中空球状有機顔料の特性　（第 1報）
－塗工紙の光学特性と印刷物の色彩科学的因子の制御－

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Characteristics of Hollow Sphere Plastic Pigment (Part Ⅰ)
- Optical Properties of Coated Paper and Colorimetric Control in Printing -

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ABSTRACT

With a view to investigate the influence of hollow sphere plastic pigments upon the printed color on coated paper surface, the hollow sphere pigments were compared with filled ones in a variety of experimental approaches.

Coated papers containing the hollow sphere pigment in their coatings improved optical properties like gloss and brightness. Optical parameters solely of the coating accounted well for this finding. An equation derived from the Kubelka-Munk equation provides optical parameters from two measurements of the reflectance of a coated paper over two substrates of different reflectances. This method permits to predict the brightness of coated paper having the same kind of coating with the known one at a different coat weight.

The colorimetric parameters of solid-printed surfaces of the coated papers are closely related to the optical and structural properties of coated papers. The color of printed surfaces was dominated by the smoothness and brightness of coated papers.

The hollow sphere pigments proved to improve optical properties of coated paper and to control minutely colorimetric parameters of printed surfaces.

KEYWORDS

Brightness, Coated papers, Coatings, Colorimetric parameters, Hollow sphere pigments, Kubelka-Munk equation, Latex, Optical properties, Printed surfaces, Smoothness

INTRODUCTION

Latex, namely, an aqueous dispersion of polymers such as synthetic rubbers, is generally produced by emulsion polymerization. Hollow sphere pigments of latex developed recently[1-3] began to be applied as a plastic pigment to paper coating to take advantages of light weight, compliance with calendering[4] and good optical properties[5,6]. For these reasons, the author expects that its unique optical characteristics will improve color reproduction in printing. Those advantages stem mainly from the hollow structure. Hollow sphere pigment has a structure with a core of water surrounded by a shell of hard polymer. On drying, the inside water evaporates, leaving an air-filled core that further scatters light at the air-polymer interface. In the case of hollow sphere pigments, both particle size and void volume have positive effects on coating performance. Brown[7] reported that the direction of the particle size effect on sheet gloss after calendering is in the opposite direction to the filled sphere pigment. As the particle size of the filled sphere pigments increased, the gloss decreased significantly. However, in the case of hollow sphere pigments, the gloss increased with increasing particle size. Brightness and opacity tended to exhibit a peak at around 500nm. In our experiments, latex samples with the optimum particle size for optical performance were selected.

In this study, with a view to elucidate mechanism of occurrence of the advantages of hollow sphere pigments over the filled ones, colloidal and structural properties of the latices, optical properties of the latices, the coatings and the coated papers containing the latices, and colorimetric parameters of solid-printed coated paper were examined.

EXPERIMENTAL

Latex samples

Two kinds of pigment latices, i.e. hollow and filled, were used in this work as shown in Table 1.

Colloidal and structural properties of latices

Zeta potential and particle size distribution

Zeta potential and particle size distribution were measured as a function of pH, using ZETA SIZER 3000 (Malvern Instruments, UK). pH was adjusted by adding a solution of either HCl or NaOH.

Microscopic observation

For the purpose of observing the shape of latex particles, scanning electron microscope (SEM) was applied. A 0.01%-solids emulsion of these latices was dropped on a grid precovered with a collodion film. The grid had been etched with an ion coater in advance for providing hydrophilicity to get the emulsion spread over spontaneously. Then, the emulsion on the grid was freeze-dried overnight. After the grid was osmium-coated for providing electric conductivity, it was observed by SEM (S-4000, Hitachi, Japan) at an accelerating voltage of 10 kV.

Figures 1 and 2 are SEM photographs of particles of anionic hollow and anionic filled sphere pigments of latex, respectively. The particle shape of either of the latices was a sphere. The particle diameter of the latices was estimated to be 1000 nm and 350 nm, respectively.

Optical properties of coated papers

Coating

The coating color was preliminaly formulated with 70 pph of kaolin clay (UW-90, Engelhard, USA), 30 pph of calcium carbonate (Brilliant-15, Shiraishi kogyo, Japan), 0.2 pph of a dispersing agent (Aron T-40, Toagosei, Japan), 0.25 pph of NaOH and 10 pph of binder latex (LX407G, Nippon Zeon, Japan). Two types of pigment latex, anionic hollow sphere pigment and anionic filled one, were added separately to this color. The amount of the pigment latex was 5, 10 and 20 pph. The coatings were drawn down on a base sheet (Woodfree paper, 65 g/m^2, Nippon Paper Industries, Japan) with a wire bar using a sheet-fed coater equipped with a synchro-starting dryer (PM9040MC, SMT, Japan). The coat weight was targeted at 9 g/m^2. The coated papers were dried at 120℃ for 10 sec, and supercalendered at 50℃ under a linear pressure of 49.1 kN/m.

Oken smoothness（Modified Bekk method with a water column, Asahi Seiko, Japan）, sheet gloss (Spectrophotometer PF10, Murakami Color Research Laboratory, Japan) and reflectance (Spectrophotometer TC-1800, Tokyo Denshoku, Japan) of the coated papers were measured. The measurement conditions of reflectance were D65 diffuse illuminant / 2° normal observer. The surfaces of these coated papers were observed using SEM. The cross-section of the coated paper was prepared with a focused ion beam and observed by Scanning Ion Microscope (SIM, SMI-9800, SII, Japan). The SIM observation followed this procedure: chemical vapor deposition of tungsten for surface protection, coarse cross-sectioning with gallium ions, fine cross-sectioning with gallium ions to 30 μm below the surface and the SIM observation at a tilt of 60 degrees.

