Ink dot formation in coating layer of ink-jet paper with modified calcium carbonate

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Abstract

Commercial ink-jet papers are made from silica or alumina as a coating pigment, both of which give high image quality, but are expensive. The present work aims at efficient use of calcium carbonate as an alternative of silica for ink receptive coating layers. Commercial calcium carbonate was ground mechanically or dissolved partially with hydrochloric acid to reduce and equalize the aggregates size. Trial ink-jet papers were prepared and some of them were plasma-etched to give a hydrophilic property. The trial ink-jet papers were evaluated in terms of dynamic behavior of ink droplets ejected from a test ink-jet head visualized by a microscopic high-speed video camera system and of ink penetration depth determined by confocal laser scanning microscope (CLSM). Particle size reduction of calcium carbonate pigment by mechanical grinding and hydrochloric acid dissolution decreased ink dot area and dot roughness on the papers. This result suggests that particle size reduction improves image quality. Based on the criterion standard that the smaller the dot area, the better the image quality, the efficient processes were mechanical grinding, hydrochloric acid dissolution and plasma-etching in the decreasing order. It is concluded that particle size reduction decreases pore size of the coating structures and consequently ink droplets tend to penetrate deep in coatings rather than spread laterally along surfaces.

Keywords

Coating layer, confocal laser scanning microscope, ink-jet printing, grinding, plasma-etching

Introduction

Nowadays, ink jet printing systems are widely used not only for personal printing, but for advanced commercial printing capable of outputting variable information continuously, prepress of offset printing and non-contact printing on curved surfaces of packages. Moreover, they are spreading to various applications in other areas like microcontact printing to form a self-assembled monolayer and micro- to nano-patterning for semiconductors.

Ink-jet paper, as a representative of ink-jet media, is rapidly developing and now capable of reproducing photo-like images. But, ink-jet paper does not seem to keep pace with improvements in printing speed and size reduction of ink droplets developed by novel ink-jet head technology. On the other hand, a part of market is demanding inexpensive versatile ink-jet paper compatible with most printers even at current print quality grades.

Most of commercial ink-jet papers are manufactured from silica or alumina as a coating pigment because of resultant high water absorbency and high optical density of ink dots. However, silica and alumina are expensive. In place of these expensive pigments, calcium carbonate may be an alternative, but general types of calcium carbonate cannot give a high print quality. Adequacy as an alternative pigment is probably related to hydrophilicity, particle size and dispersibility. To evaluate calcium carbonate from these aspects, commercial calcium carbonate was modified and the relationship between characteristics of the particles and geometry of ink dots formed on ink-jet papers was examined. Parameters of pigment required for high image quality were discussed in terms of dynamic penetration behavior of ink droplets obtained using a microscopic high-speed video camera system[1] and the three-dimensional shape of ink dots in paper obtained using a CLSM[2-4].

Experimental

Samples

Processing of calcium carbonate

To provide commercial precipitated calcium carbonate (PCC), PZ, Shiraishi Kogyo Kaisha. Ltd., with ink-jet printability, it was modified in terms of wettability, reduction and equalization of particle size, and porosity of pigment coatings. PCC tends to form heterogeneous aggregates in size. First, we tried to break down aggregates into smaller ones by mechanical grinding. Calcium carbonate PZ was dispersed into water to 40 % consistency. This pigment slurry was poured into a cylindrical container with six balls of about 10 mm diameter all made of agate. The container was set to the ball mill, Planetary Ball Mill P-7, Fritsch-Japan and the pigment was ground. Table 1 shows three grinding conditions.

Another size reduction of calcium carbonate was conducted by dissolution with hydrochloric acid. The concentration of the hydrochloric acid was altered with a

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constant ratio of the dilute hydrochloric acid volume to calcium carbonate mass. The concentration used was 0.1, 0.2 and 0.4 M to dissolve about 5, 10 and 20 % of calcium carbonate.

Table 1 Grinding conditions of calcium carbonate and their surface

Grinding condition			Specific surface area, m^2/g (Nitrogen adsorption method)
Revolution, rpm	Time, min	Repetition	
850	15	3	19.8 (Intensive Grinding)
550	10	3	17.6 (Medium Grinding)
250	5	3	15.4 (Light Grinding)
0	0	0	13.5 (Untreated)

Preparation of trial ink-jet paper and plasma etching

Trial ink-jet paper was prepared from untreated, ground partially-dissolved calcium carbonates. Calcium carbonate of 100 pph (parts per hundred of pigment) with sodium polyacrylate of 0.8 pph as a dispersant were dispersed for 5 minutes using a disperser, Hybrid Mixer HM-80, Keyence Corp. and defoamed for 10 seconds. Polyvinyl alcohol of 10 pph as a binder, poly-DADMAC of 20 pph as an ink fixative were added and mixed to a coating color at 40 % solids. This color was coated on a base (copy paper) with a motor-driven wire bar coater followed by hot air drying for 60 s.

