

PAPER VII

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In: Colloids and Surfaces A: Physicochemical and Engineering Aspects 2011(380)1–3, pp. 79–88.
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Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Absorption and adsorption of dye-based inkjet inks by coating layer components and the implications for print quality

T.T. Lamminmäki^{a,*}, J.P. Kettle^{a,1}, P.A.C. Gane^{b,c,2}^a VTT Technical Research Centre of Finland, P.O. Box 1000, 02044 VTT, Finland^b Aalto University, School of Science and Technology, Faculty of Chemistry and Materials Sciences, Department of Forest Products Technology, P.O. Box 16300, FIN-00076 Aalto, Finland^c Omya Development AG, CH-4665 Oftringen, Switzerland

ARTICLE INFO

Article history:

Received 4 January 2011

Received in revised form 7 February 2011

Accepted 11 February 2011

Available online 24 February 2011

Keywords:

Diffusion
Absorption
Adsorption
Ionic charge
Permeability
Inkjet printing

ABSTRACT

Inkjet printed surfaces should have good ink fastness properties so that the printed paper can be finished and remain durable during post-treatment and use. To achieve this, the ink colorant requires adequate fixing to the paper surface. In the case of coated inkjet papers, the coating layer surface is engineered to generate good printability using parameters of pore network structure, surface area and surface chemistry of coating pigment(s), and polymer additive properties. The aim of this work was to clarify how the ionic charge, and particularly its distribution in the coating layer, combines with binder to impact on the dye fixation properties of dye-based inkjet inks. The studied pigments were a specially chosen ionically surface-inert organo silica and a modified calcium carbonate (MCC) and binders were non-ionic polyvinyl alcohol (PVOH) and anionic styrene acrylate (SA) latex. Additionally, surface treatment, by applying a cationic polymer (polyDADMAC), was used to study the effect of surface charge on the ink penetration and the resulting print quality. The absorption/adsorption of ink colorant was studied with UV–VIS spectroscopy to evaluate the absorbance resulting from ink dye mixed with model coating structure suspensions, which were prepared by grinding, sieving and suspending in aqueous dispersion. The results showed that addition of PVOH into a coating formulation based on anionically dispersed coating pigment increased the colorant absorption/adsorption. The PVOH supports interpolymer diffusion of the polar ink vehicle, which opens the polymer matrix so that the colorant can transfer into the binder network and remain there. Additionally, providing an opposite charge between the coating and inkjet ink is well known to act to bind the colorant most effectively. When applied to paper, the use of a cationic additive application specifically to the coating layer surface slowed down the ink penetration into the paper structure, by reducing coating permeability, and bound the anionic colorant at the top layer by charge interaction, so that reduced bleeding and improved water fastness could be achieved.

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1. Introduction

There are many different kinds of inkjet inks used in the field across the range of inkjet presses, including both aqueous and solvent-based vehicles, adopting dye and/or pigment colorant. In home and office printers, as well as the first generations of high-speed presses, anionic aqueous-based dyes are commonly used. This means that, to enable the effective fixing of colorant into the top part of a coating layer, it requires a coating which has an opposite ionic charge than that of the ink colorant. In the case of anionic ink, a cationic charge is needed, and it is usually provided by adding

a cationic poly(diallyl dimethyl ammonium chloride) (polyDADMAC) into the coating color [1–5]. Other cationic additives have also been used [6,7], and the role of cationic binder, for example cationic starch, has also been considered [8,9]. The cationic additive application to the top of the coating layer has been studied by Nguyen et al. [10]. The opposite ionic charges mean that the colorant can fix to the coating structure by ionic interactions, by means of long range electrostatic forces (Coulombic attraction).

Kallio et al. [11] studied the adsorption of disazo (Food Black 2) dye onto coating pigments, which did not have dispersant, from polar liquids, such as water (distilled), ethanol, acetone and ethylene glycol, and non-polar cyclohexane. They noticed that the electrostatic interactions are the predominating driving force for the colorant adsorption to kaolin, precipitated calcium carbonate, amorphous SiO₂, TiO₂ and Al₂O₃. In the case of hydrophobic talc, the driving force is hydrophobic interaction. The studied pigments had both acidic and basic surface groups. However, the presence of polar liquid reduced the influence of Lewis acid–base

* Corresponding author. Tel.: +358 40 578 1479; fax: +358 20 722 7604.

E-mail addresses: taina.lamminmaki@vtt.fi (T.T. Lamminmäki), john.kettle@vtt.fi (J.P. Kettle), patrick.gane@aalto.fi, patrick.gane@omya.com (P.A.C. Gane).¹ Tel.: +358 40 593 6013; fax: +358 20 722 7026.² Tel.: +41 62 789 2422; fax: +41 62 789 2410.

interactions. It seems that the adsorption was prevented by the competitive adsorption of polar liquid molecules. Hartus [12] studied the adsorption phenomena with paper fibres and pigments and noticed that the fibres (eucalyptus, deinked pulp (newsprint), softwood sulphate pulp, birch sulphate pulp and TMP) adsorbed diazo type dyes (Food Black and Fast Black) less than the pigments (precipitated calcium carbonate, Kaolin and Talc). The cationic starch had the highest absorption capability.

The surface chemistry of the coating layer affects the liquid and vapour water movement on the surface, for example, how the moisture hydrogen bonds to the surface. In the particular case of dispersed pigments the hygroscopy of the dispersant polymer layer needs to be considered as a dominant factor. As water moves in the porous structure, it itself influences the surface chemistry. The polarity increases with water content increase and this reflects the adhesion of polar components of ink, mottling and rub/abrasion resistance [13].

Donigian et al. [14] showed, furthermore, using thin layer chromatography that silica and precipitated calcium carbonate (PCC) coatings fix inkjet dyes by different mechanisms and the binding strength depends on the pigment type. Their study included coating colors having different amounts of fully hydrolyzed PVOH. The results showed further that the fluid holding capacity is different with these studied silica and PCC pigments. Silica pigments provide a high pore volume for ink and a large specific surface area on which the dye can fix during the ink imbibition. The silica absorbs both diluent/solvent and dye, whereas PCC anchors the dye on the pigment surface while the diluent/solvent penetrates deeper into the coating or base paper [8,14,15]. The binder addition in the coating color can play a role in dye adsorption. The addition of cationic additive in the pigment slurry was shown to retard dye migration in the resulting coating structure.

The objective of this work was to clarify how the ionic charge of the pigment coating structure system combined with either non-ionic polyvinyl alcohol or anionic styrene acrylate latex coating binder influences anionic dye-based inkjet ink adsorption and adsorption. The absorption and/or adsorption of the ink colorant by each coating component was studied using UV–VIS spectrometry, by monitoring the change in absorbance when ink is mixed with an aqueous suspension of previously ground dried coating. The study also considered how a cationic additive on the coating layer surface, when applied to paper, affects the dye and vehicle distribution. The connection to the final print quality was explored by printing with a desktop printer (dye-based inks).