Prediction of brightness of coatings [8-12)]

An equation was derived to predict brightness solely of a coating. Equation (1) is the basic Kubelka-Munk equation relating R (reflectance) to R_∞ (brightness) and SW (scattering coefficient multiplied by coat weight). Transforming equation (1) in terms of SW gives equation (2).

$$R = \frac{(R_g - R_\infty)/R_\infty - R_\infty (R_g - 1/R_\infty)\, e^{SW(1/R_\infty - R_\infty)}}{(R_g - R_\infty) - (R_g - 1/R_\infty)\, e^{SW(1/R_\infty - R_\infty)}} \qquad Eq.(1)$$

$$SW = \frac{1}{1/R_\infty - R_\infty} \ln \frac{(RR_g R_\infty - RR_\infty{}^2 - R_g + R_\infty)}{(RR_g R_\infty - R - R_g R_\infty{}^2 + R_\infty)} \qquad Eq.(2)$$

Two kinds of reflectance of coated paper over two substrates with different reflectances (R_{g1} and R_{g2}) were measured and substituted into equation (1). Transforming the two resultant equations in terms of R_∞ gives equation (3).

$$R_\infty = \frac{c - \sqrt{c^2 - 4}}{2} \qquad Eq.(3)$$

$$where \quad c = \frac{(R_{g1} + R_2)(R_1 R_{g2} - 1) - (R_1 + R_{g2})(R_2 R_{g1} - 1)}{R_1 R_{g2} - R_2 R_{g1}}$$

$$and \quad R_1 < R_2$$

Using this equation, we can predict the brightness solely of coating.

Definition of symbols

R_i : the reflectance of a layer (coating in this work) which has behind it a surface (background) with a reflectance of $R_{g\mathrm{i}}$, where black cavity for i = 1 and sufficient number of base paper sheets for i = 2 were used in this work.

$R_{g\mathrm{i}}$: the reflectance of surface of the i-th background

R_∞ : the brightness of coating = the reflectance of ideal coating ,whose the layer is thick enough that further increase in thickness does not change the reflectance = reflectivity

S : specific scattering coefficient

W : coat weight

Colorimetric parameters of printed papers

Printing on coated papers were conducted on a RI printing tester (Ishikawajima Sangyo Kikai, Japan) with a conventional process cyan ink for off-set. RI printing tester permits every sample within the same run to be compared under the same condition of nip pressure, speed and ink volume on a plate. The colorimetric parameters such as lightness (L^*), a^*, b^*, chroma (C^*_{ab}), hue (H^*_{ab}) and the differences in each parameter between printed and non-printed surfaces were measured using the spectrophotometer.

Quantification method of ink amount on paper[13)]

The content of copper included in a cyan ink printed on paper was measured as an intensity of the peak in an X-ray fluorescence spectrum measured by an X-ray fluorescence analyzer (MESA-500, HORIBA, Japan). The proportional relationship between the copper content and the transferred ink amount measured gravimetrically was confirmed. Applying this relationship, the amounts of the cyan ink printed on the prepared coated papers were determined.

RESULTS AND DISCUSSION

Zeta potential and particle size distribution

Figure 3 shows the effect of pH on the value of zeta potential and the particle diameter. For both of the anionic latices, regardless of either filled or hollow, the zeta potential showed a negative value in the entire pH range. The negative zeta potential is probably due to adsorption of hydroxyl ions and ionization of carboxyl groups on the latex polymer. The particle size distribution for both of the anionic latices was very stable with elapse of time. The measured particle diameters were consistent with the results from the SEM photographs.

Microscopic observation of coated papers

Figures 4 and 5 are SEM photographs showing a particle shape in coated paper surfaces. For the filled sphere pigment, many concave particles were observed. The particles of the hollow sphere pigment appear to be circular and black. To appear black assumes that surfaces of hollow sphere pigment particles tend to be flattened during calendering, as customarily seen on coated paper surfaces.

Figure 6 is a SIM photograph of a cross-section of coated paper containing the hollow sphere pigment. The particles of the hollow sphere pigment in the coating were perfectly spherical. This suggests that the hollow structure of the hollow sphere pigment in coating was maintained even after calendaring. However, the particles of the hollow sphere pigment near coated paper surface were a little collapsed and the surface was flattened. This result was consistent with the SEM photographs of coated paper surfaces.

Optical properties of coated papers

Figure 7 shows that Oken smoothness increased with increasing amount formulated in the coating for the hollow sphere pigment, but decreased for the filled sphere pigment. It seems that the surface of the coated paper with the hollow sphere pigment became smoother during calendering because hollow particles deform easily to gain flat surfaces. Figures 8 and 9 show that the sheet gloss and the reflectance of the coated paper increased with increasing the formulated amount of pigment. The hollow sphere pigment showed higher values than those of the filled one.

Figure 10 shows the relation between the brightness (R_∞) and the specific scattering coefficient (S) of the coatings. Both of the parameters increased with increasing formulated amount of pigment latices. The hollow sphere pigment showed higher values than the filled one in both of the parameters. The total number of hollow sphere pigment in the coating was theoretically about one sixteenth of the number of the filled one at the same formulated amount. However, because the hollow sphere pigment had an air-filled core surrounded by a shell of hard polymer even in the dry state, the total surface area of the hollow sphere pigment in the coating was about 14% larger than that of the filled one. Considering that a larger interface area provides more light scattering, a coating with the hollow sphere pigment showed higher light scattering efficiency resulting in a higher reflectance of the coated paper. This means the brightness of the coated paper would be higher as well. Figure 11 shows the relation between the coat weight and the reflectance of the coated papers that would be attained if they were formulated at 20 pph. It can be predicted that the hollow sphere pigment will show a higher reflectance than the filled one at any coat weight.

Colorimetric parameters of printed papers

Figure 12 shows that lightness (L^*) increased slightly with increasing amount for the hollow sphere pigment formulated in the coating, but decreased slightly for the filled sphere pigment. The chroma increased with increasing formulated amount for both of the latices. In comparison between the latices, these parameters were always higher for the hollow sphere pigment than for the filled one. Figure 13 shows changes in color difference (ΔE^*_{ab}) and hue difference (ΔH^*_{ab}). The color difference increased slightly with increasing formulated amount, and the hue difference decreased both for the two latices.