Some of the trial ink-jet papers prepared from untreated calcium carbonate were plasma-etched to give hydrophilicity. Plasma ions emitted by alternating current corona discharges strike a surface of the trial ink-jet papers and generate positive ions. The positive ions and hydroxyl ions of water bind together and the surface becomes hydrophilic. Practically, polyvinyl alcohol formulated as a binder is considered to become hydrophilic rather than calcium carbonate. Plasma etching was conducted in the atmosphere of 20 Pa by applying 400 V alternating current. Three levels of etching strength used were, in the increasing order, [1] 6 to 8 mA for 30 s, [2] 6 to 8 mA for 60 s and [3] 18 mA for 120 s.

Properties of processed pigments and trail ink-jet papers

Processed pigments were subjected to analyses such as scanning electron microscopic (SEM) observation, determination of BET specific surface area by the nitrogen adsorption method, Nova 4000, Quantachrome Instruments, and measurement of particle size distribution by the laser dynamic light scattering method, Zetasizer 3000, Malvern Instruments. For trial ink-jet papers, contact angle between a paper surface and water was measured as well as the ink penetration analysis described in the following section.

Microscopic high-speed video recording and dynamic analysis of ink penetration

In ink-jet printing, penetration of ink-jet inks with relatively low viscosities is a very rapid phenomenon. So, efforts to capture ink-jet ink penetration using a high-speed camera have been made by several researchers[5, 6]. Photo 1 is an overview of the video recording device developed in this work. A test ink-jet head, HEK-1, Konica Minolta, was used for printing. Voltage data for ejecting ink droplets were adjusted in order to minimize satellite occurrence. The volume of one ink droplet is about 30 pL, corresponding to about 40 μm in diameter. Aqueous black inks for ink-jet, BCI-6BK, Canon, were used.

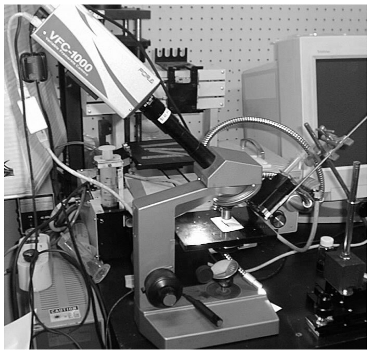

Photo 1 Microscopic high-speed video camera system for dynamic ink penetration

A high-speed video camera, VFC-1000 black-and-white model, For-A, was fitted into a common optical microscope with a tenfold objective lens, Olympus via tenfold attachment lens MA44S, Elmo. Ink behavior was recorded at a speed of 500 frames/s and a shutter speed of less than 1/1000 s. The ink-jet head was fixed at an about 45 degree angle from the paper sheet plane. Cool light illumination was introduced at an about 20 degree angle. The distance between the objective lens and a paper surface must be about 5 mm for optimum focus, but it is too short for the head to be inserted in-between. The head was set about 20 mm distant from the landing location, thus reducing the collision speed of collision considerably in contrast to about 1 mm for practical printers. The video images were decomposed to individual images, each of which was subjected to the following image analysis.

General print quality-related parameters calculated by image analysis applied to printed characters are area, perimeter and intensity, namely, optical density[7]. Area, perimeter and optical density reflect print sharpness, degree of wicking and the uniformity of the text, and ease of visual perception, respectively. In this work, the dot images were first binarized based on the dynamic threshold level defined by the moving average method. Ink dot area was filled and closed when there were holes made apparently by light reflection, secondly. Pattern region (ink dot region in this case) analysis was made to calculate geometrical parameters like ink dot area and these parameters were saved in the CSV format for statistical evaluation using Excel, Microsoft. Parameters calculated for each individual ink dot were ink dot area and ink dot roughness. The former was calculated in square micrometers by converting from the pixel scale. The latter is defined as the ratio of true perimeter to envelop perimeter indicating the degree of perimeter roughness of the pattern region, where the envelop perimeter means the curve connecting peripheral pixels externally without any dent. Dot roundness, a ratio of area to perimeter squared, is also often used to indicate print quality[8], but for non-coated paper with fiber orientation, elliptic dots do not always mean poor print quality. Therefore, dot roughness was adopted here. These two parameters were averaged from 5 ink dots per paper sample. The series of image analysis was done using software, PopImaging Ver.3.40, Digital Being Kids.

