PAPER IV

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Absorption Capability and Inkjet Ink Colorant Penetration into Binders Commonly Used in Pigmented Paper Coatings

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ABSTRACT: The absorption of coating binders used in inkjet coatings plays an important role apart from that of the porosity and pore structure of the pigment coating layer. The aim of this work is to clarify how different binder films absorb water-based dye-containing inks and how changes in the ionic nature of both ink dye and binder films affect the ink absorption capability and the final colorant location in the binder film. The studied commercial binders were one carboxylated, and a range of partially hydrolyzed and fully hydrolyzed polyvinyl alcohol (PVOH), and these were compared to an anionic styrene acrylic latex. The hydrolysis modifies the effective crystallinity and hence the swelling tendency. The results show that as the hydrophobicity of the PVOH binder increases, the less the binder absorbs the water-based ink vehicle and the colorant of the ink locates/fixes more on the top part of the coating structure. Both ink vehicle and dye colorant diffuse into the binder film. It was observed that the carboxylated PVOH film produces the most intense coloration (darkest blue color of cyan ink) as the greater ink vehicle absorption promotes the high colorant amount in the film. The combination of opposite charges of the binder film and dye-based ink colorant fixes the colorant most effectively to the top part of the film by the action of chromatographic separation and adsorption.

INTRODUCTION

The high specific surface area of inkjet coating pigments requires binders that have a high binding capacity. The most common binder used in inkjet coatings is polyvinyl alcohol (PVOH). The binding strength of PVOH depends on the degree of hydrolyzation.[1] The peel strength of PVOH is higher when the degree of polymerization is also high.[2] Modified PVOH has also been used: carboxylic-, sulfonic-, acryl amide-, cationic-, and silicone-modified PVOH. The use of other types of pigments in the inkjet area has brought some other binders: polyvinyl pyrrolidone, poly(acrylic acid), polyacrylamide, methylcellulose, cellulose derivatives, gelatin, polyvinyl acetate latex, vinyl acetate ethylene, and cationic starch.[3−8]

The role of binder has mainly been studied in the coating layers. Svanholm[9] studied silica pigments with PVOH binder in coated fine papers. He noticed that the silica pigments with large internal pore diameters require more binder than pigments with smaller pores in order to get the dye colorants to remain on or near the top of the coating. The PVOH can form a film in the top part of the coating, where the colorant of inkjet ink can become fixed. A partially hydrolyzed and higher molecular weight PVOH gave the best color gamut and the sharpest line edges, and also sufficient binding strength. The effect of binder type was studied by Ström et al.[10] They showed that binder type affects the water imbibition on the silica surfaces and the PVOH and starch containing coatings have a linear relationship between absorption amount and the square root of time, indicating that they followed the Poiseuille equilibrium flow inherent in the Lucas−Washburn equation. The latex bound coatings, in contrast, had a linear absorption response with time. Additionally, it must be remembered that diffusion also follows a square root of time dynamic, and this is often overlooked in such studies, and could have alternatively been a potentially key difference between these coatings based on binder type. Vikman and Vuorinen[11] studied light fastness of the inkjet printed surface using PCC and kaolin, and their blends. The binders were PVOH and cationic starch with cationic styrene acrylate latex. With dye-based inks, the significance of structural properties of the coating layer in the light fastness decreased when the strength of the chemical paper-ink interaction increased. The dyes benefit from a dense coating structure, whereas a coarse structure of the coating appears to be advantageous for pigment-based inks.

Pinto et al.[12] studied inkjet ink colorant location in the binder film layers by using Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). They mainly studied polyvinylpyrrolidone (PVP) and its copolymers, but there are also some results with PVOH-containing films. They concluded that both PVP and PVOH engage in intermolecular hydrogen bonding interactions. The cross-sectional images of samples containing PVP restricted the ink colorant to the media surface.

Oka and Kimura[13] introduced four different mechanisms to describe how an acid red dye (anionic) can set on a silica pigment that has been covered with PVOH. First the colorant can attach onto the PVOH layer. In the second mechanism, the colorant can dissolve in PVOH, and in the third, colorant forms a complex

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with adsorbed cationic polymer (dye-fixing agent) and stays in the PVOH. In the last two mechanisms, the PVOH does not have an effect on the final colorant location. The colorant attaches on the silica pigment and adsorbs on silica with cationic polymer present. They concluded that most of the used dyes form a complex with dye-fixing agent, and this disperses in the PVOH layer and, thus, this is the dominant phenomenon. The rest of the dye remains as a colorant layer on the PVOH surface. We supported in our hypothesis the ideas of Oka and Kimura, but we assume that the colorant can follow the diffused water molecules into the binder network.

