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# COLLOIDAL PROPERTIES OF HOLLOW LATICES AND THEIR ROLES IN CONTROLLING COLORIMETRIC PARAMETERS OF COATED PAPER SURFACE

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## ABSTRACT

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

Colloidal properties of latices were determined by measuring zeta potential and particle size distribution. For the amphoteric filled sphere pigment of latex, the polarity was reversed from the negative side to the positive side with decreasing pH. An extraordinarily high peak in the particle size distribution of the amphoteric filled evidenced aggregation between latex particles near the isoelectric point, depending on the electrolyte concentration and pH of the suspending medium.

Coated papers containing the hollow sphere pigment in their coating improved optical properties like gloss and brightness. Optical parameters solely of the coating could account for this finding. An equation derived from the Kubelka-Munk equation calculated them from twice measurements of reflectance of a coated paper over two substrates of different reflectances. This method permitted to predict brightness of coated paper of which coat weight would be different from the actual one.

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

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

## 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[5-7], the last of which are reported to improve color reproduction in printing. Those advantages stem all from the hollow structure. Hollow sphere pigments have 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 this study, with a view to elucidate the advantages of the hollow sphere pigments over the filled ones, colloidal properties of the latices, optical properties of their coatings and the coated papers, and colorimetric parameters of the solid-printed surfaces were examined.

## EXPERIMENTAL

### Latices

Table 1 shows the properties of the latices used in the experiments.

Table 1 Properties of latices

| Latex | Particle diameter (nm) | pH | Monomer components |
|---|---|---|---|
| Anionic hollow (HP-1055*) | 1000 | 9 | Styrene and Acrylic acid |
| Anionic hollow (MH5055**) | 500 | 8.5 | Styrene and Acrylic acid |
| Anionic filled (V1004**) | 320 | 8.5 | Styrene and Butadiene |
| Amphoteric filled (LX407K**) | 135 | 9 | Styrene and Butadiene |

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

### 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 and ionic strength of the suspending medium, using ZETA SIZER 3000 (Malvern Instruments, UK). pH was adjusted by adding a solution of either HCl or NaOH. For controlling the ionic strength, NaCl was used. Table 1 lists all the latices used.

***SEM observation***

For the purpose of visualizing the shape of the latex particles, the latices were observed using scanning electron microscopy (SEM). The latices used were the anionic filled and the anionic hollow (MH). A 0.01%-solids emulsion each of these latices was dropped on a grid precovered with a collodion

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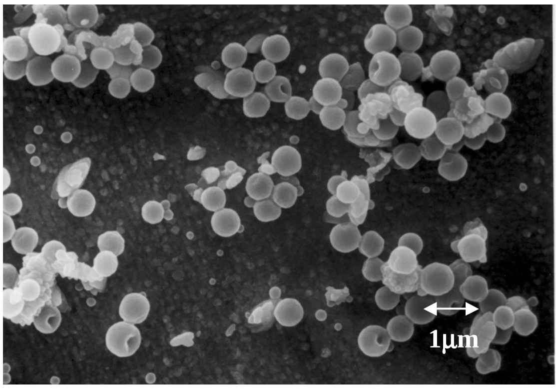


Fig. 1 Secondary electron micrograph of anionic hollow sphere pigment (MH) fixed with osmium tetroxide.

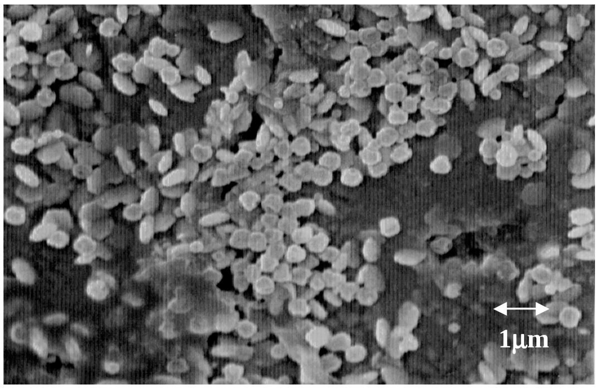


Fig. 2 Secondary electron micrograph of anionic filled sphere pigment fixed with osmium tetroxide.

film. The grid had been etched by an ion coater in advance for providing hydrophilicity to get the emulsion spread over spontaneously. Then, the emulsion on the grid was exposed to osmium tetroxide vapor in a dessicator for 2 hours and dried with silica gel in a dessicator over night. Before the SEM observation, the grid was platinum-coated for providing electric conductivity.

Figures 1 and 2 are SEM photographs of particles of the anionic hollow and the anionic filled sphere pigments of latex, respectively. The particle diameter of the latices was apparently 500 nm and 350 nm, respectively. For the anionic hollow, 20 to 30 % of the particles were concave. The shape of the anionic filled was not a perfect sphere, but a sphere with wrinkled surfaces. Both of the apparently deformed shapes are perhaps due to shrinkage during drying.

