

Relationship between initial absorption behavior of ink-jet inks and three-dimensional distribution of the fixed inks in paper

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Abstract

Novel techniques for examining fixation processes of a dye ink dot on paper and three-dimensional geometry of the fixed ink dot were developed and applied.

Most magenta and black dye 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.

Microscopic high-speed video capture system was established to visualize ink drop spread on and penetration into paper. Changes in ink dot area and dot roughness with time were evaluated from microscopic video images. Ink drop behavior on trial coated paper from commercially available calcium carbonate pigment and from its ball-milled pigment was recorded. Small particle size by ball milling reduced the dot area, but dot area continued to change for a longer time than that for the untreated sample, as is explained in terms of small pore size according to Lucas-Washburn's equation.

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 finally settled ink as well as its optical properties. The final ink setting is dependent on the chemical and physical interaction between ink and paper. A system of high-speed video camera attached to an optical microscope was built to clarify short-range behavior of an ink drop immediately after landing on paper. Turning to ink dots already set, dye inks are difficult to handle to determine the ink distribution. Dye 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 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 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 profile¹ and fiber network structures^{2,3}. Observation of trace constituents contained in paper is also in the scope of CLSM. Location of epichlorohydrin resin for high wet strength in paper⁴ and bacteria⁵ in a food-packaging paperboard was determined.

With regard 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 as exemplified by offset ink locations by stereoscopic backscatter imaging of scanning electron microscopy⁶ and a thin printed ink layer in a cross-section made with a focused ion beam^{7,8}. The latter technique was extended to observe ink-jet dye inks in matte and high gloss type papers using a combination of SEM, electron probe microanalyzer and optical microscope⁹ though it is very complicated. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been applied to determine the extent of ink penetration in model coatings¹⁰.

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.

Table 1. List of ink-jet paper samples

| Key | Grade | Basis weight, g/m ² | 60° Gloss |
|-----|-----------------|--------------------------------|-----------|
| A | Photo quality | 295.9 | 39 |
| B | Photo quality | 232.3 | 32 |
| C | Photo quality | 251.1 | 36 |
| D | High gloss type | 183.5 | 57 |
| E | Medium | 108.6 | 3 |

Laser scanning 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 to 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.

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 mm² with a thickness of a single confocal plane of 0.60 mm. 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. Rhod and Cy5 modes suit observation of magenta and black ink dots well, respectively. Table 2 shows a default condition

such as wavelength ranges of exciting and fluorescent lights for magenta and black inks. 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.

Table 2. Optical condition applied for measuring ink dot shape by fluorescence method.

| Color of ink-jet ink emitting fluorescence | Magenta | Black |
|--|-----------------------|----------------------|
| Optimum exciting wavelength, nm | 550 (green) | 650 (reddish yellow) |
| Maximum fluorescence wavelength, nm | 580 (greenish yellow) | 667 (red) |
| Wavelength of irradiation laser, nm | 543 (100 %) | 633 (80 %) |
| Wavelength of color filter for detection, nm | 560-615 | >650 |
| Pseudo-color in image | Red | Blue |

Trial calcium carbonate coated paper for ink-jet

Commercially available calcium carbonate, PZ, Shiraishi Kogyo, Japan, with a nominal mean particle diameter of 0.15 µm was used as a coating pigment. A hundred parts of the calcium carbonate with 0.8 pph (parts per hundred parts of pigment) of dispersant was dispersed and then defoamed with a sun-and-planet mixer, HM-80, Keyence Corp., Japan, for 5 min and 10 s, respectively. As other constituents, 2.5 pph of polyvinyl alcohol and 20 pph of ink fixative were added to this pigment slurry and dispersed with the same mixer to be a coating color of 40 % solids. This color was applied to wood-free base paper with a motor-driven wire bar coater and the coated paper was dried with hot air for 60 s. This sample will be referred to as "untreated". To provide a high surface smoothness, this coated paper was calendered with a test calender, KRK, Japan at a steel roll temperature of 70 °C and an oil pressure of 687 kPa for two passes. This sample will be referred to as "calendered". The calcium carbonate was ground for a smaller mean particle size with a stronger sun-and-planet mixer of a ball-mill type, P-5, Fritsch, Germany. Milling for 10 min and a rest for another 10 min were repeated three times. Coated paper was prepared from this fine calcium carbonate as a coating pigment. This

sample will be referred to as “ground pigment”. The coat weight was all about 25 g/m².

