTIR-ATR loadings presented in Fig. 7 appear mostly at the same wavenumbers as in the case of PVA-poly-DADMAC coatings (Fig. 5). The two FTIR-ATR contributions at 1555 and 1427 cm^{-1} (Fig. 7), and the UVRRS contributions at 1593 and 996 cm^{-1} (Fig. 8) might possibly correspond to the triazine structure (Larkin et al. 1999) referred to already in the context of PVA-poly-DADMAC coatings. Furthermore, the FTIR-ATR contributions at 3350 , 1651 , 1427 , 995 and 980 cm^{-1} might originate at least partially from the cationic starch, because the starch grade used in this study has FTIR bands at 1653 and 1419 cm^{-1} , and several strong bands in the $1190\text{-}960\text{ cm}^{-1}$ region, as Fig. 9a illustrates. Similarly, the negative contribution in the UVRRS plot (Fig. 8) at 1639 cm^{-1} might correspond to the 1642 cm^{-1} band in the UVRR spectrum of the cationic starch (Fig. 9b). Finally, there are two additional negative contributions at 2916 cm^{-1} and 2851 cm^{-1} , which can be associated with CH_2 groups (Lin-Vien et al. 1991). Neither DY86 colorant nor any of the coating components have bands at these specific wavenumbers, so these bands might possibly originate from some photo-degradation product.

Discussion

Role of Physical Paper-Ink Interactions

In the sample set of the present study, the structural properties of the model coatings were varied by altering the PCC:kaolin pigment ratio. In addition, their surface chemical properties were modified by using two different coating polymer systems. According to the literature (Bugner 2002), pigmented inks are generally thought to form a filter cake on the surface of the coating, instead of penetrating into the coating with the carrier phase, which is typical of dye-based inks. Hence, it would seem justified to assume that the dye-based inks would benefit from the dense coating structure, whereas a coarse structure would protect the pigment particles physically from light fading. Some evidence of this kind of behavior could already be found in the previous studies (Vikman 2003a; Vikman and Vuorinen 2004).

The results of the present study indicate that the physical properties of the coating have opposite influences on the light fastness of dye-based and pigmented inks. Moreover, their role depends on the ink-coating combination in question. The PLS model on PVA-poly-DADMAC coatings suggests that the most important paper-related variables with regard to the light fastness of dye-based inks would be the θ_a micro roughness and polarity, and that light fastness would be improved as the polarity of the coating decreases and its surface gets smoother. On the other hand, the macroscopic structural properties of the coating, or the average pore diameter, Bendtsen air permeability and Bendtsen roughness, would play a minor role according to the model. According to the data presented Table 3, two most important paper-related variables are Bendtsen roughness and Bendtsen air permeability, which both correlate well with the PCC:kaolin ratio of the coating. In contrast, the variation of θ_a micro roughness, average pore diameter and polarity is small, and they do not seem to correlate well with the pigment ratio of the coating. Consequently, it appears that light fastness of the studied dye-based model inks on the PVA-poly-DADMAC coatings is primarily dependent on the chemical paper-ink interactions rather than on the structural factors of the coatings. The θ_a micro roughness and polarity arguably describe only the remaining small variation between the light fastness values obtained with certain ink composition on coatings with different pigment ratios. On the other hand, the light fastness of the pigmented ink PY83 is improved as porosity and roughness at macroscopic scale increase, and as the pore size decreases. This would suggest that the chemical paper-ink interactions would play a only minor role in the light fastness of the pigmented ink.