2. Materials and methods

In the first part of our study, we determined the sorption of ink dye into fine particulate “mini-structures” of coating. The pigments used to form the coating layers in this case were either modified calcium carbonate (MCC, OMYAJET B6606³) or epoxy silane colloidal silica (silica, Bindzil CC 40⁴). The silica was not designed for application in inkjet, but we wanted to have a coating pigment that would not adsorb charged ink dye itself and so could permit a study directly of the action of PVOH addition. The MCC was in the form of a dry pigment powder, and the hydrophobised silica pigment was dispersed as slurry by the pigment supplier using an ionic wetting agent/surfactant having an anionic charge (Table 1). This silica was used to provide an inert surface to dye, but that the surfactant present to provide dispersion in water, being anionic, may display some residual attraction for cationic dye. The MCC had a weight median particle diameter of 2.70 μm ($d_{50\%}$) and silica 12 nm. The

specific surface area (BET, ISO 9277) of MCC was 46 $\text{m}^2 \text{g}^{-1}$ whereas with silica it was 220 $\text{m}^2 \text{g}^{-1}$. Polysalz S⁵, sodium polyacrylate, was used as an anionic dispersing agent. Cationicity, when required, was provided by the cationising agent poly(diallyl dimethyl ammonium chloride) (polyDADMAC, Cartafix VXU⁶). The amount of agent used for providing the chosen charge was 0.5 pph. The binder was either non-ionic polyvinyl alcohol (PVOH, Mowiol 40-88⁷) or anionically stabilised styrene acrylate latex (SA, CHP 212⁵). In this work, each pigment with a given dispersing agent or pigment with dispersing agent and a chosen binder is referred to as the respective “coating structure system”. In the case of MCC pigment, the coating color contained 7 pph of binder, and in the silica case it was 15 pph to provide sufficient binding power due to the higher surface area.

The ink was formulated by ourselves, to be sure that it contained only one colorant. The ink contained 5 wt% anionic colorant (Basacid Blue 762, Cu phthalocyanine), 5 wt% polyethylene glycol (PEG 200), 5 wt% diethylene glycol, 0.3 wt% Surfynol 465⁸ (surface active agent) and the rest being water. The surface tension of the ink was determined to be 49.5 mN m^{-1} (23 °C) using a Bubble Pressure Analyser KSV BPA800⁹ tensiometer.

The anionic dye-based ink sorption (in the case of PVOH there exists both absorption and adsorption) as studied with a PerkinElmer UV/VIS/NIR spectrometer (Lambda 900¹⁰). The ultraviolet–visible (UV–VIS) spectroscopy has been utilized in the study of adsorption by Shi et al. [6] and Backfolk et al. [16], but they concentrated on the sorption of inks with different salt-addition to the pigment surfaces, not how the addition of binder on the pigment particle surface affects the UV absorbance of inkjet ink colorant. The UV–VIS spectroscopy quantified the relation of the intensity of incident, I_0 , and transmitted, I , radiation as a function of wavelength in the ultraviolet–visible spectral region. The idea was that the inkjet ink colorant adsorbs in respect to the coating structure system during their mixing as ink is distributed amongst aqueous suspended pre-ground dried coating, and we can detect this as a change of colorant absorbance in the liquid phase with the UV–VIS.

Fig. 1 introduces the sample preparation and analysis procedure that we used. Coating color formulations were first formed into layers. The layers of studied pigment with different dispersing agents and/or different binders were produced in Teflon[®] moulds by letting the slurry dry at room temperature (23 °C). This meant that all components of coating colors remained in the coating layer structure after drying. The dried coating layer was then ground for 2 min with a homogenizing mill (Retsch MM301 Mixer mill), adopting three grinding balls with diameter of 1 cm and at a rotation frequency of 30 s^{-1} . By grinding the pigment coating structure systems we wanted to avoid the extended pore network structure effect present in coating cakes or layers, which normally acts to limit accessibility to the constituent surfaces over time in respect to permeation, thus enabling the structure surface-related phenomena to be isolated. We assumed that the grinding effect was similar for each coating layer, and that this subsequent sample treatment was assumed to provide a sufficiently homogeneous distribution of structural components despite the potential for some soluble species migration during drying. The grinding of the pigment coating systems might also expose new surfaces of the pigment that

⁵ BASF Aktiengesellschaft, Paper Chemicals, 67056 Ludwigshafen, Germany.

⁶ Clariant International AG, Rothausstrasse 61, CH-4132 Muttenz 1, Switzerland.

⁷ Kuraray Specialities Europe GmbH, Building D 581 D-65926, Frankfurt am Main, Germany.

⁸ Air Products PLC, Hershaw Place Technology Park, Molesey Road, Hershaw, Walton-on-Thames, Surrey KT12 4RZ, United Kingdom.

⁹ KSV Instruments Ltd., Höyläämötie 11 B, FIN-00380 Helsinki, Finland.

¹⁰ PerkinElmer, 940 Winter Street, Waltham, Massachusetts 02451, USA.

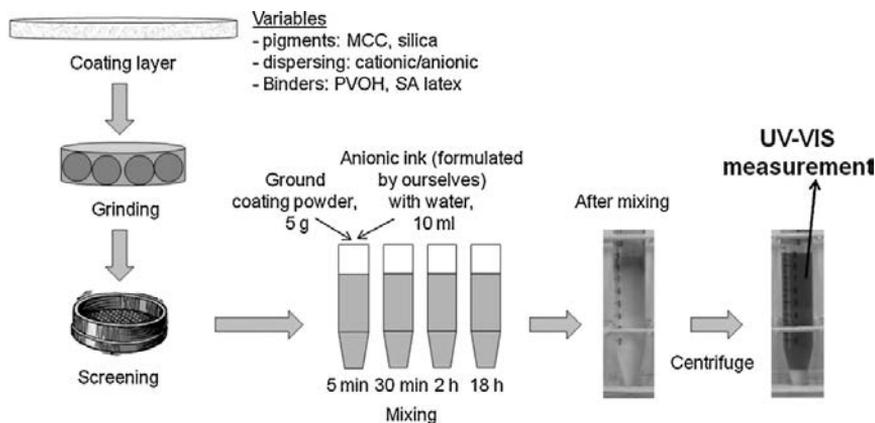
¹¹ Polytetrafluoroethylene, Du Pont.

³ Omya AG, Postfach 32, CH-4665 Oftringen, Switzerland.

⁴ Eka Chemicals AB, Industrial Specialties, SE-44580 Bohus, Sweden.

Table 1The studied MCC and silica coating structure systems. Zeta-potential was measured with AcoustoSizer II^a.

