Plain Paper Quality of Encapsulated Color Pigmented Inks

Takehiro Tsusumi, Ryuma Mizushima, and Makoto Sakakibara, Kao Corporation, Performance Chemicals Research Laboratories, Wakayama, Japan

Abstract

Color pigmented inks have the advantage in durability and are used in many printing industries. But for ink jet inks, they are used limitedly because of the necessity of specific combination with the media. Actually the color pigmented ink jet inks were first developed for wide format printer with the special coated paper. Remove of the restriction of media is needed to expand the possibility of color pigmented ink jet inks. For this expansion, encapsulated pigment had been proposed having durability independent of the media.[1]

In this paper, pigment dispersions with different amount of desorbed polymer are investigated to maximize the optical density on the plain paper. The amount of the desorbed polymer in the ink is found important to improve the print quality on the plain paper.

Introduction

Drop on demand Ink jet printer has become much more attention for digital printing. Good image quality can be achieved using a cheap apparatus by good combination of ink and media. Some ink jet printers produce photographic images that could not be distinguished from silver halide photographs and some printer produce a black text almost the same quality as that of the laser beam printer. The combination of ink and media is the key for good print quality in the ink jet printing system. On the other hand the restricted combination limits the application.

There are two types of colorant used for ink jet printers, dye based inks and pigmented inks. Dye base inks shows excellent color gamut on the special papers and recently gained enough durability for practical use by dye chemistry technology and media technology. But dye base inks still have the problems with the plain paper, such as poor waterfastness, lightfastness and sharpness.

Pigmented inks have advantages in waterfastness and lightfastness independent of the kind of the media and are used for the application required high durability. But pigmented inks have some restriction on the combination with the media. Because pigment particles in the ink remain on the surface of the print, the prints have the tendency of low gloss and poor rub resistance on the coated media. Consequently pigmented inks are sometimes used with overcoat for special papers.

Pigmented inks have also difficulties in the combination with the plain paper. Pigment particles have the tendency to run down between the paper fibers along with the ink vehicle and not to remain on the top the paper. Control the surface tension of the ink is an approach and high surface tension inks are used for black inks. High surface tension inks bring high optical density but cause the problem of inter-color breeding. High surface tension black inks are tolerated with the combination of reactive color inks. As the print speed increase, the breeding problem will become seriously.

Pigmented color inks have the problem on the plain paper quality and unfortunately high surface tension system is impossible. Consequently some improvement of the color ink was demanded for the plain paper quality.

Many investigations on pigment chemistry, polymer chemistry and dispersion chemistry have been made to solve the problem of color pigmented inks with the plain paper. Crystal size and shape control technology and surface modification technology were investigated[2] from the pigment chemistry. Structured polymeric dispersant[3] and encapsulating technology[1] were developed from the dispersant chemistry. As the result of these investigations, many suitable color pigment dispersions for ink jet inks became available and color pigmented inks become to be used not only for wide format printers but also for personal printers today. But the mechanism of the plain paper quality had not yet proposed closely.

Water soluble dispersant has the absorption equilibrium in the dispersion. A polymer absorbs on the pigment surface and a polymer exists in the disperse phase freely. The absorbed polymer keeps the pigment particles apart in the ink and stabilizes the dispersion. The desorbed polymer does not affect as a dispersant and sometimes causes the flocculation. On the other hand, water insoluble dispersant, which has no solubility to the disperse phase, has no equilibrium in the dispersion and is suitable for high performance pigment dispersion.

The print speed of ink jet printer becomes faster and become to compete with the laser beam printer in some application, such as office printing. For this application, higher optical density is also demanded. Besides the surface modified pigment, most of the pigmented inks on the market today are made with polymeric dispersant and containing some amount of desorbed polymeric dispersant. An understanding of the relation between the desorbed polymeric dispersant in the ink and pigment distribution in the paper are useful to maximize the print quality. In this report, we studied the optical densities of the inks having different amount of the desorbed polymer with the relation of the depth profile of the pigment in the paper.

Experimental

Polymer Preparation

Styrene graft acrylic polymer was synthesized by solution polymerization with MEK solvent. A quarter of mixed solution of methacrylic acid, butyl methacylate, styrene, styrene macromonomer (Mn = 2,300), mercaptoethanol, and 2,2'-Azobis(2,4-dimethylvarelonitrile) was pored into the 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 the droplet of all monomer solution, polymer solution was heated to 80°C and added a small amount of initiator 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.

Pigment Dispersion

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 the beads mill. The dispersion was concentrated with the evaporator by removing the MEK and some water and centrifuge to remove the large size particles. The content of the dispersion were adjusted to 20wt% by adding ion exchanged water.

