Ink jet paper prepared by using surface-modified calcium carbonate

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Abstract

Varied reaction condition parameters of the carbonation process provide various particle diameters and shapes of the calcium carbonate products. Those calcium carbonates are potential to replace silica and alumina used for commercial ink-jet paper. Ultra-fine particles of calcium carbonate were so synthesized in the aim of improved print quality that could not be attained by conventional types of calcium carbonate. Nevertheless, the ultra-fine particles tended to provide smaller pore size and thus low rate of liquid absorption to the coat layer of paper. Therefore, the surface properties were altered for enhancing ink absorption rate and improved printability. Trial ink-jet paper prepared from the novel calcium carbonate with modified surfaces was evaluated in terms of print quality and microscopic ink dot shape using confocal laser scanning microscope.

Introduction

Ink-jet paper for digital printing demands quick absorption of ink droplets ejected from an ink-jet head and reliable fixation of the dye or pigment in the ink on the paper surface. Commercial ink-jet papers are made from silica or alumina as a coating pigment, both of which give high ink absorption rate and high color density. These pigments can give high image quality by much finer primary particle size and much pore volume, but they have low production efficiency and high cost.

Synthetic (precipitated) calcium carbonate is manufactured as a product of the reaction between carbon dioxide gas and calcium hydroxide obtained from natural limestone by calcination and hydration. Varied reaction condition parameters of the carbonation process provide various particle sizes and shapes. In place of silica and alumina, synthetic calcium carbonate may be an alternative, but conventional types of calcium carbonate cannot give a high print quality [1,2].

Adequacy as an alternative pigment was evaluated by hydrophilicity, particle size, dispensability of pigment, the relationship between characteristics of pigment and geometry of ink dots on a coating layer. In the present study, ultra-fine particles of calcium carbonate were synthesized and the surface properties were altered for improved printability. Trial ink-jet paper prepared from the novel calcium carbonate with modified surfaces was evaluated in terms of print quality and microscopic ink dot shape using confocal laser scanning microscope [3].

Experimental

Modification of calcium carbonate

Specific surface area of commercial calcium carbonate for coating pigment is normally 7 to 20 m^2/g. However, in the case of ink-jet printing, much smaller ultra-fine particles are better for high image quality [4]. Therefore, ultra-fine particles of calcium carbonate with specific surface area of more than 60m^2/g were synthesized (PCC-A). On the other hand, the ultra-fine particles tend to provide smaller pore size and a low rate of liquid absorption (c.f. Lucas-Washburn's equation).

$$\frac{V}{A} = \phi \sqrt{\frac{R\gamma\cos\theta}{2\eta}t} \qquad (1)$$

V: liquid volume A: contact area γ : liquid surface tension
η : liquid viscosity θ : contact angle ϕ : porosity

Besides, finer particles tend to have higher total surface energy and aggregate in the drying process so that pore volume becomes smaller. Therefore, to enhance the liquid absorption rate by lowering the surface energy, namely, decreasing the contact angle, a surfactant (PCC-B) or silica particles (PCC-C) were adsorbed to calcium carbonate surfaces. And, the ultra-fine particles of calcium carbonate were controlled to decrease aggregation caused by drying process (PCC-D) for changing the liquid absorption rate.

Surface energy or hydrophilicity of particle surfaces was evaluated by measuring contact angle using a method that 100pph of pigment with 3pph of polyvinyl alcohol were dispersed and coated on PET film. After drying, contact angle was measured between coated layer surface and droplet of distilled water of 4μl 100ms after contact.

Preparation and properties of trial ink-jet paper

Trial ink-jet paper was prepared from 100pph of calcium carbonate PCC-A, B, C, or D with 3pph of poly-DADMAC (diaryldimethyl ammonium chloride) as an ink fixative and 5pph of PVA (polyvinyl alcohol) as a binder. For reference, another ink-jet paper was prepared silica (FINESIL X-45).

