Three-dimensional distribution of ink-jet inks in paper acquired by confocal laser scanning microscope

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ABSTRACT

A new method of determining three-dimensional distribution of dye-based inks for ink-jet was demonstrated. In this method, fluorescence emitted from dyes is detected in a laser scanning microscope. Most magenta and black dye-based inks for ink-jet contain fluorescence agents or use fluorescence dyes specific of the color. Fluorescence emitted from those of the ink-jet inks provides a three dimensional ink distribution by the optical slicing function of a confocal laser scanning microscope. Its characteristic high sensitivity owes to intense light emission even from trace fluorescence dyes as compared to observation with a regular optical microscope. However, it keeps easy sample preparation, as is a merit of optical microscopy. In applications, several facts were revealed. Ink dot shape was like a coin with a constant thickness on photo quality paper, ink spreads over crack surfaces on high gloss type paper a few times deeper than the normal penetration and ink dots had rugged edges with their tips intruding between fibers in the base paper for medium grade paper. Three-dimensional image analysis is potential to be a useful measure to clarify more dye-based ink penetration mechanisms.

KEY WORDS

Dye-based inks, Fluorescence dye, Image analysis, Optical slicing, Photo quality paper, Silica coatings

INTRODUCTION

Mechanisms of ink penetration and setting are very important in all kinds of printing methods considering how prints appear to human eyes depends on morphology of the settled ink as well as its optical properties. Ink-jet prints recorded in dye-based inks are difficult to handle to determine the ink distribution. Dye-based inks bond, on the molecular level, with pulp fibers or coating pigments via cationic polymers to ensure the bonding even when moisturized. Both the inks and cationic polymers dissolve in water and they have no shape after drying. So, it is difficult to determine a dye-based ink distribution from a standpoint of solid morphology, unlike pigment inks. In this work, attention was paid to fluorescence dyes formulated in ink-jet inks with regular colored dyes. These fluorescence dyes facilitate observation ink geometry in a confocal laser scanning microscope (CLSM) without any

staining the sample.

CLSM application is a novel and unique technique for observing ink-jet ink distribution, but has been utilized in paper science for different other purposes. The most common purpose is geometrical measurements like surface profile and fiber network structures. Beland et al. [1] measured surface profiles of matte-coated paper three-dimensionally using the confocal function and related perception of gloss to the surface topography. Aggelidis et al. [2] visualized fiber network deformation caused by calendering to correlate the changes with the macroscopic compressible elasto-viscoplastic response of paper coatings. Xu et al. [3] determined paper layer structures from discrete layers made by optical sectioning followed by a dynamic thresholding method for separating fibers from air and artifacts. Observation of trace constituents contained in paper is also in the scope of CLSM. Ozaki [4] stained polyamide epichlorohydrin resin in paper with Sulfo rhodamine 101 selectively and observed the resin distribution in the sheet. Suominen et al. [5] found that the bacteria were mainly localized in the interface area between the polyethylene layer and the cellulose fiber web of a food-packaging paperboard stained with acridine orange.

Turning to ink penetration analysis, the most popular method is making a cross-section of a sheet printed and observation with an optical microscope. But, sectioning needs manipulative skills and is nearly impossible to sample a pinpoint targeted dot of ink. Several other methods were applied to clarify ink penetration. Helle and Johnsen [6] clarified microscopic offset ink locations by stereoscopic backscatter imaging with micrographs obtained by scanning electron microscopy (SEM). Energy dispersive X-ray analysis (EDX) combined with SEM is also a valuable mean to detect elements contained in inks to obtain two-dimensional distribution. Uchimura et al. [7, 8] developed a new technology of making a smooth cross-section of a paper sheet with a focused ion beam without any destruction and applied this technique to clear observation of a thin printed ink layer on paper for the first time. Furthermore, they [9] extended this technique to ink-jet recording and tried to observe dye-based inks that penetrated matte and high gloss type papers using SEM. However, it is very complicated to combine SEM observation with electron probe microanalyzer (same with EDX) and optical microscope to determine ink distribution. Pinto et al. [10] applied time-of-flight secondary ion mass spectrometry (TOF-SIMS) to determine the extent of ink penetration in model coatings from their cross-sectional images and correlated the effect of a water-soluble polymer on dye binding.

