

Impact of Binder Composition on Inkjet Printing Paper

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This article is focused on the impact of different binder mixtures on the performances of paper surface and printability. The coating properties were studied with the chosen silica pigment, and the binder consisted of vinyl acetate copolymer and polyvinyl alcohol with different ratios, followed by the measurement of smoothness, whiteness, and surface strength. The inkjet image quality was assessed using water-based inks. The print density, dot gain, and line quality were analyzed. The results showed that the surface performance and printability were affected by the composition of the binder. With the decrease of vinyl acetate copolymer and the increase of polyvinyl alcohol, the surface smoothness and strength decreased, and the penetration and diffusion of the ink changed as well. When the binder mixture was used with proper ratio, a larger solid density, smaller dot gain, and higher definition can be achieved, which were better than using either one of them alone.

Keywords: Inkjet paper; Binder compositions; Penetration and diffusion; Density; Dot gain; Definition

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INTRODUCTION

Inkjet technology is becoming increasingly common in high-speed commercial printing. In order to produce inkjet prints in high quality, the use of coated papers is, as a rule, essential (Ridgway and Gane 2002; Desie and Van Roost 2006). Currently, the mainstream of the inkjet printing is based on spreading and penetrating of aqueous-based ink, no matter which dye or pigment inks are being used. Paper coating becomes the key factor affecting the quality of the final products (Lamminmäki *et al.* 2012).

Ink drop imbibition within the paper sheet structure is a complex process (Arthur *et al.* 2011). As the solvent in the ink droplet penetrates into the coat of the paper, the colorant remains on the surface or the inside of it. Good pigment and dye fixing will result in better printing density, larger color gamut, and improved abrasion and water resistance (Tang and Li 2009), but the proper penetrating and spreading of the solvent, as well as good colorant fixing, depend fully on the coating of paper, consisting of pigments, binders, and fixing agents. As a result, studies on the components, types and properties of the binders in coating, and their relationships with the surface strength and ink absorption have become more and more important.

The major function of the binder is to maintain a certain degree of stability and flowability of the coating suspension to ensure success of the coating process (Dreyer *et al.* 2011), and to make sure that the binder can improve the surface strength (Chen and Guo 2010) of the inkjet printing paper. The type, dosage, and properties of the polymer generally will produce obvious differences in the surface strength. The binder can also modify the ink absorption of the coating.

To a certain extent, ink penetration depth and diffusion extension depend on binder type and dosage. It is possible that the binder swells under the influence of the ink. This acts to close the nano-size pores and therefore affects the ink penetration and diffusion in the coating structure (Lamminmäki *et al.* 2010).

Svanholm noticed that the binder can even form a film on the top of the coating, where the colorant of ink can become fixed (Svanholm *et al.* 2006). Lamminmäki *et al.* (2011) explained that as the water diffuses into this region, the binder will swell and open the linked structure of the binder polymer, the colorants in the ink will follow the water molecule's diffusion into the structure, and they will become fixed after the evaporation of the water. Proper colorant fixation can lead to high quality of optical print density, brilliance of the colors, image edge sharpness, as well as good resistance to water and light (Vikman 2003; Vikman and Vuorinen 2004; Kettle *et al.* 2010).

Image analysis can be used to study the impact of the binder on the printing quality from the microscopic point of view. Anson (1997) successfully evaluated the apparent quality of papers by studying the microscopic three-dimensional features of the surface through 3-D laser scanning. Chen *et al.* (2004) analyzed the porosity of printing papers, the solid dots, and lines of printing by extracting and testing the printed ink color with an image analysis method. Morea-Swift and Jones (2000) designed a method with letter 'E' as the study subject and evaluated the definition of the printed image. In the present article, the rendering of fine lines on coating paper with different binder composition is evaluated using image analysis technology.

As is well known, most of the relevant studies, domestic and abroad, have focused on the impact of the binder on the spreading and penetrating of aqueous-based inks, especially for single-component binders. However, the printing quality of coated paper with mixtures of different binders has rarely been analyzed or evaluated in detail. In fact, binders differ from one another in terms of performance. Besides that, a single type of binder may not meet the requirements of the inkjet printing paper quality. Therefore, this article is focused on the effects of binder mixtures with different compositions on paper performances and printability, including the density, dot gain, and fine lines qualities.

EXPERIMENTAL

Materials

Silica (Grace P508, US) was used as the pigment in the experiment; it has a specific surface area of 300.6 m²/g and pore volume of 1.51 cm³/g. The images of figures (SEM) and particle size distribution are shown in Figs. 1 and 2.

The binders were polyvinyl alcohol (PVOH, Kuraray 318 provided by Helen Chemicals (Suzhou) Ltd.) and vinyl acetate copolymer (VAE, Vinnapas 5588 provided by Wacker Chemicals (China) Co.). Table 1 shows the properties of the binders.

The specific surface area and porosity of these materials in the experiment were measured using nitrogen absorption method (BET, ISO 9277) with a model 2020 specific surface and porosity analyzer from Micromeritics Instrument (Shanghai), Ltd. The particle size distribution was measured with MIE scattering theory using a laser particle size analyzer from Dandong Bettersize Instruments, Ltd.