Different kinds of additives have been widely used in inkjet coatings as cationic components[4,5,7,12,14,15] and cross-linkers.[2,16] The reason for using the additives has been to adjust the colorant fixing or the adsorption properties of the coating layers and/or the rheology of coating colors. Ryu et al.[14] showed that the cationic additives increase the viscosity of typical coating colors. The inkjet print density remained more or less the same and, among the studied cationic additives, polyDADMAC improved the water fastness of the printed surface the most. The polyDADMAC-containing coating also had less color bleeding than the coating without additive. However, there are only a few studies in which the colorant of inkjet inks fixes in the binder layers. The occurrence of the separation of ink vehicle and colorant has not been studied.

The aim of this work is to clarify how anionic and cationic dye-based inks absorb into the different polyvinyl alcohols tested, compared with anionic styrene acrylate latex. The observations were made using binder films, and the role of ionic change in the films is linked to colorant location. The dye separation phenomenon was additionally studied using Time of Flight Secondary Ion Mass Spectrometry.

■ MATERIALS AND METHODS

The binders in this work were chosen from different types of polyvinyl alcohols (PVOH), one being carboxylated and the others ranging in degree of hydrolysis, provided by Kuraray (Kuraray Specialties Europe GmbH, Building D 581 D-65926, Frankfurt am Main, Germany) and one anionic styrene acrylate latex from BASF (BASF Aktiengesellschaft, Paper Chemicals, 67056 Ludwigshafen, Germany). PVOH contains vinyl alcohol and vinyl acetate units (Figure 1). The resulting polymer has crystal and amorphous parts in the structure, and the greater the degree of hydrolysis the more there form crystal regions within the polymer matrix.[17] In the K-Polymer KL-318 (PVOH) polymer, a carboxylic monomer (COO^-Na^+) has been added. Table 1 shows the properties of the binders. The charge of the binders was adjusted by adding either anionic sodium polyacrylate [Polysalz S (BASF AG, Paper Chemicals, 67056 Ludwigshafen, Germany)], having a molecular weight of 4000 $g \cdot mol^{-1}$, or cationic poly(diallyl dimethyl ammonium chloride) (polyDADMAC, Cartafix VXU (Clariant International AG, Rothausstrasse 61, CH-4132 Muttenz 1, Switzerland). The content of additives was set at two values, 1 and 4 pph.

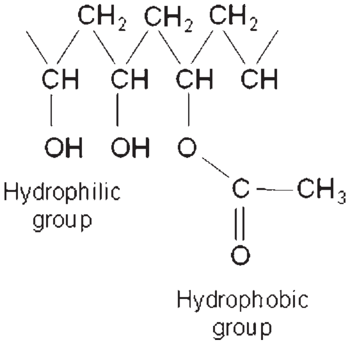


Figure 1. Chemical structure of polyvinyl alcohol.

The PVOH binder films were produced by cooking the respective polymer and drying it in Teflon (Polytetrafluoroethylene, Du Pont) molds at 23 ± 2 °C. The latex film was subsequently made with an Erichsen (Erichsen GmbH & Co., Am Iserbach 14, D-58675 Hemer, Germany) film applicator (Model 288) followed by drying them in an oven at 105 °C for 5 min. The thickness of the films was 205−260 μm.

The inks were self-made and they contained 4 (cationic) or 5 (anionic) wt-% colorant, 5 wt % polyethylene glycol (PEG 200), 5 wt % diethene glycol, 0.3 wt % Surfynol 465 (surface active agent from Air Products (Air Products PLC, Hersham Place Technology Park, Molesey Road, Hersham, Walton-on-Thames, Surrey KT12 4RZ, U. K.) and the remainder was water. The colorants were anionic (Basacid Blue 762, Cu phthalocyanine) and cationic (Basonyl Blau 636, Victoria Blue FBO, Basic Blue 7, triarylmethane) dyes provided by BASF. There was a slight difference between the surface tensions of the inks: the anionic ink had 49.5 $mN \cdot m^{-1}$ and the cationic 55.9 $mN \cdot m^{-1}$ (23 °C). This can have an effect on the colorant location due to the wetting characteristics in relation to the binder surface energy. The observably different tone of blue of anionic and cationic cyan colorants came from the basic properties of the dyes.

