Control of the Dot Height of Pigmented Ink for Good Clarity

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Abstract

Clarity is one of the important physical parameters to characterize the quality of a print image. The print at low clarity will be recognized lacking in glossiness. Generally the pigmented ink is inferior to the dye-based ink in clarity of printing.

The present paper studies the clarity of print of the pigmented ink both theoretically and experimentally and shows that the clarity of print at low duties is determined predominantly by the height of ink dots formed on a paper. In addition, we propose techniques to control the dot height and show possibilities to improve the clarity of the pigmented ink.

Introduction

Owing to the progress in technology of printers and inks, ink-jet printing systems have extended rapidly in the printing market for the past several years. The speed of printing of some ink jet printers is now comparable to that of personal laser printers. Furthermore some ink jet printers show photographic images that cannot be distinguished from silver halide photographs. Although ink jet printers have many advantages, waterfastness and lightfastness of ink jet print often become problematic particularly when color printing is made with water-soluble dye-based ink.

To avoid this problem, there have been attempts to apply color pigments to ink jet colorants because pigments have better waterfastness and lightfastness. Many studies related to pigment chemistry, polymer chemistry and dispersion chemistry have been conducted. On the pigment chemistry, crystal size and shape control technology and surface modification technology were investigated[1)]. In the field of the dispersion chemistry, structured polymeric dispersant[2)] and emulsion-based technology[3)] were developed. The technology to attach a variety of nucleophilic materials to pigment surface chemically was also developed[4)]. From the dispersion technique, some new methods were proposed[5)]. As a result, pigmented dispersion suitable for ink-jet ink has become available and now pigmented ink is used not only in wide format printers but also in personal printers.

There is an insufficiency in the pigmented ink, however, in that it shows lower clarity of printing than the dye-based ink. The print at low clarity will be recognized lacking in glossiness; this is noticeable when the printing is made on a coated paper rather than a plain paper. It is an essential subject to improve the clarity of printing of the pigmented ink for widening its application.

For this purpose, we studied the clarity of printing both theoretically and experimentally and sought possibilities to improve the clarity of the pigmented ink. First, we analyzed theoretically the relationship between the clarity of a print and the height of dots of pigmented ink formed on a paper. Then we tried experimentally to control the dot height of pigmented ink by 1)changing the particle diameter of pigments, 2)adjusting the viscosity of the ink, 3)reducing the amount of free polymers that are not adsorbed on the surface of pigments. Finally, we prepare a series of pigmented inks showing different dot heights and experimentally elucidate the relationship between the clarity of print and the dot height.

Experimental

Preparation of encapsulated pigment dispersion

To make encapsulated pigment dispersion, we adopted styrene graft acrylic polymer as water-insoluble polymers that was synthesized by solution polymerization with MEK solvent. A quarter of a mixed solution of methacrylic acid, butyl methacylate, styrene, styrene macromonomer (Mn=2,300), mercaptoethanol, and 2,2'-azobis(2,4-dimethylvarelonitrile) was poured into a separable flask filled with nitrogen and heated at 75°C. The rest of the mixed solution and MEK were dropped into the flask with a dropping funnel over a period of three hours and polymerized at 75°C. After that, the polymer solution was heated at 80°C and a small amount of initiator was added for running out of the monomer residue. The polymer composition used for this study was MAA/BMA/St/St-macromonomer=15/15/30/40wt% with the weight-average molecular weight of 56,000.

At the next step, 20g of the neutralized polymer and 80g of Pigment Red 122 (or Pigmnet Yellow 74 or Pigment Blue 15:3) were mixed with 100g of MEK and 400g of ion exchanged water. The mixture was dispersed with a beads mill. The dispersion was concentrated with an evaporator by removing MEK and some water, and centrifuged to remove the particles of large size. The solid content of the dispersion was adjusted to 20wt% by adding ion exchanged water. Average particle diameters of cyan, yellow and magenta colorants were 89nm, 110nm and 100nm, respectively.

Encapsulated colorant with high viscosity under concentrated condition that used polymer (MAA/BMA/St/St-macromonomer =20/15/30/35wt% with the weight-average molecular weight of 52,000) was also prepared similar to above-mentioned encapsulated colorant.

The encapsulated cyan colorants having different particle diameters were prepared by changing the strength of beads mill, or by concentrating the constituent except subsidence using super-cyclone separator. Average particle diameters of cyan colorants were 24nm, 43nm, 45nm, 108nm and 150nm.

