Application of CLSM observation technique to multicolored ink-jet dots

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Abstract

To improve print quality, it is important to analyze the mechanisms of ink fixation on paper. First of all, the three dimensional (3D) fluorescence spectra of excitation and fluorescence were obtained by a fluorescence spectrophotometer. The optical condition for observing ink-jet prints by CLSM was found through the characterization of three-dimensional fluorescence spectra of ink. The distributions of dye-based and pigment-based ink-jet inks were observed as fluorescence images by CLSM, whereas cross-sections of these ink-jet prints prepared by FIB were observed as light-reflected images by the optical digital microscope. By comparing light-reflected cross-section images of prints with reconstructed images of prints by CLSM, the distribution of ink-jet inks on the glossy photo ink-jet paper could be evaluated. In the case of pigment-based inks, the inks were fixed on the paper. On the other hand, in the case of dye-based inks, the inks were penetrated into the ink acceptable layer on the paper. In addition, inks tended to penetrate to depth proportional to the diameter of the ink dot.

Introduction

Depending on factors such as information source, output size and type of users, printing is classified into large-scale commercial printing and personal printing. Large-scale commercial printing has been popular ever since Gutenberg's invention, whereas personal printing is rapidly increasing with the advance of innovative information technology. In the case of commercial printing, the source of information traditionally exists as a manuscript on paper, and the printing efficiency has always been defined as mass production at high speed. In the case of personal printing, information, such as documents made on a computer or acquired from web site, has been output to paper by ink-jet printing or laser printing. However, printing for personal use is taking the place of large-scale commercial printing more and more because the printing speed has recently increased and it need not make a plate [1].

Image-Switch was developed by the National Printing Bureau of Japan. This technique can secure the originality of documents printed using common pigment-based ink-jet printer and laser printer [2]. Image-Switch has the advantage of no need of special paper or ink. In the case of a color laser printer, most of color toners do not penetrate the paper, but they are only fixed on the surface. As a result, the topography of toner layers is hardly affected by the topography of paper, and stable prints can be easily obtained. However, in the case of ink-jet printers, the actual output is different from the input data because the ink penetrates and spreads inside the paper. Therefore, it is important to elucidate the ink fixing mechanisms in order to improve the quality of prints.

So far, regarding the fluorescence property of magenta and black inks used in ink-jet printing, it has been reported that it is possible to observe the three-dimensional ink distribution using a Confocal Laser Scanning Microscope (CLSM). [3]. We could also observe the distribution of four process colors (cyan, yellow, magenta and black) on XY plane by CLSM in the limited condition [4].

To focus on the ink penetration into paper, the cross-section of printed paper was prepared by microtome, and this cross-section was observed by the optical microscope. However, it was very difficult to obtain the cross-section on the particular portion desired. In addition, printing ink often dissolved into the embedding resin used in the microtome method. Uchimura et al. developed a new technique for preparing cross-sections of prints by focused ion beam (FIB)[5,6]. Cross-sections of a particular portion of a printing sample could be directly prepared by the FIB technique. The ink penetration could also be observed clearly by the optical microscope because the cross-section of prints obtained by FIB was very smooth. The distribution of dye-based ink-jet ink could be observed in matt and glossy ink-jet papers using an optical microscope, scanning electron microscope (SEM) and electron probe micro-analyzer (EPMA)[7].

In this study, the distribution of dye-based and pigment-based ink-jet inks was observed as three dimensional fluorescence images by CLSM on the base of fluorescence spectra of ink-jet inks. In addition, actual cross-sections of these ink-jet prints prepared by FIB were also observed as light-reflected images by the digital microscope. By comparing the fluorescence images with the light-reflected images, the penetration of the ink-jet inks was characterized.

Experimental

Samples

Photo grade glossy ink-jet paper commercially available was used. Printed samples were prepared by outputting a line of 0.1 mm in width by two ink-jet printers (printers A and B). The resolution of the output was adjusted to 600 X 600 dpi. In the case of printer A, all inks (cyan, magenta, yellow and black) were pigment-based inks, while, in the case of printer B, only the black ink was pigment-based and the other inks (cyan, magenta and yellow) were dye-based. Each ink was removed from its cartridge, and the fluorescence properties of the inks were measured.