The effect of the physical properties of the coating on light fastness is somewhat different for weakly cationic latex-starch coatings. This can be rationalized by taking into account the more hydrophobic and less polar nature of the latex-starch coatings compared to the PVA-poly-DADMAC coatings. This supposedly has an influence on the behavior of the studied aqueous model inks when they are in contact with the coating. The PLS results would suggest that the light fastness of DY86 TEG ink is predominantly controlled by the mechanical properties of the coating, with a decrease in pore size and an increase in Bendtsen roughness and air permeability being pre-eminently beneficial. On the other hand, the light fastness of the other dye-based inks would primarily be controlled by the polarity and θ_a micro roughness of the coating, so that light fastness is improved as polarity and micro-scale roughness increase. One possible explanation for this behavior might be the more hydrophobic nature of the TEG ink compared to the other inks. The data presented in Table 3 indicate that the latex-starch coatings are clearly hydrophobic. Consequently, it would seem plausible that the hydrophobic nature of an ink would facilitate its spreading and penetration into the coating, and ultimately obtaining physical protection from photo-degradation. Therefore, the structural properties of the coating are apparently more important for the light fastness of the TEG ink than the polarity or micro-roughness of the coating. In contrast, the spreading and penetration of the other, more hydrophilic dye-based inks is facilitated as the polarity of the coating increases.

For the pigmented ink on latex-starch coating, the results of the PLS analysis indicated that the most important factors are polarity, Bendtsen roughness and average pore diameter. Light fastness is improved as polarity decreases, macro-scale roughness decreases and pore size increases. This contradicts the results obtained on PVA-poly-DADMAC coatings but could again be rationalized by taking into account the clearly more hydrophobic nature of the latex-starch coating. Apparently, the decrease in polarity influences the spreading and penetration of the ink into the coating.

Role of Chemical Paper-Ink Interactions

The role of chemical paper-ink interactions for the light fastness of ink jet prints was studied in terms of dye-based DY86 inks. As is well known, pigmented inks have better light fastness than dye-based inks because of their crystalline structure (Kuramoto 1996). The results of the present study also support this conclusion.

The FTIR-ATR and UVRRS spectroscopic measurements performed for the unexposed and light-exposed ink jet prints on both coating sets suggest that these samples differ in terms of the contributions related to the DY86 colorant. The bands originating from the colorant are generally more abundant in the spectra of unexposed prints, which indicates degradation of the colorant as a result of light exposure. However, the results also seem to suggest that certain chemical groups of the colorant would be more vulnerable to light-induced degradation than others. According to the spectroscopic data, the sulphonate groups and the aromatic and naphthalene rings of the DY86 colorant appear to be more abundant in the unexposed prints than in the light-exposed prints. In contrast, some evidence could be found for both PVA-poly-DADMAC and SA latex-starch coatings that the bands related to the triazine groups would emerge in the spectra of the light-exposed prints. These observations are consistent with the literature, which suggests that the aromatic structures decompose at least partly in the photo-oxidation reaction of the azo colorants (Griffiths and Hawkins 1972; Griffiths and Hawkins 1977; Kuramoto 1996), whereas S-triazine is known to be resistant to light fading (Hu et al. 2003). Moreover, studies on the photocatalytic oxidation of anionic triazine-containing azo dyes in waste waters (Hu et al. 2003) have indicated that the substituents attached to the naphthalene group of a dye molecule were hydroxylated to form organic acids easier than those linked to the triazine group. In particular, this was found to apply to the C-N bond of an azo group and the C-S bond of a sulphonate group.

The possible reasons for the suggested photo-degradation behavior of the DY86 colorant are nevertheless not completely evident. According to the literature, an increase in the hydrogen bonding capability of the host polymer has proven to reduce the fading of certain azo dyes (Clifton and Nugent 2000). Moreover, polymers can act as a barrier towards oxygen, like PVA (Wnek et al. 2002). On the other hand, cationic polymers like PVP and poly-DADMAC have been suggested to destabilize azo colorants (Yuan et al. 1997; Lavery et al. 1998; Shaw-Klein 1998). Another study indicated that the relatively low light fastness of ink jet prints on media consisting of nitrogen-containing polymers would result from the minor aggregating tendency of nitrogen-containing dyes when they are in contact with nitrogen-containing polymers (Wang et al. 1999). The results of the previous studies (Vikman 2003b; Vikman and Vuorinen 2004) indicated that the sulphonic acid groups of the anionic DY86 dye might form ionic bonds with poly-DADMAC. Consequently, these interactions could possibly reduce the tendency of the DY86 colorant to form hydrogen bonds with the surrounding media, primarily with PVA binder, and also its capability to form colorant-colorant aggregates, both