Control of the amount of free polymer

We prepared colorants without free polymer that did not stick to the surface of pigments by dispersing the deposit of super-cyclone separator. We controlled the amount of free polymers in colorant by adding free polymers as the occasion.

Ink preparation and printing

Inks for this study were made from 30% (Magenta and Yellow) or 25% (Cyan) of pigmented dispersion, 10% of triethyleneglycolmonobutylether, 1% of acetyrenol E100 (Kawaken Fine Chemicals Co.,Ltd.), approximately 10% of glycerin which could control ink viscosity and the rest of water. All inks were filtrated with membrane filter (1.2μm) just before the experiments.

We got the evaluation print using the Epson ink jet printer (EM-930C) and PM photo paper (EPSON) as a coated paper.

Measurement

The clarity of prints was measured using Image Clarity Meter (SUGA TEST INSTRUMENTS Co. Ltd.; ICM-1T, width of slit; 2°). Dot height and dot dump were measured using AFM (KEYENCE CORPOTATION, NANOSCALE HYBRID MICROSCOPE VN-8000).

Results and Discussion

1. Theoretical calculation

We consider scattering of light by a number of small dots of the pigmented ink randomly residing on a paper. It is assumed that the paper surface is flat and smooth and that the height of all dots is *H*. We suppose that the incident light of a monochromatic plane wave with a wave number vector $\mathbf{k}_{\text{in}}$ and an amplitude E_{in} impinges on the paper. Then the scattered light can be expressed by a superposition of plane waves with various wave number vectors having the same magnitude as $\mathbf{k}_{\text{in}}$. The amplitude of the plane wave with a wave number vector $\mathbf{k} \equiv (k_x, k_y, k_z)$, $E_{\mathbf{k}}$, can be expressed by the following integral:

$$\frac{E_{\mathbf{k}}}{E_{\text{in}}} = F\left[R_I \int_{\text{ink}} e^{i(v_x x+v_y y+v_z H)}dxdy + R_P \int_{\text{paper}} e^{i(v_x x+v_y y)}dxdy\right] \Bigg/ \int_{\text{ink+paper}} dxdy \quad (1)$$

Here the *x* and *y* axes are taken on the paper surface, and $\int_{\text{ink}}$, $\int_{\text{paper}}$ and $\int_{\text{ink+paper}}$ mean the surface integral over the dot area, that over the paper area, i.e. the dot-free area, and that over the whole area, respectively. A vector $\mathbf{v} \equiv (v_x, v_y, v_z)$ is defined by $\mathbf{v} = \mathbf{k}_{\text{in}} - \mathbf{k}$, and R_I and R_P are amplitude reflectances of light at the ink surface and at the paper surface, respectively. F is given by

$$F = \frac{1+\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\theta_3}{\cos\theta_1(\cos\theta_1+\cos\theta_2)} \quad (2)$$

where θ_1 is the incident angle of the incident light,

$\theta_2 = \cos^{-1}\left(k_z \Big/ \sqrt{k_x^2+k_z^2}\right)$ and $\theta_3 = \cos^{-1}\left(k_z \Big/ \sqrt{k_y^2+k_z^2}\right)$; θ_2 and θ_3 express the direction of the wave number vector $\mathbf{k}$ of the scattered light.

We can use the strength of the regular reflection wave as a measure of clarity because an image of a light source is formed by the regular reflection wave. In this case, it is conventional to use the incident light with the incident angle $\theta_1 = 45°$. Also $\mathbf{k}_{\text{in}}$ may be assumed to lie in the *xz* plane without loss of generality.

Hence one may have $v_x = v_y = 0$, $v_z = -2\sqrt{2}\pi/\lambda$ and $F = 1$ for the regular reflection wave, where λ is the wavelength of the light. Thus eq.(1) becomes

$$\frac{E_{\mathbf{k}}}{E_{\text{in}}} = R_I e^{-i2\sqrt{2}\pi H/\lambda}\chi + R_P(1-\chi) \quad (3)$$

where

$$\chi = \int_{\text{ink}} dxdy \Bigg/ \int_{\text{ink+paper}} dxdy = 1 - \int_{\text{paper}} dxdy \Bigg/ \int_{\text{ink+paper}} dxdy \quad (4)$$

Consequently the strength of the regular reflection wave is given by

$$\left|\frac{E_{\mathbf{k}}}{E_{\text{in}}}\right|^2 = \left[R_I^2\chi^2 + R_P^2(1-\chi)^2 + 2R_I R_P \chi(1-\chi)\cos\left(-2\pi\frac{\sqrt{2}H}{\lambda}\right)\right] \quad (5)$$

Here R_I and R_P are assumed real for simplicity. Eq. (5) particularly describes the dependence of clarity on the dot height *H* under given values of R_I, R_P and χ.