Measurement of ink penetration depth

Distance of penetration of ink droplets ejected from the test ink-jet head into paper was measured with the CLSM. Fluorescence at around 667 nm wavelengths emitted from the black ink by irradiation of laser at the 633 nm wavelength permits to slice ink dots in paper optically by the confocal system and the three-dimensional shapes were measured. For each slice image, the ink component was judged to be present when the fluorescence intensity (gray level of the dot) was over a certain value that was common to every slice image. This threshold value was determined as the most suitable threshold gray level to binarize the vertically central slice image. The penetration depth was calculated from the slice thickness of 1 μm. This CLSM method is one of the most useful techniques for measuring ink penetration depth although there are some other methods like simulation of ink penetration effects on spectral reflectance and chromatic appearance[9], experimental evaluation of chroma and hue of printed colors[10], time-of-flight secondary ion mass spectroscopy (TOF-SIMS) to evaluate effects of polymers on binding ink-jet dyes[11] and Raman spectroscopy without fluorescence interference[12].

Results and discussion

Properties of ground calcium carbonate

Photo 2 is scanning electron micrographs of calcium carbonate pigment before and after grinding. Because water was evaporated in the atmospheric conditions to prepare the SEM samples, it is noted that the carbonate tended to coagulate. Considering this drying method, the untreated carbonate is found to have formed heterogeneous aggregates of up to about 10 μm in diameter while the intensively-ground carbonate shows reduction and equalization of particle size in spite of large aggregates present partly. Figure 1 shows normalized particle size distributions for the carbonate pigments before and after intensive grinding. The grinding process decreased larger particles and increased smaller particles both relatively. Table 1 includes BET specific surface areas measured by the nitrogen adsorption method. It shows that the specific surface area increased as the grinding intensity increased.

Dynamic analysis of ink penetration into trial ink-jet paper

Figure 2 shows changes of ink dot area on the trial ink-jet papers prepared from the ground carbonate pigments. Time scale for the horizontal axis was calculated from the number of image frames. The initial frame including the ink droplet on paper was assumed to be

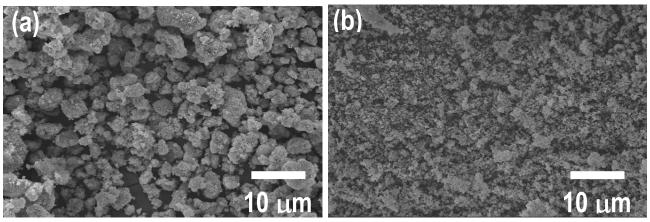

Photo 2 Scanning electron micrographs of calcium carbonate before (a) and after (b) grinding

2 ms after the landing. Mean values of several ink dots are plotted although the ink droplets taken into the mean calculation were not always ejected from the identical nozzle. The leveled-off area was the largest for the untreated carbonate pigment. Even light grinding was found to have an effect on dot area reduction. Comparison between commercial ink-jet papers coated with silica pigments, in our previous work[1], smaller dot area resulted in better image quality. Therefore, the finding that dot area decreased as grinding intensity increases implies that particle size reduction leads to a good image quality. The dot area for commercial photo-quality papers ranges approximately between 1100 and 1300 μm^2 and that for the coated paper prepared from the carbonate ground the most intensively also falls into this range. But, the time until dot area has leveled off was 8 to 20 ms for the commercial ink-jet papers while it was as long as 40 to 60 ms for the ground carbonate pigments, as is meaning slow ink absorption. Ink absorption slowness would cause ink mixture resulting in poor image quality in high-speed printing. Ink absorption rate is considered to be related to porosity and binder distribution of coatings as well as hydrophilicity of pigment surfaces.

Figure 3 shows changes in ink dot roughness that represents the degrees of ink bleeding and heterogeneous ink penetration due to heterogeneous microstructure of coatings deriving, for example, from a pigment aggregate shape. The dot roughness values for the ground carbonate pigments were lower than those for untreated carbonate pigment, but all the values for the carbonate pigments were much higher than for commercial photo-quality ink-jet papers. It took about 60 ms for the dot roughness values to level off for the carbonate pigments. This fact suggests that

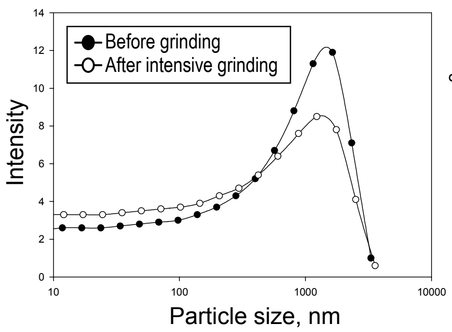

Fig. 1 Particle size distribution of calcium carbonate before and after grinding

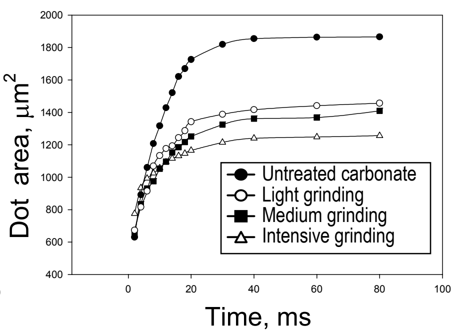

Fig. 2 Dot area changes with time for trial ink-jet papers coated with calcium carbonate ground at three

