Observation of the Ink Vehicle Penetration into Coated Paper by Confocal Laser Scanning Microscope

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Keywords: Ink, Vehicle, Penetration, Coated, Paper, Laser, Scanning, Microscope

SUMMARY

A good understanding of the final location of ink pigments and oils is important to improve print quality and to understand the mechanisms of ink setting. A new method to characterize the location of ink pigments and ink vehicle after printing is developed using a confocal laser scanning microscope (CLSM). Magenta dyes and pigments are natural to detect and characterize. Offset ink oils and coating layers are stained with distinct fluorescent dyes before imaging. Simultaneous observation of the coating and the ink vehicle is possible.

Inkjet dyes are found to penetrate through the coating layer into the fiber network for standard coating layers. Even for grades developed for inkjet printing, the dyes are found to penetrate over ten μm into the coating in high density ink areas, but pigmented inkjet inks show little penetration of pigments into the coating layers. The dye used to tag ink oils is found to separate from the oil as the oil moves through the coating layer. However, correction to the results is possible. In offset inks, the ink oils are found to accumulate around kaolin pigments and in bubbles inside the coating layer.

INTRODUCTION

The mechanisms of ink setting and penetration are important to understand to improve the quality of various printed products. The final location of ink vehicle, dyes and pigments indicate the setting mechanisms and influence the print quality. Coated papers, such as high grade printing paper and inkjet paper have high printability requirements. Current methods to characterize the location of ink components are tedious and expensive.

For conventional offset printing, the pigments and resins are thought to remain at the surface of the coating layer. However, it is not clear how deep the vehicle will penetrate into the coating and if some resin is transported into the coating layer. For inkjet printing, penetration of dye or pigment into the paper causes a loss of ink density.

Current methods to characterize ink penetration uses some type of cross sectioning of the sample. The methods to cross-section samples may lead to artifacts. In addition, it takes a long time for preparing the cross section even by the focused ion beam (FIB) [1, 2]. Also, in the cross sectional images, a wide area cannot be observed at one time. Ström *et al*. [3] and Preston *el al.* [4] used conventional spectral chemical analyses to confirm that pigments and resins for the most part stay at the surface of the coating layer. However, these techniques give an average result over an area and not detailed three-dimensional information. These earlier results are important, but there is a need for more detailed understanding, especially as more details with regard to ink setting are understood. There is a need for a quick method to characterize ink penetration that does not damage the sample, and can see a significant amount of the sample at one time.

Printing samples can be observed by the confocal laser scanning microscope (CLSM). Some applications of prints have previously been studied by CLSM [5], but the main topic was to characterize surface roughness. CLSM is established as a valuable tool for obtaining high-resolution images and three-dimensional reconstruction of a variety of specimens, especially in the field of medicine and biology. While the laser beam (Ar or He-Ne laser) is scanning the printed surface, the emitted fluorescent light is detected by photodetector. Because a pinhole is placed in front of the photodetector, out-of-focus information is reduced. The plane of focus is selected by a computer-controlled fine-stepping motor that moves the microscope stage up and down. The three-dimensional image can be reconstructed by stacking two-dimensional images collected in series. Enomae *et al.* has recently studied about the penetration of inkjet ink by CLSM [6]. In their study, the reconstructed images were observed. We have also studied to observe the ink penetration into uncoated paper by the reconstructed images of CLSM [7]. In this case, the fluorescence stain technique was utilized to observe the ink vehicle.

In the other method of CLSM, XZ frame as the cross-section image can be directly obtained and XZ frames in the Y-direction are taken. Both methods do not need any preparation of the cross-section. The cross-section image of XZ frame has higher resolution than that of the reconstructed image. Although the measuring times depend on the number of steps and the accumulation times, it takes about three to five minutes for one sample. Sample preparation time is minimal.

In this work, ink penetration in the coated grades is reported using CLSM. In this technique, the penetration of ink could be observed by three-dimensional images. In addition, the penetration of magenta inkjet pigments and magenta inkjet dyes in the inkjet-grade papers are characterized by XZ frames directly. In order to discriminate between coating and ink vehicle, a double-staining technique was also developed.