phenomena known to be beneficial for light fastness. This idea is supported by the results obtained in the present study concerning the effect of the physical properties of the coating. If the light fastness of the dye-based model inks on the SA latex-starch coatings is considered, the calculated color difference values ΔE^* correlate negatively with the corresponding water fastness data presented in the previous paper (Vikman and Vuorinen 2004). Then, the interactions between the coating pigments and polymers were suggested to have an effect on the attachment of the colorant to the coating. Therefore, it would seem reasonable to assume that variation in the chemical environment of the colorant would influence the chemical stabilization of the studied dye-based model inks, and thereby light fastness. The results of the water fastness study led to the postulation that particularly the weakly cationic starch would play a role in the attachment of the colorant to the coating. The interactions between the cationic moieties of the coating polymers were suggested to be strongest with kaolin. The FTIR and UVRRS results of the present study give some indications that starch-originated bands would appear also in the spectra of the light-exposed prints. Therefore, the seemingly stronger interaction between DY86 and starch might have a negative influence on the stabilization of the colorant against light fading. Furthermore, FTIR data on the weakly cationic latex-starch coatings also suggest that aliphatic alkyl groups might be present in the light-exposed prints but not in the unexposed prints. Similar behavior was observed in the earlier study (Vikman 2003a) with an unprinted, light-exposed anionic SA latex coating, which did not contain starch. One possible explanation for these new bands might therefore be light-induced degradation of the styrene moieties of the latex. It has been suggested in the literature (Wing-sum Kwan 1999) that UV light absorbers such as styrene might be able to destabilize azo colorants.

Conclusions

The aim of this paper was to obtain an understanding of the mechanisms influencing the light fastness of ink jet prints on modified conventional coatings. This was studied with FTIR and UV resonance Raman spectroscopy and multivariate analysis methods, using experimental inks and coatings with known compositions.

The results indicated that the effect of the PCC:kaolin ratio of the coating on light fastness is dependent on the ink-coating combination. The pigment ratio had a clear influence on the light fastness of the pigmented ink PY83 on PVA-poly-DADMAC coatings, and on the light fastness of dye-based inks on weakly cationic latex-starch coatings. In these cases, the improvement in light fastness could be related to the increase in the amount of PCC in the

coating. The results suggest that the light fastness of pigmented ink is clearly better than that of dye-based inks. Moreover, with both PVA-poly-DADMAC and SA latex-starch coating sets, the physical properties of the coatings have opposite influences on the light fastness of dye-based and pigmented inks. In general terms, the data imply that the dye-based inks would benefit from a dense coating structure, provided that they have penetrated into the coating layer, whereas a coarse structure of the coating would be advantageous for pigmented inks, owing possibly to the different type of penetration into the coating.

The role of chemical paper-ink interactions was found to be rather complex, though some general conclusions can be drawn. On average, the spectra of unexposed and light-exposed prints differed in terms of the contributions related to the DY86 colorant. Particularly, the amounts of sulphonate groups and aromatic moieties were found to decrease as a result of light exposure, whereas some evidence on the presence of the triazine group in the light-exposed prints could be found. This would suggest a partial degradation of the colorant molecule. The effect of the coating composition on photo-fading is not completely clear, but the interactions between the colorant and the coating polymers apparently play a role. The clarification of the exact degradation and stabilization mechanisms of the DY86 colorant nevertheless require more detailed studies with model compounds.

To summarize, the light fastness of the studied model inks was found to be dependent on several factors, which illustrates the intricate nature of the phenomenon. As a rule, the chemical paper-ink interactions seem to have greater influence on light fastness than the physical paper-ink interactions. However, as the chemical interactions weaken, the contribution of the physical properties of the coating becomes stronger.

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Table 1. Compositions of model coatings.