In the absorption measurement, a binder film, sized 2.0 × 2.0 cm, was immersed into the self-made cationic or anionic dye-based inkjet ink. After each defined measuring time, the sample was removed from the ink and dried lightly between two blotting boards. The weight of film was measured before and after the immersions. The absorption amount is defined as the difference between the absorbed and the dry weights, with initial adjustment made for the moisture content of original binder film. This was then divided by the weight of the film to give a specific uptake, i.e., per unit weight of film. The measurement was made under standard conditions of relative moisture content 50% RH and temperature 23 °C. The result is composed of three parallel measurements.

The colorant and water separation was studied using Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). In the measurement, the partially hydrolyzed PVOH binder (Mowiol 40−88) film was immersed in a commercial anionic ink (Versamark VX5000e cyan ink) or this same anionic ink with an addition of 1 $g \cdot dm^{-3}$ lithium for 5 min time and subsequently dried at 23 ± 1 °C and 50% RH overnight. We assumed that the lithium, with its very low molecular weight (small atomic radius) followed the water molecules, and so could be used as a tracer for the vehicle imbibition path. The ink absorbed binder films were embedded in a LR White resin (Electron Microscopy Sciences, P.O. Box 550, 1560 Industry Road,Hatfield, PA-19440, U.S.). The samples were then cross-sectioned and covered with platinum and polished. In the ToF-SIMS measurement 10 ns pulse, ions/electrons are released from the surface. ToF-SIMS analyzes the chemical compounds of the cross-sectioned sample as a function of depth, *z*. By measuring the gray scale values of the

Table 1. Properties of the Studied Polymers

binder	fully hydrolyzed PVOH (Mowiol 20−98)	partially hydrolyzed PVOH (Mowiol 40−88)	carboxylated PVOH (K-polymer KL-318)	styrene acrylate latex (Latexia 212)
degree of hydrolysis, mol-%	98.4 ± 0.4	87.7 ± 1.0	87.5 ± 2.5	
density, g·cm^{-3}	0.4−0.6 [a]	0.4−0.6 [a]	0.4−0.6 [a]	1.03
glass transition temperature, °C				−20
viscosity (4% solution, 20 °C, DIN 53 015), mPas	20.0 ± 1.5	40.0 ± 2.0	25.0 ± 5.0	
ash content maximum (calculated as Na_2O), %	0.5	0.5	N/A	N/A
chemical nature	nonionic	nonionic	anionic	anionic

[a] Measured according DIN 53 468 by Clariant International AG from the granulates.

location of different components in the *z*-direction of the sample, we generated information about the distribution of each constituent chemical compound.

The water type, i.e., free or bound water in the binder film moisture content after absorption, was measured with a differential scanning calorimeter [DSC, Mettler DSC 30 (Mettler-Toledo, Inc., 1900 Polaris Parkway, Columbus, OH 43240, U.S.)], which measures the difference in the amount of heat required to increase the temperature of a sample by a defined amount. In the measurement, the freezing of unbound water was analyzed by the latent heat effect at −0.5 °C. The bound water was then identified as the total moisture content of the film found under drying by heating minus the amount of unbound water. We recall here that the binder films under test were polyvinyl alcohol (Mowiol 40−88) and styrene acrylate latex (Latexia 212). In DSC and absorption measurements, we have to remember that part of the PVOH films may dissolve and this can have some effects on the results. In our earlier study,[18] we showed that after a 30 s absorption time, the dissolving part of polymer can be about 5% of the initial weight of PVOH, whereas the SA latex dissolves only about 1%, and this latter amount is related primarily to surfactants, residual monomers, oligomers, and so forth, rather than the binder itself.

■ RESULTS AND DISCUSSION

Absorption Amount into Binder Films. The amount of ink absorption into the binder films was studied for the self-made anionic and cationic dye-based inks. The highest absorption amount was reached with carboxylated PVOH film (Figure 2). Then came partially hydrolyzed and fully hydrolyzed, with the SA latex film had the lowest absorption. As the absorption time increased, a higher amount of ink was absorbed into the films. The order of the films remained the same regardless of absorption time, indicating no chemical change occurred. The amount of absorbed ink had a linear relation to the square root of time, as shown in Figure 2. The addition of cationic or anionic additive in the binder film has only a very minimal effect on the absorption properties. The more important aspect seems to be the hydrophilic nature of the binder polymer itself. This can indicate that the additives do not fix to the PVOH hydroxyl groups and so do not prevent the water molecules and/or colorant fixing to the binder molecules.