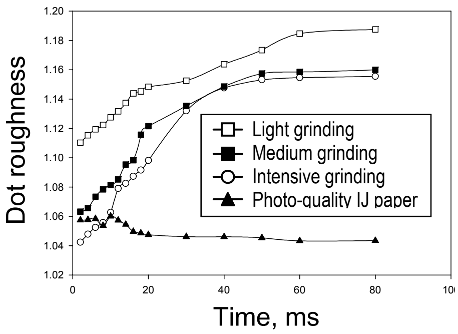

Fig. 3 Ink dot roughness changes with time for trial ink-jet papers coated with calcium carbonate ground at three levels

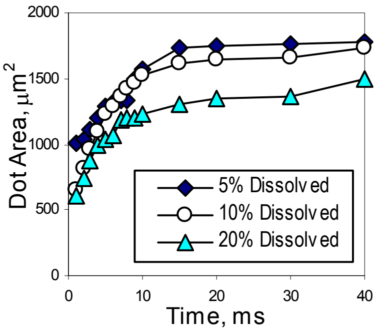

Fig. 4 Dot area changes with time for trial ink-jet papers coated with calcium carbonate dissolved partially with hydrochloric acid

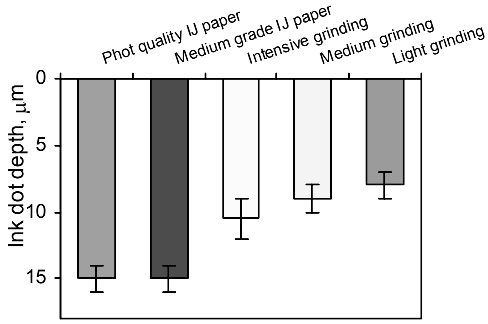

Fig. 5 Ink penetration depth for trial ink-jet papers coated with ground calcium carbonate pigments compared to those for commercial ink-jet papers

ink spread very slowly on the dot periphery although dot area had hardly increased any more well before this time.

Figure 4 shows changes of ink dot area on the trial ink-jet papers prepared from the partially-dissolved carbonate pigments. Dot area tended to decrease as the amount of dissolved carbonate increased to be small particles. It is highly likely that coating structures prepared from pigments with smaller particle sizes include pores with shorter radii and consequently lower the penetration speed with lateral spread suppressed, regardless of whether the particle size is reduced by grinding or dissolution.

Contact angle between water and plasma-etched surfaces of the trail ink-jet papers prepared from the untreated carbonate pigment decreased as the etching strength was raised. The etching process hardly changes the porous structure, so surface chemical modification of coated paper is expected to improve image quality.

Measurement of ink penetration depth

Distance of ink penetration into paper was measured with the CLSM technique. Figure 6 shows the comparison in the ink penetration depth of trial ink-jet papers from the ground carbonate pigments with photo-quality and medium grades of commercial ink-jet papers. For commercial ink-jet papers using silica pigment, ink penetrated to 15 μm in depth. In contrast, it was 8 to 11 μm for the trial ink-jet papers using the ground carbonate pigments. Between the trial ink-jet papers, the ink penetration depth tended to be greater for smaller particles processed by more intensive grinding.

Conclusion

Particle size reduction of calcium carbonate pigment by mechanical grinding and hydrochloric acid dissolution decreased ink dot area and ink dot roughness in ink-jet printing. This finding implies that these processes improve image quality of ink-jet. Assuming that smaller ink dot area provides higher image quality, mechanical grinding had the greatest effect, hydrochloric acid dissolution the second and plasma-etching the last. As for the coating pore structure, it was experimentally elucidated that smaller pores due to particle size reduction tends to make an ink penetrate deep into a coating structure rather than spread laterally along the surface.

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Biography

Toshiharu Enomae graduated from The University of Tokyo in 1984, and received M.Sc. in 1986 and Ph.D. in 1993 regarding "Evaluation of coated paper structure". For 1993-1995, post-doctorate fellow for Dr. Pierre LePoutre at Univ. of Maine, USA. Backgrounds are paper coating, paper physics etc. Current interests are "Application of new minerals developed by hybridization with inorganic compounds to paper coating" etc.