Coating	PCC:kaolin ratio (pph)	Binder	Dispersant	Coating color pH
P0:100	0:100	PVA 10 pph	Poly-DADMAC 3 pph	10.4
P20:80	20:80			10.1
P40:60	40:60			9.9
P60:40	60:40			9.9
P80:20	80:20			9.5
P100:0	100:0			8.2
S0:100	0:100	Weakly cationic	Weakly cationic	10.2
S20:80	20:80	SA latex 10 pph	starch 4 pph	10.0
S40:60	40:60			9.9
S60:40	60:40			9.6
S80:20	80:20			9.0
S100:0	100:0			8.1

Table 2. Compositions and properties of model inks. The abbreviation 2-p refers to 2-pyrrolidone, DEG to diethylene glycol and TEG to tetraethylene glycol.

Ink Code	Colorant Type	Added Co-solvent		Distilled Water, wt. %	pH	Surface Tension, mN*m ⁻¹	Viscosity, mPas
		Type	Amount, wt. %				
DY86 2p1	DY86	2-p	10	86	7.75	58.13	2.41
DY86 2p2	DY86	2-p	20	76	7.50	56.84	2.75
DY86 DEG	DY86	DEG	10	86	7.96	52.08	2.54
DY86 TEG	DY86	TEG	10	86	7.47	58.53	2.77
DV107	DV107	2-p	20	76	8.12	37.76	2.79
PY83	PY83	PG	15	-	7.75	43.97	1.83

Table 3. Data on paper properties and light lastness. In the paper sample notation, P refers to the PVA-poly-DADMAC coating polymer system and S to latex-starch coating polymer system.

Paper	Porosity		Roughness		Surface chemical properties		Light fastness ΔE^* (100 h)					
	Bendtsen air permeability [ml/min]	Average pore diameter [μm]	Bendtsen roughness [ml/min]	θ_a [deg.]	Polarity	Contact angle [$^\circ$ deg.]	DY 86 2-p 10%	DY 86 2-p 20%	DY 86 DEG 10%	DY 86 TEG 10%	DV 107 2-p 20%	PY 83
P0:100	43	0.10	121	3.4	0.43	38.0	14.6	14.1	17.8	10.9	19.9	9.8
P20:80	68	0.11	168	4.0	0.56	14.2	17.0	20.2	25.6	15.9	25.4	9.9
P40:60	167	0.11	218	3.6	0.56	9.6	16.6	18.6	24.0	11.8	23.6	7.8
P60:40	202	0.10	251	3.5	0.57	12.8	14.5	14.0	22.4	13.5	24.4	6.9
P80:20	346	0.11	282	3.9	0.56	19.7	16.9	15.6	21.3	13.5	25.2	9.0
P100:0	419	0.08	304	4.1	0.56	7.2	16.1	17.4	26.6	15.1	26.1	5.1
S0:100	12	0.12	80	3.3	0.01	93.3	21.3	21.0	27.8	20.1	20.4	2.2
S20:80	23	0.12	156	3.7	0.12	107.8	20.4	14.1	26.1	14.2	23.1	4.9
S40:60	40	0.11	226	3.7	0.3	103.0	10.8	12.3	17.5	10.9	12.2	5.2
S60:40	140	0.10	197	3.9	0.35	98.0	13.3	12.5	18.3	11.9	13.5	3.6
S80:20	273	0.09	250	3.6	0.07	106.7	15.1	13.6	19.7	9.9	17.2	8.0
S100:0	378	0.09	220	3.3	0.01	106.3	15.3	13.0	20.4	9.1	18.5	3.4