Figures 14 and 15 show the tendency of changes in the parameters (L^*, C^*_{ab}, ΔE^*_{ab} and ΔH^*_{ab}) of several strips of commercial coated paper with a basis weight of 104.7 g/m^2 and a coat weight of 10 g/m^2 printed all in the same manner but ink amount. The changes in every colorimetric parameter with increasing ink amount were roughly the same as the changes with increasing formulated amount of filled sphere pigment. This finding suggests that the volume of transferred ink increased and the lightness decreased as a result with increasing formulated amount of filled sphere pigment.

Figure 16 shows that ink deposit on the coated paper decreased with increasing formulated amount of the hollow sphere pigment in the coating, but increased for the filled sphere pigment. The ink deposit was determined by the X-ray fluorescence method.

From these results, the changes in lightness of solid-printed surfaces could be explained in terms of the ink transfer-smoothness relation for both hollow and filled sphere pigments. For the coated papers containing filled sphere pigments, the smoothness decreased with increasing formulated amount. Therefore, the transferred ink volume increased and the lightness decreased as a result. For the coated papers containing hollow sphere pigments, the smoothness increased with increasing formulated amount, the transferred ink volume decreased and the lightness increased. Furthermore, specific scattering coefficient increased with increasing the formulated amount, thus inducing high lightness. So, this increase in lightness of the coated paper is considered to help increase lightness of a printed surface, maintaining a contrast to a non-printed surface. From these results, it is concluded that color of a printed surface is dominated by smoothness and brightness of the underlying coated paper.

CONCLUSIONS

The effects of hollow sphere pigments of latex on the properties of the coated papers and their prints were examined and compared to the filled type.

Addition of the hollow sphere pigment increased smoothness, gloss and light reflectance of the coated paper. This effect was more striking than that of the filled one. This is because the surface of coated paper containing the hollow sphere pigment is flattened during calendering, as shown by the SEM and SIM photographs. However, the cross-section of coated paper in the SIM photograph showed that the particles of the hollow sphere pigment in coating were close to perfectly spherical. It was suggested that the hollow structure of the hollow sphere pigment was maintained even after calendering. Therefore, light is scattered at the air-polymer interface, the hollow sphere pigment show a higher value than the filled one in both brightness and specific scattering coefficient solely of the coatings, which leads to higher brightness of the coated paper.

As for colorimetric parameters of printed surfaces of coated papers, lightness increased with increasing formulated amount for the hollow sphere pigment, but decreased for the filled one. The changes in lightness could be explained in terms of the ink transfer-smoothness relation for both the hollow and the filled sphere pigments. It was concluded that color of a printed surface, in terms of lightness, was dominated by smoothness and brightness of the underlying coated paper.

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Table 1 Properties of latices

Latex	Particle diameter (nm)	pH	Monomer components
Anionic hollow (HP-1055*)	1000	9	Styrene and Acrylate
Anionic filled (V1004**)	320	8.5	Styrene and Butadiene