Coating structure system	Dispersing agent, amount	Binder, amount	Zeta-potential, mV
MCC powder in water	–	–	21
Anionic MCC	Sodium polyacrylate, 0.5 pph	–	–37
Anionic MCC + 7 pph PVOH	Sodium polyacrylate, 0.5 pph	PVOH, 7 pph	–12
Anionic MCC + 7 pph SA	Sodium polyacrylate, 0.5 pph	SA latex, 7 pph	–37
Cationic MCC	polyDADMAC, 0.5 pph	–	24
Cationic MCC + 7 pph PVOH	polyDADMAC, 0.5 pph	PVOH, 7 pph	11
Silica	N/A	–	–22
Silica + 15 pph PVOH	N/A	PVOH, 7 pph	–19

^a AcoustoSizer II is a product name of Colloidal Dynamics/Agilent, Technologies (Finland Oy), Linnoitustie 2B, FI-02600 Espoo, Finland.**Fig. 1.** The treatment of coating structure before UV–vis analysis in the UV absorbance study.

would otherwise be covered with binder polymer, or break the binder films, which in the porous coating system would have been unavailable for the colorant. However, given the relative low energy of homogenizing, this is expected to be minimal. The ground powder was screened through a 300 μm slit screen, to ensure that the coating powders did not contain inhomogeneous lumps and that the particles of the resulting coating “mini-structures” were as monosize as possible.

The anionic formulated ink was diluted with water (7 cm^3 ink per dm^3 water, the original ink contained 5 wt% dye colorant). 10 cm^3 diluted ink was mixed with 5 g of the produced coating structure system powder, to produce a suspension of the powder particles in the diluted ink. The mixing was continued for a series of such samples over selected times (5 min, 30 min, 2 h and 18 h). Each mixture was centrifuged and the remaining dye concentration in the filtrate was analyzed in the UV–VIS spectrophotometer. The experiments were carried out at room temperature (23 ± 2 °C).

In the other part of this study, the connection between cationic charge of the paper coating surface, as it appears on the paper itself, and the print quality was assessed by surface application of polyDADMAC (Cartafix VXU⁶) with an Erichsen¹² film applicator (Model 288) followed by drying in an oven at 105 °C for 5 min. The applied polyDADMAC amount was 2.0–3.2 g m^{-2} . The polyDADMAC was applied on the same double-coated fine papers (pre-coating 7 g m^{-2} and 8 g m^{-2} top-coating, base paper 67 g m^{-2}) as reported by Lamminmäki et al. [17]. The top-coating of double-coated paper contained 100 pph inkjet PCC (OMYAJET B5260³) and either PVOH (Mowiol 40–88⁷) or SA latex (Latexia 212 provided by

Table 2

The recipes and properties of top-coating colors.

Component	Coating color			
	7 pph PVOH	30 pph PVOH	7 pph SA	30 pph SA
Inkjet PCC	100	100	100	100
PVOH	7	30	–	–
SA	–	–	7	30
Polysalz S	–	–	6	6
<i>Measured values</i>				
Solids content, %	25.1	22.2	28.1	30.9
Zeta-potential ^a , mV	2.4	2.6	–37.0	–32.8
pH	8.4	8.4	8.5	7.9

^a Measured with AcoustoSizer II.

Ciba Specialty Chemicals¹³). The formulation of the top-coatings is shown in Table 2. The zeta-potentials of the coating colors were measured with an AcoustoSizer II by using a dilution ratio of 1:1000 (de-ionized water). The pre-coating had 100 pph of ground calcium carbonate with a narrow particle size distribution having 60 wt% < 1 μm (Covercarb 60³), 12 pph styrene-butadiene latex (DL966¹⁴) and 0.6 pph carboxymethylcellulose (Finnfix 10¹⁵).

The sorption properties of the surfaces of cationically treated, and the same coating without treatment, were analyzed with a capacitance-based Clara device, as previously described by Lamminmäki et al. [17] using water (de-ionized) and the same formulated cyan dye-based ink that was used in the UV–VIS analyses. As the liquid permeates the pore structure, so the capacitance of the dielectric coating structure changes. The temperature of water was

¹² Erichsen GmbH & Co., Am Iserbach 14, D-58675 Hemer, Germany.¹³ Ciba Specialty Chemicals, Klybeckstrasse 141, CH-4002 Basel, Switzerland.¹⁴ Dow Suomi Oy, Urho Kekkosenkatu 7 B, PL 117, 00101 Helsinki, Finland.¹⁵ Finnfix is a trademark of Noviant Oy, Malminkatu 34, 00100 Helsinki, Finland.

23 °C. Two different temperatures of the ink were studied, 23 °C and 40 °C, to establish any effect that might occur in commercial inkjet printing presses, which can operate at elevated temperatures (40 °C is typical for an ink in a Versamark® press, for example). An ink at higher temperature may have different viscosity, dynamic surface tension and drying speeds. In the Clara measurement, the applied amount of liquid in the chamber of the device was 5 cm³. The measurements were made after equilibration under a relative humidity of 50%RH and 23 °C temperature. The result is expressed as a curve of capacitance change during time as the liquid penetrates through the sample in the z-direction. The resulting curve is an average of five parallel measurements. The external pressure was 0.10 bar, which is the calculated pressure that the 15 pl size droplet having a speed of 15 m s⁻¹ (density 1000 kg m⁻³) creates at the paper surface as the droplet hits to the paper surface (used in a Versamark® press). The pressure was estimated by utilizing the common pressure, density and speed formula.

The without and with polyDADMAC addition samples were printed with an HP DeskJet 3940 desk-top inkjet printer using constant settings (the substrate was kept as “plain paper” and the print quality “normal”). The printing was carried out at room temperature 23 ± 2 °C. The print quality was evaluated by print density (GretagMacbeth D196) as well as ink bleeding in respect to line width and raggedness, analyzed with a QEA personal IAS¹⁶ system. The observed line width is defined in relation to an original target line width, where the extra width has been caused by the spreading and/or mixing of the inks as measured by the gray values following the standard ISO 13660. The raggedness describes the uniformity of the line edge area.

A water fastness test was used as an indication of colorant fixing properties to the paper coating surface. The printed single-color compact area was immersed for 5 min into de-ionized (23 °C) water. After that the samples were left hanging to dry in the dark at 23 °C temperature and 50%RH moisture content overnight (at least 17 h). Similar methods have been used in other studies [18–20]. The color change ΔE^* was measured with a GretagMacbeth SpectroEye¹⁷ spectrophotometer. In the spectrophotometer we used a configuration of 2° measuring angle, D65 illuminant, UV-filter on and the coated unprinted paper defined as a white area. CIELab* values and print densities were measured before and after the water-treatment. ΔE^* was calculated following the standard equation of SCAN-P 89:03.