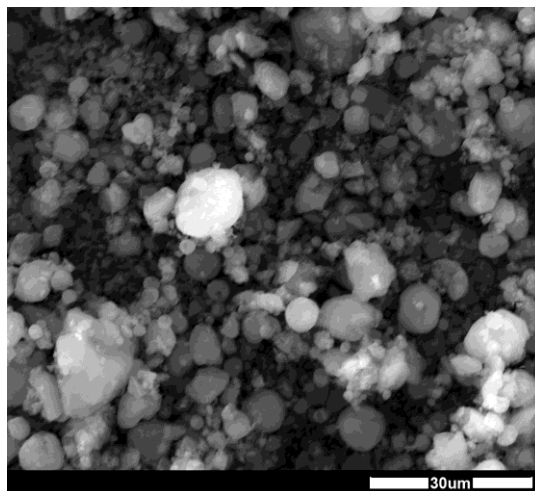


Fig. 1. SEM image of silicon dioxide pigment

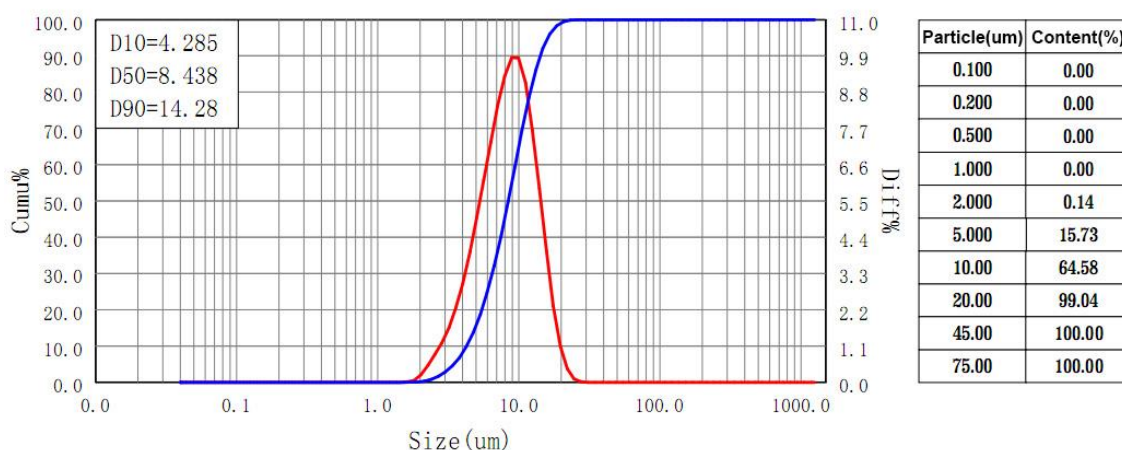


Fig. 2. Particle size distribution of silicon dioxide pigment

Table 1. Properties of the Studied Binders

Binder	Solid Content (%)	Viscosity (mPa.s)	pH	Glass Transition Temperature (°C)	Degree of Alcoholysis (mol-%)	Particle Size (D50 um)
VAE	55.37	600	4.65	5±1.0	-	0.9
PVOH	10.46	2550	5.79	-	87±1.0	-

Coating

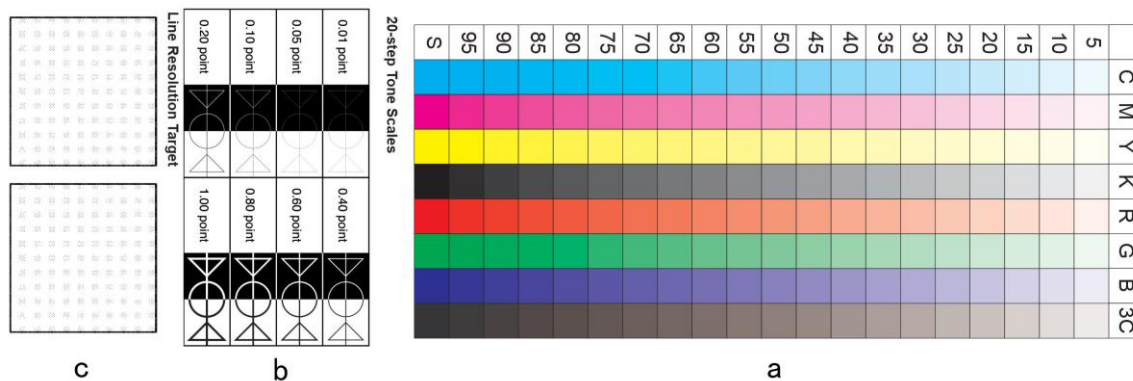
The coating was conducted on a base paper made in China (108 g/m²) using a small electric coating machine operating at a speed of 14 m/min, under the conditions of 25 °C and 60% of relative humidity (RH). The solid content of the coating was 20%, the ratio by weight of coating pigment to total amount of binder was 100:40, and the amount of coating was 6 to 7 g/m². The coated paper was placed flatly into an oven for 10 s at 105 °C, then taken out and air-dried naturally (Svanholm 2007). The different proportions of VAE and PVOH are listed in Table 2. The coating solution viscosity, paper surface strength, whiteness, smoothness, and contact angle were measured according to the TAPPI standard methods T 230 om-99, T 459 om-99, T 525 om-92, T 479 cm-99, and T 458 cm-94, respectively.