Manufacturers: *Rohm and Haas Japan and ** Nippon Zeon

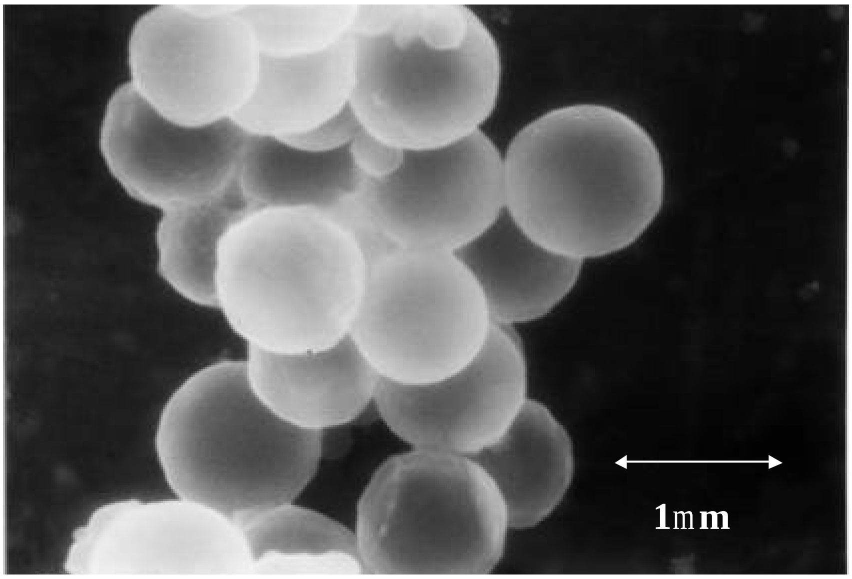

Fig. 1 Scanning electron micrograph of anionic hollow sphere pigment

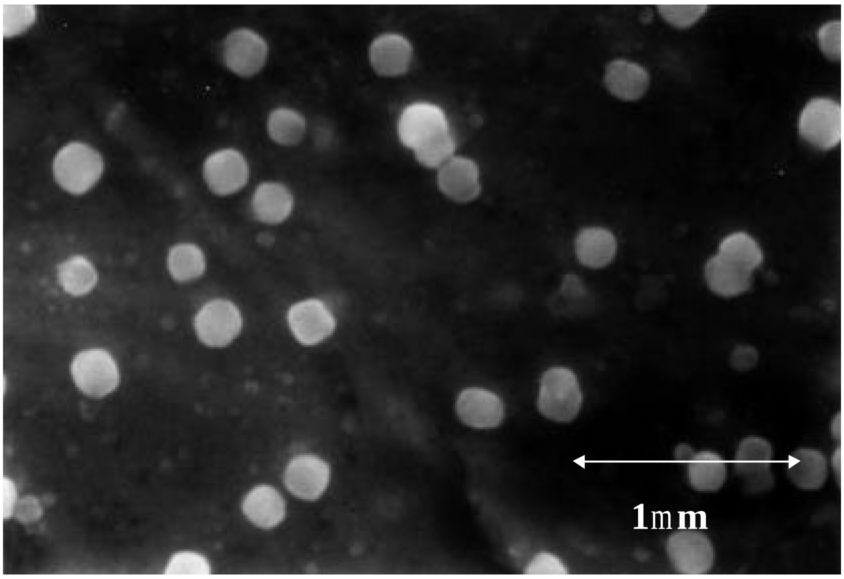

Fig. 2 Scanning electron micrograph of anionic filled sphere pigment

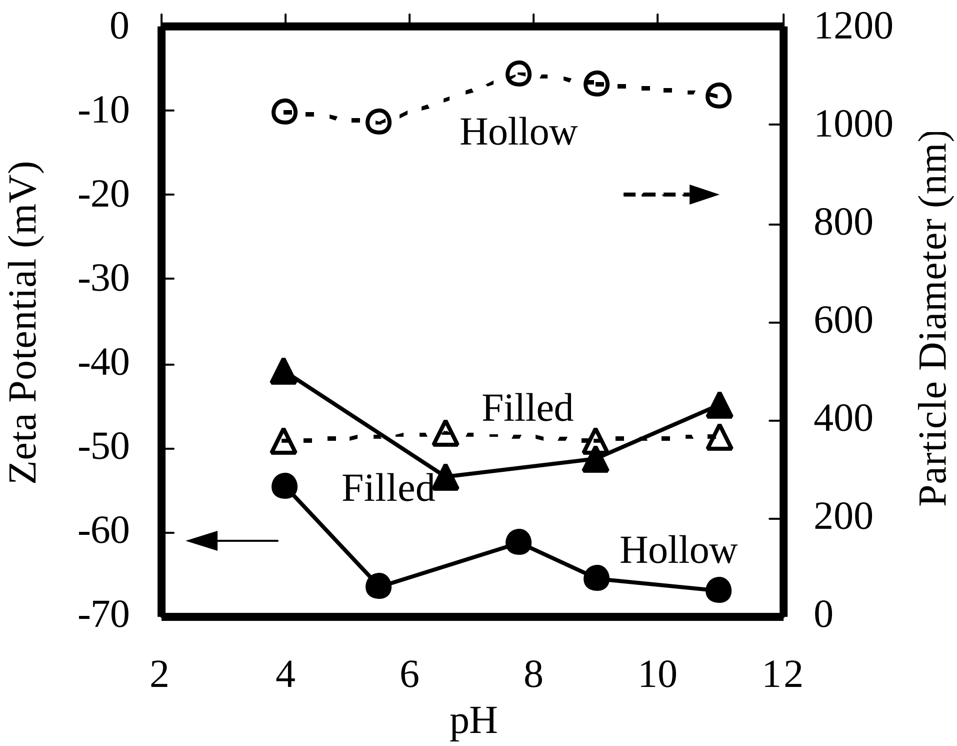

Fig. 3 Effect of pH on zeta potential and particle diameter

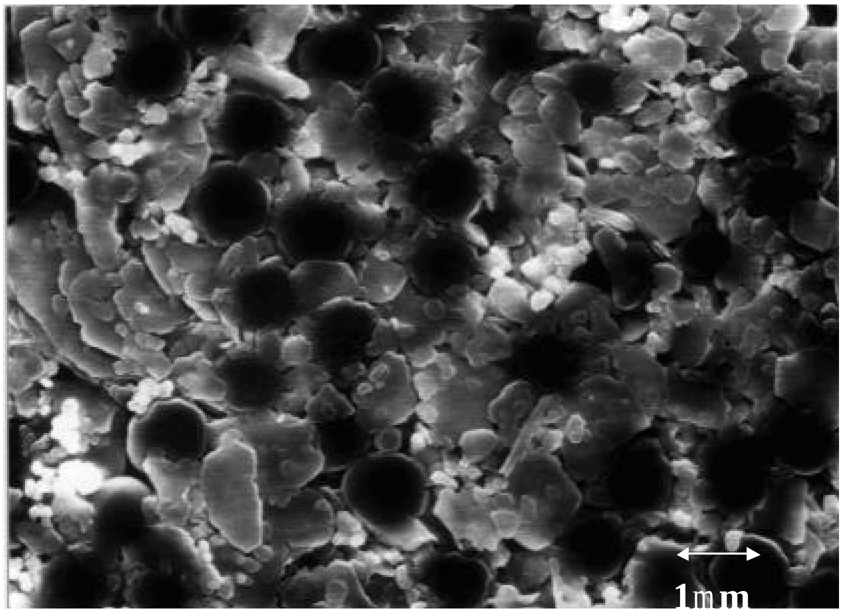

Fig. 4 Surface of coated paper containing 20 pph of anionic hollow sphere pigment

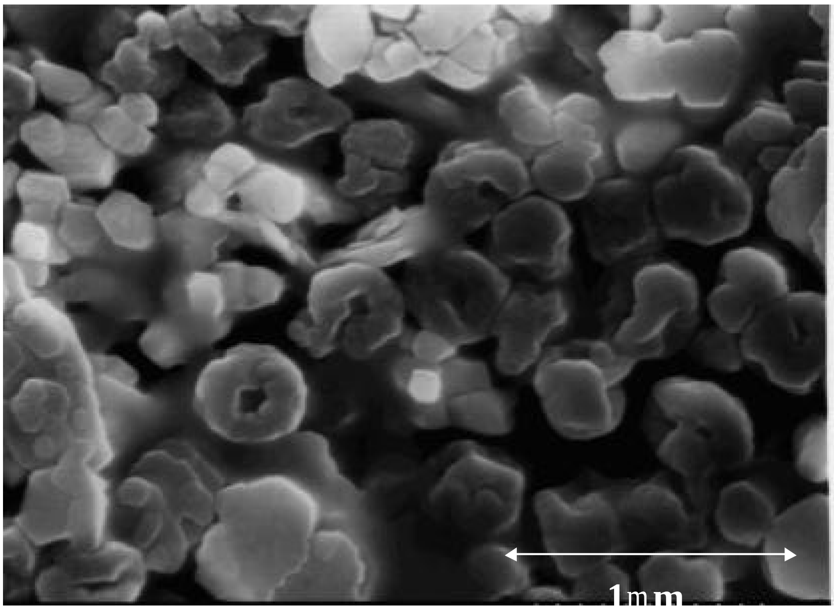

Fig. 5 Surface of coated paper containing 20 pph of anionic filled sphere pigment