Determination of fluorescence from ink-jet inks

The three dimensional (3D) fluorescence spectra of excitation and fluorescence were obtained by a fluorescence spectrophotometer (Hitachi: F-2500). Measurement conditions were indicated in Table.1. The 3D measurement technique is accomplished by measuring the emission spectrum of a sample while changing the excitation wavelength. The properties of excitation and fluorescence of ink-jet inks were measured as the dilute solution by deionized water.

Table 1 Measurement condition of fluorescence spectrophotometer

Items	Conditions
Measurement mode	3 dimension
Data mode	Fluorescence
Excitation start wavelength	400.0 nm
Excitation end wavelength	700.0 nm
Excitation sampling interval	5.0 nm
Fluorescence start wavelength	400.0 nm
Fluorescence end wavelength	700.0 nm
Fluorescence sampling interval	5.0 nm
Scan speed	230 nm/min
Excitation side slit	5.0 nm
Fluorescence side slit	5.0 nm
Voltage of photo-multidetector	400 V
Response	2.0 nm

Observation by CLSM

Images were obtained using a CLSM (Leica, TCS-SP5) equipped with an X63 oil－immersion objective lens (HCX PL APO, NA 1.40). The immersion oil (Refractive Index: 1.518) was supplied by Leica. The Z-resolution of the oil-immersion lens is three times better than a lens with air between the sample and the objective lens. Therefore, it is possible to obtain an optical resolution in the z direction to less than 0.6 µm using an oil-immersion lens [8]. Excitation wavelengths of 488 nm from an Ar laser and 405 nm from a diode laser were primarily used for the observation of the prints by CLSM. The pinhole diameter was set to 151.6 µm. 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 0.15µm intervals in the z-(thickness) direction and was reconstructed using software. 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 3.6 µm intervals. Each frame size was all 512 x 512 pixels. Although the length of measurement time depends on the number of steps and accumulation and the sequential scan mode, it takes about 3 to 10 minutes.

Cross-sectioning and observation of prints

FIB (Hitachi; FB-2000A) was used to prepare cross-sections of samples. The acceleration voltage for a high etching rate was 30 kV, which was attained using liquid gallium metal as the ion source. A beam with an object aperture of 500µm at an electric current of approximately 12nA was irradiated on samples.

Light-reflected cross-section images were obtained by the optical digital microscope (Keyence, VH-8000). Back-scattered electron images of cross-sections were obtained using SEM (Hitachi, S-300N). The electron beam was supplied at an acceleration voltage of 15 kV at the low vacuum (25 Pa), and the working distance was 19.2 mm.

Results and Discussion

Determination of fluorescence of ink-jet inks

Pigment-based ink-jet inks

Figure 1 shows the three dimensional fluorescence spectra of the deionized water and magenta pigment-based ink (Printer A). The linear swollen part in the center indicates the scattering of exciting light. The scattering light of magenta ink was saturated because the scattering light of magenta ink was much stronger than that of the deionized water. Fluorescence usually comes longer than the excitation wavelength. The deionized water had no fluorescence (Fig1-a), whereas the magenta ink had the fluorescence on the wavelengths between 550 nm and 600 nm in the excitation wavelength from 500 to 580 nm (Fig.1-b).

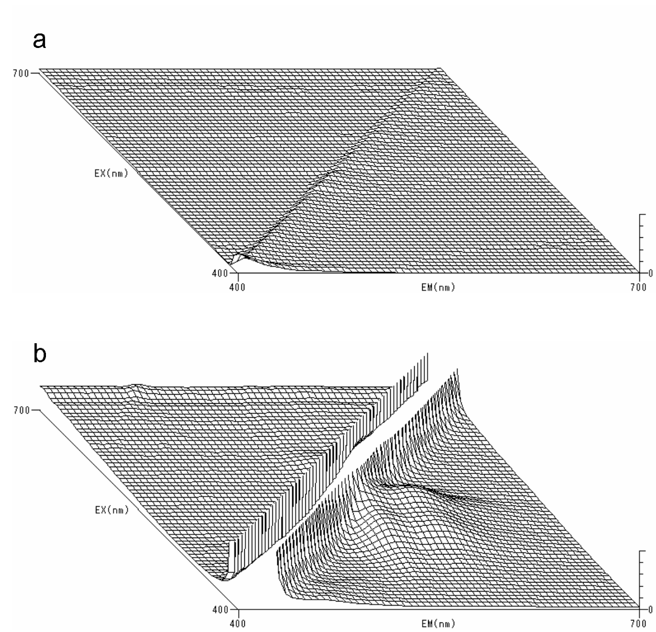

Figure 1. Three dimensional fluorescent spectra
(a) Deionized water, (b) Pigment type magenta ink for Printer A