We see in Figure 2 that the lines are parallel in the cases where absorption takes place, indicating equal absorption rates. However, they have different heights in relation to the *y* axis. These differing heights indicate that another phenomenon has occurred prior to the first measurement time. This phenomenon is therefore occurring at different rates within the different binder films. We can only speculate what this might be, but suspect a polymer swelling effect once exposed to moisture. Interestingly, one combination stands out as being differently sensitive to this shorter time scale effect—that of cationic ink as a function of highly cationically treated fully hydrolyzed PVOH. Similarly, we see that cationic ink also lifts the line for partially hydrolyzed PVOH when no added cationic agent is present, though the effect is less marked. It could be that the network strength of the PVOH is being affected. To study this further, the binding strength could be evaluated.

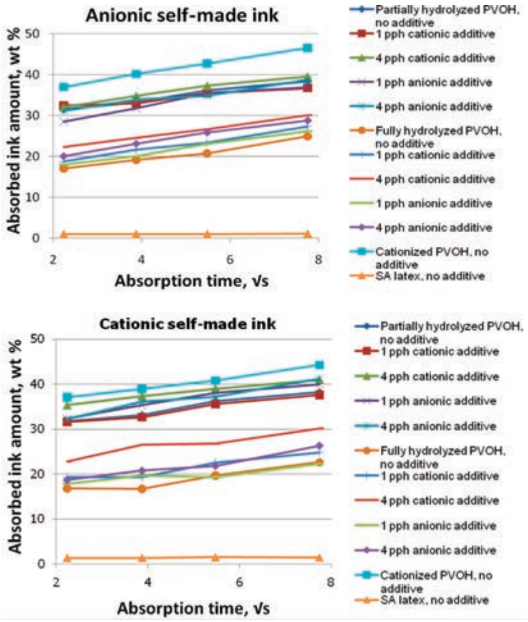


Figure 2. Absorption of anionic and cationic self-made inks into the PVOH and SA latex films, expressed as the weight fraction of film weight. The standard deviation of absorbed ink amount was at maximum 2 wt %, but in most cases, it was about under 1wt %.

The amount of amorphous and crystalline regions in the polymer affects the content of absorbed moisture.[19,20] At any given relative moisture content, a polymer with a low crystallinity absorbs more moisture than one with high crystallinity.[20,21] This confirms that the amorphous region of the polymer can bind water molecules readily, whereas the crystalline part cannot. Our results in Figure 2 illustrated that the fully hydrolyzed PVOH, with more crystalline structures,[17,20] absorbed less of the inkjet inks than the partially hydrolyzed: the water diffuses and fixes to the amorphous region of PVOH causing swelling of the polymer, whereas in the crystalline part, the small size water molecules penetrate through the adjacent PVOH structures without binding there. Water molecules are small enough to fit into the polymer network without disrupting it.

If the movement of water molecules in the binder film is studied in terms of bound and unbound water, then we notice that the water molecules diffuse in the polyvinyl alcohol polymer network and they can hydrogen bond to the hydrophilic groups of PVOH.[8] This can happen only in the noncrystal regions of the polymer.[17] At certain water content, the PVOH film has both free

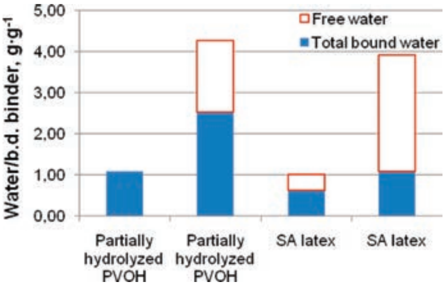


Figure 3. The water type (bound versus unbound) in PVOH and SA latex films, as measured with DSC. The dissolving of PVOH likely has some effect on the results.