When the incident light is white light, the strength of the regular reflection wave, that is, clarity, is expressed by the sum of $\left|E_{\mathbf{k}}/E_{\text{in}}\right|^2$ with various wavelengths. A typical example of the dependence of clarity on H is shown in Figure 1, in which $R_I = 0.4$, $R_P = 0.2$ and $\chi = 0.2$ are assumed independent of λ. It should be noted that the clarity has a minimum (becomes worst) at around *H*=200nm. This is caused by the interference between the light reflected at the paper and that at the dot.

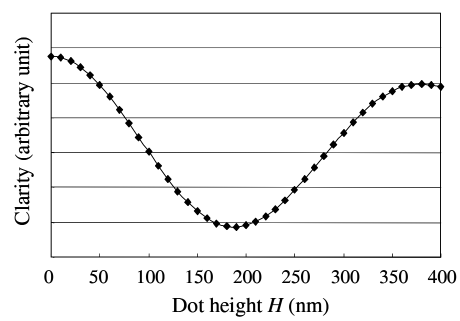

Figure 1. *Theoretical calculation of the dot-height dependence of clarity*

2. Control of dot height

After landing on the surface of a coated paper, the pigmented ink partly penetrates into the inside of the paper and the remaining ink forms a dot on the paper. It is therefore expectable that the dot height can be reduced by enhancing the penetration of the ink into the paper.

We presumed that this enhancement could occur when reducing the size of pigments in the ink and when lowering the viscosity of the ink. We therefore made a series of experiments to study the influence of the diameter of the pigment particle and the ink viscosity on the dot height. In addition, we study the effect of decreasing the amount of free polymers included in the pigmented ink.

2-1. Particle diameter

It can be expected that smaller pigments penetrate into the paper more easily because they can flow in a narrower void between silica particles residing on the surface of the coated paper. Regarding the penetration of the pigments, we supposed that there existed a critical diameter of the pigment particle; that is, pigments larger (smaller) than the critical diameter cannot (can) penetrate into the coated paper.

Using the cyan pigmented ink with an average particle diameter of 89nm, we evaluated the critical diameter via the volume of the solid content of the ink, the volume of a dot formed on the paper and the distribution of the particle diameter of the pigments. As a result, the critical diameter has been found about 60nm, as shown in Figure 2. For the pigmented ink with an average particle diameter of 108nm, we made the same experiment and obtained the critical diameter of about 60nm again.

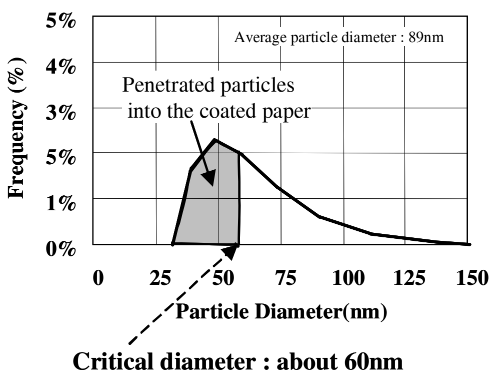

Figure 2. *Distribution of the diameter of pigment particles in cyan ink with an average particle diameter of 89nm*

From the result above, 60nm may be considered as a good criterion for designing the size of the pigment particles in the ink. Pigment particles less than about 60nm in diameter penetrate into the paper predominantly and hence the ink composed of those pigment particles can achieve low dot height.

To study this in more detail, we prepared cyan pigmented inks with average particle diameters of 24nm and 45nm and printed the inks on a coated paper. Most pigments included in these inks have diameters less than 60nm. Triangles and circles in Figure 3 show the dot height and the volume of the ink penetrating inside the paper respectively for several values of the solid content of the ink; filled symbols are for the ink with an average diameter of 24nm and open symbols for that of 45nm.