3. Results and discussion

3.1. Anionic colorant absorption/adsorption in the coating structures

The zeta-potentials of the studied coating formulations are introduced in Table 1. The highest anionic charge was seen for the coating color formulations having anionically dispersed MCC or anionic MCC with SA latex. The addition of polyvinyl alcohol seems to decrease the anionic charge, although the PVOH has a non-ionic nature. This suggests that the PVOH is associating with the charged species. The highest cationic charge was observed with the MCC pigment with cationic dispersing.

The value of the UV–VIS absorbance peak was detected at a wavelength of 610 nm (Fig. 2), where the sorption maximum of cyan dye was located (actually, the “orange” region). The maximum absorbance ($A = -\log(I/I_0)$) value of colorant at 610 nm was about

3.7. Repetitive trials showed that the values varied between ±0.2 from the average value.

We did not calculate the adsorption amount of dye per sample surface area as, for example, Shi et al. [6] did, because the target was to define the differences between the coating structure systems as they would appear during the wetting regime, i.e. the pigment with cationic/anionic dispersing and the pigment with different dispersing system combined with different binder type addition at the ambient moisture condition. This was because the specific surface area of each coating structure system, which would have been required to define specific adsorption, could not be measured reliably using the BET method under the condition of application, due to loss of structural moisture during the evacuation necessary for sample preparation. The calculated theoretical greatest dye amount that the coating structure system could adsorb in our method was 0.698 mg (dye) g⁻¹ (coating structure system), assuming that the color change in the liquid phase is caused solely by the colorant adsorption into the coating structure system and not the other components in the ink. The calculation is based on the information that the original dye contained 5 wt% of colorant and 7 cm³ of ink was mixed into 1 dm³ water. In the UV–VIS analysis, 10 cm³ of this diluted ink was mixed with 5 g of the respective coating structure system. However, it is very likely that the other components of ink move into the filtrate, too, but they have probably a very small influence in the measured color because they were effectively transparent components in the color region. The effect of cationic polyDADMAC fixing to the coating pigment was clarified by washing the pigment with 0.5 pph polyDADMAC repeatedly, each with 20 cm³ de-ionized water (per washing time).

Fig. 3 shows how the anionic ink adsorbed amongst the different coating structure systems as a function of time. The absorbance of the filtrate from the MCC pigment powder (as received from the pigment manufacturer) was increased from 2.3 to 2.9 during the increase of mixing time, indicating some loss of sorption with time. When 0.5 pph of anionic dispersing agent was added, the absorbance value of the extracted filtrate rose to the level of 3.1 meaning that dispersing agent prevented colorant adsorption especially at the shorter time, below 2 h. The addition of 7 pph PVOH in the anionic dispersed MCC decreased the absorbance values showing that it supported the sorption process. Similar effects of PVOH were detected with silica. On the other hand, the SA latex containing coating structure mix had very similar results to that of the anionic dispersed MCC containing structure. Latex had no effect on absorbance, suggesting that it plays an inert role in respect to dye interaction. When the MCC pigment was dispersed with the cationic dispersing agent, the absorbance results were clearly lower, confirming the strong adsorptive tendency.

Fig. 3 shows that addition of anionic dispersing agent increased the light absorbance of the anionic colorant in the filtrate from the MCC pigment powder-in-ink suspension. The increase of light absorbance means that a reduced amount of colorant has adsorbed within the pigment coating structure system and so more colorant stays in the liquid phase. The result indicates that the MCC pigment powder has a surface chemistry, for example dispersing agent, already before dispersion in the ink which could attract, to some extent the colorant, whereas the anionic dispersing agent in the pigment system makes the pigment less attractive for the anionic colorant. However, the MCC pigment had quite similar zeta-potential (measured from the mixture where MCC pigment powder was mixed into water) as that of the cationically dispersed MCC, but still the colorant sorption remained on a higher level as in the case of cationic MCC or cationic MCC with PVOH. This indicates that in the case of MCC powder the cationic groups are not as available as in the cationically dispersed MCC systems. They could, therefore, be either in the pigment intra-particle pore space, and thus harder for the ink colorant to fix there as the colorant might need first of

¹⁶ Quality Engineering Associates, Inc., 99 South Bedford Street #4, Burlington, MA 01803, USA.

¹⁷ Electron Microscopy Sciences, P.O. Box 550, 1560 Industry Road, Hatfield, PA 19440, USA.

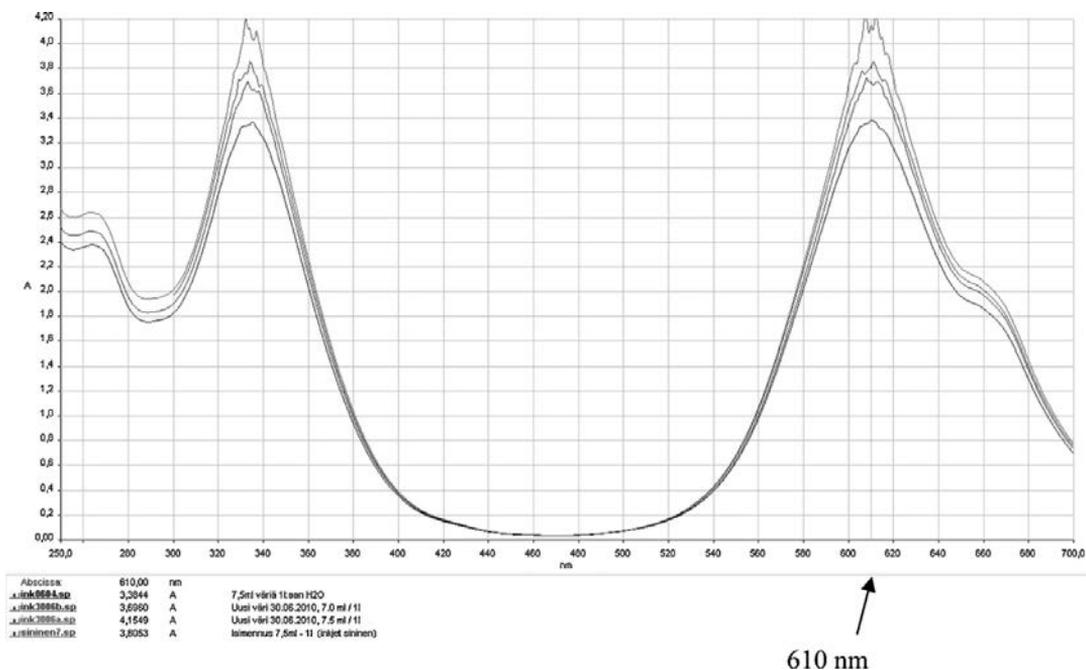


Fig. 2. An example of UV-vis result curves from different concentration of colorant dye.