EXPERIMENTAL

Paper samples and printers

Photo quality, high gloss type and medium grade of paper all with a silica coating exclusively for ink-jet were used. **Table 1** lists paper samples used. Specular gloss at 60 degrees was measured with a glossmeter GM-268, Konica Minolta. The mean value of gloss in the machine and cross directions is shown in the table. Homogeneous color patterns with a dot area ratio of 10 % or 20 % were printed on each sheet in cyan, magenta, yellow and black inks. Ink-jet printers used were Pixus 950i, Canon Inc., Japan and PM-970C, Epson, Japan. For quantitative analysis of a single dot shape, the dot was printed

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with an ink-jet head assembled in HEK-1, a printing device for testing, Konica Minolta, Japan.

Microscope and observation

Confocal laser scanning microscope, LSM 510 with an upright body named Axioplan 2, Carl Zeiss, Germany was used. Functions characteristic of this type of optical microscope to obtain three-dimensional (3D) images are optical slicing in the transverse direction by the confocal system and intensive power of laser beams to compensate for resultant insufficient illumination. The term "confocal" means "collecting light exclusively from a single plane in focus with a pinhole that eliminates light reflected from others than the focal plane". Laser beams fall on the front of a sample, then reflect and enter the detector to provide a fluorescence image. A 3D image is constructed from a series of single confocal images accumulated digitally.

A piece of printed sample cut to about 15 by 15 mm² was mounted on a slide glass. Then, a drop of fluid paraffin was put on its corner or edge to allow it penetrate the sample spontaneously to the other end, leaving as less as possible air bubbles. A cover glass was mounted on it and subjected to observation. As an impregnation liquid in the case of silica-based ink-jet coatings, fluid paraffin was selected because its refractive index is about 1.47 that is close to that of silica being about 1.45. A light beam does not refract at an interface between substances with equal refractive indices, but passes straight. Even a porous material appears transparent when such a liquid fills its inside pores. Aniline may be preferred as an impregnation liquid for base paper because its refractive index is 1.58 that is close to that of pulp fibers ranging between 1.57 and 1.60. Note that aniline is toxic and take care not to touch it or inhale its vapor.

To know a specified material distribution in an optical microscope, a fluorescence dye is commonly applied to mark the material in prior to observation. However, some kinds of ink-jet inks contain a fluorescence dye formulated in its manufacturing processes for bright coloration and security reasons to distinguish printers in cases of banknote forgery.

In observation, the objective lens selected was mainly Plan-Neofluar 40X/0.75. At this magnification, one XY-plane image corresponds to 230.3 by 230.3 μ m² with a thickness of a single confocal plane of 0.60 μ m. The speed of laser scanning was about 30 or 60 s per single image of 1024 by 1024 pixels. The choice of laser beams was set to the FITC/Rhod/Cy5 mode from the fluorescence probe database. **Table 2** shows a default condition such as wavelength ranges of exciting and fluorescent lights for this combination of dye type setting. These dyes were not applied practically to the ink-jet inks or paper at all. The ink-jet inks happened to have a fluorescence dye of the same condition of wavelength of exciting light and color filter in detection with the fluorescence agents registered in the database. Resultantly, there was no ink having the same pattern of excitation and fluorescence with FITC. But, acrydine orange, a general fluorescence dye to stain pulp fibers is excited at wavelengths around 480 nm and emits fluorescence at wavelengths around 530 nm. This pattern is almost the same with the FITC pattern. So, FITC/Rhod/Cy5 setting was maintained even when no fiber was in the view.

In the quantitative analysis, binarization and count of the number of dots were performed using a

shareware application, PopImaging V.3.1, Digital being kids, Co. Ltd., Japan.

RESULTS AND DISCUSSION

Figure 1^{*} shows example images of ink-jet dots of four colors; cyan, magenta, yellow and black. The image on the left side is a regular reflected light image acquired with a digital camera. The image on the right side is a fluorescence image acquired in synchronization with a laser scan. Although the two images are not for the identical location, it was found that the magenta ink emits fluorescence in greenish yellow, the black ink emits fluorescence in red, and neither cyan nor yellow ink emits fluorescence from the correspondence between the ink colors and the pseudo-colors. Ink dots in cyan appear black in the fluorescence image, but this is not for fluorescence. Its outline appears clear against the homogeneous light-red background presumably for weak fluorescence from a certain constituent in the paper coating. Against this background, outlines of light-cyan and light-magenta dots are also visible. A lot of fluorescent brightening agents are very commonly used for pigment coatings to increase paper brightness. They are excited by a broad range of ultra-violet rays with the most efficient wavelength of around 380 nm and emit a blue band of fluorescent light with the most brightness-intensifying wavelength of around 460 nm. However, the light-red background is far from the possible range of fluorescence from the fluorescent brightening agents, because even the 505 to 530 nm range of fluorescence was not detected. After all, this observation ensured that fluorescence emitted by at least magenta and black inks can be a measure to determine 3D ink dot distribution. Dye-based inks of the same colors used for Epson ink-jet printers were confirmed to exhibit the same fluorescence behavior.