Figure 2 shows the fluorescence spectra of pigment-based ink-jet inks. The excitation wavelength of each ink was selected on the basis of 3D fluorescence spectra. Each spectrum indicates the intensity relative to the maximum value of fluorescence intensity. The magenta and yellow inks emit strong fluorescence at the excitation wavelength of 488 nm. The yellow ink had a peak at the fluorescence wavelength of 550 nm while the magenta ink had two peaks at 548 nm and 590 nm (Fig2-a, b). The cyan ink had a fluorescent peak at 480 nm for the excitation wavelength of 405 nm (Fig2-c). However, pigment-based black inks of both printers A and B showed no fluorescence at any excitation wavelengths.

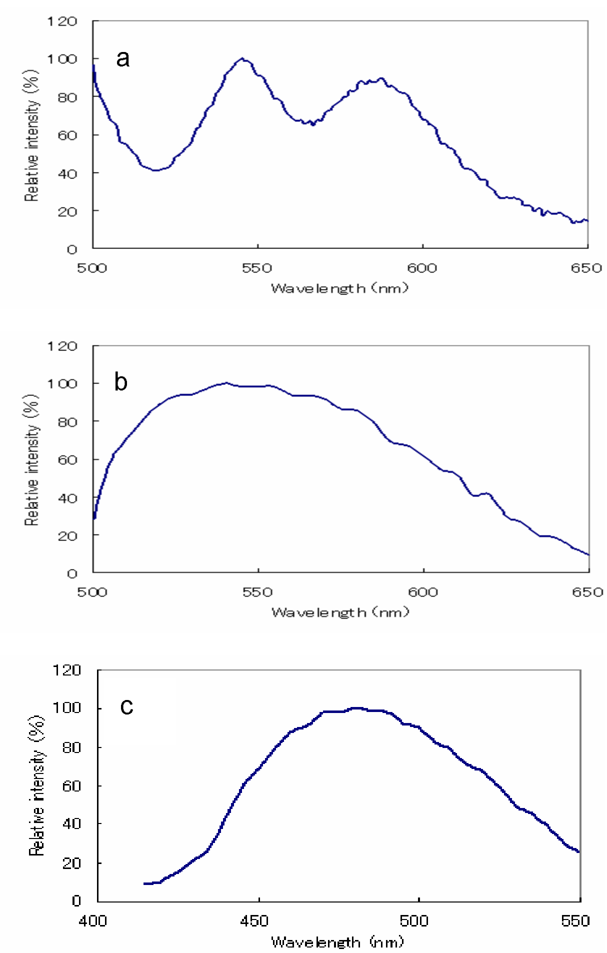

Figure 2. Fluorescence spectra of pigment-based ink-jet inks
(a) Magenta ink (Excitation wavelength of 488 nm)
(b) Yellow ink (Excitation wavelength of 488 nm)
(c) Cyan ink (Excitation wavelength of 405 nm)