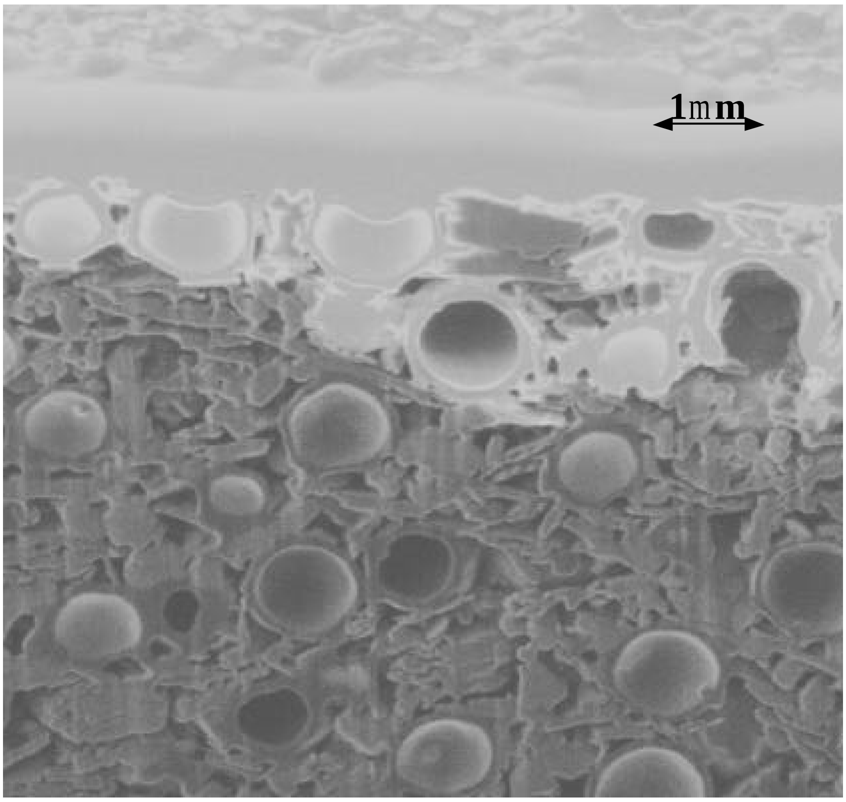

Fig. 6 Cross section of coated paper containing 20 pph of hollow sphere pigment observed in Scanning ion microscope after cross-sectioning by a focused ion beam