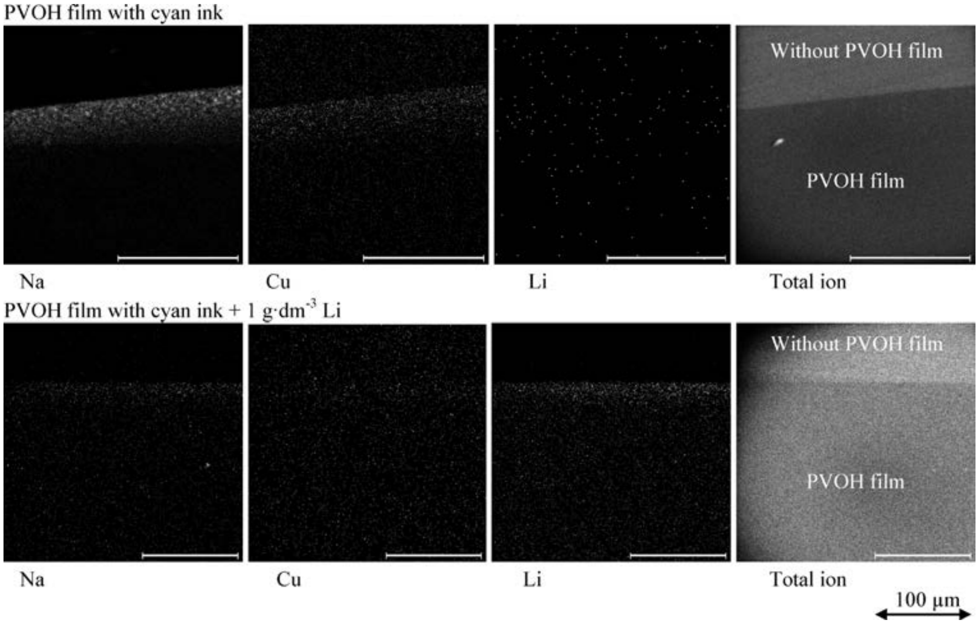


Figure 4. The location of sodium, lithium, and copper in the PVOH film analyzed with Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The ink was Versamark VX5000e cyan ink, which contained copper and sodium. Lithium was used as a tracer in the water (made from $Li_2SO_4 \cdot H_2O$).

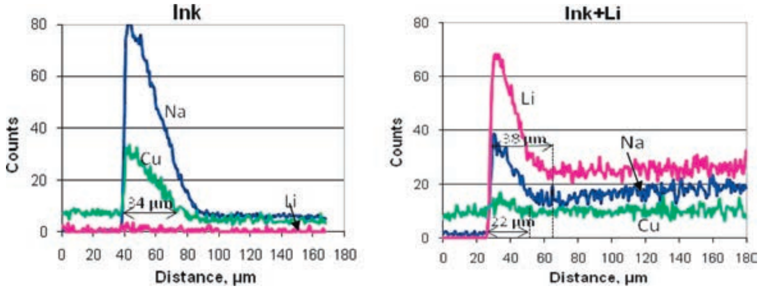


Figure 5. The location of ink (Cu and Na) and water (Li) in the PVOH film layer. Measured with ToF-SIMS.

water and bound water. The results of differential scanning calorimetry, in Figure 3, show that the PVOH film has, at the moisture content of 1%, only bound water, whereas the latex film has some bound and some unbound. At the 4% moisture content, the PVOH film still shows proportionally more bound water than the SA latex film. Latex does not have chemical groups that can fix the water molecules to the same extent as the PVOH. This kind of difference in the fixing capability between the binders must also exist in the practical inkjet ink setting stage.

Separation of Colorant and Water. The ToF-SIMS analysis of the sample having absorbed commercial ink indicates the location of water and colorant in the PVOH film. The amount of colorant was so low, however, that it was very difficult to locate the colorant with certainty. The colorant molecule contained copper and sodium. However, Figures 4 and 5 indicate that the tracer lithium can be found deeper in the binder film structure than copper. Thus, there is a falling concentration gradient of colorant within the film in relation to the ink vehicle front. We can conclude, therefore, that there is a chromatographic separation, and hence adsorption of colorant to the polymer network.

Interestingly, in Figure 5, the case where lithium salt is added, the picture is not so clear regarding the sodium trace. Compared with the situation where no lithium ion was added, the sodium distribution appears to penetrate deeper into the layer. This suggests that sodium is being released from a complex in partial exchange equilibrium with the lithium.

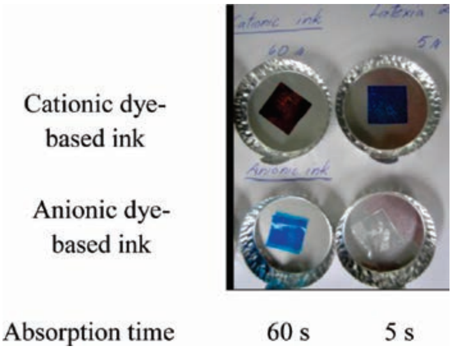


Figure 6. The self-made cationic and anionic dye-based ink absorption into the anionic latex film after 60 and 5 s absorption times, respectively.