EXPERIMENTAL

A commercial photo gloss-type inkjet paper (IJP), a commercial matte-type IJP, and a commercial coated paper (104.7g/m^2) were used as papers for inkjet printing. A commercial coated paper was also used for offset printing.

Dye-type and pigment-type printers were used as the inkjet printers. The dye-type printer was a Stylus Photo 820 (EPSON Inc.), and the pigment-type printer was a Stylus C84 (EPSON Inc.). Printing was performed by the best photo mode for photos and graphics with high print quality. Both magenta low concentration part and magenta high concentration part in the printed samples were observed by CLSM.

A commercial coated paper was stained with Acridine Yellow. A 0.03 wt% of Acridine Yellow was dissolved in ethanol. The coated papers were soaked for 3 minutes in this solution, rinsed with pure ethanol for 5 minutes, and dried. Rhodamine B was used as a fluorescent dye for staining the ink vehicle due to its successful application in a previous study [7]. A 0.03wt% of Rhodamine B was added to the ink and was stirred. Before printing, the ink was held to stain completely for 24 hours. The stain ink was printed on the stain coated paper. Offset printings were carried out with a KRK printing tester with printing speed of 1m/s and printing pressure of 100 kgf. The amount of ink transfer was $1.3 g/m^2$.

In addition, coating was prepared from a calcium carbonate pigment (Carbopaque, IMERYS), a kaolin pigment (KCS Kaolin IMERYS) and a styrene-butadiene latex (620NA, Dow Chemical Co.). The coating color formulation was compounded from CaCO3 50%, kaolin 50%, and SB-latex 15%. Coatings were applied on the polyethylene (PE) film using a rod drawdown coater. The coating weight was $65 g/m^3$.

Images were obtained using a CLSM (Leica TCS-SP2). A x63 oil-immersion lens (HC PL APO, NA 1.32) and a x100 oil-immersion objective lens (HCX PL APO, NA 1.40) were used. Immersion oil (Refractive Index: 1.518) was supplied by Leica. The Z-resolution of the oil-immersion lens is more than three times better than that of a dry lens which has air between the sample and the objective lens. Therefore, it is possible to obtain an optical resolution in the z direction to less than 0.6µm using an oil-immersion lens [6]. Oil-immersion lenses have been previously used to observe pulp fibers [9, 10]. Excitation wavelengths of 458nm and 514nm from an Ar laser (power: 50mW) were used for the observation by CLSM. The detected wavelengths ranged from 535nm to 635nm for the excitation wavelength of 514nm, while the detected wavelength ranged from 470nm to 600nm for the exciting wavelength of 458nm. The excitation wavelength of 514nm was used for the observation of magenta ink and cyan ink vehicle, and the excitation wavelength of 458nm was used for the observation of coated layer on the coated paper. A dichroic beamsplitter, which separates the fluorescent wavelength from the excitation wavelength, was used (DD458/514). The pinhole diameter was set to 50µm. The shoulders of this detection window were assumed to be sufficiently away from the excitation wavelength to limit any crossover. Digital zooms of x1, x2 and x4 were used. Confocal images were obtained using both XYZ and XZY scan modes. In the case of XYZ mode, a sequence of XY (plane of the paper) frames was obtained at 0.1µm intervals in the Z-direction (thickness) and was stacked as a maximum intensity projection (Z-stack image). In the XZY mode, XZ images were obtained through rapid depth scanning and XZ (paper cross-section) frames in the Y-direction were taken at 2.5 µm intervals. The pixel count of each frame was 1024×1024-pixel images.

RESULTS AND DISCUSSION

Penetration of Inkjet Ink

Two inkjet inks were characterized, one is dye-type printer and the other is pigment-type ink. Because magenta dye and magenta pigment have fluorescence on the excitation wavelength of 514nm, the distribution of ink could be directly observed by CLSM with no staining. Figure 1 shows the Z-stack (maximum intensity projection) images of magenta low concentration parts (A) and magenta high concentration parts (B) of dye-type ink on the photo gloss paper. Dark parts overlapped with cyan ink. In the case of low concentration parts (Fig.1A), ink dots could be observed.

