The Effect of Properties of Encapsulated Pigment Inks on Optical Density

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Abstract

If an ink jet is applied to an office printer, it is important to obtain high optical density on plain paper, consistent with that of a laser beam printer. Also, on the point of durability and water resistance, pigment inks have advantages for office use over dye inks. Encapsulated pigment inks that are coated with water-insoluble polymers in particular can achieve high optical density, compared with conventional pigment inks, which are dispersed by water-soluble dispersants.

For this paper, to use these encapsulated pigment inks effectively, we prepared several encapsulated pigment inks, which had different wettability and penetration ability on plain paper, and investigated the relationship between their properties and their optical density on plain paper. We found that inks with both high wettability and low penetration ability indicate high optical density. To confirm the cause(s) of these results, we measured the ratio of white spot to solid image by image processing. We also examined the depth profile of the pigment from the paper surface by TOF-SIMS analysis.

Introduction

With the increasing popularity of digital cameras, an ink jet printer for home use has been developing recently. Now it is considered that the photo quality of ink jet printing for photo media has reached that of silver halide photography. On the other hand, ink jet technology for office use has been developing recently with the advantage of low cost, low energy, small space, low maintenance over the laser beam printer (LBP). The office printer needs to produce easily readable document files on plain paper, so high optical density is one of the most important factors in this field.

For office use, pigment inks that have waterfastness and lightfastness are suitable for storing document files. In particular, encapsulated pigment inks that are coated with water-insoluble polymers have excellent printing performance of optical density, rub resistance and highlighter-fastness on plain paper, because they form hydrophobic film on the paper surface, compared with conventional pigment inks dispersed with water soluble polymers.

However, compared with LBP toner where almost all pigment remains on the paper surface, ink jet inks tend to exhibit lower optical density because they penetrate to the inside of plain paper, so the amount of effective pigments for color strength decreases. Therefore, to get high optical density, it is necessary to control the penetration of pigments to the inside of plain paper and various means have been tried. The relationship between the distribution of pigment on penetration and optical density is an important point.

Another challenge with ink jet printing in getting high optical density, is decreasing the printing part where ink doesn't spread and doesn't cover the surface of plain paper (we call it "white spot"). To solve this problem, it is necessary to wet the ink to the paper fiber and to spread ink dot on the paper surface as much as possible. The relationship between white spot and optical density becomes another key point.

Therefore, this study shows how the distribution of pigment on penetration and white spot on the paper surface influence optical density on plain paper. To accomplish this study, we prepared several encapsulated pigment inks, which had different wettability and penetration ability on plain paper. Then we investigated the relationship between their properties and their optical density on plain paper. We estimated the ratio of white spot to solid image by image processing and also examined the depth profile of the pigment from the paper surface by TOF-SIMS analysis.

Experimental

Preparation of encapsulated pigment dispersion

To make encapsulated pigment dispersion, we adopted styrene graft acrylic polymer that was synthesized by solution polymerization with MEK solvent for water-insoluble polymers. 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 nitrogen purged separable flask and heated to 75°C. The rest of the mixed solution and MEK was 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 to 80°C and a small amount of initiator was added for running out of the monomer residue. The polymer compositions used for this study was MAA/BMA/St/St-macromonomer=15/15/30/40 with the weight-average molecular weight of 56,000.

At the next step, 20g of the neutralized polymer and 80g of Pigment Red 122 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 the evaporator by removing MEK and some water, and centrifuged to remove the large size particles. The content of the dispersion was adjusted to 20wt% by adding ion exchanged water.

Ink preparation and printing

Inks for this study were made from 30% of pigment dispersion, 10% of triethyleneglycolmonobutylether, 1% of acetyrenol E100 (Kawaken Fine Chemicals Co.,Ltd.), 1% of various organic agents (such as alcohol or ether) which can change ink property, approximately 10% of glycerin which can control ink viscosity and the rest of water. All inks were filtrated with membrane filter (1.2 µm) just before the experiments.

A Print test was made with an Epson ink jet printer (EM-930C). Xerox 4024 was used as the plain paper. We printed a solid pattern and measured optical density.