Table 2. Ratios of Binders

NO.	VAE:PVOH (Quality Ratio)
1	10:0
2	8:2
3	6:4
4	4:6
5	2:8
6	0:10

Printing

A Canon 6300 inkjet printer with dye-based aqueous inks was used for printing the image, as shown in Fig. 3, which is divided into three parts. From the right to the left, Fig. 3a refers to dot proportion from 5% to 100%, including step scale of yellow, magenta, cyan, black, red, green, and blue colors for measuring the print density and dot gain. Figure 3b shows eight widths of dark lines and reverse lines for testing the ink edge definition to the indication of ink infiltration and diffusion. Figure 3c indicates the black dot that printing line density is 72 lpi and the dot proportion is 1% for shape testing. The color management function was closed under ‘print setting’ of Adobe Illustrator CS6 software, and ‘Epson high quality glossy photo paper’ was selected as the ‘printing media’ in the printing process. The printing was carried out using the picture with large ink volume to test the printability of the paper. The lines were photographed through a 40x optical microscope to compare the rendering of those lines (Shuichi *et al.* 2000).

**Fig. 3.** Printing picture: 1% to 100% step scale; eight different widths of dark and reverse lines

Spectroscopic Measurements

A GretagMacbeth SpectroEye spectrophotometer was used to measure the printing quality parameters, including the optical solid density and dot gain, using a configuration of 2° measuring angle, D65 illuminant, UV-filter, and white area defined as the coated unprinted paper.

Microscopic Image Extraction and Analysis

An Olympus microscope and Panasonic CCD were used for taking photos of the Fig. 3b about six kinds of papers which contain different ratios of binders. Then six photos were compared visually. Olympus microscope, Panasonic CCD, and DT2000 V2.0 image analysis program were used for the measurement corresponding to results shown in Fig. 3c pertaining to roundness and circumference.

RESULTS AND DISCUSSION

Impact of Different Binder Composition on Coating Suspension Viscosity and Paper Surface Performance

As shown in Fig. 4a, the coating suspension rheology changed with the increase of PVOH. When PVOH was above 60% in the experiments, coating suspension was difficult to stir. When binder was VAE alone, the viscosity was only 10 mPa.s. However, when PVOH was used alone, the viscosity reached up to 400 mPa.s, which was 40 times higher than VAE only used as binder. Thus, the PVOH had a great effect on coating suspension viscosity.

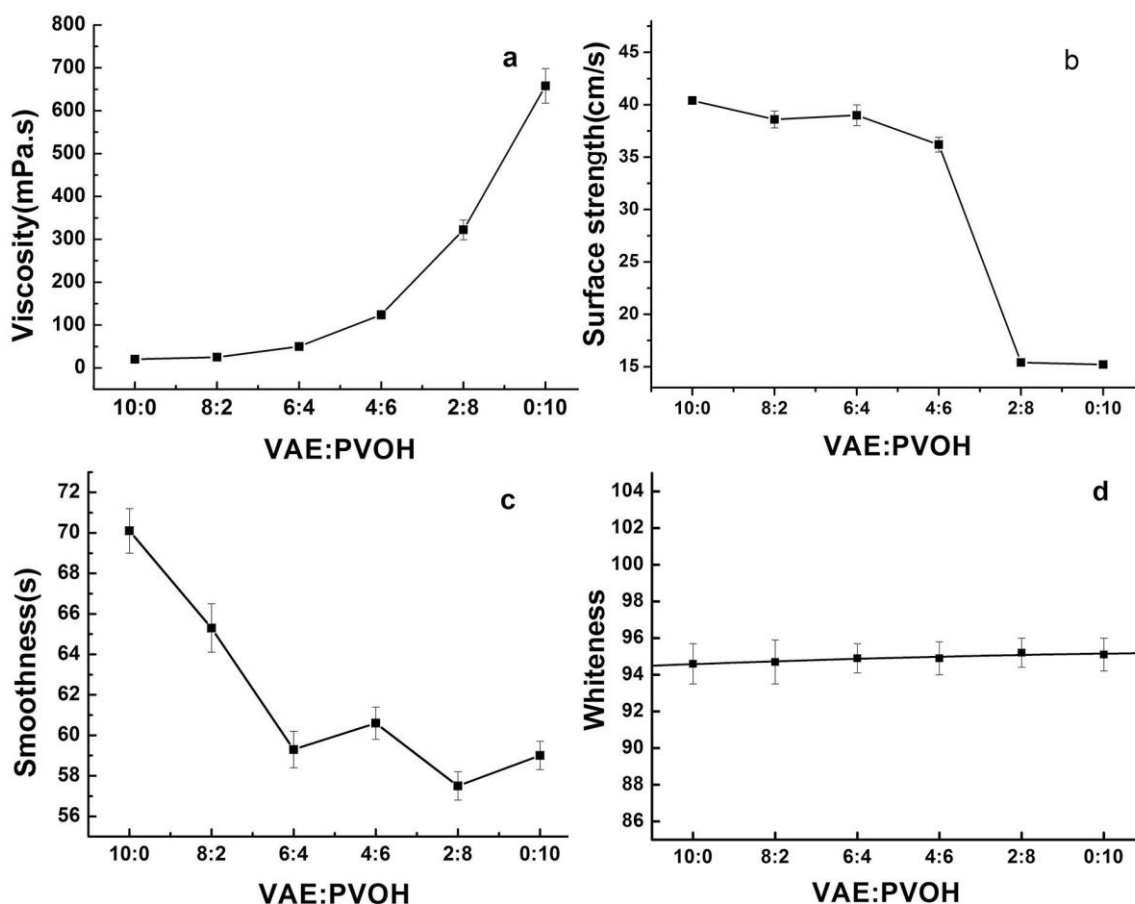


Fig. 4. Impact of different binder compositions on coating suspension viscosity, smoothness, surface strength, and whiteness of the coated paper