Figure 2 shows the cross-section (XZ) images of magenta low concentration parsts (A) and magenta high concentration parts (B) of dye-type ink on the photo gloss paper. The penetration of dye ink could be directly observed by XZ image of CLSM. Dye-type ink penetrated into photo gloss paper. It was obvious that the penetration of magenta dye ink of the low concentration parts was different from that of the high concentration parts. The increase penetration depth on the high concentration must be a simple result of capacity of the coating layer; more of the coating layer is needed to set the ink. However, Fig. 2B demonstrates that dye molecules do penetrate into the coating layer even for this grade intended for inkjet printing.

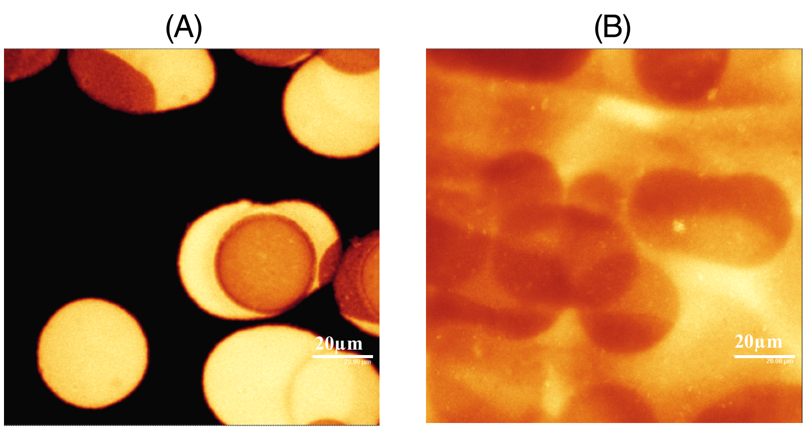

Figure 1 The Z-stack (maximum intensity projection) images of magenta low concentration parts (A) and magenta high concentration parts (B) of dye type ink on the photo gloss paper. (Oil-Immersion Lens X63, Digital Zoom X 2)

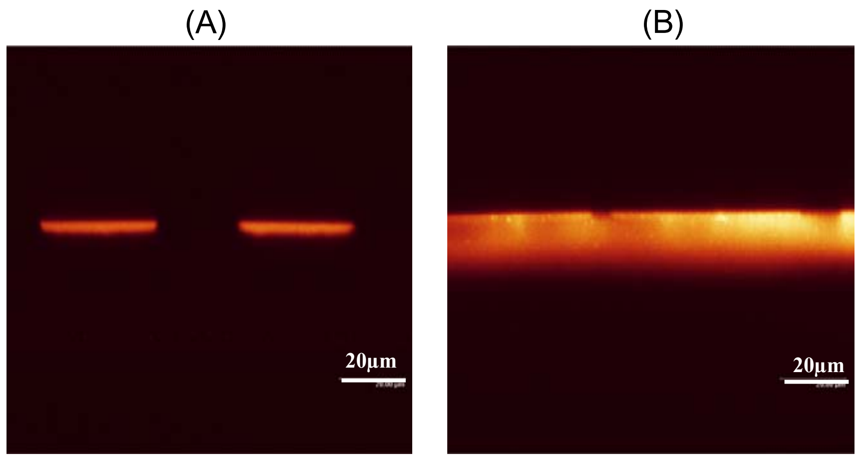

Figure 2 The cross section (XZ) images of magenta low concentration parts (A) and magenta high concentration parts (B) of dye type ink on the photo gloss paper Oil-Immersion Lens X63,Digital Zoom X 2

Figure 3 shows the cross section (XZ) images of magenta low concentration region (A) and magenta high concentration region (B) of pigment type ink on the photo gloss paper. The striking difference from the dye based ink is that the ink pigments stay on the paper surface even for high density printing. Even the overlap of the ink with the cyan ink is clear from Fig. 3B as shown as the non-planar region denoted with an arrow. From this shape, the results indicate that that the magenta ink was stacked on the cyan ink.