Measurement of Ink properties

We measured surface tension of several inks and contact angle of these inks to the plain paper as ink properties. We could measure contact angle stably because we could delay ink penetration by the use of plain paper that was pressed under a calendar roll to decrease air space.

TOF - SIMS analysis

TOF-SIMS analysis was applied to measure the depth profile of pigment in paper penetration. To make a cross section of plain paper, printing paper was stiffened by polyethylenetelephtalate resin (PET) and was cut with a diamond cutter. As pigment spectra, we selected Mw = 311.25 spectra of Quinacuridone.

TOF-SIMS data were recorded on a TOF-SIMS IV instrument (ION-TOF GmbH, Munster, Germany) and imaging data were recorded by scanning an analysis area of 200 × 200 μm using lateral resolution 3μm. Line profiles of the pigment were performed using corrected images and average profiles of 3 samples were calculated.

Image processing

To evaluate the ratio of white spot in solid image printing, we used an image processing system IAS-1000 (QEA corp.). At first, solid image was taken in the image processor with a CCD camera. The image processor operated at an optical density of 1 pixel (3.54 μm × 3.54 μm). We call it "pixel optical density". This measurement was done at 296100 pixels on a 3500 μm × 2600 μm area. Then, we estimated the ratio of white spot from a histogram of pixel optical density by Image processing.

Result and Discussion

1. Properties of inks and optical density

It is assumed that an ink drop spreads by wetting on the paper surface at first, then penetrates to the inside of the paper. Therefore we can assume that the behavior of an ink drop is expressed to the following equations (1), (2). The work function of spread by wetting on the paper surface is expressed by Young's equation (1). On the other hand, penetration to the inside of paper is described by Lucus-Washburn's equation (2) of capillary phenomena between paper fibers.

Work function of spread by wetting $W = \gamma (1 - \cos\theta)$ (1)

Penetration length $L = \sqrt{(r t \gamma \cos\theta / 2\eta)}$ (2)

γ : surface tension, θ : contact angle, L : penetration length, t : time, r : capillary diameter, η : viscosity

According to these equations, if ink viscosity is constant, we can recognize that the behavior is determined by only surface tension (γ) and contact angle (θ) in ink properties.

The smaller the work function of spread by wetting becomes and the smaller the penetration length becomes, the higher the optical density indicated. This means that smaller $\gamma (1 - \cos\theta)$ in equation (1) and the smaller $\gamma\cos\theta$ in equation (2) are effective for high optical density (Figure 1).

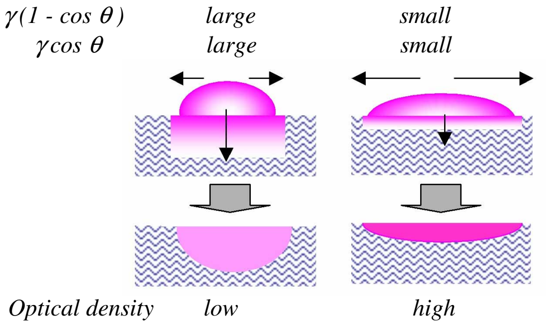


Figure1. Image of spread by wetting and penetration of pigment with change of ink properties

To confirm whether this model is correct, we prepared several encapsulated pigment inks that have different surface tension and contact angle to change wettability and penetration ability. Then, we discussed the relationship between $\gamma (1 - \cos\theta)$ and $\gamma\cos\theta$ and optical density (Figure 2).