Figures 2 and **3** are combined images of orthogonal projection for magenta ink dots on photo quality papers A and B, respectively. In each of the combined images, the bottom left picture is the front elevational view in XY-plane at Z equal to the center of most dots in the thickness direction, the top picture is for XZ-plane when the sample is sectioned virtually along the green line (the horizontal line in the XY-plane image) and the bottom right picture is for YZ-plane when sectioned along the red line (the vertical line in the XY-plane image). In addition to planar dot shape and size, these combined images give individual dot thickness information from the XZ- and YZ-plane images. The thickness is estimated to be constantly about 4 μ m for both of the papers. The density distribution inside the dots in XY-plane for paper B is less homogeneous than that for paper A, suggesting that paper B absorbs ink less homogeneously or fixes the dye less homogeneously possibly due to inhomogeneous silica pigment distribution.

Figures 4 and **5** show an orthogonal projection for high gloss type papers C and D. Some bright curved lines are visible around dots for both of the papers. These are a part of the ink dye that spread over surfaces of cracks present in the coating surface and became concentrated there. Cast coating methods seem to be used to manufacture these papers to give gloss higher than that for the photo quality papers (refer to Table 1), but tend to incur defects like those cracks on their surfaces. The ink

^{*} All colored figures available at http://psl.fp.a.u-tokyo.ac.jp/hp/enomae/publish/pdf/2004panpac_enomae.pdf

is estimated to spread over the crack surfaces two to three times farther than normal penetration in coatings with no defect from bright long legs seen in dot cross sections in XZ- and YZ-planes. This undesirable ink spread may decrease color density.

To visualize them more clearly to human perception, the projection images were converted to bird's-eye views at an angle of 18 degrees from the horizontal plane as illustrated by **Figure 6**. **Figure 7** shows the bird's-eye views of ink dots shape for six ink-jet papers. Judging from the views, photo quality papers were found to give ideal coin-shaped dots. High gloss type papers C and D were found to give remarkable long legs attached to a coin-shaped body of ink dots. The ink dot size for paper D looks smaller than paper C. But, the ink used for paper C was exceptionally black and the brightness setting was adjusted to be low in image acquirement. So, the dot size was not actually as different as sensed from these two pictures. Medium grade papers E and F with a coating on a paper-made base gave unclear outlines of dots. The ink dots appear to be separated into small segments, presumably because large secondary particles of silica inhibited the ink to penetrate the coating homogeneously. Paper F gives a rather better dot shape moderately like a coin than paper E.

Approach to quantitative analysis

Figure 8 is a composite image of fluorescent and transmitted white lights for a single dot of Canon black ink. The diameter of dots printed with this testing head is larger than that printed with the most recent printers. This image in XY-plane is one of the 32 slices across which the ink dot extends. From the composite image, the ink appears to have spread out as avoiding large secondary particles of silica. One of the typical problems of CLSM is attenuation of fluorescence with depth in 3D image construction. The deeper is the location in the sample, the weaker is the fluorescence. This is because laser and fluorescence go through a longer path with absorption and scattering of light. Xu and Parker [11] applied a method of fitting a curve to the experimental intensity versus depth data and made easier and more exact assessment of cross-sections of wood fibers and paper sheets. In our work, fluorescence reduction was slight enough to determine locations of ink dot fragments in deep slices because fluid paraffin was applied to coatings for transparency and the observed region of the coatings was thinner than that of paper.