Purification of the Pigment Dispersion

2.0Kg of pigment dispersion was purified by membrane filtration using Vibratory Shear Enhanced Process (VSEP), New Logic International Inc., with polysulphone membrane having the exclusion molecular weight of 4,000. The pH value and the solid content of the dispersion were kept constant during the purification by adding the neutralizer and ion exchanged water.

Ink Preparation and Printing

Inks for this study were made from 30% of pigment dispersion, 10% of triethyleneglycolmonobutylether, 10% of glycerin, 1% of acetyrenol E100 (Kawaken Fine Chemicals Co., Ltd.) and the rest of water. All inks were filtrated with membrane filter (1.2 μm) just before the experiments. Print test was made by the Epson ink jet printer (EM-930C). Xerox 4024 was used as the plain paper.

Measurements

Digital microscope, VH-6300C, Keyence Japan, was used to visualize the colorant on the print. Attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR) method was measured with Horiba FT-710 spectrometer, Horiba Seisakusho Co., Ltd. ATR-FTIR spectra were detected with Dura Sample IR II, Sens IR Technologies. Fourier-transform infrared photo-acoustic spectroscopy (FTIR-PAS) spectra of the print were obtained by Bio-Rad Laboratories step-scan FTIR spectroscopy type FTS60A/896. The PAS cell was MTEC Co. Ltd. type 300 photo-acoustic detectors. Spectra were measured at 8 cm^{-1} resolution with 32-256 scans and a mirror velocity of 2.5, 5, 10, 20, 40 KHz.

Result and Discussion

Purification of Microcapsule Pigment

Three kinds of purified pigment dispersion were made by the membrane filtration technique. The membrane filter passes the water soluble polymer in the disperse phase effectively.[4] The amount of the desorbed polymer could be controlled by increasing the amount of the filtrate. Figure 1 shows the amounts of desorbed polymer measured as the solid content of filtrate. Physicochemical properties of sample dispersions are listed in Table 1.

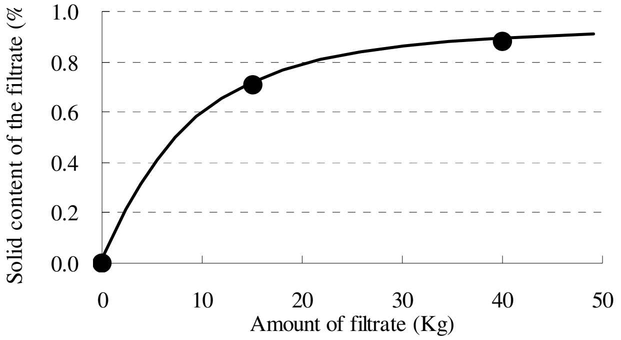

Figure 1. Efficiency of the purification.

Table 1: Physicochemical Properties of Pigment Dispersions

	Amount of filtrate (Kg)	Viscosity (mPa.s)	S. T. (mN/m)	Diameter (nm)	pH
Sample A	0	3.0	43.7	155	8.8
Sample B	15	3.0	47.3	148	8.8
Sample C	40	3.2	50.2	152	8.8

Physicochemical properties other than surface tension did not change by the purification. The change of the surface tension represented that the desorbed polymer had surface activity and the purification was made effectively.

Ink Performance of Purified Microcapsule Pigment

To study the effect of the desorbed polymer in the microcapsule pigment dispersion, the stability and print performance of inks were investigated (Table 2). The stability of the inks was very goof independent of the amount of desorbed polymer. Because the microcapsule pigment had enough stability, the flocculation did not occur by the water soluble desorbed polymer. On the other hand, the optical density was influenced significantly by the amount of the desorbed polymer. Because the optical density of the pigmented ink depends on the amount of the pigment on the paper surface, the desorbed polymer, which was surface active to reduce the surface tension, was presumed to accelerate the imbibition of the pigment particle into the paper. The evaluated inks contained surfactant as a penetrant. The difference of the function between the desorbed polymer and the surfactant was not clear but the structural analogy to the pigment dispersant might have some influence on the wettability of the dispersion to the paper fiber.

Table 2: Ink Test of Sample Dispersions

	Ink Stability Test *		Print Test
	Changes of viscosity	Changes of particle diameter	Optical density
Sample A	102%	104%	0.97
Sample B	101%	106%	1.05
Sample C	103%	102%	1.12

*: changes were measured after 70°C x 1month

Figures 2 and 3 shows the surface and cross section image of the paper. The amount of the pigment on the print surface and the pigment distribution in the paper could not differentiate between samples.