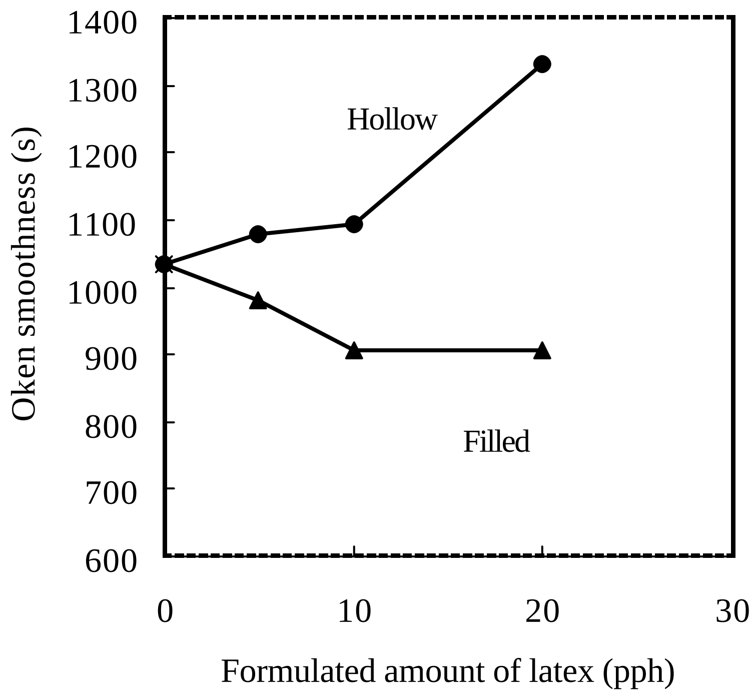

Fig. 7 Oken smoothness vs formulated amount of latex

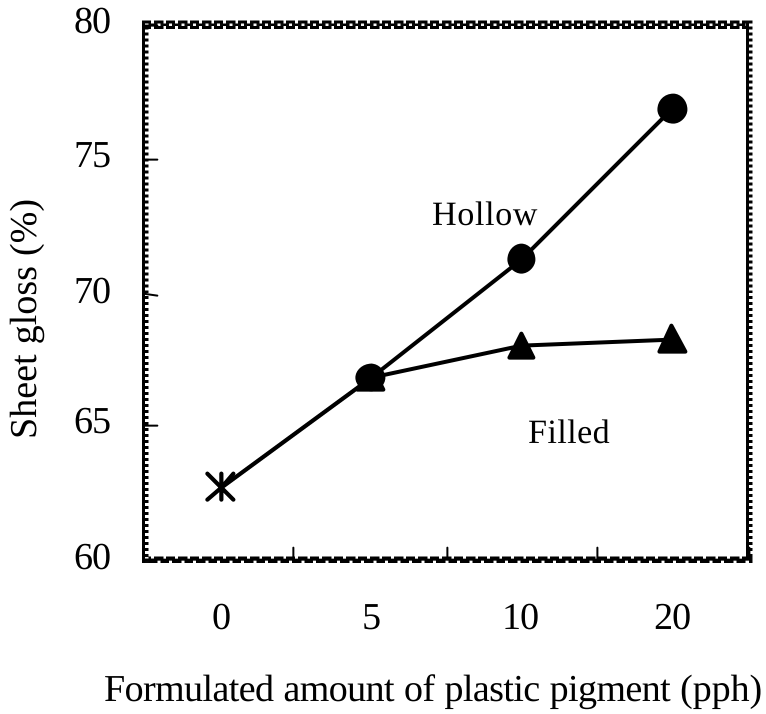

Fig. 8 Sheet gloss vs formulated amount of plastic pigment

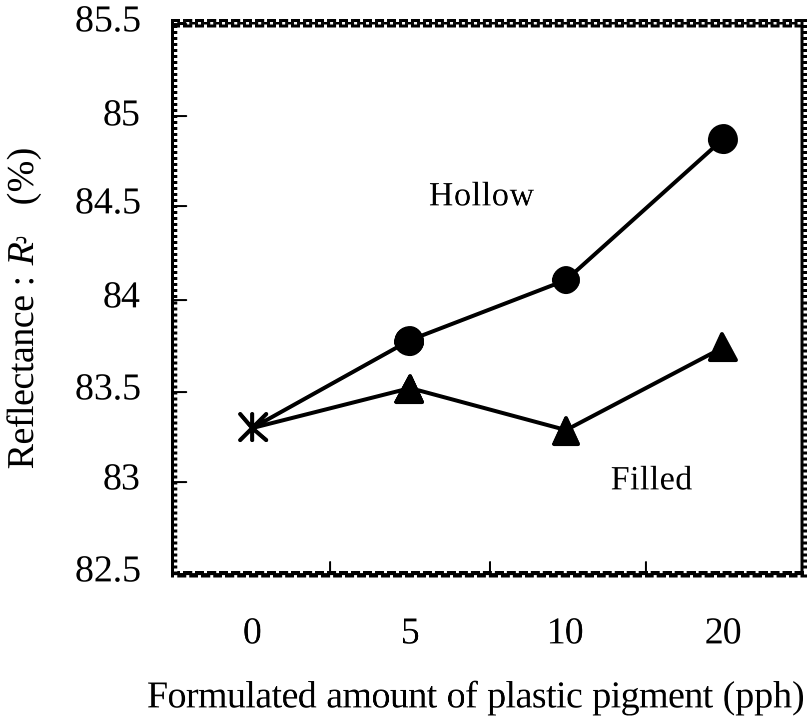

Fig. 9 Reflectance of coated paper backed by sufficient number of sheets of bas paper (R_2) vs formulated amount of plastic pigment

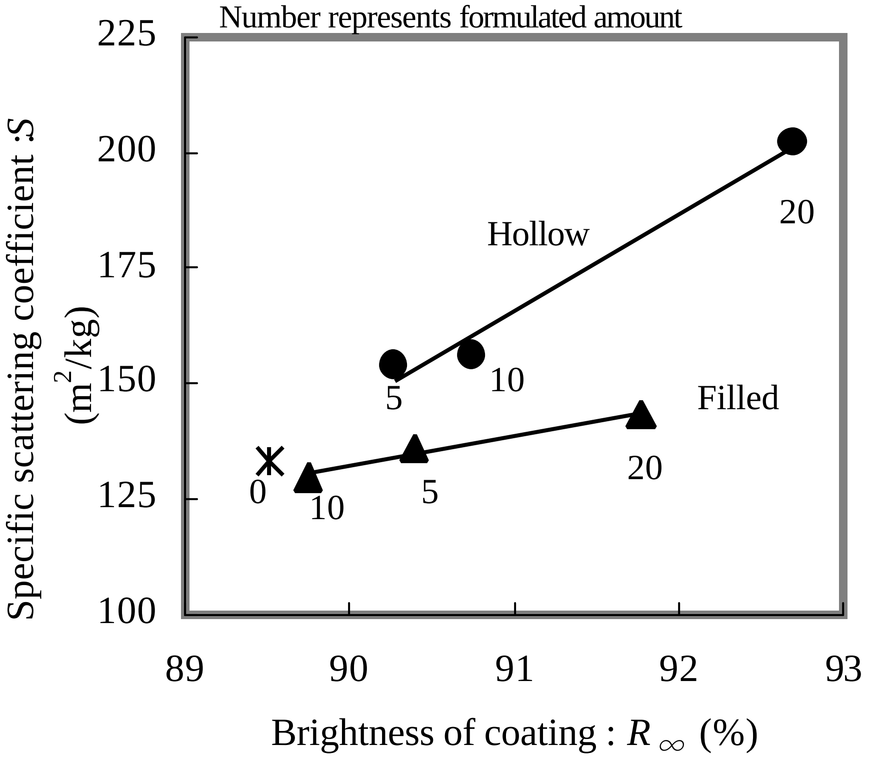

Fig. 10 Specific scattering coefficient (S) vs brightness (R_∞) both of the coatings