Colorant Fixing to the Binder Films. Figure 6 shows how the anionic nature of SA latex prevented the anionic colorant from fixing to the film after the short ink exposure time of 5 s. The anionic SA film had no colorant at all, whereas cationic ink adhered to the anionic latex film. After the 60 s absorption time, both anionic and cationic ink showed blue coloration of the SA latex film, though a much darker blue color was achieved with the longer 60 s absorption time for the cationic dye. The PVOH films, however, always displayed a blue color independent of the ionic nature of the colorant (Figure 7). When the various PVOH films were immersed, each with one dye, it was noticeable that the coloration of the films was very similar. The cationic or anionic additive did not change the observed color intensity.

Figure 8 shows how the anionic dye-based colorant located within the top part of the PVOH films. It did not penetrate in any case through the whole film. The anionic colorant located even more on the top part of the binder film when the cationic additive had been added to the binder (Figure 8 in the middle). The higher the additive amount, the narrower the area of colorant

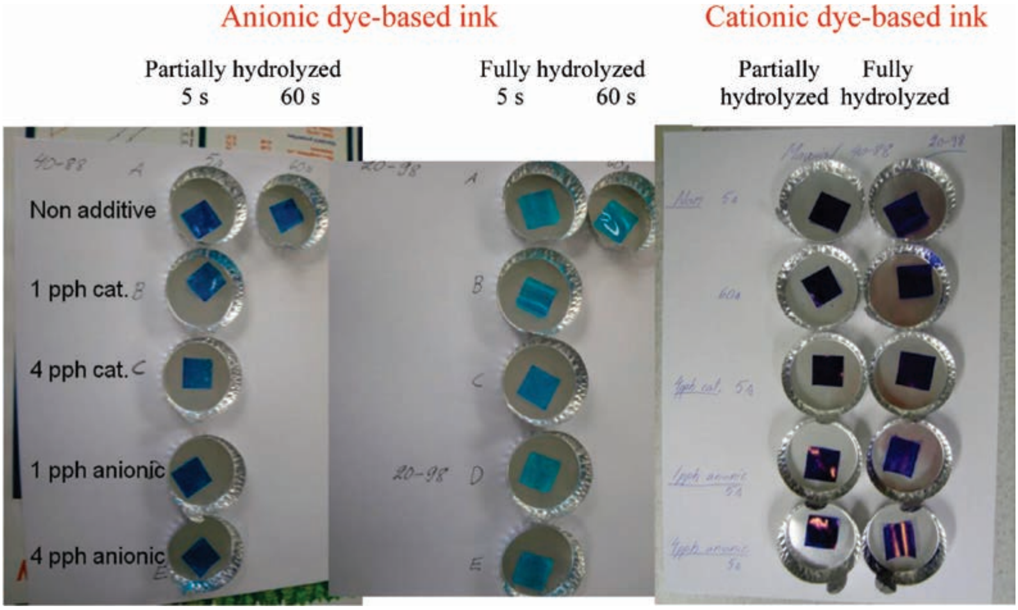


Figure 7. The color of partially and fully hydrolyzed PVOH binder films after the self-made anionic and cationic ink absorption measurement. Absorption times were 5 and 60 s, respectively.