It has been reported that a sharp viscosity increase may occur during the mixing of PVOH with silica suspension, which is due to the hydrogen bonds between silanol groups located on silica and hydroxyl groups on PVOH, as well as the polymer bridging (Schempp *et al.* 1975; Boylan 1997; Backfolk *et al.* 2006). The PVOH molecule can be regarded as a simple straight line. There are a large number of hydroxyl groups at the outer side of the molecule. For this reason it is easy for PVOH to cross-link with the silica in the coating. The molecule structure of the H-bond binding between PVOH and silica is shown in Fig. 5. In the experiments, with the increment of the PVOH dosage, the

hydroxyl content increased. Therefore, there were more cross-linking points, which then led to greater viscosity of the coating suspension, lower flowability, and difficulties in stirring and coating.

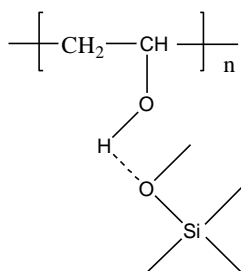


Fig. 5. H-bond binding between polyvinyl alcohol and silica

Surface strength and smoothness are important factors influencing interfacial properties of coating paper for inkjet printing (Al-Turaif *et al.* 1995; Jarnstrom *et al.* 2007; Wang *et al.* 2009). Figures 4b and 4c show the surface strength and smoothness for different binder compositions of coating papers. They became stronger with the increment of VAE dosage in binder mixture, probably due to the difference in coating structure. As can be seen in Fig. 6, there was precipitation of silica in VAE binder when well-distributed coating emulsion was allowed to sit quietly for a certain time, but there was no precipitate in PVOH binder. Similarly, this phenomenon would also take place during the processes of coating and paper drying. Such effects can be tested by X-ray photoelectron spectra (EDS) of the surface of paper (Fig. 7) and the proportion of elements (Table 3.).

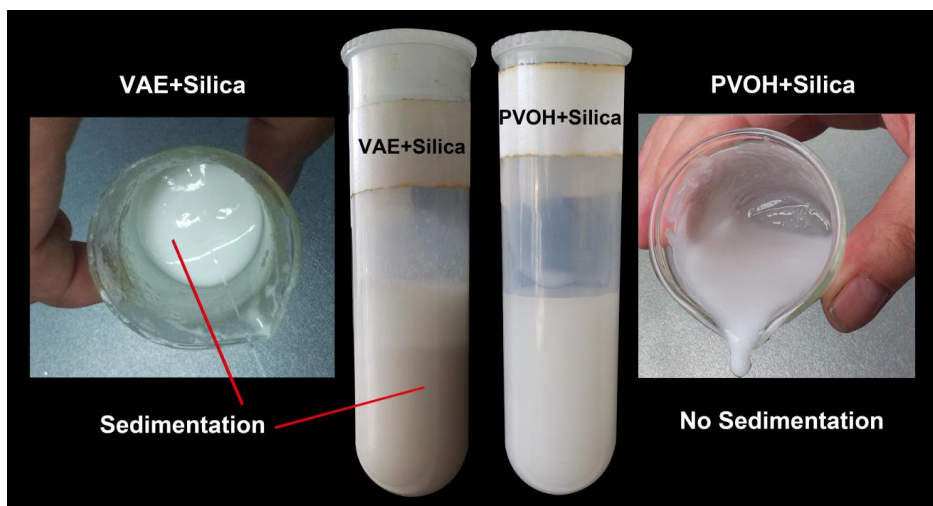


Fig. 6. Coating emulsions with VAE and PVOH as binder standing quietly for 24 h

The main chemical elements of the coating surface were C, O, and Si, because of the mixture of silica, VAE, and PVOH in the coating. Among them, Si was from the silica in the coating suspension, whereas C (hydrocarbon) was from VAE and PVA. As can be seen in Table 3, a comparison of paper with different ratios of VAE:PVOH showed that the weight of C was more and Si was less than for paper with PVOH as the sole binder.

There were more VAE particles in the top-coating of the paper with VAE as the sole binder; therefore, the strength and smoothness of paper surface was on a relatively higher level. On the contrary, with the PVOH binder alone, the silica particles were dispersed uniformly and steadily. And there was more silica on the surface of the coating. Thus, relatively, the strength and smoothness were lower.

Additionally, as shown in Fig. 4d, the VAE-to-PVOH ratio had little impact on the whiteness of the coating.