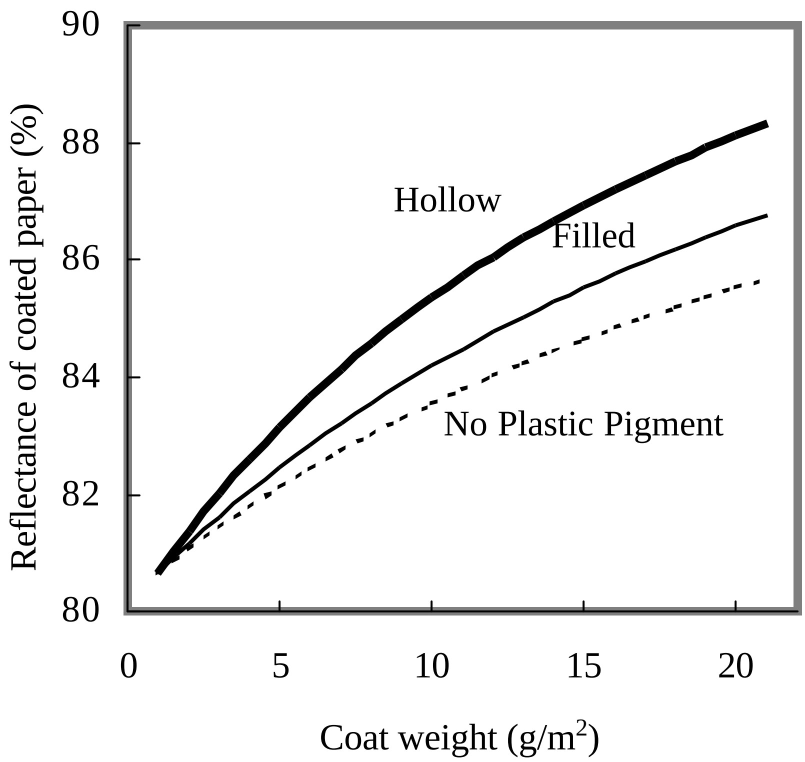

Fig.11 Predicted reflectance of coated paper

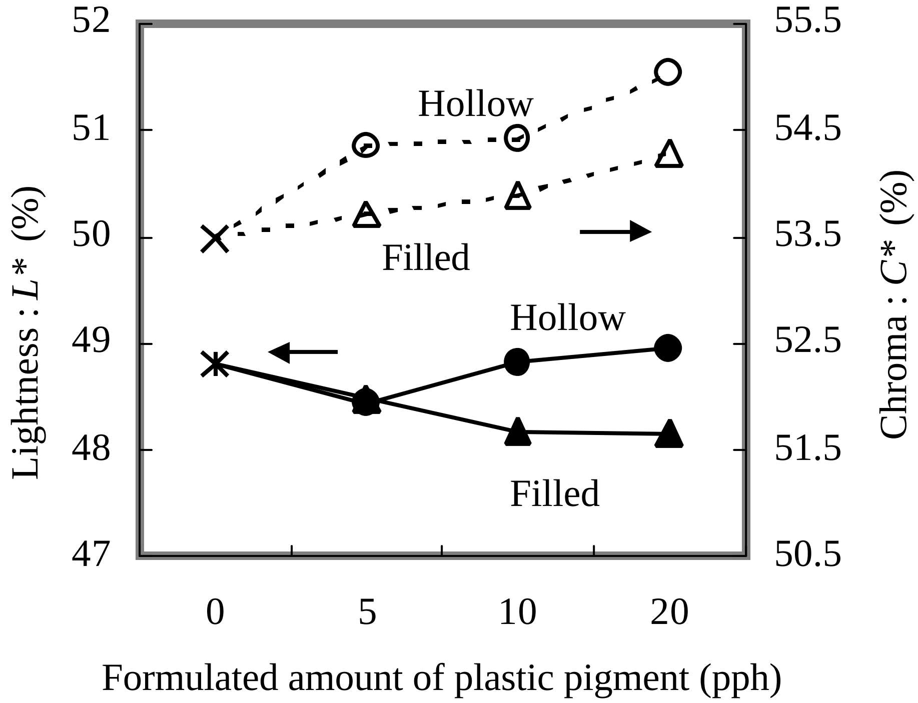

Fig. 12 Lightness (L^*) and Chroma (C^*) of printed surface of coated paper

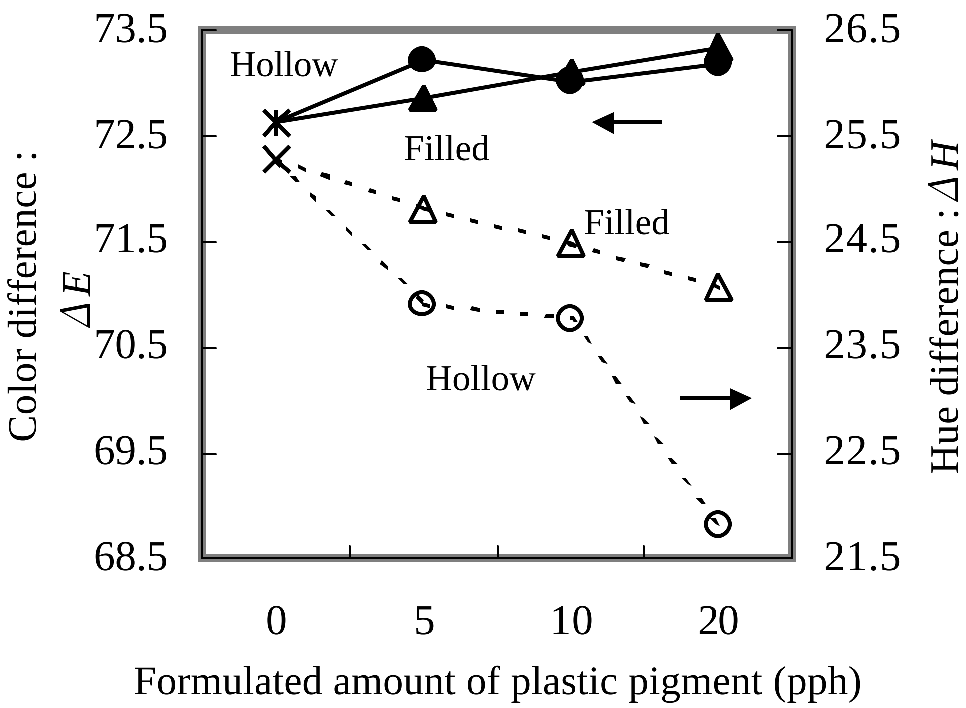

Fig. 13 Color difference (Δ E) and Hue difference (Δ H) (difference between printed paper and non-printed) of printed surface of coated paper