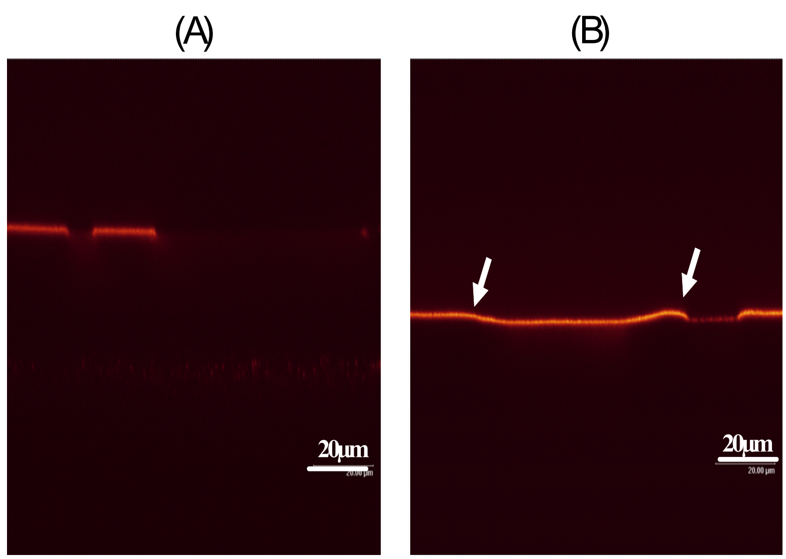

Figure 3 The cross section (XZ) images of magenta low concentration parts (A) and magenta high concentration parts (B) of pigment type ink on the photo gloss paper Oil-Immersion Lens X63,Digital Zoom X 2. Arrows show bulges in the ink film layer, likely caused by ink overlap with cyan ink.

Figure 4 shows the cross section (XZ) images of dye type ink and pigment type ink on the magenta low concentration part into the IJP matte paper. Dye type ink penetrated into the SiO_2 flocks, while pigment type ink stayed around SiO_2 flocks even for the IJP matte paper. It was clear that cross section images by XZY method show the penetration of ink directly.

(A) (B)

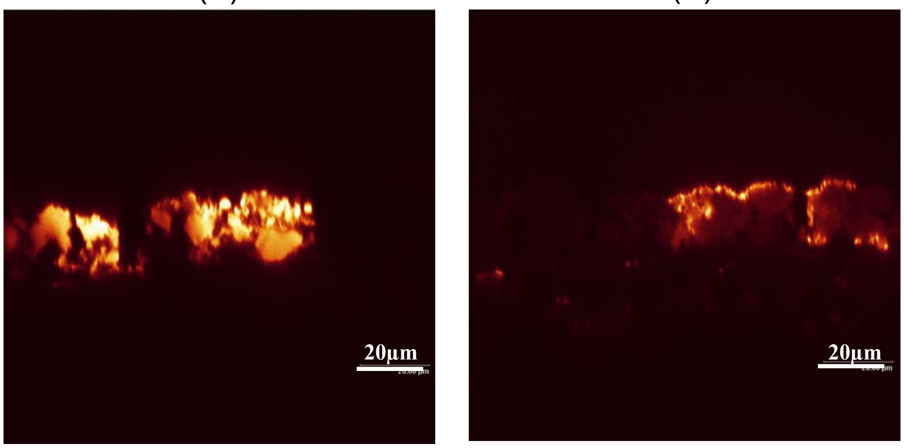

Figure 4 The cross section (XZ) images of dye type ink and pigment type ink on the magenta low concentration part into the IJP matte paper
(A) Dye type ink, (B) Pigment type ink, Oil-Immersion Lens X63, Digital Zoom X 2

Figure 5 shows the cross section (XZ) images of dye type ink and pigment type ink on the high concentration region printed on the commercial coated paper. Pigment type ink penetrated into the coated layer a small amount, about 2 μm, as Fig. 5B shows. In the case of the pigment type ink, printing quality was good even on the commercial coated paper. On the contrary, dye based inks penetrated not only into coated layer but also into base paper: this result is indicated in Fig. 5A because fiber cross sections are visible due to the magenta dye surrounding them. In the case of dye ink, printing image was poor on the commercial coated paper because the coated layer couldn't capture dye ink on the high concentration parts. The penetration of dye ink into the coated papers can be easily estimated by XZY method of CLSM; in Fig. 5A, we estimate the depth to be around 18 μm.