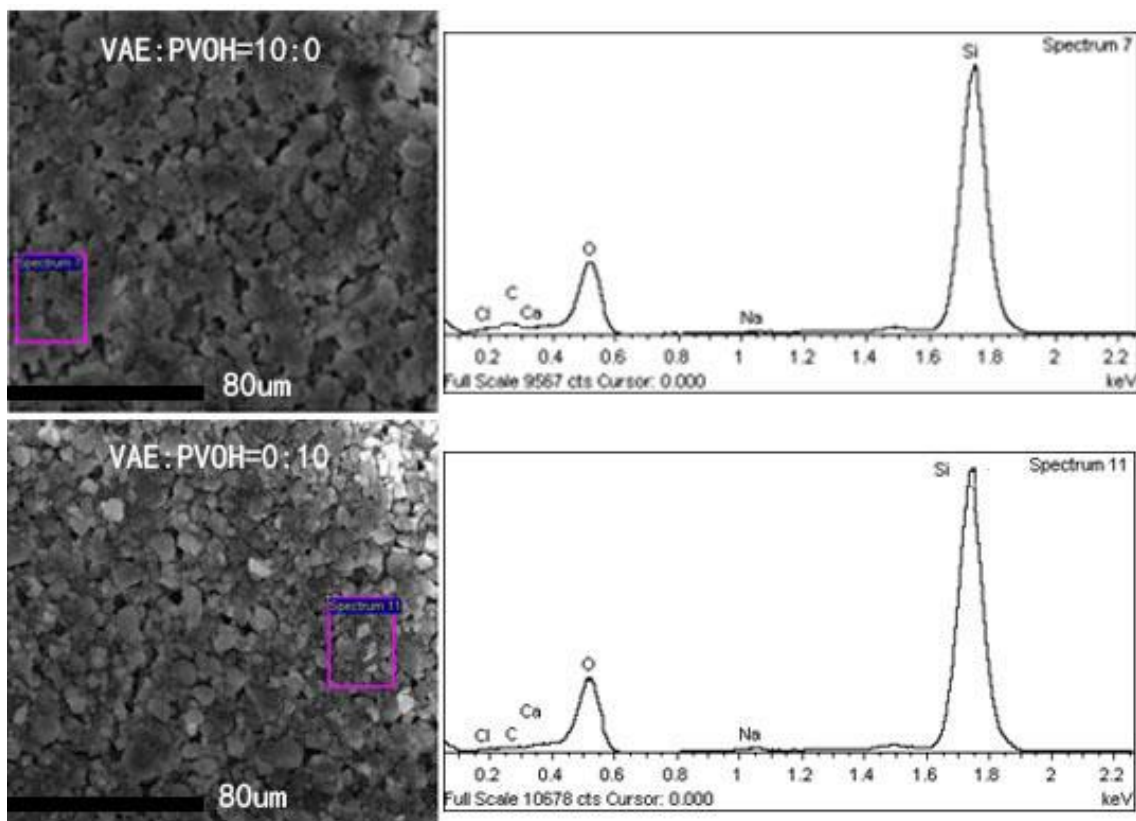


Fig. 7. X ray photoelectron spectra (EDS) about surface of paper

Table 3. Proportion of Selected Elements on the Paper Surface

Ratio of Binder	C Weight%	C Atomic%	Si Weight%	Si Atomic%
VAE:PVOH=10:0	5.83	8.95	27.58	18.72
VAE:PVOH=0:10	1.23	0.57	36.28	24.79

Impact of Different Binder Compositions on Printing

Optical solid density

Optical solid density is the print density measured with a reflection densitometer when the dot area coverage of printed matter is 100%. Solid density depends on ink layer thickness and substrate materials. As the ink layer becomes thicker, the density becomes higher within a certain range. The value of solid density depends on the ink absorption property of the coating on the paper, the penetration of the ink, and the retention of the colorant. The solid densities of cyan, magenta, yellow, and black in the six paper samples coated with different coating formulation used in the experiments are shown in Fig. 8.

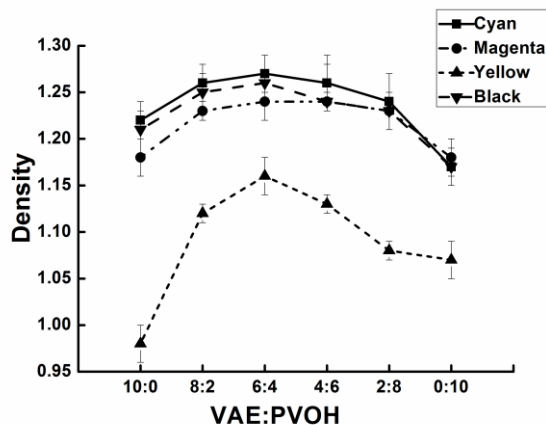


Fig. 8. Solid density of the six paper patterns

The coating using VAE or PVOH as binder alone produced the lowest print density with cyan, magenta, yellow, and black ink. Otherwise, the print density results from the coating VAE-to-PVOH ratio was 6:4 were on a high level. This was probably due to the difference of the pore properties in the coating.

As shown in Table 4, the use of PVOH binder resulted in lower specific surface and pore volume than with VAE binder.

Table 4. Specific Surface Area and Pore Volume of Three Silica Coated Papers

Samples	Specific surface area(m ² /g)	Pore volume (cm ³ /g)
Coating paper (VAE: PVOH=10:0)	8.2678	0.0401
Coating paper (VAE: PVOH=8:2)	7.3364	0.0382
Coating paper(VAE: PVOH=6:4)	5.7211	0.0326
Coating paper (VAE: PVOH=4:6)	5.9674	0.0348
Coating paper (VAE: PVOH=2:8)	6.3048	0.0362
Coating paper(VAE: PVOH=0:10)	6.5402	0.0377

This is attributed to the ability of PVOH to go into the intraparticle pores (pore diameter of 20 to 60 nm) of specialty porous silica pigments, such that some of the smallest pores were closed up (Lamminmäki *et al.* 2010). Instead, VAE cannot transfer to the same extent as PVOH. Because the particles were too large (900 nm) to flow into the pores of the silica, they only filled in the gaps between silica particles. Furthermore, coating using VAE as binder alone was not as uniform as in the case of PVOH binder (Fig. 6), so coating with VAE binder retained a larger specific surface and pore volume.