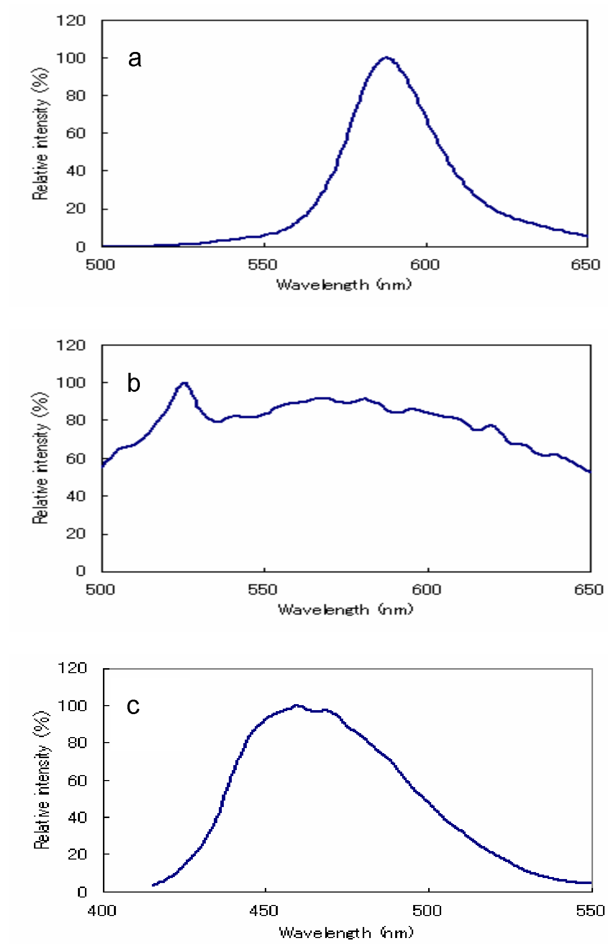

Figure 3. Fluorescence spectra of dye-based ink-jet inks
(a) Magenta ink (Excitation wavelength of 488 nm)
(b) Yellow ink (Excitation wavelength of 488 nm)
(c) Cyan ink (Excitation wavelength of 405 nm)

Dye-based ink-jet inks

Figure 3 shows the fluorescence spectra of dye-based ink-jet inks obtained from the similar procedure for the pigment-based inks. The excitation wavelengths for the dye-based inks were the same with those for the pigment-based inks. The magenta dye-based ink emitted a strong fluorescence having a peak at 590 nm. The yellow ink had a broad peak from 500 nm to 650 nm and another sharp peak on the wavelength of 525 nm. This might mean that two components in the yellow ink emit fluorescence. The cyan ink has a fluorescence peak at 460 nm at the excitation wavelength of 405 nm.

Characterization of ink fixation and ink penetration

Figure 4 shows the SEM image of the cross-section of a pigment-based magenta print. Layer “a” indicates the ink acceptable layer while layer “b” indicates the resin coat layer. The base paper was observed under layer “b”. The thickness of the ink acceptable layer was determined from the SEM image. The depth of ink penetration was calculated from the light-reflected cross-section image of digital microscope and the reconstructed XZ and YZ images of CLSM on the basis of the thickness of the ink acceptable layer.

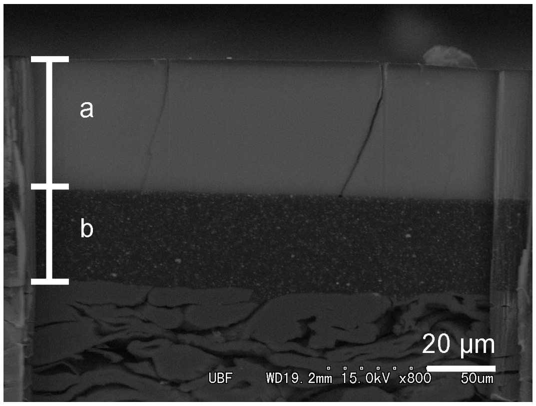

Figure 4. SEM image of cross section of pigment type magenta prints
a: Ink acceptable layer, b: Resin coat layer
Cross section was prepared by FIB.

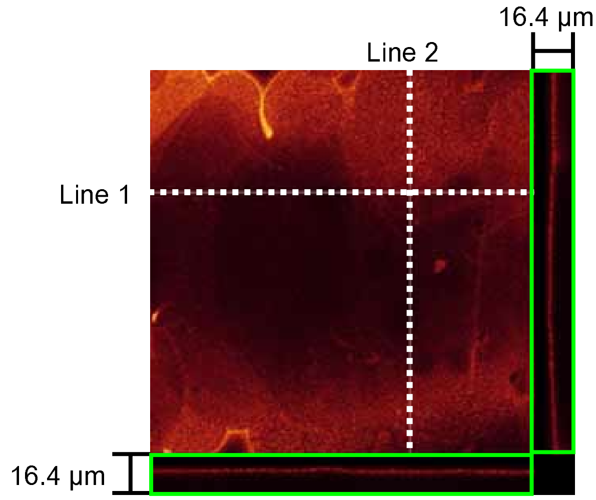

Figure 6. Reconstructed image of magenta printing sample obtained from XYZ scan mode of CLSM

Pigment-based ink-jet inks

Figure 5 shows the light-reflected cross-section image of a pigment-based magenta print by the optical digital microscope. The blue (dark in monochromatic print) layer indicates the ink acceptable layer. The thickness of the ink acceptable layer was approximately 40 µm. The ink is observed to be fixed on the ink acceptable layer. The thickness of the ink layer was calculated approximately 3 µm.