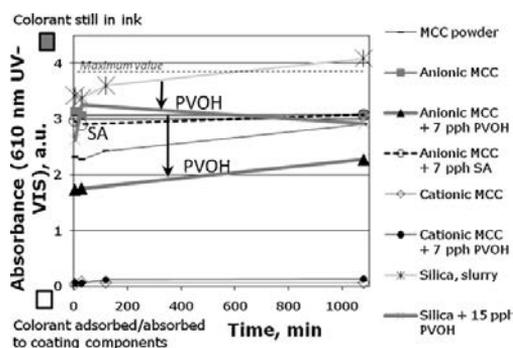


Fig. 3. The UV-vis light absorbance of liquid containing anionic cyan dye after the mixing procedure of different pigment systems. The absorbed liquid contained 7 cm³ ink which was diluted to 1 l water.

all to pass by anionically charged outer surfaces, or the cationic charge sites are distributed together with neighbouring anionic sites, which would act to repel the dye so making an approach to sorption sites also limited. In the case of cationically dispersed MCC the cationic additives and original cationic sites now locate all over the pigment surface and the anionic colorant can bind more easily without neighbouring charge repellancy.

Fig. 4 illustrates that not all the cationic polyDADMAC was fixed on the surface of MCC pigment. After the eight washings of the pigment coating structure system there was no further polyDADMAC extracted in the filtrate. This can indicate that during the inkjet ink imbibition in practice some excess may also be released away into the water phase. From the data in Fig. 4 it was possible to calculate that 15.7% of the originally added 24.9 mg g⁻¹ was recovered during washing.

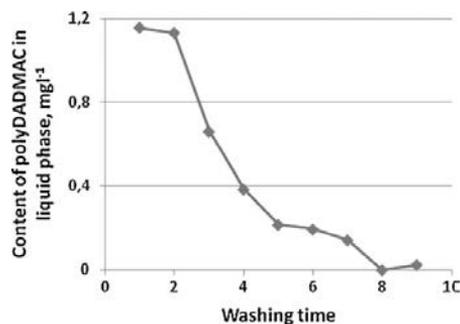


Fig. 4. The content of polyDADMAC in the filtrate after washing. At first, 5 g of pigment (dispersed with 0.5 pph of polyDADMAC) was mixed with de-ionized water (20 cm³) for 1 min, followed by transfer to a Büchner funnel and filtration. The filtrate was dried and the grammage was measured. After that a further 20 cm³ of water was added and the filtrate analyzed. The procedure of water addition was repeated eight times with analysis repeated after each dilution (call here washing). We assumed that the pigment remained on the filter paper (the filtrate was after each washing was transparent).

The addition of 7 pph PVOH in the anionically dispersed MCC pigment increased the colorant transfer into the pigment mixture (Fig. 3). A similar difference was noticed with the comparison of silica pigment and silica with PVOH. Both PVOH-containing coatings still had anionic charge, as the zeta-potential results indicated. The PVOH has non-ionic nature and so ionic interaction cannot explain the higher sorption. One explanation is that the diffusion of water molecules opens the PVOH polymer network so that the colorant can follow the water molecules into the amorphous part of the PVOH network and therefore this pigment coating structure system can take up more colorant. The colorant remains in the PVOH network (Fig. 5). However, when the added binder was anionic

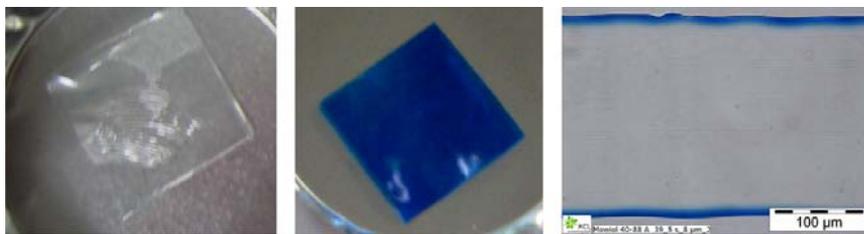


Fig. 5. The anionic colorant ink absorption is seen to occur into the PVOH film, but not into the SA latex film (thickness 205–260 μm): observation recorded after 5 s contact.

styrene acrylic latex the absorbance was very similar to the anionically dispersed MCC pigment. There are no opposite ionic charge groups which could bind the anionic colorant and the hydrophobic nature of SA latex prevents the diffusion of water molecules into the polymer network and so also the colorant diffusion into the binder polymer.

As the MCC pigment was dispersed with extra cationic dispersing agent and this pigment system was analyzed with UV–VIS spectrophotometer, the colorant sorption was clearly greater than in any anionic system and even in the original cationic pigment case. The UV–VIS results of additionally cationically dispersed MCC pigment after 2 h mixing time were on the level of 0.07 and the addition of 7 pph PVOH into this system increased it a little further to the level of 0.12. The addition of PVOH to the cationically dispersed MCC had a minimal effect on the results, and the added PVOH does not prevent the colorant sorption. The differences are not statistically significant. It seems that the cationic charge of the coating pigment system binds the anionic colorant effectively even in the lower zeta-potential area (11 mV) when the non-ionic PVOH polymer is either on the pigment surface, and/or within the intra-particle pores and/or distributed throughout the structure. This demonstrates the preferential action of Coulombic attraction over a distance rather than the contact-dependent diffusion into the binder polymer matrix. On the other hand, the water molecules diffuse into hydrophilic PVOH network and the colorant transfers into the polymer network in the same way as in the case of the anionic pigment coating structure system. The long mixing time did not significantly release the colorant from the pigment system, supporting the expected good water fastness.

The values of absorbance in Fig. 3 seem to increase somewhat in the cases of the anionic structures over time. The long time (18 h) of physical mixing releases some of the adsorbed colorant molecules back to the liquid. The non-permanence could be related to competitive adsorption between polyacrylate and the anionic dye. It may be assumed that simple addition of polyacrylate does not ensure complete adsorption within energetic mixing. Thus, the progressive adsorption of excess polyacrylate, its larger polymer structure displacing the dye competitively, could be responsible for dye release. The absorbance results of cationic structures, on the other hand, stayed very similar, also after the longest mixing time. The colorant has bound so fast to the pigment system that the long physical mixing time fails to release any more of the colorant.

The use of the organo silica, although not designed for inkjet application, allows us to assume that its surface is virtually inert in terms of charge-driven sorption – much like the polymer of the latex binder – and so makes an excellent control pigment for determining if there are any intrinsic charge properties of the MCC by means of comparison. The UV–VIS results of the filtrate extract from the mixes with anionically dispersed intrinsically hydrophobic silica pigment were on a higher level than the results of anionic MCC pigment, indicating that MCC pigment system adsorbed more ink colorant than the organo silica, even though the silica slurry had lower zeta-potential (less anionic, -22 mV) than MCC (-37 mV).