When VAE and PVOH were mixed at a 6:4 ratio, the surface area and pore volume of the paper was smallest. Inks had minimum penetration in this type of coating, leaving more colorants on the surface of the paper, resulting in the largest solid density.

Dot gain

The dot gain is important for tone rendering of a picture. Inkjet printing is a non-contact printing process. The dot gain is mainly caused by the spreading of aqueous-based inks on the surface of the paper. Serious dot gain may result in the loss of picture tones. From the dot gain curve of cyan, magenta, yellow, and black (Fig. 9), the ratio of binder affected dot gain in light and middle tones. Using PVOH alone as coating binder resulted in the largest dot gain, while the smallest was observed when using VAE alone. With the increasing ratio of PVOH in binder, dot gain was intensified.

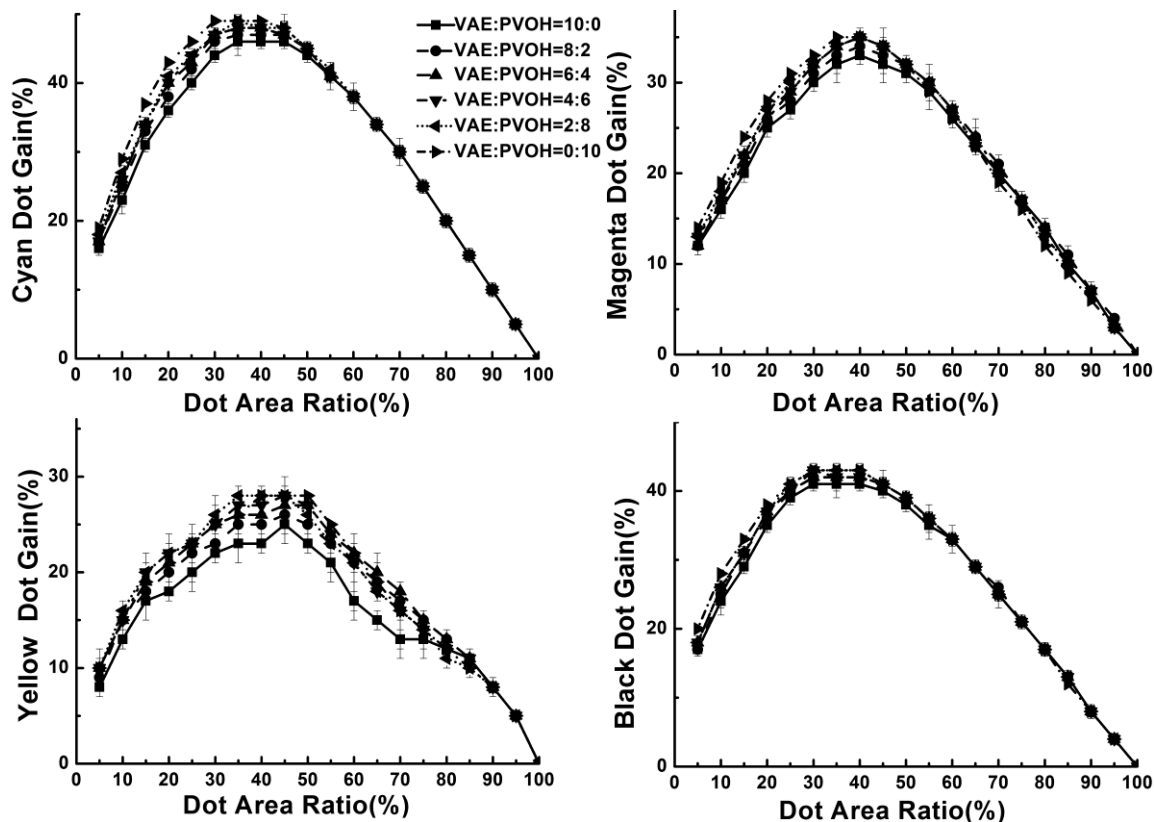


Fig. 9. Dot gain curves of cyan, magenta, yellow, and black for six coating papers with different ratios in VAE and PVOH, respectively

1% dot data on paper samples with different binder ratio were sampled randomly. By threshold segmentation and edge extraction of 30 ink dot, the roundness and circumference were measured. Figure 10 shows the results of ink dot processing.

To every single ink dot, the larger the ink dot roundness achieved, the more regular the ink dot shape was; the longer the ink dot circumference was, the less smooth the ink dot edge became. As shown in Fig. 11, the ink dot quality was the best when the ratio of VAE and PVOH was as 6: 4 with the shortest circumference and the largest roundness of an ink dot.

The structural as well as chemical differences of coating layers affect the final inkjet print quality (Lamminmäkiet *al.* 2010). The stronger the hydrophobicity of the binder is, the less the water-based ink absorption and diffusion (Di Risio and Yan 2006; Järnströmet *al.* 2010). Therefore, the increment of PVOH, which has a strong water absorption, could result in the enhancement of the dot area and dot perimeter.