Microscopic high-speed video for ink drop dynamics

High-speed video capture system was established to record behavior of an ink drop by following an example of the past work¹¹. Ink drops were ejected from ink-jet printing head, HEK-1, Konica Minolta, Japan. Landing on paper, penetration and lateral spread of the ink dot were captured using a high-speed video camera, Motion Meter 1000, REDLAKE MASD, Inc., USA attached to an optical microscope with an eye-piece attachment and an objective lens both of 10X magnification. The ink-jet head was set at an angle of 45 degrees and at an adequate position so that an ink drop lands on paper right under the objective lens to be within the scope. The distance between the edge of the ink-jet head and the drop-landing site was about 20 mm. The ink drop on paper was illuminated with a cold light at an angle of about 20 degrees from the paper surface. The recording rate was 500 frames per second. Water-based black ink, BCI-6Bk, Canon Corp, Japan was used.

Recorded video images were digitized and resolved into each frame. For every image in each frame, dot area and dot roughness were determined by image processing using a shareware application, PopImaging V.3.1, Digital being kids, Japan. Dot area and dot roughness defined as a ratio of a perimeter to a convex perimeter were evaluated in processes of pattern region analysis. For each dot parameter, results of at least 3 dots were averaged.

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 white light reflected 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

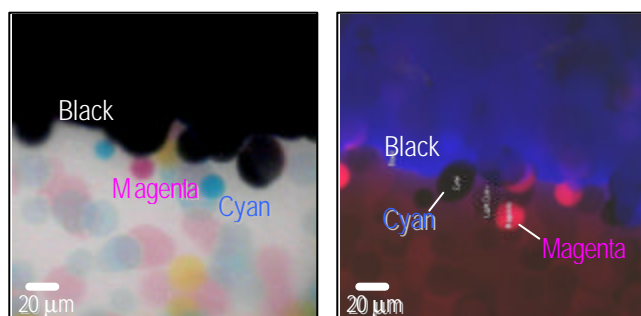


Figure 1. Ink jet dots of cyan, magenta, yellow and black in reflected light (left) and fluorescence (right) image, not for identical location

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 could be measures to determine 3D ink dot distribution. Dye inks of the same colors used for Epson ink-jet printers were confirmed to exhibit the same fluorescence behavior.

Figure 2 is combined images of orthogonal projection for magenta ink dots on photo quality papers A and B, and high gloss type paper D, 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 µm 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.

In the orthogonal projection for high gloss type paper 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 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 paper surface plane. Figure 3 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 paper D was found to give remarkable long legs attached to a coin-shaped body of ink dots. Medium grade paper E with a coating on a paper-made base gave unclear outlines of dots. The ink dots have rugged edges with their tips intruding between fibers in the base paper. In addition, 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.

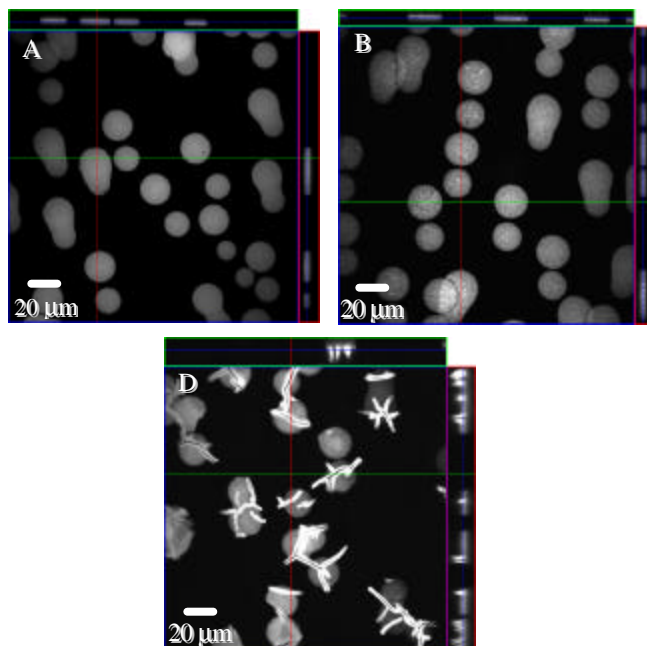


Figure 2. Dots of magenta ink on photo quality papers A and B, and high gloss type paper D