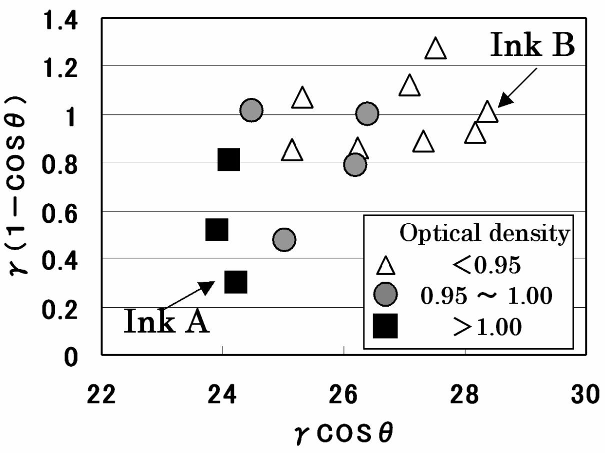


Figure 2. Relation of optical density to γ(1 - cos θ) and γ cos θ

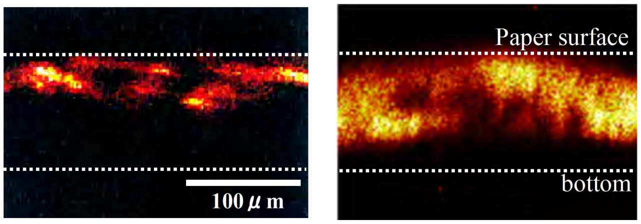
The range of surface tension (γ) was from 25 to 30 mN/m and the range of contact angle (θ) was 10 degrees to 30 degrees. The results of this evaluation suggested that optical density becomes high when both $\gamma (1 - \cos\theta)$ and $\gamma\cos\theta$ are small. So, this model can explain one facet of the relationship between ink properties and optical density. Therefore there are suitable surface tensions and contact angles for high optical density.

We discuss each effect of spread by wetting and penetration to the inner individually in the next section.

2. Penetration depth of pigment

To confirm the change of penetration length by differences of ink properties, we investigated depth profile of pigment in the cross section of paper by TOF-SIMS analysis. Until recently, the direct measurement of depth profile of pigments from the paper surface hasn't been done, though there are many reports that image of pigment distribution was measured indirectly by ATR-FT-IR or IR-PAS and that the cross section of printing was observed by microscope.

TOF - SIMS analysis that we adopted, can measure depth profile of pigment directly because segment ions from pigment in the area of cross section are determined. We compared Ink A and Ink B in Figure 2 that have a big difference in optical density. Figures 3 and 4 show the image of spectra strength from pigments and the depth profile of their spectra strength.



Ink A Ink B

Figure 3. Image of pigment spectra strength measured by TOF-SIMS analysis

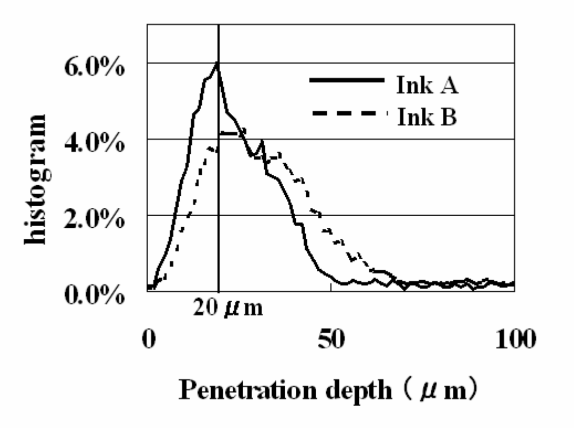


Figure 4. Depth profile of spectra strength by TOF-SIMS analysis

Ink A (that indicated high optical density) had the larger amount of pigments in the shallow part from the paper A was controlled. We considered that this difference of penetratio surface, compared with Ink B. So, the penetration of pigment in Ink n depth was derived from the difference in ink properties.

On the other hand, we have found (by our other investigation of comparison with toner pigments and ink pigment) that pigments within 20 m depth can contribute to optical density. The use efficiency of pigment in Ink A was 45% and that in Ink B was 35% (Table 1).

This result proved that more than half of pigments didn't work for optical density. It might be a key point in getting high optical density, that we control the penetration depth of pigments to within 20 μm, to get high use efficiency of pigment.

Table 1. Penetration depth and use efficiency of pigment

	Optical density	Penetration depth	Use efficiency (within 20μm)
Ink A	1.01	50 μm	45%
Ink B	0.88	70 μm	35%

3. White spot

We inspected white spot resulting from limited spread by bad wetting. We assumed that white spot changes according to ink properties. We then confirmed the relationship between optical density and white spot.