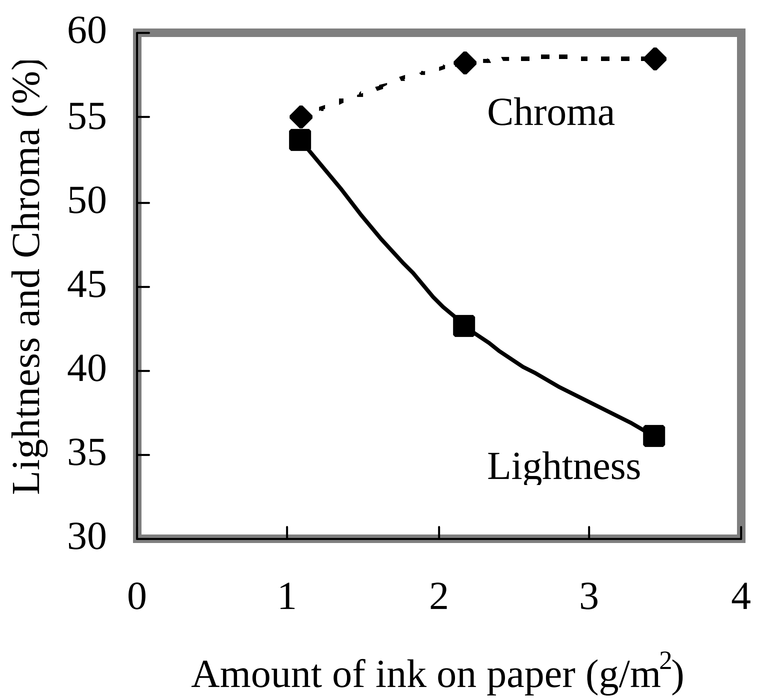

Fig. 14 Changes in lightness and chroma with ink amount on the commercial coated paper

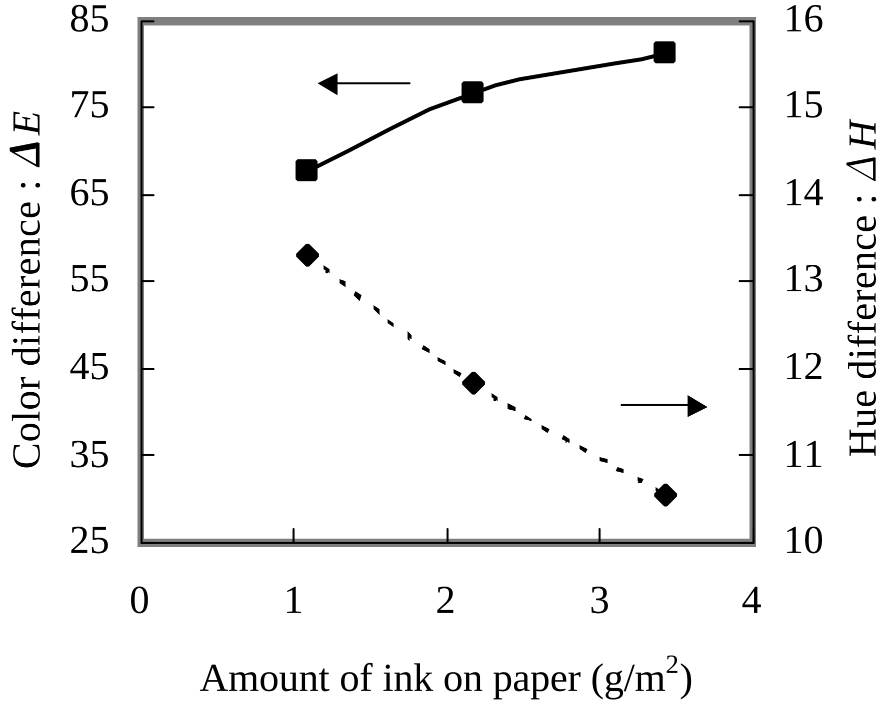

Fig. 15 Changes in color and hue difference with ink amount on the

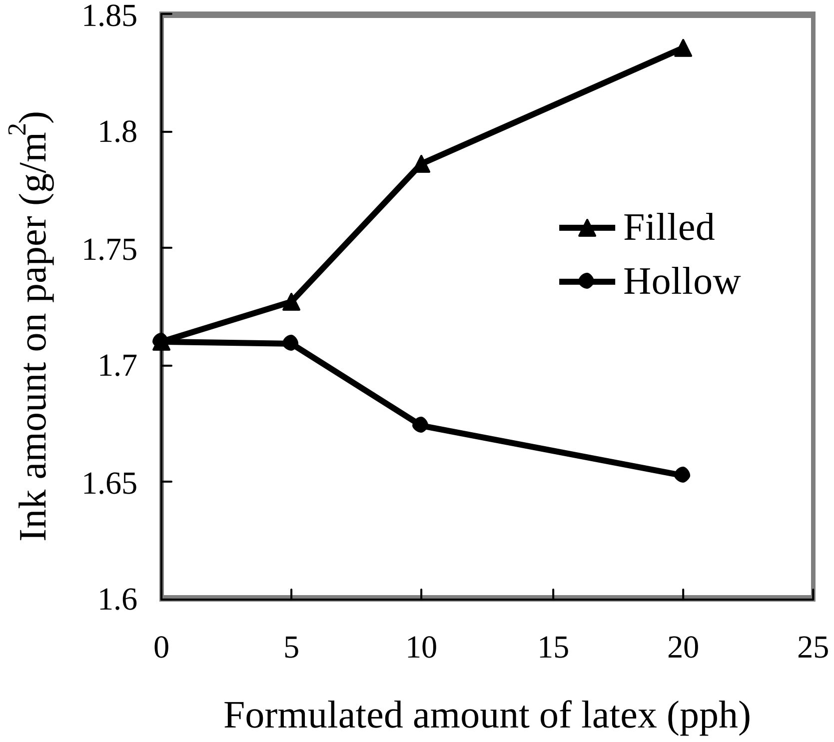

Fig. 16 Ink amount on paper vs formulated amount of latex