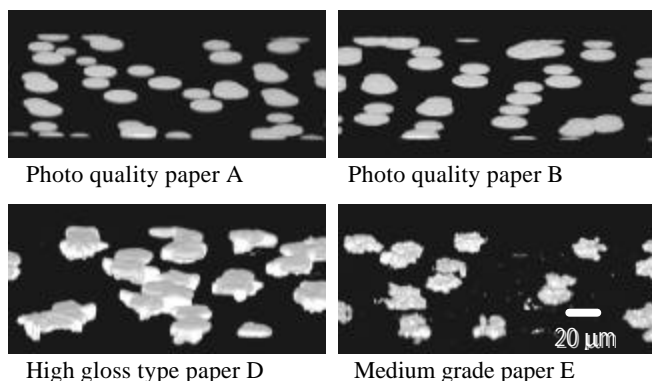


Figure 3. Bird's view images (18° from paper surface plane) of magenta ink dots

Video images and processing

Figure 4 shows video images of ink dot spread and penetration in discrete frames for the three kinds of photo quality ink-jet paper. But, note that the ink used for these video images was oil-based cyan ink, while the water-based black ink was used for the later image processing. A bright part in a bottom half of dots in early frames is specular reflection of illuminating light. Afterwards, the tip of the optical fiber light was covered with a sheet of paper to make diffuse light. This modification was useful to avoid specular reflection for accurate calculation of the dot parameters. There is a concentric ring observed inside each circular ink dot in later frames. This ring is considered to be a liquid ink film left un-penetrated on paper. This ink film was found to become smaller in diameter with time in accordance with the results of dye inks presented previously¹².

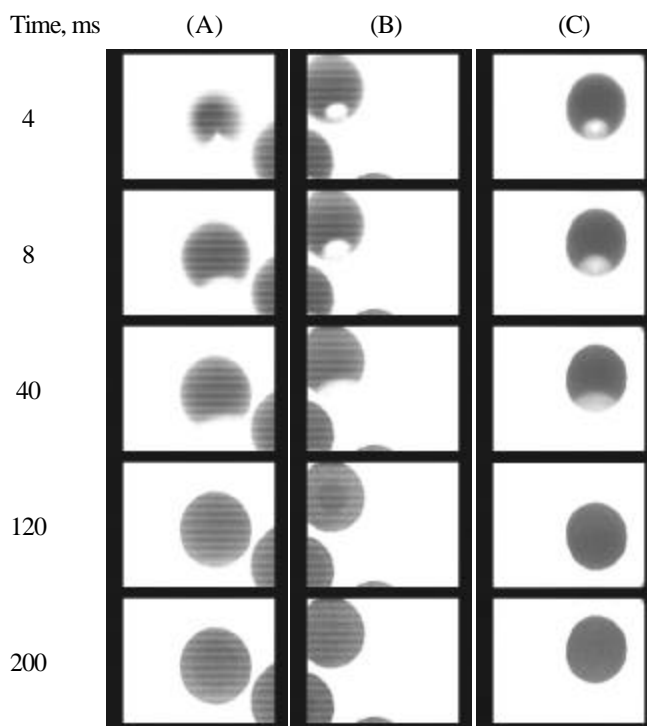


Figure 4. Microscopic video images showing change of ink dot with time for photo quality ink-jet papers (A), (B) and (C)

Figure 5 shows the image processing for calculating dot area and dot roughness of ink dots in each frame. The original dot image (1) is one example of an ink dot. Each frame has actually only half the nominal vertical resolution because of interlaced scan lines. So, Gaussian filter, a blurring filter, was adopted to compensate for blank lines (2) and then, binarization with a dynamic threshold value (3) and reversing the whole image and filling inside holes (4) were done successively.

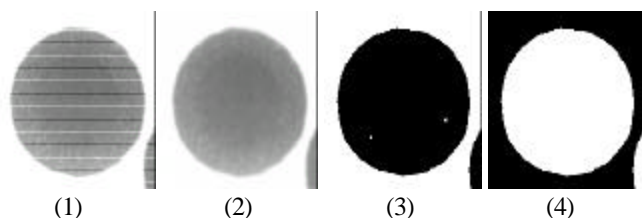


Figure 5. Image processing for determining dot shape; (1) original, (2) Gaussian-filtered, (3) binary with dynamic threshold and (4) reversed and filled images

Behavior of ink drop on calcium carbonate coated paper

To prepare calcium carbonate coated paper as a trial, commercial PCC (precipitated calcium carbonate) was used as a coating pigment. To examine an influence of particle size, it was ball-milled for a smaller particle size. Figure 6 is scanning electron micrographs of the two pigments.