This indicates that the MCC pigment has some cationic components on the pigment surface that could attach the colorant molecules, which are clearly lacking in the case of the organo silica. The PVOH addition did not change the situation. In this case, there are also differences between the binder content. If we assume that binder forms a uniform layer on the pigment surface, we can calculate that the 15 pph PVOH addition could theoretically produce about 0.47 nm thickness of a uniform binder layer on the silica pigment surface, and the 7 pph PVOH on the MCC surface a 1.13 nm thick layer. In this calculation, we recall that the specific surface area of pigment was $220\text{ m}^2\text{ g}^{-1}$ for the silica and $46\text{ m}^2\text{ g}^{-1}$ for the MCC, and the specific gravity of PVOH was 1.26 g cm^{-3} . In the thicker PVOH layer, the swelling of binder permits the opening of the polymer network more. This kind of sorption difference in the results could be seen during the first 2 h. However, the binder content increase from 7 pph to 15 pph meant that the sorption properties of the coating layers were changed. In the case of the studied coatings, the sorption speed of the top-coatings applied on the pre-coated paper surface, as measured with drop penetration (CAM 200⁹) using a $6\ \mu\text{l}$ water drop, decreased from $0.47\text{ mm s}^{-0.5}$ to $0.17\text{ mm s}^{-0.5}$, respectively. This can also have some effects on the studied formulation powders, especially for the larger particle size agglomerates or when soluble PVOH binder is itself adsorbed onto the coating pigment surfaces.

3.2. The effect on liquid ink penetration of cationic additive applied directly to the paper coating surface

The application of a few grams per square metre of polyDADMAC on the double-coated fine paper surface slowed down the speed of water and dye-based ink sorption into the structure (Fig. 6). The polymer acted to close up the surface layer, i.e. reduce permeability, so that it took more time for liquid to penetrate into the structure. The water produced the lowest capacitance values in the Clara equipment, then the anionic dye-containing ink at the temperature of $23\ ^\circ\text{C}$, and the quickest sorption was seen using the same ink at the higher temperature of $40\ ^\circ\text{C}$. Fig. 7 shows two examples of the variation of the Clara results.

Fig. 6 shows that cationic additive application on the anionic PCC coating, which had 7 pph of SA latex as a binder, has partially decreased the liquid penetration through the sample comparing to the penetration of the surface without the cationic additive. Clearly, the addition of polyDADMAC has dampened the capillary effect as the curve becomes monotonic. The difference exceeds the variations in the results. The $2.0\text{--}3.2\text{ gm}^{-2}$ polymer layer did not totally cover the coated paper surface, so that the liquid has possibilities to penetrate through “holes” into the structure. On the other hand, the ink vehicle can diffuse into the polymer layer, go through it and continue the penetration into the coating part of the structure by permeation flow. The polyDADMAC surface has a minimum at the 40 ms time. This could be the surface between the applied polymer and the coating layer. On the other hand, Fig. 4 shows that some of the polyDADMAC washed out from the MCC pigment coating

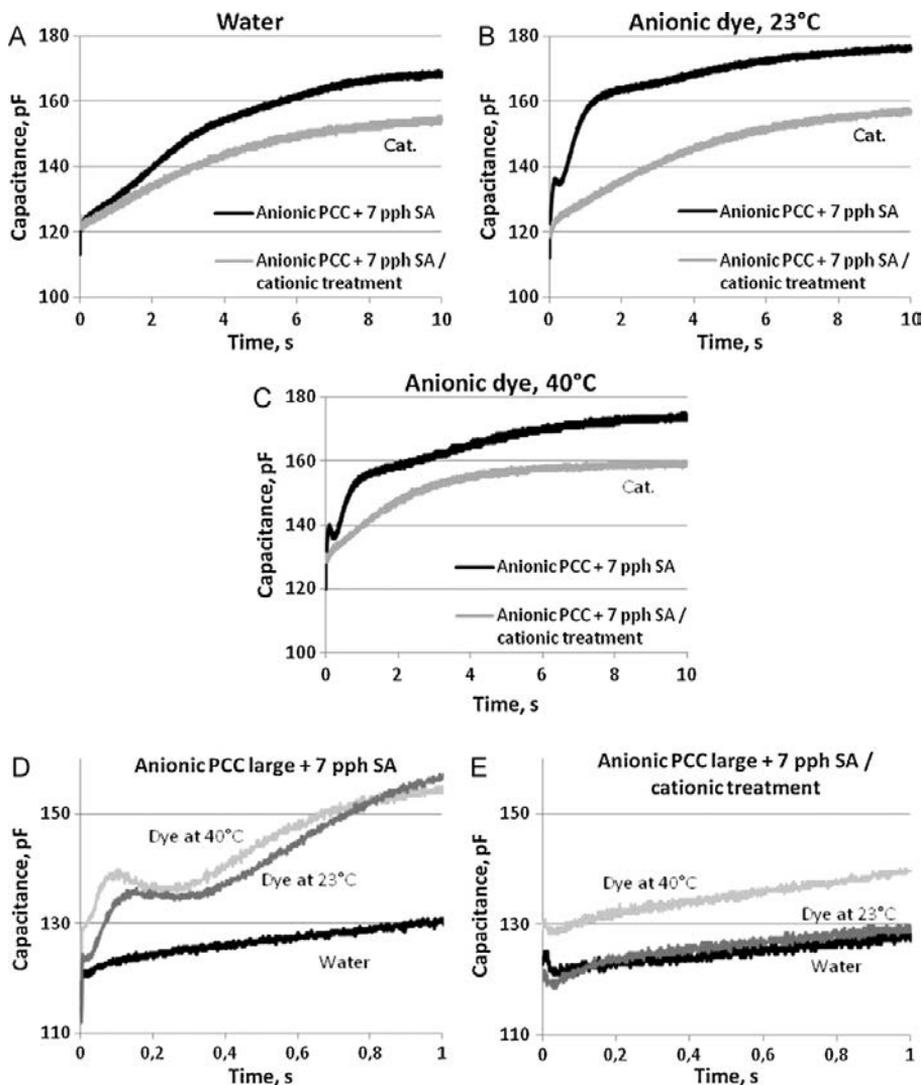


Fig. 6. The capacitance changes of a top-coated paper, having a top-coat of anionic PCC + 7 pph SA latex, and same surface with the added polyDADMAC (cationic) treatment plotted against the time. A, B, C – the liquids were water, anionic self-made cyan dye ink at 23 °C and the same ink at 40 °C, respectively. The penetration of water and dye-based inks (23 °C and 40 °C) into the anionic PCC coating (D) and polyDADMAC applied surface (E). The external pressure was 0.10 bar.

structure. Therefore, it is possible in this case of far excess polymer that some of the polymer transfers with ink vehicle into the coating layers and there affects the liquid penetration. The washing out can affect the properties of ink vehicle by increasing the viscosity, changing the surface tension or increasing the cationicity, and this could reflect in the location of local minimum. Additionally, the measurement method relies on the definition of capacitance under constant geometrical conditions, i.e. capacitance $C = \epsilon A/d$, where ϵ is the dielectric constant and A and d are the geometrical parameters of planar area and sample thickness, respectively. Swelling of polymer dispersants and additives, as well as of the underlying fibrous matrix, clearly can affect the result strongly, especially in respect to increasing structural thickness.