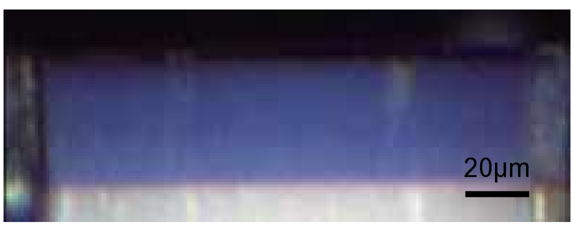

Figure 5. Light-reflected cross section image of pigment-based magenta prints by the digital microscope

Figure 6 shows the reconstructed image of magenta prints obtained in the XYZ scan mode of CLSM. The fluorescence of ink portions is represented in quasi-color. The square image shows the XY plane. The cross-section image at the bottom represents the XZ plane image along line 1 of the XY plane image, and the other cross-section image represents the YZ plane image along line 2 of the XY plane image. The thickness of ink layer was estimated to be 3.1µm because the Z-depth of reconstructed cross-section images in figure 6 was 16.4µm. The thickness of the ink layer obtained by the digital microscope was almost equal to that obtained by CLSM. By comparing the light-reflected image with the reconstructed cross-section images of CLSM, it was confirmed that the distribution of the ink pigment fixed on the ink-jet paper was observed as a fluorescence image. Although the presence of two fluorescent intermolecular components were suggested from the fluorescence spectrum in Figure 2(a), these components were not observed inside the paper. This was why two kinds of fluorescence were emitted from the ink fixed on paper.

Figure 7 shows the light-reflected cross-section image of yellow prints using the digital microscope. The fixation of yellow ink was similar to that of magenta ink. The thickness of the yellow ink layer was estimated as 3µm.

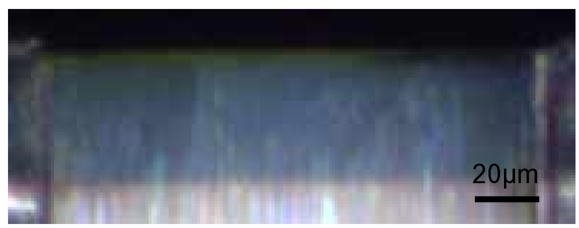

Figure 7. Light-reflected cross section image of yellow prints using the digital microscope

Figure 8 shows the reconstructed image of yellow printing sample obtained in the XYZ scan mode of CLSM. The thickness of the ink layer was estimated to be approximately 4 µm because the Z-depth of reconstructed cross-section images was 13.5 µm.

In the case of the yellow ink, the thickness of the ink layer observed by the light-reflected image was 1µm shorter than that by the fluorescence image.

That is why fluorescence of the yellow ink was detected more sensitively than that of the magenta ink through the pinhole of CLSM because the fluorescence intensity of yellow ink is much higher than that of magenta ink. It was confirmed that the thickness of ink layer estimated by CSLM technique slightly vary in fluorescence intensity of ink.

The fluorescence of the cyan ink could not be discriminated from that of paper because the fluorescence intensity of the ink was very weak. As a result, the pigment-based cyan ink fixed on paper could not be observed by CLSM.

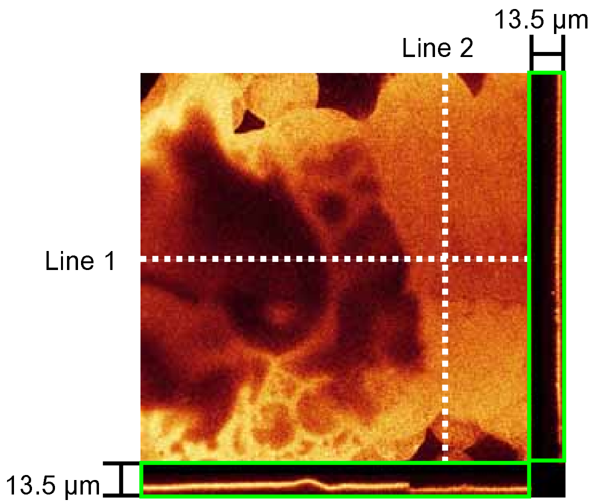

Figure 8. Reconstructed image of yellow print obtained in the XYZ scan mode of CLSM