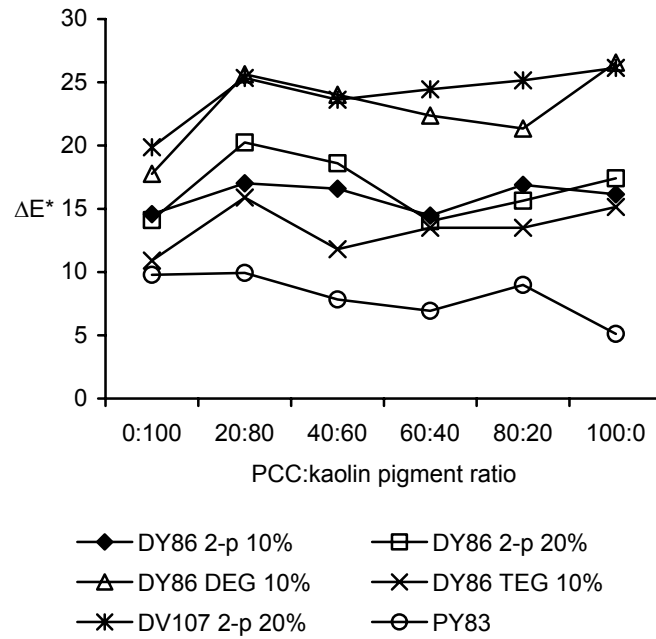


Fig. 1. Light fastness of experimental ink jet inks on cationic PVA-poly-DADMAC coatings. Large ΔE^* denotes poor light fastness.

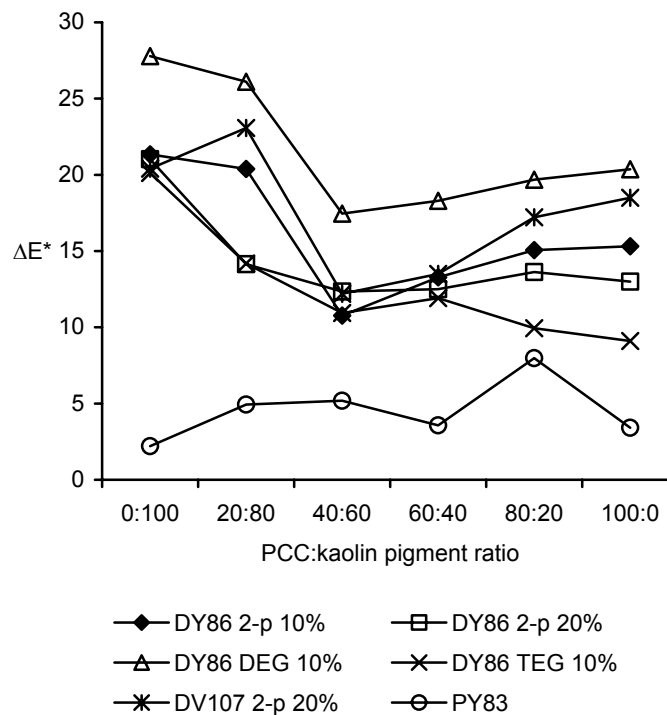


Fig. 2. Light fastness of experimental ink jet inks on weakly cationic SA latex – starch coatings. Large ΔE^* denotes poor light fastness.

Table 4. PLS model for PVA-poly-DADMAC and weakly cationic SA latex – starch coatings. R^2X , R^2Y and Q^2 denote the explained variation of X- and Y-variables, and the predicted variation, respectively.

Polymer system	PC	R^2X	$R^2X(\text{Cum})$	Eigenvalue	R^2Y	$R^2Y(\text{Cum})$	Q^2	$Q^2(\text{Cum})$
PVA-poly-DADMAC	1	0.644	0.644	3.863	0.438	0.438	0.131	0.131
	2	0.179	0.823	1.075	0.303	0.741	0.190	0.296
	3	0.137	0.960	0.824	0.071	0.812	-0.054	0.296
SA latex–starch	1	0.502	0.502	3.012	0.648	0.648	0.456	0.456
	2	0.445	0.947	2.671	0.072	0.720	-0.170	0.456
	3	0.027	0.975	0.164	0.151	0.871	0.203	0.566