(A) (B)

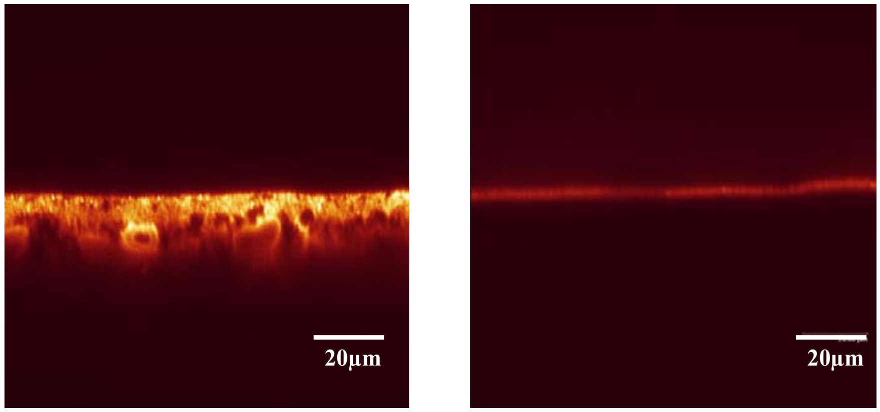

Figure 5 The cross section (XZ) images of dye type ink and pigment type ink on the high concentration part into the commercial coated paper
(A) Dye type ink, (B) Pigment type ink, Oil-Immersion Lens X63,Digital Zoom X 2

Simultaneous observation of offset ink vehicle and coated layer

Rhodamine B is added to the offset inks to tag or mark the location of the ink mobile phase. However, the dye may not totally stay with the ink oils because of some interactions with the coating layer. In the companion paper, Rhodamine B is found to adsorb to Styrene-Butadiene latex, but not much to kaolin or calcium carbonate [11]. The separation of Rhodamine B from ink vehicle by the coating layer was characterized here in order to estimate the error that may be caused by the separation.

The edges of the coated layer on plastic film slips were soaked in ink stained with Rhodamine B and were held for several days. The boundary of the ink on the coated layer was observed by CLSM and optical microscope. Figure 6 shows the CLSM Z-stack image and optical microscope image of 24 hours later after soaked in ink. The averaged intensity projection Z-stack image was obtained on the excitation wavelength of 514nm. The optical microscope image was obtained by transmitted light. The same location was observed. The distance from the edge of the ink pigment/coating interface to the top of the fluorescence detection is denoted “a” which is the distance that the Rhodamine B climbs. The distance that the vehicle actually climbs, detected by an opacity change, is denoted “b”.

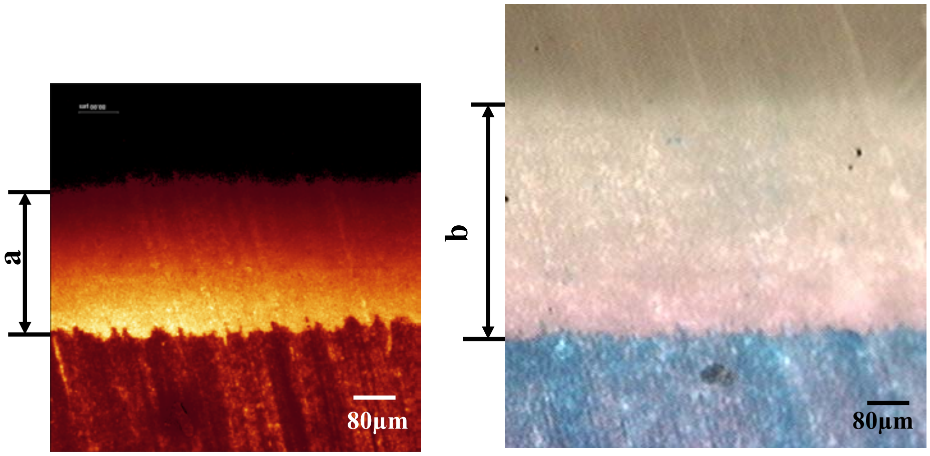

Figure 6 The CLSM Z-stack image and optical microscope image of the coated sample of 24 hours later after soaked in ink
Left: CLSM Z-stack image, Right: Optical microscope image by transmitted light
a : Distance of Rhodamine B Climbing, b : Distance of Vehicle Climbing

Figure 7 shows the relative affinity between the coating layer, the ink vehicle and Rhodamine B. Rhodamine B was somewhat trapped by the coating layer compared to the ink vehicle. Actually, the distance of Rhodamin B climbing is 50 % less than the ink vehicle climbing. This means that the penetration depth of ink vehicle could not be directly measured with this technique, but can be estimated based on Fig. 7. The distribution of ink vehicle can be observed by this stain technique because fluorescence dye would be also penetrated to the half depth of ink vehicle.