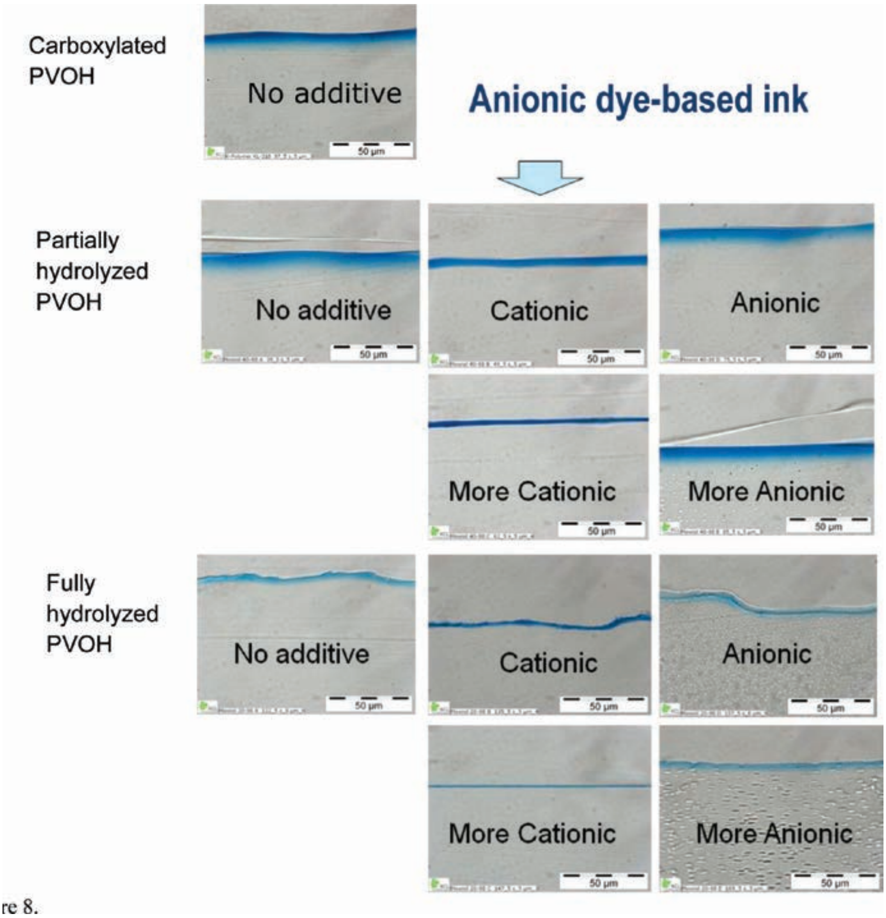


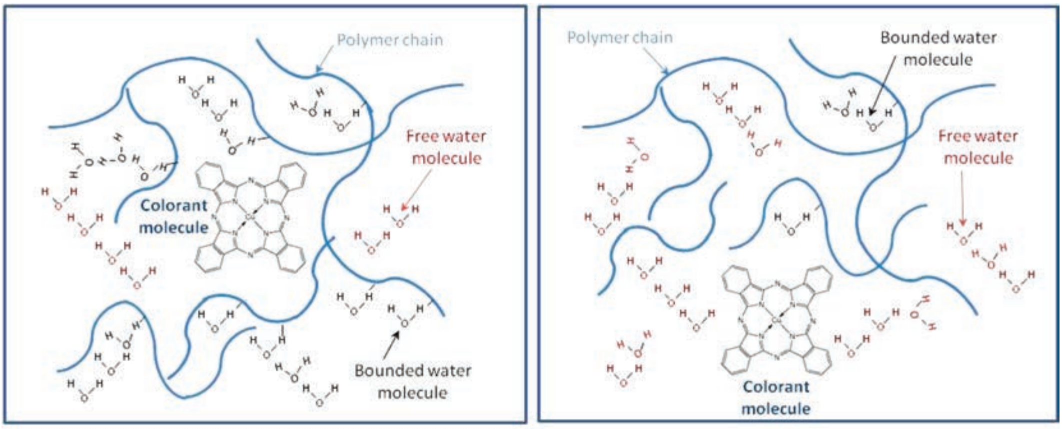
Figure 8. The cross-section optical microscopy images of polyvinyl alcohol films after 5 s self-made anionic ink absorption. The additive amount was 1 pph (cationic or anionic) or 4 pph (more cationic or more anionic).

thickness on the top of the film became. The lowest blue color of the binder film was achieved with fully hydrolyzed PVOH film, indicating a holdout of colorant. The optical direct observation was so definitive that it was not necessary to resort to instrumentation for color determination. Similar colorant location in the top part of the binder film could be seen when the ink had cationic nature and the binder contained anionic additive (not shown here).

The cross-section images in Figure 8 show that colorant locates in the top part of the binder film even in the case when the colorant and binder film have same anionic nature. This suggests that in the coating layers, we could get an acceptable uptake of ink with any type of PVOH binder. The opposite ionic nature of PVOH and colorant is not essential to bring the colorant into the coating layer, i.e., it is carried in the water. However, the opposite ionic nature promotes the colorant fixation more in the top part of the structure. In addition, the cross-section figures illustrate that the darkest blue color locates on the top of the film by a concentration gradient decreasing (fading) into the *z*-direction of the film. In the absorption, the colorant accumulates more within the first encountered surface, which necessarily has had a longer contact time to the ink. The colorant follows the ink vehicle into the film and there occurs a chromatographic separation of colorant molecules from ink vehicle. This result agrees well with the results of Oka and Kimura.[13] The results of ToF-SIMS also indicate that the greatest colorant content located at the top of the film and the separation of dye and water can take place during the absorption.