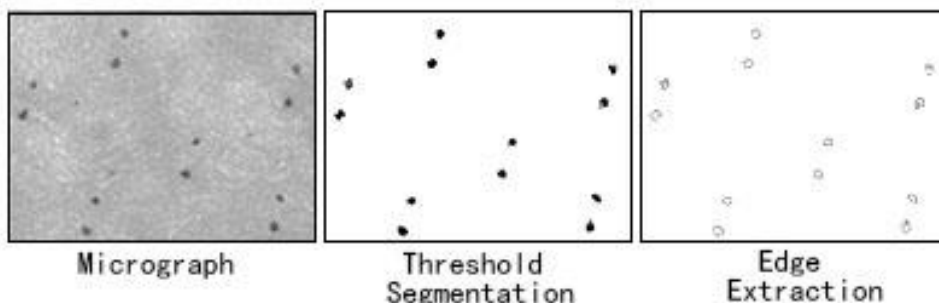


Fig. 10. Image processing of 1% Dot (72 lpi)

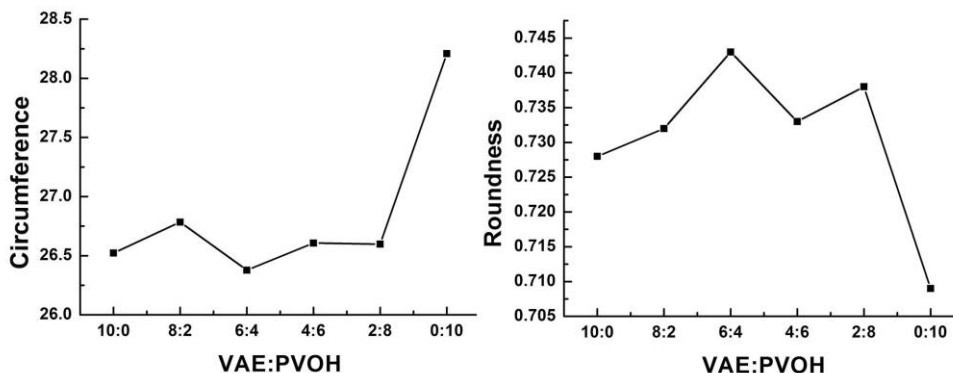


Fig. 11. Perimeter and roundness of 1% Dot (72 lpi) in different ratio of VAE and PVOH

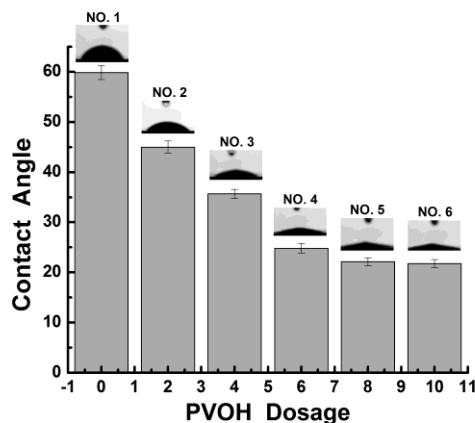


Fig. 12. Contact angles and shapes of deionized water droplets of six paper samples