Dye-based ink-jet inks

Figure 9 shows light-reflected cross-section images of dye-based magenta, yellow and cyan prints by the optical digital microscope. The pigment-based inks could be fixed on the glossy photo ink-jet paper (Figs. 5 and 7), whereas the dye-based inks penetrated the ink acceptable layer of the glossy photo ink-jet paper (Fig. 9). Although the ink acceptable layer appears pale blue, the cyan dye-based ink could be distinguished from the ink acceptable layer due to the clear contrast.

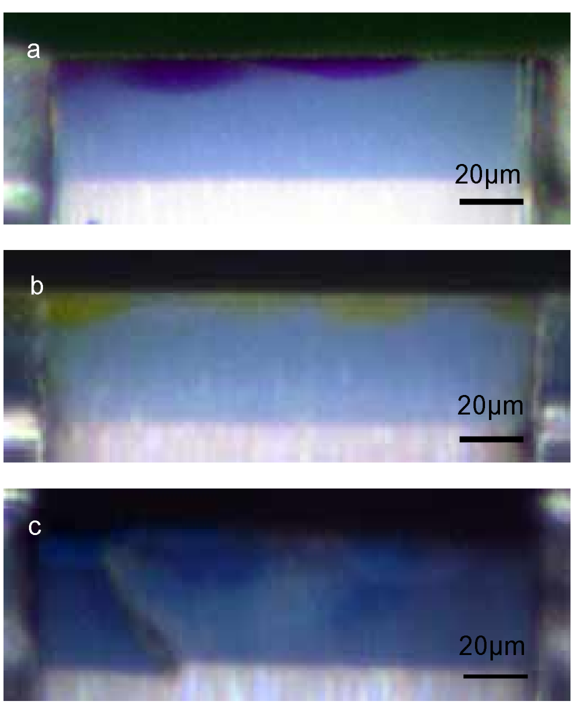

Figure 9. Light-reflected cross section images of dye-based ink print obtained by the digital microscope
a: Magenta ink, b: Yellow ink, c: Cyan ink

As well as the pigment-based inks, figure 10 shows the reconstructed images of magenta prints and yellow prints which were obtained in the XYZ scan mode of CLSM. The z-depth of the reconstructed cross-section images of yellow and magenta prints were 22.08 µm and 18.46 µm, respectively. And the ink penetration depth was from 6µm to 11µm. In addition, inks tended to penetrate to a depth proportional to the diameter of the ink dot. Figure 11 shows an XZ plane image of the cyan print which was obtained in the XZY scan mode. The distribution of the cyan ink was observed directly using the scan mode of XZY because the fluorescence of cyan dye was easily degraded by the laser beam. This method can be used even for magenta and yellow prints. The dye-based cyan ink in the glossy photo ink-jet paper could be observed by CLSM because this cyan dye had sufficient fluorescence intensity and paper had no fluorescence. In the case of wood free paper, however, the penetration of cyan dye-based ink could not be observed because optical brightening agents contained in paper emitted strong fluorescence at the excitation wavelength of 405 nm.