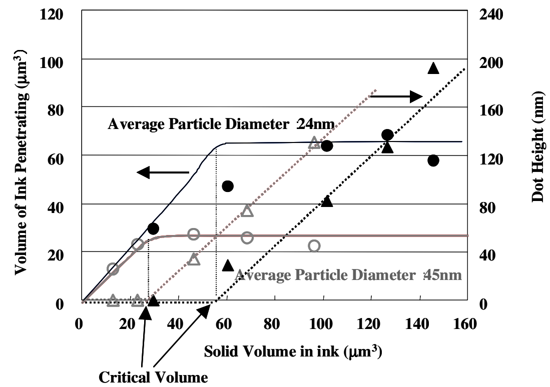

Figure 3. *Dot height and volume of ink penetrating inside the paper vs. volume of solid content of ink (average particle diameter 24nm or 45nm)*

It is observed that up to a certain volume of the solid content of the ink, the dot height remains zero, which means that all the pigments penetrate into the paper. Above this volume, say the critical volume, the volume of the ink penetrating inside the paper saturates and instead the dot height increases with the volume of the solid content of the ink. This means that the critical volume corresponds to the maximum limit of the ink volume that can penetrate into the paper. This critical volume decreases with the size of pigments in the ink; the ink with an average diameter of 24nm exhibits a larger critical volume than that of 45nm. It is noted that this makes smaller pigments more advantageous for obtaining lower dot height and hence higher clarity.

We then examined the effect of pigments larger than 60nm in diameter on the dot height. It is probable that these large pigments added to the ink prevent small pigments from penetrating into the paper. We therefore prepared mixed inks by mixing the cyan ink composed of small pigments with an average particle diameter of 43nm and that of large pigments with an average particle diameter of 150nm with the total volume of the pigments kept constant. Figure 4 shows the dot height and the volume of the ink penetrating inside the paper vs. the ratio of the small-pigment ink to the mixed ink; triangles represent the dot height and circles do the volume of the ink penetrating inside the paper.

If small pigments can penetrate into the paper without hindered by large pigments, the dot height should be constant when the ratio of the small-pigmented ink is large enough for small pigments in the mixed ink to fill the critical volume, as shown by a gray dotted line. On the contrary, experimental data in Figure 4 show that the dot height increases monotonically as the large-pigment content of the ink increases. This means that large pigments hinder the penetration of small pigments into the paper and should be preferably eliminated from the pigmented ink for obtaining low dot height.

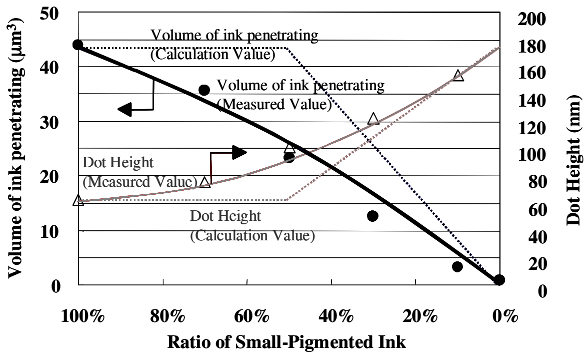

Figure 4. Dot height and volume of ink penetrating inside the paper vs. ratio of the small-pigmented ink to the mixed ink

2-2. Viscosity

It is expectable that the viscosity of ink will also affect the penetration of the ink into the paper; ink with a lower viscosity should penetrate into the paper more rapidly. Here we have to note that the viscosity of the ink is not constant during penetration but should increase as the ink penetrates into the paper, being concentrated during penetration.

We prepared two pigmented inks whose viscosities are initially same but different from each other when concentrated, and printed each ink on a coated paper. Figure 5 shows the critical volumes introduced in section 2-1 for the two pigmented inks. Viscosity of each ink when concentrated up to 25% is shown in the parenthesis. As expected, the ink with a lower viscosity shows a larger critical volume. This result suggests that the viscosity of the pigmented ink, which is tunable by the selection of vehicle and dispersant, is also a key factor to control the dot height.