The same 7 pph SA latex-containing coating layer was analyzed in our previous paper, Lamminmäki et al. [17], about two years ago.

In both measurement series, the same cyan dye-based commercial ink and same external pressure, 0.10 bar. The only difference was that the paper was stored for two years at a temperature 23 ± 2 °C and relative moisture content 50 ± 5 RH%. In the previous measurement, we did not notice a local minimum at 0.2–0.3 s. The reason behind this can be in the ageing of latex polymer and the weakening of fibre–fibre bonds.

Fig. 5 illustrates that the 40 °C ink penetrated quicker through the paper than the lower temperature ink. The velocity of particles and macromolecules depends on temperature, viscosity of the surrounding fluid and size of particle/macromolecule. The diffusional motion of macromolecules is greater with the 40 °C ink than with 23 °C ink. The ink imbibition is accelerated by use of a warmer ink, as viscosity also falls exponentially with temperature. Another advantage of using higher temperature ink is the possibility to speed up

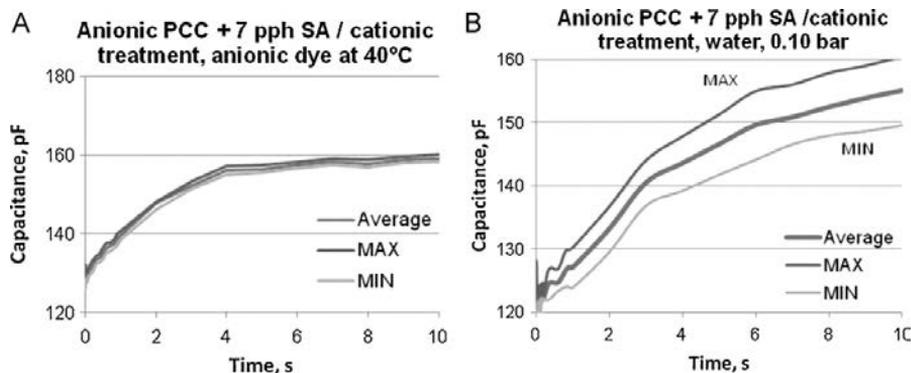


Fig. 7. The variation of the capacitance values of anionic PCC + 7 pph SA latex with the polyDADMAC (cationic) treated surface. External pressure was 0.10 bar and the liquid was anionic dye at 40 °C (A) and water (B).

the drying of the ink. In the real printing process, the ink amount is limited, and a warmer ink can start to evaporate/dry more quickly than a colder one. There may also be dependence of surface tension of the ink on temperature, especially if this is defined by surfactant action, which itself is diffusion dependent.

3.3. The effect of surface applied cationic additive on the inkjet print quality

The results of print densities are illustrated in Fig. 8. The pre-coating surface alone produced the lowest print density with both cyan and magenta dye-based ink because the colorant can penetrate through the pre-coating which is not designed for inkjet purpose (not enough pore volume, no suitable cationic charge). Otherwise, the print density results from the top-coated samples were on a high level, indicating that the applied ink amount was high and well distributed on and in the coating surface structure. On the anionic SA-containing coating, the cationic polyDADMAC surface treatment produced a higher print density than the same coating layer without surface cationic additive (7 pph SA-containing coating). In the case of PVOH-containing coatings, the cationic additive application seems to decrease slightly the print density of cyan color, but the magenta surface remained similar. The higher amount of the soluble PVOH binder (30 pph) closed the coating layer structure. However, in this case there appeared places where the PVOH had formed film-like structures, as expected, but, in the middle of such localised film-like structures, a round hole was frequently observed. The colorant of the ink can penetrate through

this hole deeper into the coated paper, and therefore the print density became lower when using 30 pph PVOH than when using 7 pph PVOH despite the expected average decrease in permeability. The non-uniformity of the 30 pph PVOH coating was reflected also in the mottling values.

There are slight differences between the print densities of the cyan and magenta of cationic additive treated SA latex-containing surface and the same coating without cationic additive as well as on the 30 pph SA latex-containing coating layer. The difference behind these results can be the ionic charge contrast of dye and surface, but it is more likely that the printed surfaces have already so much dye-based ink that sufficient colorant remains on the top of the coating layer whatever the charge and the binder.

The bleeding was measured from the magenta line (Fig. 9), which was either printed as the first color laid on the paper surface (line spreading on the coating surface) or onto the pre-printed yellow surface (ink mixing). The magenta ink line width decreased as cationic additive was applied on the coated paper surface, both for the single color and the magenta on yellow cases. The cationic additive application did not decrease the raggedness of the magenta/yellow line, but the magenta line on the coated paper had less raggedness on the polyDADMAC treated surface than on the 7 pph SA-containing coating. However, the standard deviation of PCC + 7 pph SA with cationic additive was large indicating that there were some non-uniform areas in the polyDADMAC layer.

The results of line spreading and raggedness on the coating layer (Fig. 9: magenta/paper) show that cationic additive provides a narrower and sharper line than the anionic SA latex-containing coating. The opposite charge of the surface and ink (electrostatic forces) binds the anionic colorant effectively on the surface so that the colorant cannot spread in the x, y -direction of the surface although the polyDADMAC treated surface slowed the penetration of ink vehicle. Svanholm and Ström [21] showed that the addition of cationic additive into the coating color did not always diminish bleeding tendency of dye-based inkjet ink printed coatings. The cationic additive in the coating color does not necessarily locate in the top part of coating layer because, during the consolidation process, the additive can transfer deeper into the coating layer or even to the base paper, and so it cannot effectively take part in the fixing of colorant as it spreads on the surface. On the other hand, the porous properties of the coating layer affects the ink spreading by providing rapid sorption of the ink vehicle, and in the cationic additive containing coating layer the capillary and permeation flow competes more strongly with the ionic interactions than in the polyDADMAC surface treated coating layer. The only exception to the overall advantage of surface treating with cationic

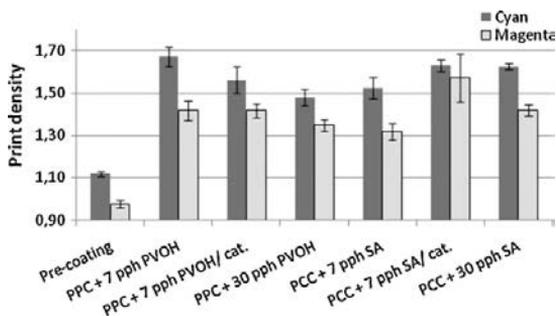


Fig. 8. Print density of cyan and magenta on the PCC coated surfaces and same surfaces, i.e. PVOH- versus SA latex-containing treated with cationic additive. Printed with HP DeskJet 3940 adopting dye-based inks.