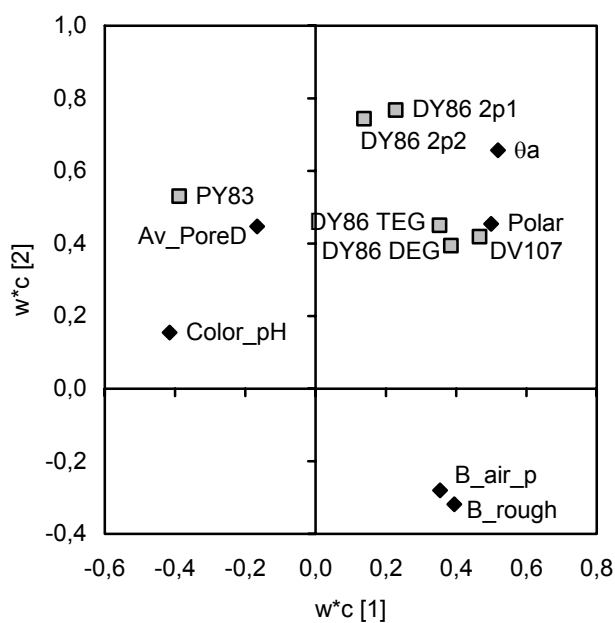


Fig. 3. PLS model depicting the effect of coating properties on light fastness on PVA-poly-DADMAC coatings.

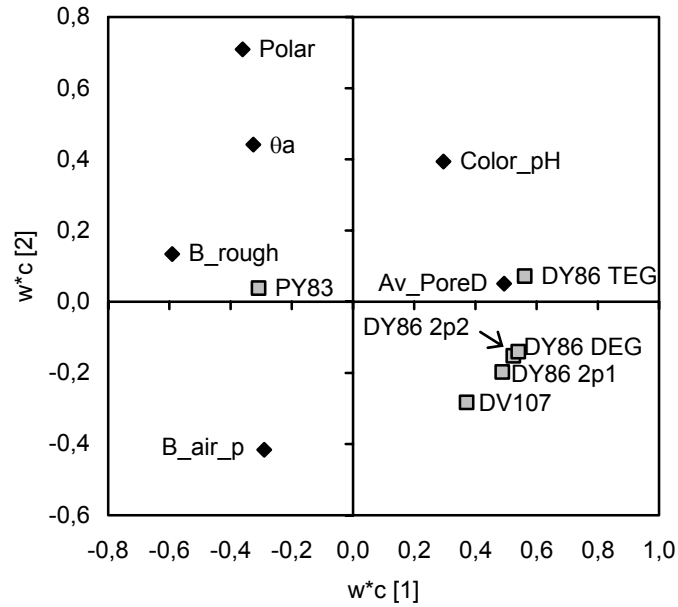


Fig. 4. PLS model depicting the effect of coating properties on light fastness on weakly cationic SA latex–starch coatings.

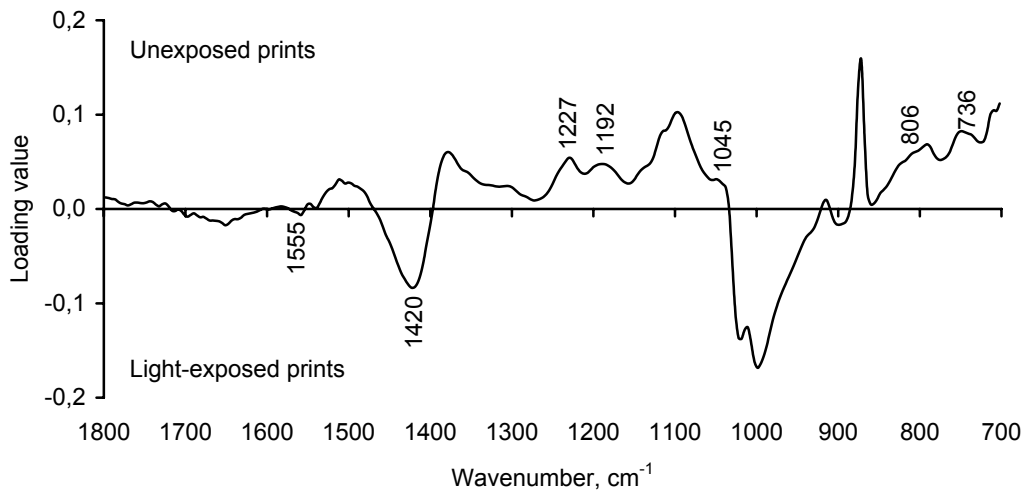


Fig. 5. Loading values of untreated and light-exposed prints on cationic PVA-poly-DADMAC coatings (FTIR-ATR spectra, DY 86 deg ink, all PVA-poly-DADMAC coatings).