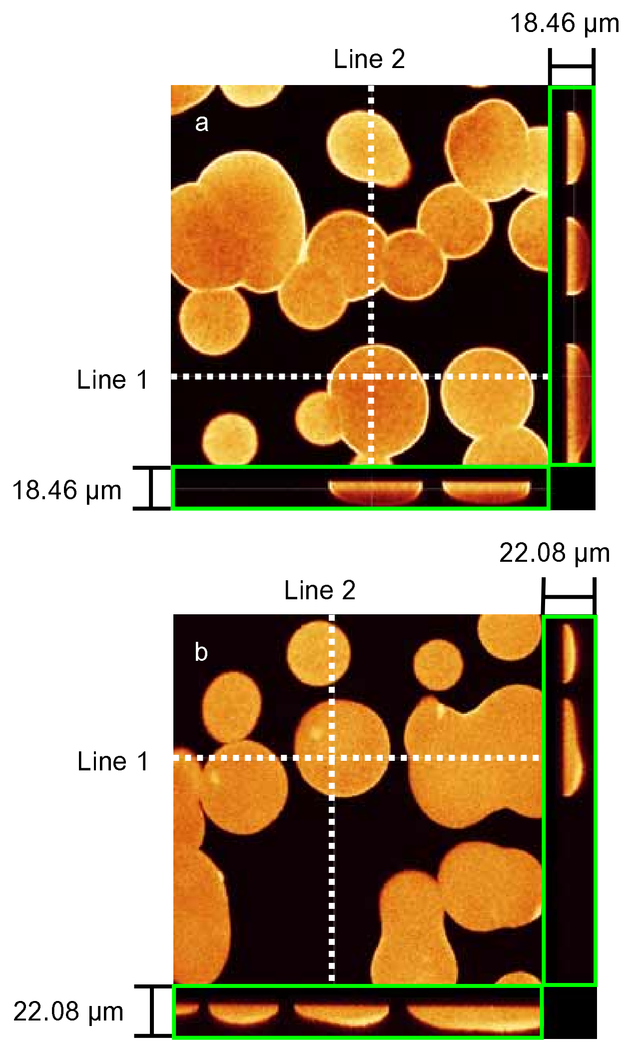

Figure 10. Reconstructed images of prints obtained in the scan mode of XYZ of CLSM
a: Magenta ink, b: Yellow ink

Figure 11. Reconstructed images of cyan prints obtained in the XZY scan mode of CLSM

Conclusions

(1) The optical condition for observing ink-jet prints by CLSM was found through the characterization of three-dimensional fluorescence spectra of ink. In the case of magenta and yellow inks, the fluorescence was obtained in the range between 500 nm and 650 nm at the excitation wavelength of 488 nm, whereas, in the case of cyan ink, the fluorescence was obtained in the range between 500 nm and 650 nm at the excitation wavelength of 405 nm.

In addition, the pigment-based black ink could not be observed by CLSM because the pigment-based black ink had no fluorescence at any excitation wavelength.

(2) By comparing light-reflected cross-section images of prints with reconstructed images of prints by CLSM, the distribution of ink-jet inks on the glossy photo ink-jet paper could be evaluated. In the case of pigment-based inks, the inks were fixed on the paper. On the other hand, in the case of dye-based inks, the inks penetrated the ink acceptable layer on the paper. In addition, the dye-based inks tended to penetrate to a depth proportional to the diameter of the ink dot.

References

[1] Enomae, T., "Penetration behavior of ink drop", Vol.31 No.2, Sikoku pulp and paper research technical letter, 2(2005)

[2] Nagashima, H., "A Novel Half-Tone Screening for Anti-counterfeiting", Vol.41 (4), J. Printing Sci.& Tech. of Japan, 217 (2004)

[3] Enomae, T. Ivutin, D. and Isogai, A., "Three-dimensional distribution of ink-jet inks in paper acquired by confocal laser scanning microscope", APPITA Annual conference & Exhibition Proceedings, 577-588 (2004)

[4] Naito, M. Enomae, T. Isogai, A. Nagashima, H. "Observation of ink-jet ink distribution using confocal laser scanning microscope" J. Printing Sci.& Tech. of Japan, 91-95(2006)

[5] Uchimura, H. Kimura, M., "A Sample Preparation method for Paper Cross-sections using a Focused Ion Beam" , Sen'i Gakkaishi, Japan, 54(7) : 360-366(1998)

[6] Uchimura, H., "Preparation method of paper and printed paper cross-sections using a focused ion beam to observe it with microscope", J. the Imaging Society of Japan (Nippon Gazo Gakkaishi), 42(2): 168-172(2003)

[7] Uchimura, H. Ozaki, Y. Kimura, M., "Observation of the dye ink penetrated into the ink jet printing papers", International Printing & Graphic Arts Conference, 199-205(2004)

[8] Sterlzer, E. H. K., "Handbook of Biological Confocal Microscopy", Plenum Press, New York, 139-154(1995)

Author Biography

Mikiko Naito workes for the National Printing Bureau from 1996 and engaged in print technology in Odawara Plant. As for her passing in 2005 at a research institute and she studied about printability of ink-jet ink as a visiting researcher of Tokyo University in 2006. Current topic are "Three dimensional observation of ink-jet ink by confocal laser scaning microscope"etc. She is engaged to the research and development of security technology.