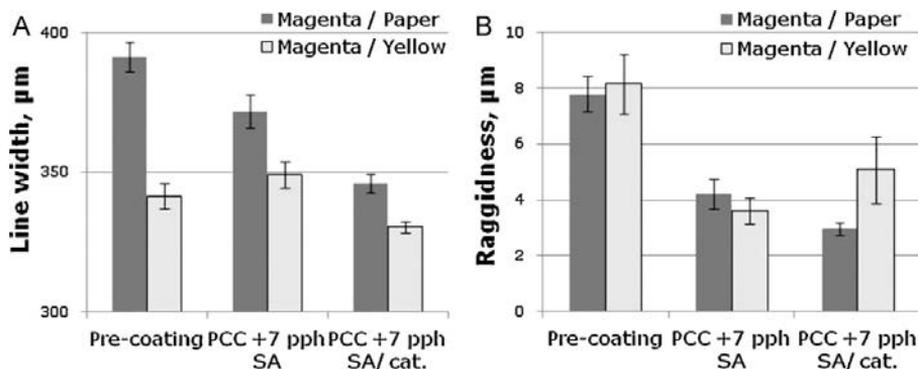


Fig. 9. The line width (A) and raggedness (B) of magenta line on the plain coated paper surface and surface with yellow compact area. Printed with HP DeskJet 3940 adopting dye-based inks.

polymer could be detected with the magenta ink on the yellow surface, where the raggedness was higher with the cationically treated surface than with the SA containing coating. This clearly indicates that once the ink is isolated from the cationic layer by a previously applied color, and the sorption of ink vehicle is slowed by the presence of the polymer reducing the permeability, the dye can migrate more freely.

The water fastness (Fig. 10) was measured with print density changes and ΔE^* of 100% cyan surface after submersion in water. The print density difference between before and after water treatment was greater on the SA-containing surfaces than on the PVOH-containing surfaces. The water treatment of printed SA-containing coating releases the colorant out of the printed surface because there are no effective interactions between the colorant and the latex, whereas there is the diffusion absorption into the PVOH. The print density change was reduced by the cationic surface treatment of SA-containing coatings. The cationic additive application on the PVOH-containing coating, on the other hand, had quite minimal influence on the results of water fastness, indicating the adequate effect of PVOH alone. Similar trends could be noticed in the ΔE^* values. On the SA-containing coatings, the polyDADMAC treated surface produced the lowest ΔE^* value, and it had very similar results to those from the PVOH-containing coatings.

The water fastness results in Fig. 10 show that the cationic polyDADMAC treated SA-containing coating surface fixes the anionic colorant more permanently to the coating layer than the anionic SA latex-containing coating alone. The ionic interactions (electro-

static Coulombic attraction) fix the colorant to the surface. The difference between the slightly cationic PVOH-containing coating and the cationic polyDADMAC surface treated PVOH-containing coating is small indicating that PVOH and polyDADMAC surface behaved very similarly in water fastness test and the cationicity does not bind anionic colorant there more effectively than polymer absorptive diffusion. The UV–VIS results, furthermore, showed that colorant can transfer into the PVOH-containing structure. The slightly cationic charge combining with the hydrophilic binder of the coating layer seems to be sufficient for an adequate inkjet ink colorant fixing, so that the colorant does not release out of the surface during the water fastness test used.

4. Conclusions

The sorption studies with the anionic dye-based ink and different coating component systems using UV–VIS spectrometry confirm that a cationic coating surface adsorbs anionic dye colorant more effectively than an anionic, as expected. The addition of 7 pph PVOH to an anionically dispersed pigment increases the sorption of colorant phase, whereas 7 pph SA latex has no effect on sorption. This indicates that colorant can absorb into the polyvinyl alcohol polymer network, even in the case when the polymer has not formed a uniform layer on the coating pigment surface, whereas it cannot undergo sorption in the SA polymer latex case.

The use of an ionically surface-inert organo silica pigment enabled a comparison to be made with an ionically surface-

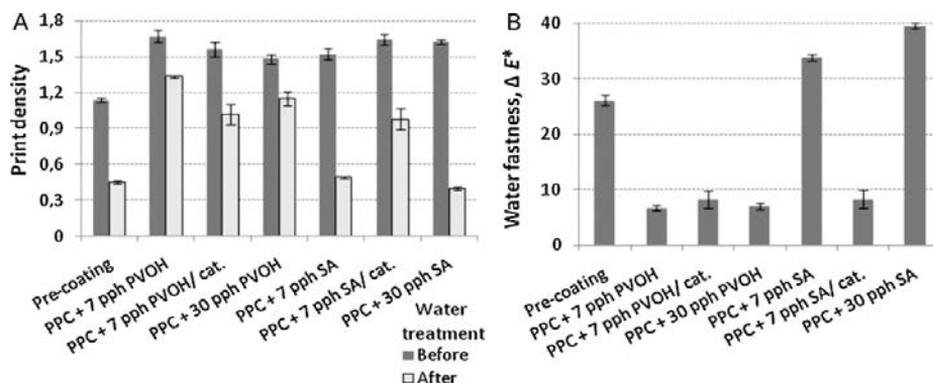


Fig. 10. The water fastness of surfaces: print density (A) and ΔE^* (B) of a 100% cyan print before and after water treatment. Printed with HP DeskJet 3940, adopting dye-based inks.

interactive modified calcium carbonate (MCC). Little to no adsorption of dye occurred in the case of the ionically surface-inert organo silica. In contrast, the limited sorption of anionic dye onto directly suspended MCC, however, indicated that the surface contained either shielded cationic sites or more likely a mixture of anionic and cationic sites, with probable nearest neighbour charge hindrance of anionic dye adsorption. Further studies of this phenomenon could reveal more precisely the charge distribution nature of the MCC surface by using selective charge interactive species.

The surface application of cationic polyDADMAC onto anionic coating layers slows down ink vehicle sorption but nonetheless reduces color spreading, due to the capture of anionic dye by the cationised surface. The opposite charge of the coating components and dye molecules binds the colorant most effectively to the top part of coating layer, producing less bleeding and improved water fastness. Ink-on-ink printing, however, acts to isolate the second laid-down ink from the surface coating charge, and combined with the reduced sorption speed of the ink vehicle, this leads to a deterioration of color-to-color bleed. Increasing the temperature of the dye ink was seen to speed up the penetration.

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