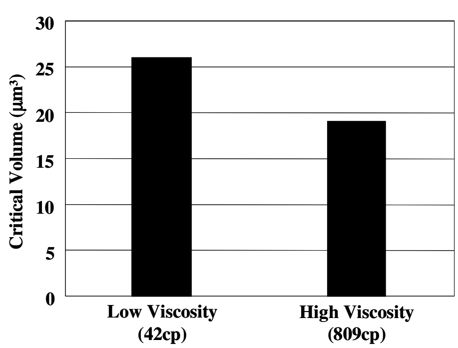

***Figure 5.** Critical volume of ink with different viscosity*

2-3. The amount of free polymer

In the pigmented ink, free polymers that are not adsorbed on the pigments are included as a constituent and may be responsible for increasing the dot height. Figure 6 shows the relationship between the dot height and the amount of free polymers included in the cyan pigmented ink. As can be seen, the dot height increases monotonically with the amount of free polymers, which suggests that free polymers remain in a dot and expand its volume.

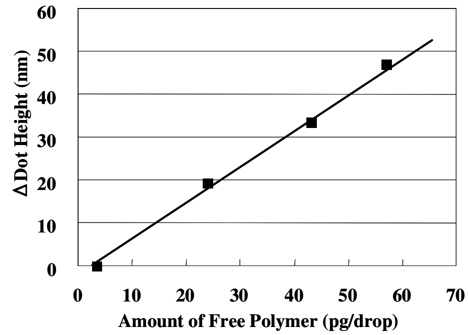

***Figure 6.** Dot height vs. amount of free polymers in cyan ink*

3. Clarity of print and dot height

We then studied the relationship between the clarity of print and the dot height, which can be controlled by the diameters of the pigment particles, the viscosity of the ink when concentrated and the amount of free polymers, as has been described in the previous section.

A series of inks with the colors of yellow, magenta and cyan were prepared with the total volume of the pigments kept constant and were printed on a coated paper at a duty of 20%, whereat isolated dots are formed on the paper. Figure 7 shows the relationship between the clarity of the print and the dot height experimentally obtained. It is observed that the clarity becomes minimal at around a dot height of 200nm. This behavior coincides with the theoretical calculation of Figure 1. Figures 1 and 7 illustrate how the clarity of print at low duties depends on the dot height and indicate the dot height suitable for obtaining high clarity.

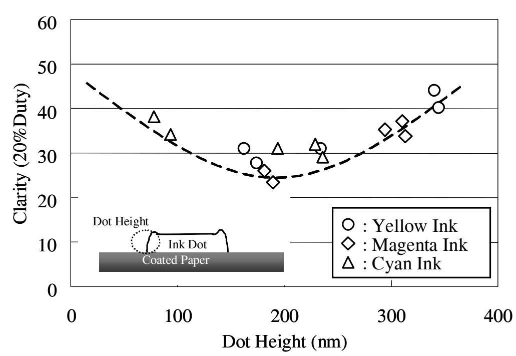

***Figure 7.** Experimental results of dot height and clarity (20% Duty)*

Figure 8 shows the relationship between the clarity of the print of 100% duty and the height of the dot bump formed on the printed surface. The clarity deceases with the height of the dot bump up to 100nm, which also resembles the behavior shown in Figure 1. At high duties, the printed surface covered with ink dots should be made as flat as possible for obtaining high clarity.

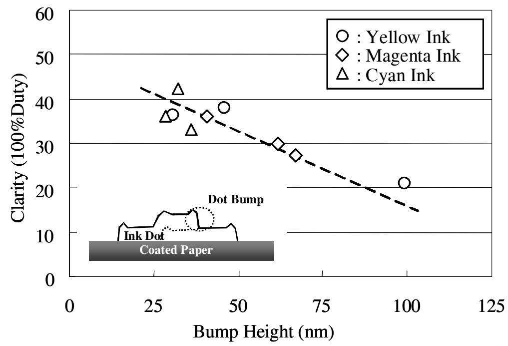

Figure 8. *Experimental results of bump height and clarity (100% Duty)*

Conclusion

We studied the clarity of print of the pigmented ink both theoretically and experimentally and sought possibilities to improve the clarity.

Our theoretical calculation predicted that the clarity was determined predominantly by the height of dots of the pigmented ink formed on a paper. We therefore sought techniques to control the dot height and found that the dot height was controllable by the size of the pigment particles, the viscosity of the ink when concentrated and the amount of free polymers included in the ink. Using this technique, we prepared a series of pigmented inks showing different dot heights and clarified the relationship between the clarity of print and the dot height. This particularly showed that the clarity becomes minimal at around a dot height of 200nm, which coincided with the theoretical prediction.

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Author Biography

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