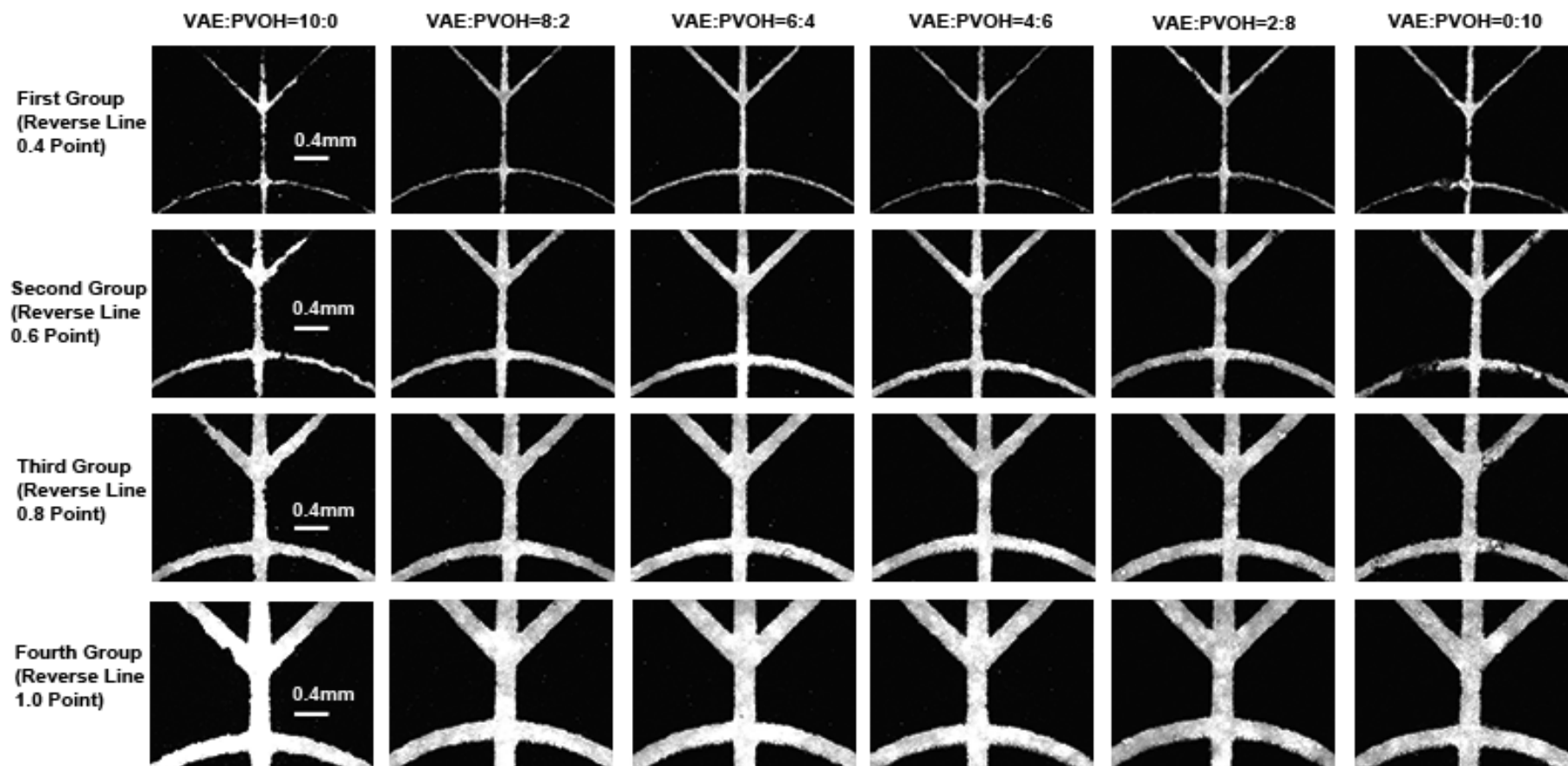


Fig. 13. Rendering of reverse lines of different width from 0.4 to 1.0 point with different VAE-to-PVOH ratios. In each group, using either VAE or PVOH alone had the worst results, with reverse line width partially shown. Images VAE-to-PVOH ratio were 8:2 and 6:4 had best line quality.

Figure 12 gives the contact angles and shapes of the deionized water droplets on the surface of six types of coated papers when the droplets were on the substrate for 100 ms. As can be seen, with the decrease of VAE and increase of PVOH contents in the coating, the contact angle decreased. The shape of the deionized water droplets changed from hemispherical to ellipsoid, and almost became flat triangle eventually. The substrate swelling gave rise to the triangular form.

The VAE molecule is hydrophobic and has weak polarity; therefore it can prohibit the water from spreading. By contrast, the PVOH molecule is hydrophilic with strong polarity; thus it helps the spreading of water (Chen *et al.* 2012; Zhu *et al.* 2012). PVOH also enhanced water-based ink spreading and resulted in serious dot gain.

Line qualities

The ISO-13660 standard prescribes blurriness and raggedness to quantify the line qualities (Shuichi *et al.* 2000). Blurriness is the appearance of being hazy or indistinct in outline. The lower the blurriness is, the better the line quality. Raggedness is the geometric distortion of an edge from its ideal position. A ragged edge appears rough or wavy rather than smooth or straight. The lower the raggedness, the better the line quality.

Figure 13 shows the rendering of four groups of reverse lines under different VAE-to-PVA ratios. In the present experiments, although there were eight widths of reverse lines, within the range of 0.01 to 1.0 point, only four groups of reverse lines with 0.4 to 1.0 point size were rendered, while the others were filled in by the ink.

By comparing the quality of reverse lines in Fig. 13, the best reverse lines with complete shape and the biggest line width, which means the least diffusion of ink can be found in each group. The reverse line reached the best quality during the ratio of VAE and PVOH as 6:4 in groups 1, 2, 3, and 4. Besides, AVE or PVOH used alone in each group all made an unclear line edge and incomplete line shape.

With strong hydrophilicity of PVOH, ink was diffused acutely; therefore, reverse lines became narrow and their quality was decreased. In the VAE latex the hydrophobic nature prevented the permeation of the ink into the polymer matrix and surface diffusion took place (Svanholm 2007; Lamminmäki *et al.* 2012). Both of them resulted in serious spreading of ink and high edge blurriness and raggedness. The pictures with VAE-to-PVA ratio of 6:4 had the lowest edge blurriness and raggedness, probably due to the appropriate hydrophilic nature of the binder mixture that held the diffusion of the ink and achieved better line quality.

CONCLUSIONS

Silica particles with a certain size distribution, when they were used in combination with VAE or PVOH, were found to achieve better print quality and higher surface strength and smoothness, also determining the coating rheology. It seems that during the aqueous-based ink absorption into the coating, a binder film that contains either VAE or PVOH alone cannot effectively hold back the spreading and permeation of the ink; however the combination of the two, with a certain ratio, may result in preferable printing quality.

The PVOH can dissolve in the water, whereas the VAE latex is hydrophobic and the polymer particle is bigger (900 nm). It is possible that the mixing of the binders can optimize the properties of coating in inkjet paper, producing appropriate homogeneity, pore volume, and hydrophilicity. The results of the six different ratios of VAE and PVOH in binder mixtures showed that the greatest optical solid density, least dot gain, and relatively clear fine lines can be achieved when VAE-to-PVA ratio is 6:4.

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