Water absorption rate was evaluated in terms of absorption rate coefficient Ka measured by ASA (automatic scanning absorptometer, Kumagai Riki Kogyo Co. Ltd., Japan). Trial ink-jet paper was subjected to printing test by using commercial ink-jet printers. The evaluated parameters on print quality were optical density of solid prints, bleeding along the boundary between adjacent black and yellow areas, bleeding around characters printed in black or magenta against yellow background.

Condition of ink-jet printing
Printer-A : Standard printing mode、
Dye ink (Bk Cy M Y), Pigment ink (PGBk)
Printer-B : Standard printing mode、
Dye ink (Bk Cy M Y LCy LM)

Print sharpness of printed images on trial ink-jet paper was evaluated by measuring bleeding in the following procedure.

Image-A as in Fig.1 was printed so that black area would be arranged on both sides of a yellow line. Area of the yellow line was measured by image analysis software, Pop imaging Ver.3.40, Digital Being Kids. The area for the calcium carbonate-coated papers relative to that for the silica-coated paper for reference was used to represent the bleeding amount from the black areas into the yellow area. The relative area to that for the silica-coated paper, assumed to be 100, means print sharpness (line).

Perimeter length of a pattern region (printed character or line) is effective to evaluate bleeding by capillary penetration because of uneven comb-shaped absorption increases it although the relative area is more closely related to lateral spread of the ink droplets on the paper surface. In this report, boundary roughness was defined and calculated as a ratio of sum of boundary length between the yellow area and the black areas to twice the length of the line segment between both ends of the boundary. Although boundary roughness is close to 1, extreme bleeding by capillary penetration decreases it to much less. Image-B in Fig.1, that is, letter “2” (12pt) was printed in black or magenta in yellow area. The area of the character relative to that for the silica-coated paper for reference, assumed to be 100, means print sharpness (character) as well. In a similar manner to the line segment mode, peripheral roughness was defined and calculated as a ratio of the true perimeter to the envelop perimeter. Fig.2 shows that the envelope perimeter means the curve connecting peripheral pixels without any concavity. Extreme bleeding decreases peripheral roughness to a value less than 1 from 1, the maximum possible.

Fig1 .Image-A(left)、B(right)

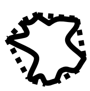


Fig2 .True perimeter (full line)
Envelope perimeter (dot line)

Measurement of microscopic three-dimensional shape of ink dots

Three-dimensional shape of ink dots of magenta was measured by use of fluorescence properties of color materials. Fluorescence at around 580nm wavelength emitted from the magenta ink by irradiation of laser at the 550nm wavelength permits to slice ink dots every 1μm in paper optically by the confocal system. Peripheral roughness of ink dots for each slice image, ink penetration depth decided by counting the number of slice images with fluorescence detected and three-dimensional shapes consisting of pixels showing fluorescence were measured.

Results and Discussion

Modification effects – properties of calcium carbonate

Fig.3 and 4 are scanning electron micrographs of the ultra-fine particles of calcium carbonate (PCC-A) and general synthesized calcium carbonate for paper as a coating pigment (right).

Table 1 shows the surface modified calcium carbonates (PCC-B, -C, -D) had lower contact angles than PCC-A, suggesting that the modified surface was wetted by water more easily. Compared with silica, PCC-B showed equivalent wettability, PCC-C and PCC-D showed lower values than silica.

Table.2 shows porosity and pore diameter measured by mercury intrusion technique. The mean pore diameters of PCC-B, -C and -D were higher than that pf PCC-A. Especially, PCC-B had the highest porosity and the highest pore diameter so that the highest water absorption rate was expected. However, note that silica provided porosity higher than any of the calcium carbonates.