Figure 9 shows the side view of a stack of circles having the same area with a dot fraction in each slice. Binary images were made for all the slices following the next steps; the threshold level determination for the central slice by applying the discrimination analysis to the Laplacian (secondary differentiation) histogram, extraction of the relevant ink dot region and finally application of this procedure to all the slices. In counting of the number of dots, the dot fraction in each slice was found to have irregular shape with inside holes and minute discrete fractions around the main one, but the hole area was excluded from and all the discrete fractions were included in portions of the ink dot. The number of dots was converted to exact volume in μm^3 considering a 3D pixel size. In the figure, every circle is justified to the center. This 3D area-equivalent stack suggests that the tapering top of the ink dot derives from surface roughness and its tapering bottom derives from ink penetration with

feathering. The largest circle is located slightly higher than the transverse center, meaning that longer feathering occurred during the ink penetration than the surface roughness level. This quantitative analysis is just an example of 3D ink distribution. Such kind of analysis would clarify mechanisms of dye-based ink penetration such as relation between transverse absorption and lateral spreading, fixing agents effects, affinity of pigments and binders for water-based inks, although it is limited to magenta and black inks as far as the examined inks are concerned.

CONCLUSION

Most magenta and black dye-based inks for ink-jet contain fluorescence agents or use fluorescence dyes specific of the color. Fluorescence emitted from those of the ink-jet inks provides a three dimensional ink distribution by the optical slicing function of a confocal laser scanning microscope. In applications, several facts were revealed. Ink dot shape was like a coin with a constant thickness on photo quality paper, ink spreads over crack surfaces on high gloss type paper a few times deeper than the normal penetration and ink dots had rugged edges with their tips intruding between fibers in the base paper for medium grade paper. Three-dimensional image analysis applied to the binary image showed that the layer with the largest cross section of an ink dot on a medium grade ink-jet paper was located slightly higher than the transverse center, meaning that longer feathering occurred during the ink penetration than the surface roughness level. This technique is potential to be a useful measure to clarify more dye-based ink penetration mechanisms.

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Table 1 List of ink-jet paper samples

Кеу	Grade	Basis weight, g/m ²	60° Gloss
А	Photo quality (Excellent)	295.9	39
В	Photo quality (Excellent)	232.3	32
С	High gloss type (Fairly Good)	193.2	44
D	High gloss type (Fairly Good)	183.5	57
Е	Medium (Good)	108.6	3
F	Medium (Good)	100.1	3

Fluorescence dye type	FITC	Rhod	Су5
Official name etc.	Fluorescein- isothiocyanate	Rhodamine	N,N'-biscarboxypentyl-5,5'- disulfonatoindodicarbocyanine
Optimum exciting wavelength, nm	490 (greenish blue)	550 (green)	650 (reddish yellow)
Maximum fluorescence wavelength, nm	520 (green)	580 (greenish yellow)	667 (red)
Wavelength and intensity of irradiation laser, nm	488 (30 %)	543 (100 %)	633 (80 %)
Wavelength of reflected light filtered, nm	505-530	560-615	>650
Color of ink-jet ink emitting fluorescence	Not applicable	Magenta	Black
Pseudo-color in image	Green	Red	Blue

Table 2 Optical condition applied for ink-jet ink distribution



Fig. 1 Ink jet dots of cyan, magenta, yellow and black in reflected light (left) and fluorescence (right) image, not for identical location.

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Fig. 2 Dots of magenta ink ejected on photo quality paper A. Greenish yellow fluorescence emitted by magenta ink is assigned to white to be discerned clearly from paper background in black.



Fig. 3 Dots of magenta ink ejected on photo quality paper B. Greenish yellow fluorescence emitted by magenta ink is assigned to white to be discerned clearly from paper background in black.



Fig. 4 Dots of black ink ejected on high gloss type paper C. Red fluorescence emitted by black ink is assigned to white to be discerned clearly from paper background in black.



Fig. 5 Dots of magenta ink ejected on photo quality paper B. Greenish yellow fluorescence emitted by magenta ink is assigned to white to be discerned clearly from paper background in black.



Fig. 6 View angle of following Bird's view images of ink dots



Photo quality paper A

Photo quality paper B



High gloss type paper C



High gloss type paper D



Medium grade paper E

Medium grade paper F

Fig. 7 Bird's view images of dots on different grades of ink-jet paper. Magenta ink was used for all papers with exception of high gloss type paper C with black ink.



Fig. 8 Black ink dots on medium grade paper E in orthogonal projection with blue zone meaning black ink dot.



Fig. 9 Distribution of diameter of a circle area-equivalent to each slice of optically-sectioned dot along depth from paper surface for black ink as shown in Fig. 8.

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