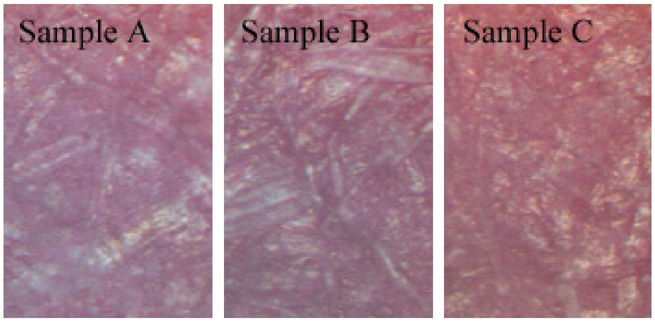

Figure 2. Surface images of print samples.

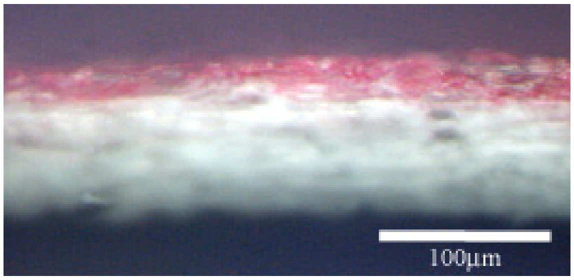

Figure 3. Cross section of print sample C.

The understanding of the relation between the pigment distribution and the print quality was thought important. The pigment distribution in the paper was measured by the FTIR-PAS method.

Measurement of Pigment Distribution in the Plain Paper

Chemical distribution in the film was measured by several methods such as X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectroscopy (SIMS). But the paper is a coarse mixture of cellulose fiber and pigment does not exist uniformly on the fiber. Then we measured the pigment distribution by the FTIR-PAS method. FTIR-PAS method can measure IR absorption of different sample depth from the surface by changing the mirror velocity (modulation frequency) and is the useful to measure the depth profile of the sample independent of the sample shape.[5] Dittmar *et al.* reported the depth profile of the polymer laminates from surface to 6 ~ 16 μm.[6] Figures 4 and 5 are the FTIR-PAS spectra of print samples.

ATR-FTIR analysis of the print sample was also made. ATR-FTIR can detect a depth of ~2μm from the surface. Then the combined analysis of FTIR-PAS and ATR-FTIR bring the depth profile of the paper from the surface to ~ 30μm.

Cellulose has the strong bending vibration absorption peaks of C-H groups at 1450 cm^{-1}. Quinacridone pigment has the absorption at 1600 cm^{-1}. Then the absorbance ratio (I_{1600}/I_{1450}) of the print sample corresponds to the ratio of Quinaqridone pigment and the paper (Table 3).

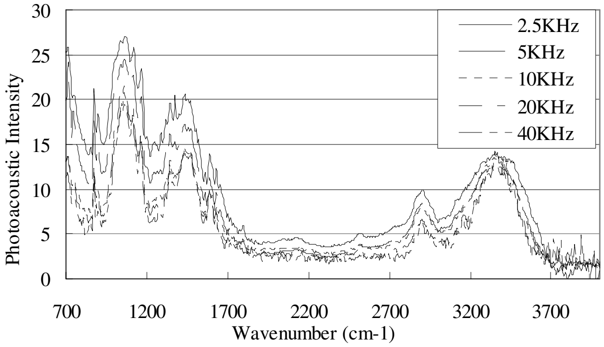

Figure 4. FTIR-PAS spectra of different frequency.

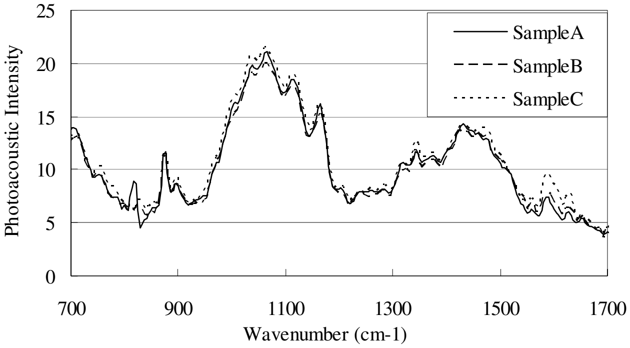

Figure 5. FTIR-PAS spectra of print samples (20KHz).

Table 3: The Absorption Ratio of I_{1600}/I_{1450}.