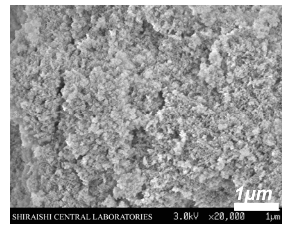


Fig.3 PCC-A

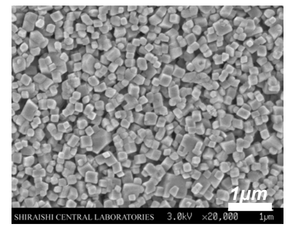


Fig.4 Calcium carbonate for paper

Table 1. Contact angle of modified calcium carbonate

	PCC-A	PCC-B	PCC-C	PCC-D	Silica
BET specific surface area [m^2/g]	65.1	67.8	76.3	75.9	292.8
Contact angle[°]	40.9	13.7	25.4	29.1	17.3

Table 2. Pore diameter and porosity of modified calcium carbonate

	PCC-A	PCC-B	PCC-C	PCC-D	Silica
Mean pore diameter [μm]	0.05	0.78	0.12	0.2	0.53
Porosity[%]	70.2	78.7	74.5	74.5	83.8

Modification effects - print quality

Fig.5 shows water absorption (Bristow) curves and absorption coefficient which are gradients Ka of the relationships between square root of contact time and volume of transferred water. The trial ink-jet papers prepared from PCC-B, C and D had higher absorption coefficients, suggesting that lower contact angles led to higher water absorption rates.

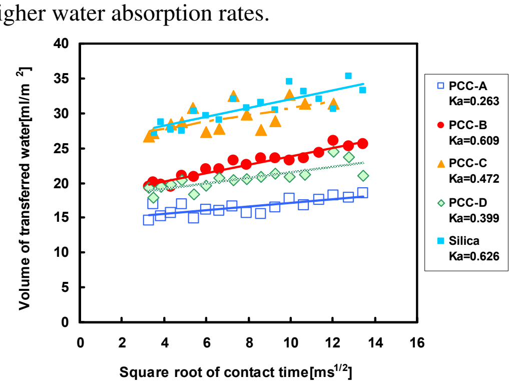


Fig.5 Comparison of water absorption rate

Fig.6 shows average optical density of Bk, Cy, M, Y solid-printed by the ink-jet printers. Compared with PCC-A, PCC-D, -C and -B show equivalent, slightly lower and fairly lower optical densities, respectively for both of the printers. Talking the result of water absorption rate as in Fig.5 into account, higher water absorption rate tends to result in lower optical densities. Dye contained in the ink was fixed deeper inside the coat layer after absorption because of the higher rate of water absorption for the coated papers with surface-modified calcium carbonate.

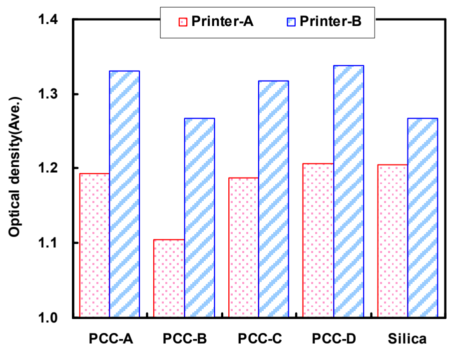


Fig.6 Optical density of coated paper

Fig.7 shows the results of relative area and boundary roughness. In the case by printer-A (7-1), PCC-B, -C and –D provided smaller relative area than PCC-A, suggesting that bleeding for them was less than PCC-A. PCC-B, -C and -D provided better boundary roughness as well, suggesting likewise that bleeding by capillary penetration was less. On the other hand, contact angle shown in Table 1 was not correlated with relative area or boundary roughness, as implied by the fact that PCC-D provided the best result of both of bleeding quality.

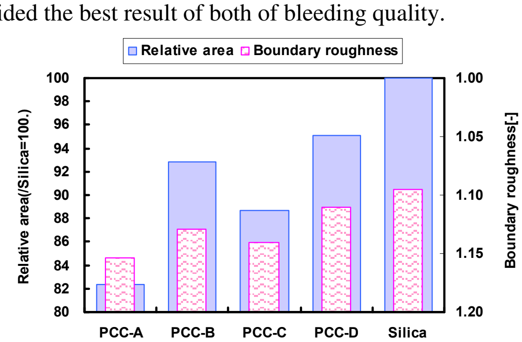


Fig.7-1 Relative area and boundary roughness (Printer-A)