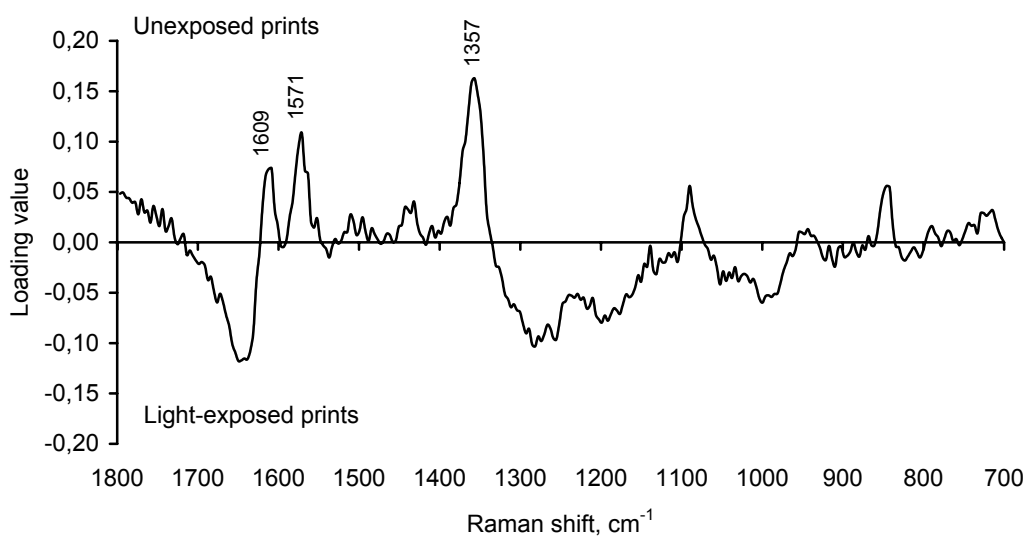


Fig. 6. Loading values of untreated and light-exposed prints on cationic PVA-poly-DADMAC coatings (UVRRS spectra, all DY 86 inks, P0:100 and P100:0 coatings)