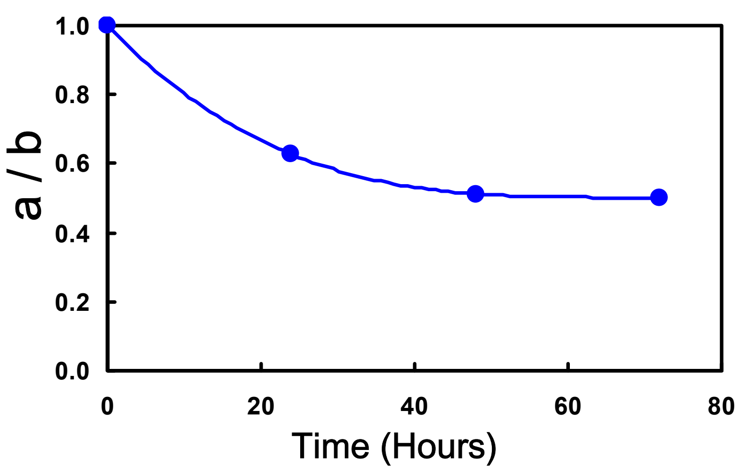

Figure 7 Relative affinity between ink vehicle and Rhodamine B in a coating layer.

In order to discriminate between coating and ink vehicle, a double staining technique was developed. Rhodamine B was used to stain for the ink vehicle. Acridine Yellow was used to stain the coated paper. Rhodamine B emits fluorescence on the excitation wavelength of 514nm. Acridine Yellow emits fluorescence on the excitation wavelength of 453nm. The ink vehicle and coated paper could be simultaneously observed by the alternate detection of Rhodamine B and Acridine Yellow.

Figure 8 shows the distribution of Acridine Yellow and Rhodamine B as the z-stack (maximum intensity projection) of CLSM. The green color expresses Acridine Yellow as coated paper, and red expresses Rhodamine B as cyan offset ink vehicle. The distribution of ink vehicle into coated paper could be observed well by the double stain technique. Some red spots, shown as arrows, were observed around the printing surface. When same ink was printed on the polyethylene film, red spots couldn't be observed. This confirms that the ink oils are well dispersed in the ink and not in the form of drops. It was expected that ink vehicle accumulated in the pores of coated layer surface. Pores between pigments may be too small to be imaged here, but larger pores or bubbles are evident. Figure 9 shows the distribution of ink vehicle and the coated layer on the frame of 0.5µm depth from printing surface. The location of this frame is the 5th step position from first signal of Rhodamine B on printing surface to z direction. Ink vehicle spreads along the surface of kaolin and even concentrates there because the surface of kaolin indicates the red color, shown as arrows in the figure. Figure 10 shows the distribution of ink vehicle and coated layer on the frame of 0.2µm deeper than XY frame in Fig.9. Ink vehicle could not penetrate into kaolin pigment; no fluorescence is obtained from inside the kaolin. Figure 11 shows the distribution of ink vehicle and coated layer on the frame of 1.2µm depth from printing surface. It was easy to discriminate between kaolin particle and bubble because configuration of bubble was sphere. Ink vehicle accumulated in the bubble of coated layer shown by the arrow.