If we calculate optical density using equation (3), (from the definition of diffusion reflection) and increase the area of white spot (we assumed optical density = 0) in solid image (we assumed optical density = 1.5), we can get the optical density curve of the rate of white spot (figure 5).

$$\text{Optical density} = -\log\left((1-\chi) / 10^{1.5} + \chi \right) \qquad (3)$$

$\chi \times 100$ (%) : rate of white spot

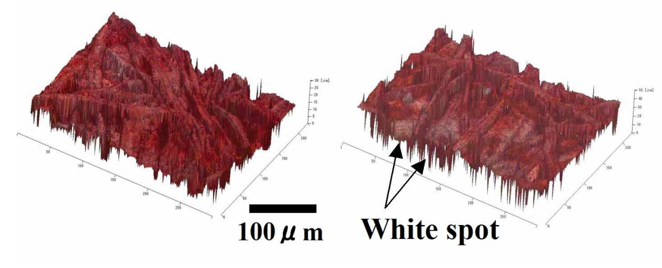
Figure 5 shows that optical density declines rapidly in the range of small white spot, so it is suggested that white spot influences optical density markedly.

Figure 5. Optical density curve of solid image calculated with increasing white spot

We also compared ink A and ink B in Figure 2 that have a big difference in optical density due to their different properties. Figures 6 and 7 show solid image of printing by laser microscope and histogram of pixel optical density on solid image, measured by image processing.

According to the results that we measured of optical density of many typical white spots in Ink B (in figure 6), we defined white spot as the area below optical density 0.78. We calculated the rate of white spot from the histogram, then the area of white spot in ink B below 0.78, which was 10.1% of the solid image.

On the other hand, the area of white spot in Ink A occupied approximately 3.1%, so it is suggested that spread by wetting of ink A was proceeding well compared with ink B. In addition, if we calculated optical density in cases where we removed the area of white spot on the histogram, the rise in optical density of Ink A is 0.04, while that of ink B is 0.08 (Table 2). This means that white spot in ink A is smaller than that in Ink B.



Ink A Ink B

Figure 6. Solid image printing on plain paper

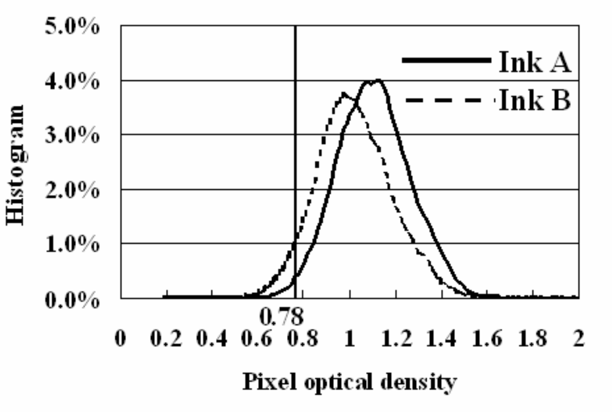


Figure 7. Histogram of pixel optical density on image

Table 2. Optical density calculated with removing white spot by histogram

	Optical density	White spot	O.D. removed white spot
Ink A	1.01	3.1%	1.05
Ink B	0.88	10.1%	0.96

Conclusion

To achieve high optical density on plain paper, it is essential to 1) increase the amount of surface-retained pigments by controlling penetration, and to 2) decrease white spot by achieving a wide spread through good wetting. Therefore, it is important to understand the influence of penetration depth of pigment and the ratio of white spot for optical density.

This study proved that TOF-SIMS analysis is very effective in determining the depth profile of pigment. It also showed that we can estimate the white spot from the measurement of pixel optical density by image processing.

In addition, this investigation showed that if we can make ink properties with smaller $\gamma (1 - \cos\theta)$ and smaller $\gamma \cos\theta$ (derived from simple work function and penetration equations), optical density becomes higher. By these measurements, we confirmed that these printings of high optical density were controlling pigment penetration and decreasing white spot.

References

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Biography

Yasuhiro Doi received his B.S. and M.S. in polymer science from Kyushu University in 1988 and 1990 respectively. In 1990, he joined Kao Corporation and has been engaged in research and development of performance chemicals. Since 2001, he has worked on research into materials application in information technology.

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