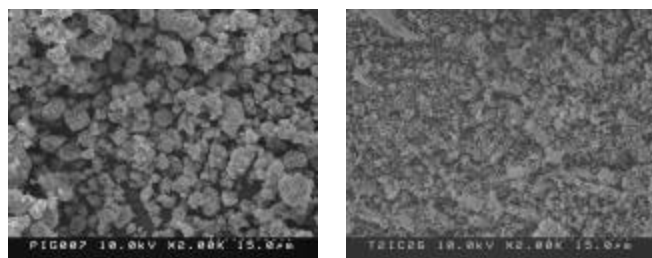


Figure 6. Commercially available precipitated calcium carbonate (left) and its ball-milled calcium carbonate (right)

Figure 7 shows dot area change with time for the three kinds of trial calcium carbonate coated paper. For this calculation, the ink used for printing dots was water-based Canon black ink. The level-off value of dot area attained at about 40 ms for the untreated sample was about $1800 \mu\text{m}^2$. It follows that the area is rather large, when compared to 1400 and $1700 \mu\text{m}^2$ for commercially available medium grade ink-jet paper with silica pigment, though the result is not shown in this paper. Generally, smaller dot areas indicate better print quality. For the calendered sample, the variation was too large as indicated by the 95% confidence level bars. This is presumably because smooth and rough sites are likely to be mixed on the surface. The area tended to continue to change for a longer time than the untreated. For the ground pigment sample, the area at 80 ms became small, and the rate of change was similar to that of the calendered. A dominant parameter affecting the rate of area change is pore size of the media. According to Lucas-Washburn's equation, the absorption rate of liquid is proportional to a square root of pore size. Calendering and further milling reduced pore size of the coating layer, and consequently reduced the ink absorption rate and presumably gave more time for the dye to be adsorbed to the fixative.

Figure 8 shows dot roughness change with time. The dot roughness for the untreated sample attained a constant value the earliest of the three samples and the value was low. For the calendered and ground pigment samples, the dot

roughness continued to increase even at an elapsed time of 80 ms like the change of dot area. But, the dot roughness value could not be discussed significantly due to the large variations because the 95% confidence intervals are too wide.

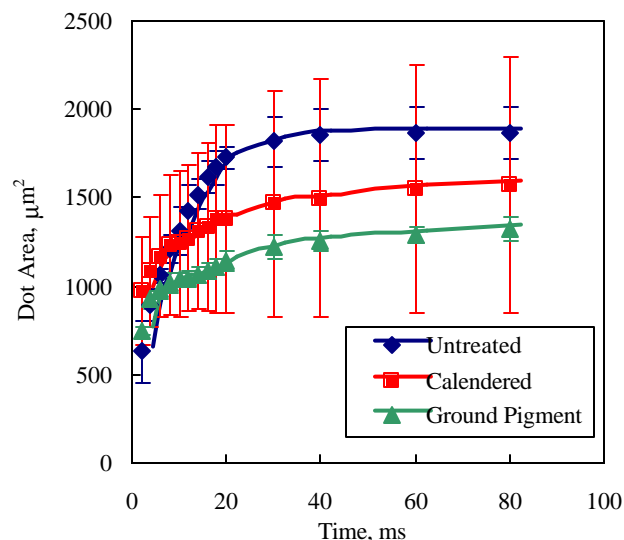


Figure 7. Dot area change with time for trial calcium carbonate-coated papers

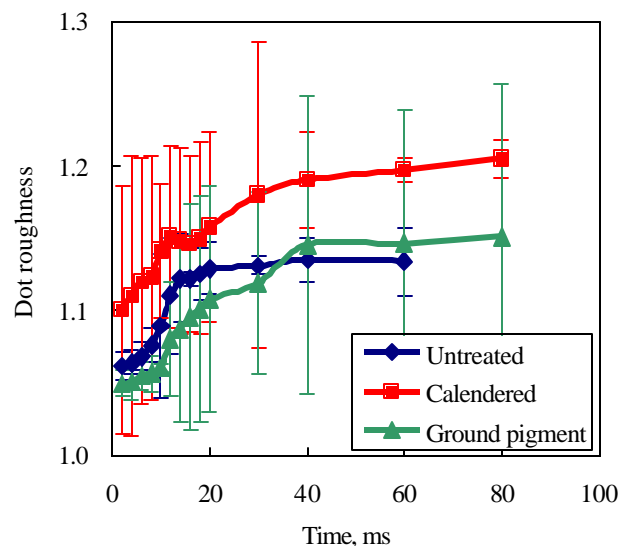


Figure 8. Dot roughness change with time for calcium carbonate-coated papers

Conclusion

Most magenta and black dye 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. This technique is potential to be useful measures to clarify dye ink penetration mechanisms for more details. Geometry of pigment ink dots is also expected to be clarified.

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Biography

Toshiharu Enomae graduated from The University of Tokyo in 1984, Received M.Sc. in 1986 and Received Ph.D. in 1993 under a title of "Studies on coating applicability of basepaper and evaluation of coated paper structure" Assistant Professor in the current department since 1987. In 1993-1995 post-doctorate research associate for Dr. Pierre LePoutre at Univ. of Maine, USA, with a topic of "Water-paper interaction". Backgrounds are paper coating, paper physics for printing and so on.

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Keywords

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