The other interesting result is that the anionic carboxylated PVOH produced the darkest blue color with both anionic and cationic ink. This suggests, especially in the anionic ink case, that the colorant follows the water into the structure, and the higher absorption capability of this binder film promotes ink colorant diffusion into the film. The absorption results show that the carboxylated PVOH absorbs more of both inks than the other studied polyvinyl alcohols. This is likely to relate to the "super absorbant" nature of sodium polyacrylate, acting to draw larger volumes of water, and hence nonadsorbed dye, through its own polymer network.

The low inkjet ink absorption amount into fully hydrolyzed PVOH (see Figure 9), which contained more crystalline regions,



Polyvinyl alcohol (PVOH) Styrene acrylate latex (SA latex)

Figure 9. A schematic representation of inkjet ink absorption into the PVOH and latex polymer network before the evaporation of water molecules.

would mean that water probably stays more in/on the top part of the film, and the polymer swelling which happens there causes further restriction acting against the colorant migrating between the polymer chains. This restriction acts to hold the colorant also near the top but will reduce the amount of colorant uptake overall, and therefore cyan color darkness will be low despite the colorant being apparently fixed near the top. This could result also in poor water fastness because the colorant locates too near the top part of polymer surface.

The results show that the cationic or anionic nature also affects the inkjet ink colorant location in binder films. When the colorant has an opposite ionic charge from that of the produced binder structure, then the colorant locates more in the top part of the film. The higher amount of counter charge additive in the film, the more the colorant locates within the uppermost top part, i.e., there exist more chemically charged groups that can fix with ionic interactions to the opposite charge groups of colorant molecules. The colorant locating more within the top surface in the coating layer means that we do not need so much ink to produce a certain print density or color gamut. The other advantage of using additives can be in the improvement of colorant fixing strength: the ionic interactions together with the hydrogen bonds produce improved water fastness.[14,15]

The Role of Binder Absorption in the Dye Colorant Location/Fixing. The results show that the water molecules absorb and fix in the binder polymer network differently depending on the hydrophilic nature of binder polymer. It seems that the water molecules diffuse in the PVOH polymer structure and open the network (Figure 9) so that the colorant molecules fit also into the swollen matrix. The size of a water molecule is 0.27−1.00 nm (depending on the amount of molecules in one cluster)[22] and the colorant molecule about 1.3 nm (taking account of the length of different bonds in the Cu phthalocyanine colorant molecule and assuming the molecule to be planar). Finally, the colorant fixes to the hydroxyl groups (hydrogen bonding) or to the opposite ionic nature groups (ionic interactions) with PVOH or just become trapped in the structure after the water evaporation.

The latex clearly has fewer chemical groups that can fix water molecules, and therefore the network of polymer does not swell (Figure 9). The colorant does not fit in the structure of the latex network and the only place where colorant can fix locates on the outside of the polymer network. We can assume that in the case of latex, the main mechanism of colorant fixing is the ionic interactions (electrostatic interactions, Coulombic attraction) on the binder film.

■ CONCLUSIONS

The hydrophilicity and absorptivity of the coating binder very strongly affects where the colorant locates after the ink setting process. When a swelling polymer, such as PVOH, absorbs the inkjet ink, the water in the ink diffuses in the polymer network structure and opens it up by an action of swelling, depending on the level of crystallinity. The ink colorant follows the water and the colorant forms hydrogen bonds or ionic interactions with the chemical groups of PVOH and/or becomes trapped in the structure after water evaporation. In the case of nonswelling SA latex, the water and colorant remain outside the polymer matrix, and the colorant cannot fix other than by external charge interaction if present.

We can affect the final ink colorant location by adding either cationic or anionic additive into the binders. The opposite ionic charge of additive and the ink colorant fixes the colorant more within the top part of the binder film. The increase of additive content from 1 to 4 pph seems to fix the colorant more toward the uppermost part of binder film provided the ink dye has an opposite charge. If the charge is similarly anionic, then the colorant passes deeper into the binder film, due to the super absorbing nature of the anionic additive (sodium polyacrylate).

It seems that during the aqueous-based inkjet ink absorption into the binder film, the binder cannot bind all of the offered water molecules, and there will be both bound and unbound water molecules in the polymer network structure. One explanation for unbound molecules is the level of crystallinity of the PVOH related to the degree of hydolysis: the crystalline areas of polymer cannot bind the water molecules. The fully hydrolyzed PVOH has more crystalline areas than the partially hydrolyzed PVOH, and therefore it is less hydrophilic and swells less during the uptake of water or inkjet ink.

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