Sample	FTIR-PAS (Frequency, KHz)					ATR-FTIR
	2.5	5	10	20	40	
A	0.28	0.28	0.29	0.30	0.32	0.39
B	0.41	0.40	0.42	0.43	0.47	0.56
C	0.46	0.45	0.47	0.51	0.56	0.73

The measuring depth of the FTIR-PAS method was calculated by equation (1) and that of ATR-FTIR was calculated by the equation (2).[5] Real depth of the paper was calculated by the equation (3).

$$d_p = e.(\kappa/\rho_c.C_p.\pi.f)^{0.5} \tag{1}$$

$$d_p = \lambda/2\ \pi n_A(\sin^2\theta - n^2_{BA})^{0.5} \tag{2}$$

$$Dp = dp.(\rho_c - 1)/(1 - \rho_{app}) \tag{3}$$

θ is the incidence angle, π the circular constant, λ the infrared ray absorption wavelength, n_A the refractive index of prism, n_{BA} the refractive index n_B (n_B, refractive index of sample), κ the thermal conductivity, ρ_c the density of cellulose, ρ_{app} the apparent density of paper and f the modulation frequency.

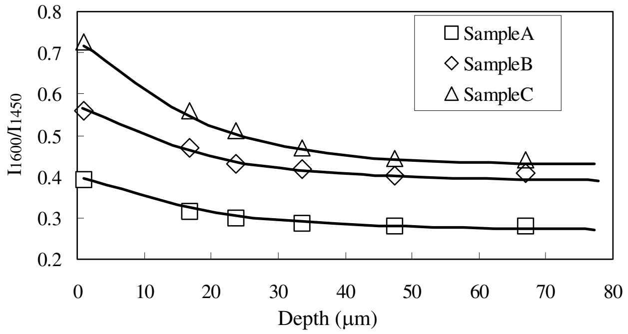

Figure 6. Integrated absorbance ratio (I_{1600}/I_{1450}) vs. sample depth.

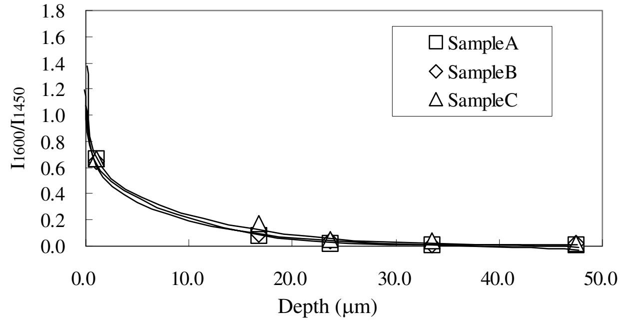

Figure 7. Depth profile of I_{1600}/I_{1450}.

Figure 6 shows the absorbance ratio (I_{1600}/I_{1450}) of the print sample versus the depth. On the FTIR-PAS measurement IR spectra was observed as integrated intensity form the surface to the designed depth. Then the subtraction of I_{1600}/I_{1450} represents the pigment distribution of the pigment in the paper (Figure 7).

The maximum depth of the pigment distribution was calculated around 30μm and had good agreement with the cross section image of the print. Unexpectedly the depth profile of the pigment distribution in the paper had not so much difference between three samples. This result suggests that the optical density of the plain paper depend on the amount of the pigment on the very top of the paper surface and the desorbed polymer affects to the remaining of the pigment on the top of the paper not to the imbibition into the paper.

Conclusion

The membrane filtration technique was used to purify the encapsulated pigment and the relation of the ink performance and the desorbed polymer were investigated. By removing the desorbed polymer, the surface tension of the encapsulated pigment rose and the optical density of the print were improved. The ATR-FTIR and FTIR-PAS methods were studied to measure the pigment distribution in the paper and found effective. The pigment distribution in the paper had not so much difference between the purified samples. Then the optical density of the plain paper was thought to depend on the amount of the pigment on the very top of the paper surface and the desorbed polymer affects to the remaining of the pigment on the top of the paper not to the imbibition into the paper.

References

1. T. Tsutsumi, M. Sawada, and Y. Nakano IS&T's 15th International Conference on Digital Printing Technologies, 133-136 (1999)
2. Belmont; James, A., johnson; joseph, E., U.S. patent 5,837,045 issued in 1998
3. Chu; I. Chang, Fryd; Michael, Lynch; Laurie E., U.S. Patent 5,231,131 issued in 1993
4. Rosental, O. M., Kardashina, L. F. Doklady Akademii Nauk (1996), 351(2), 212-214
5. Y. Kano, S. Akiyama, T. Kasemura, and S. Kobayashi, Polymer Journal, 27, (4), 339-346 (1995)
6. R. M. Dittmar, J. L. Chao, and R. A. Palmer, Appl. Spectrosc., 45, 1104. (1991)

Author Biography

Takehiro Tsutsumi received his B.S. and M.S. in Synthetic Chemistry from University of Tokyo in 1989 and 1991 respectively. He joined Kao Corporation in 1991 and has been worked on polymer dispersions. Since 1994 he has worked on ink jet ink colorants and inks.