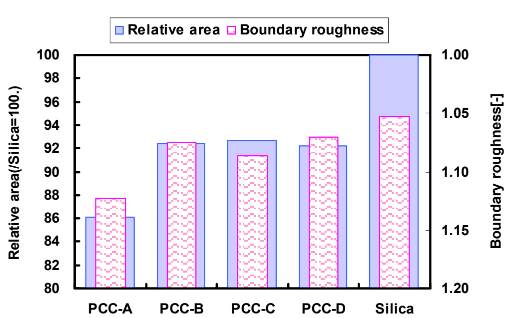


Fig.7-2 Relative area and boundary roughness (Printer-B)

In the case of printer-B (7-2), PCC-B, -C and -D provided better relative area and boundary roughness than PCC-A, but the bleeding quality was almost same among PCC-B, -C and -D and bleeding by lateral spread of ink and capillary penetration were not correlated with contact angle. The difference in bleeding quality depending on the printer seemed to be influenced by the condition of landing of ink droplets on the coat layer.

In the case of printer-A, PCC-D provided the highest bleeding quality, whose contact angle was higher and water absorption rate was lower than PCC-B, balancing surface wet ability with porosity was effective to decrease bleeding. In the case by printer-B, pore volume was not so influenced to bleeding quality, improving water absorption rate by lower contact angle was mainly effective to decrease bleeding.

Fig.8 shows the results of relative area and peripheral roughness of the characters. In the case of printer-A (8-1), PCC-B, -C and -D provided smaller relative area of black characters than PCC-A, suggesting decreased lateral spread of ink droplets. At the same time, PCC-C provided further lateral spread of ink droplets because sharpness of the characters was lower. PCC-B, -C and -D provided almost the same peripheral roughness of black characters with PCC-A and the peripheral roughness level was close to that for silica although the surface wettability was not correlated with bleeding by capillary penetration.

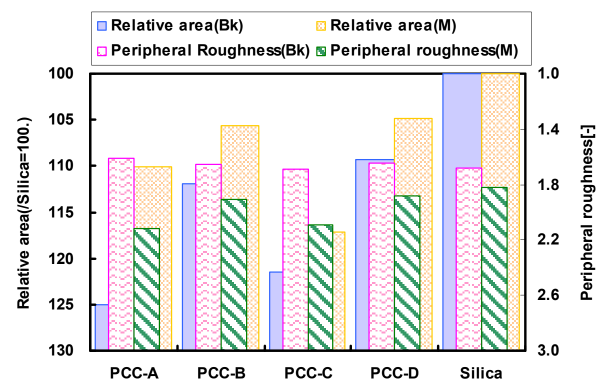


Fig.8-1 Relative area and peripheral roughness of characters (Printer-A)

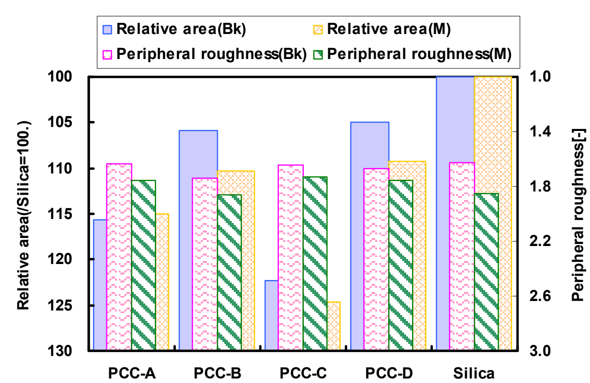


Fig.8-2 Relative area and peripheral roughness of characters (Printer-B)

In the case of printer-B (9-1), PCC-B and -D provided smaller relative areas of both black and magenta characters, suggesting that lateral spread of ink droplets decreased. PCC-C provided the largest relative area, suggesting the sharpness of characters was the lowest. Peripheral roughness of all the trial coated papers prepared from the modified calcium carbonates was almost the same with that for silica. In region of halftone dot-printed area, many droplets were absorbed as soon as they landed because of hydrophilicity of the modified pigment surface so that ink droplets were prevented from contact and mixture between each other. The amount of bleeding ink around boundaries between dots is considered to decrease. At the periphery of characters, in the case of the modification with silica particles, water absorption rate was improved but bleeding quality dropped probably because ink was considered to penetrate in the horizontal direction on the near surface.