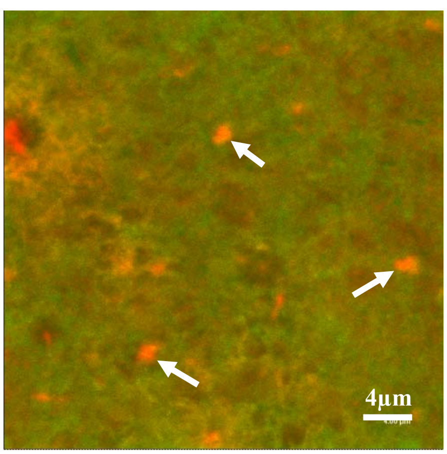

Figure 8 The distribution of Acridine Yellow and Rhodamine B as z-stack (maximum intensity projection) of CLSM.
Green color expresses Acridine Yellow as coated paper, and Red color expresses Rhodamine B as cyan offset ink vehicle.
Arrow show high vehicle concentrations.

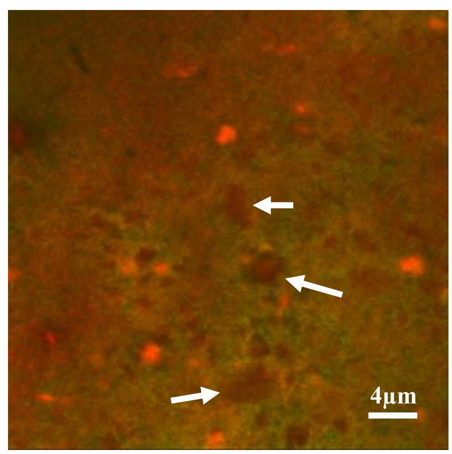

Figure 9 The distribution of ink vehicle and coated layer on the frame of 0.5µm depth from printing surface
This frame is the position of 5th step from printing surface.
Arrows show vehicle concentrated on kaolin surfaces.

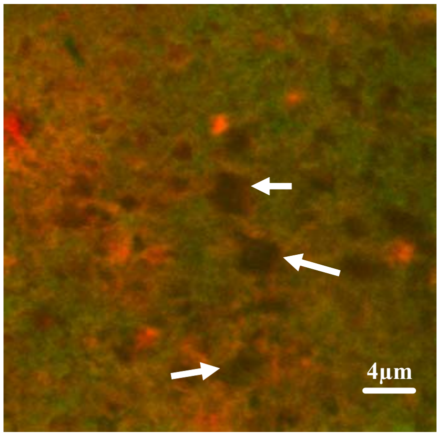

Figure 10 The distribution of ink vehicle and coated layer on the frame of 0.2 μ m deeper than XY frame in Fig.9
This frame is the position of 7th step from printing surface.
Arrows show kaolin positions.

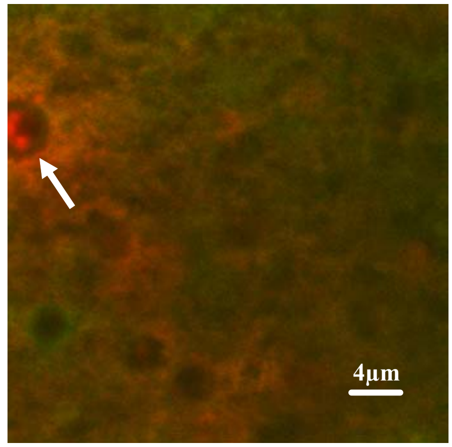

Figure 11 The distribution of ink vehicle and coated layer on the frame of 1.2 μ m depth from printing surface
This frame is the position of 12th step from printing surface. Arrows show vehicle concentrating in a bubble.

CONCLUSIONS

Magenta dye and pigments of ink jet inks could be directly observed by CLSM. Dye based inks penetrate into coating layers and into the fibers for standard coated grades, but pigmented inks tend to stay on the surface of the coating layer. Even for coating layers designed for dye based inks, dyes penetrate a significant amount into the coating layer for high density printing. For matte grade ink jet papers, ink pigments penetrate into the coating layer, but not into the silica flocs.

The behavior of offset ink vehicle stained with Rhodamine B into the coated layer was observed by CLSM and optical microscope. Rhodamine B is found to separate from ink vehicle as penetration occurs. The penetration difference was found to be 50%. The double staining technique was able to allow images that can separate out the ink vehicle from the coating layer. Vehicle was found to accumulate along kaolin surfaces and in coating layer bubbles.

ACKNOWLEDGMENTS

We thank the sponsors of the University of Maine Paper Surface Science Program for their support and discussions.

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