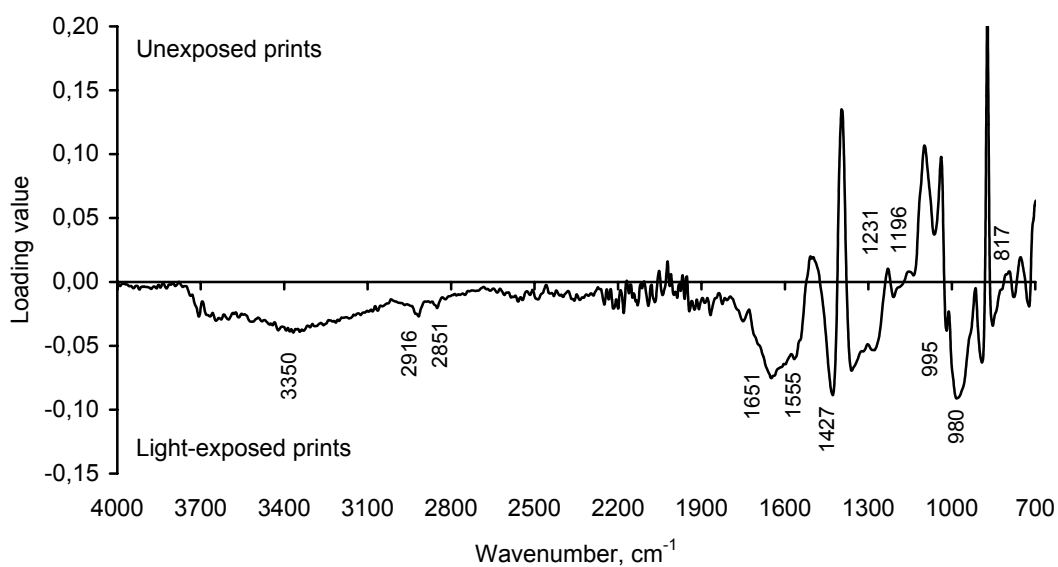


Fig. 7. Loading values of untreated and light-exposed prints on weakly cationic SA latex – starch coatings (FTIR-ATR spectra, DY 86 deg ink, all latex-starch coatings).

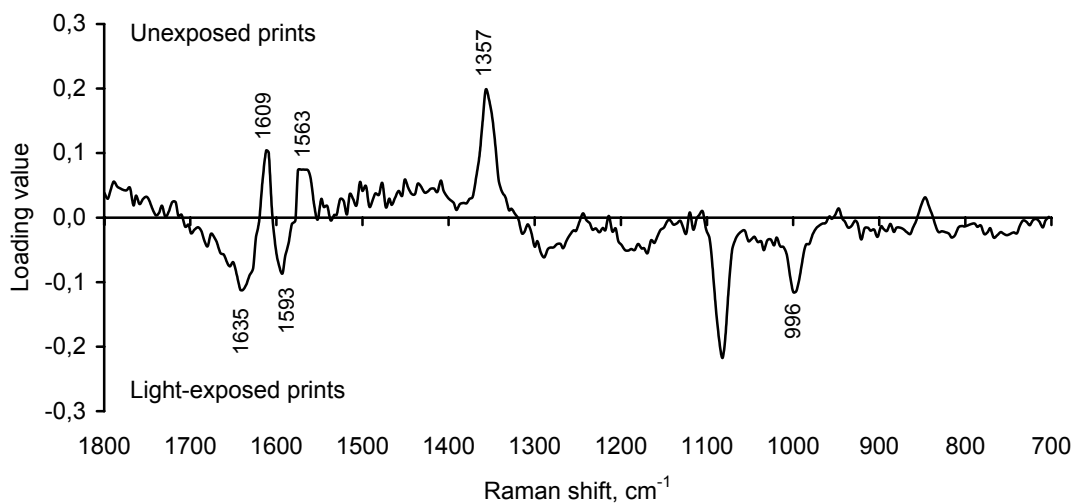


Fig. 8. Loading values of untreated and light-exposed prints on weakly cationic SA latex – starch coatings (UVRRS spectra, all DY 86 inks, S0:100 and S100:0 coatings).

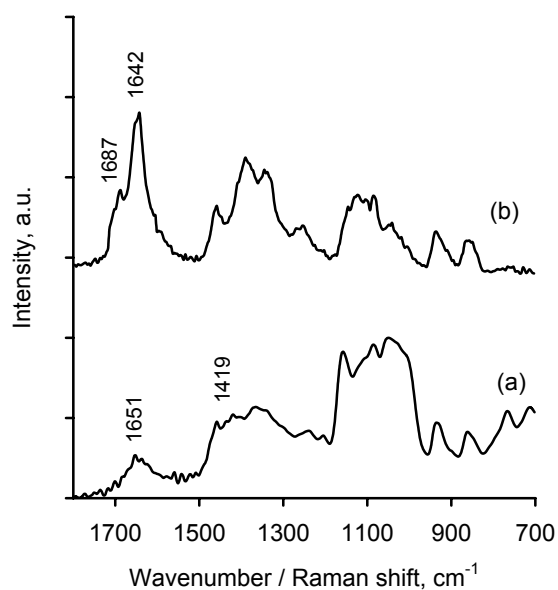


Fig. 9. FTIR-PAS (a) and UVRR (b) spectra of cationic starch. The spectra are vertically shifted for clarity.