Modification effects – microscopic three-dimensional shape of magenta ink dots by CLSM

Fig.9 shows the result of penetration depth of dye of region of printed area, optically-sliced dot image by CLSM, dot roughness of magenta ink, penetration depth of dye of region of dot alone and 3D image by bird's eye view of ink dot, whose depression angle was 30 degrees, which was analyzed each optical sliced image. This image of ink dots shows not penetrated point of ink solution but fixed point of dye.

Penetration depth of ink in the halftone dot-printed area and dot diameter of PCC-B paper was almost the same with PCC-A paper. Penetration of ink for PCC-C and -D papers was deeper than PCC-A, but the penetration depth was not correlated with contact angle or porosity. PCC-C provided a larger volume of ink dot than any other, suggesting penetration with spreading in the horizontal direction.

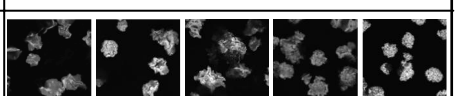
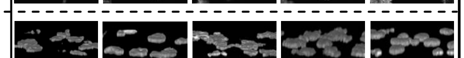
	PCC-A	PCC-B	PCC-C	PCC-D	Silica
Depth of ink μm	35	36	38	39	29
Dot diameter μm	43	43	59	43	40
depth μm	26	26	29	31	23
Peripheral roughness of ink dot	1.27	1.25	1.26	1.38	1.20
Image by CLSM					
Bird's eye view					

Fig.9 Three-dimensional image of ink dots measured by CLSM

Compared between penetration depth and optical density in the solid-printed area, PCC-B paper provided lower optical density than PCC-A paper but the same penetration depth with PCC-A paper. It was considered that the water absorption rate of PCC-B paper was faster than the fixation rate of dye so that the dye was conveyed deeper inside the coat layer, although the rate of the dye near the surface area was lower than that of PCC-A paper. PCC-C paper provided lower optical density and deeper ink penetration so that dye was considered to fix deeper inside the coat layer than PCC-A paper but the penetration was deeper than PCC-A. The optimum absorption rate of PCC-D attained by controlled porosity was considered to balance well with the fixation rate of dye.

Conclusion

In the case of using ultra-fine particles of calcium carbonate as a pigment for ink-jet paper, it was possible to improve water absorption by improved pigment surface wettability that was effective to decrease bleeding at boundary of two adjacent lines with different colors and lateral spread of ink at the periphery of printed characters. It might be possible to adjust the balance between the absorption rate of ink and fixation rate of dye by controlling porosity. For more improvement in image quality, it was considered to be important to optimize the balance between the penetration of ink dots by controlling pore size distribution of a coat layer and the fixation rate of ink by keeping high specific surface area.

References

[1] G. Moera-Swift, and S. Rose, Proc. of IS&T's NIP21, 445-447(2005)

[2] Y. Mori, T. Enomae, and A. Isogai, Proc. of IS&T's NIP22, 555-558(2006)

[3] M, Naito, T. Enomae, A. Isogai, Y. Ozaki, and H. Nagashima, Proc. of IS&T's NIP23, 580-585(2007)

[4] D. Ivutin, T. Enomae, and A. Isogai, Proc. of IS&T's NIP21, 448-452(2005)

Author Biography

Kei Matsubara works for Shiraishi Central Laboratories,. LTD. from 2000 and has been in charge of synthetic calcium carbonate for coating pigment of paper. She received her Bachelor's degree in chemical engineering from Kansai University (2000). Her work has focused on the development of calcium carbonate for ink jet paper and she studied about the relationship between ink jet printability and properties of coating pigment as a commissioned researcher of the University of Tokyo.