## Optical properties of coated papers

### *Coating*

The coating color was preliminaly formulated with 70 pph of kaolin clay (UW-90, Engelhard), 30 pph of calcium carbonate (Brilliant-15, Shiraishi kogyo), 0.2 pph of a dispersing agent (Aron T-40, Toagosei), 0.25 pph of NaOH and 10 pph of binder latex (LX407G, Nippon Zeon). Two types of pigment latex, anionic hollow sphere pigment (HP) 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 (NPi, Nippon Paper Industry) with a sheet-fed coater equipped with an synchro-starting dryer (PM9040MC, SMT) using a wire bar. The coat weight was targeted at 9 g/m$^2$. The coated paper were dried at 120℃ for 10 sec, and supercalendered at 50℃ and 49.1 kN/m.

The sheet gloss (Spectrophotometer PF10, Murakami Color Laboratory), dynamic roughness（Micro-topo-graph, Toyo Seiki）and reflectance (Spectrophotometer TC-1800, Tokyo Denshoku) of the coated papers were measured. The measurement conditions of reflectance were D65 diffuse illuminant / 2 ° normal observer. Those coated papers were observed using SEM.

### *Prediction of brightness of coatings* [8-11)]

An equation was derived to predict brightness only of a coating. Equation (1) is the basic Kubelka-Munk equation relating $R$ (reflectance) to $R_\infty$ (brightness) and $SW$ (scattering coefficient multiplied by coat weight). Solving 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 of different reflectances ($R_{g1}$ and $R_{g2}$) were measured and

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

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

$$and \quad R_1 < R_2$$

substituted into equation (1). Solving the two resultant equations in terms of $R_\infty$ gives equation (3).
Using this equation, we can predict the brightness of coating.

### *Definition of symbols*

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

$R_{gi}$ : reflectance of the surface of the $i$ -th background

$R_\infty$ : brightness of coating = reflectance of coating so thick that further increase in thickness does not change the reflectance = reflectivity

$S$ : specific scattering coefficient

*W* : coat weight

**Colorimetric parameters of printed papers**

The coated papers were printed on a RI printing tester with cyan ink. The colorimetric parameters such as lightness (L), a, b, chroma (C), hue (H) and the differences in each parameter between printed and non-printed surfaces were measured using the spectrophotometer.

## RESULTS AND DISCUSSION

### Colloidal properties of latices

***Effect of pH on zeta potential and particle size***

Figures 3 and 4 show the effect of pH on the value of zeta potential and the particle diameter. For all of the anionic latices, regardless of either filled or hollow, the zeta potential showed the negative value in the entire pH range. However, for the amphoteric filled, the zeta potential increased with decreasing pH and the polarity was reversed from the negative side to the positive side at ca. pH 5. At the isoelectric point of this pH, the ionization of both the negatively charged groups (carboxyl groups) and the positively charged groups was balanced on the surface. The negative zeta potential in the basic range of pH is undoubtedly due to the dominant ionization of the carboxyl groups on the latex polymer. The isoelectric point of a cationic latex generally appears at pH two to three higher than that of an amphoteric latex. [12)]

The particle size distribution for all of the anionic latices was very stable with time. However, for the amphoteric filled, the distribution curve had a peak at ca. pH 5 that corresponds to the isoelectric point. The particle size at this peak increased with time after pH adjustment. It seems that the latex aggregation proceeded at this pH. The particle diameters normally measured agreed with the results from the SEM photographs.

***Effect of ionic strength on zeta potential and particle size***

Figure 5 shows the effect of ionic strength on zeta

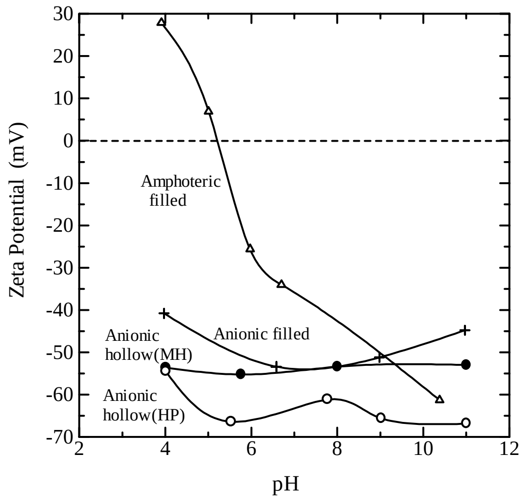


Fig. 3 Effect of pH on the value of zeta potential.

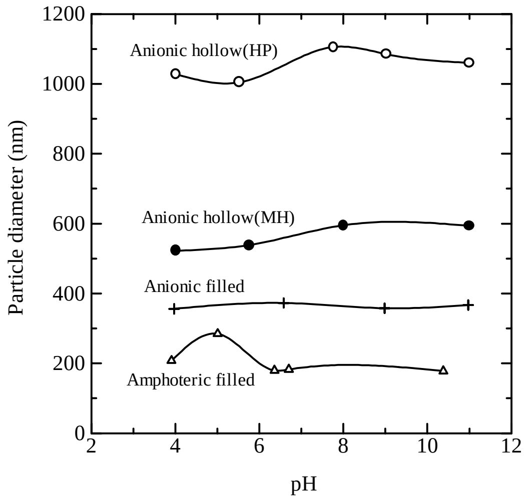


Fig. 4 Effect of pH on the average value of particle diameter.

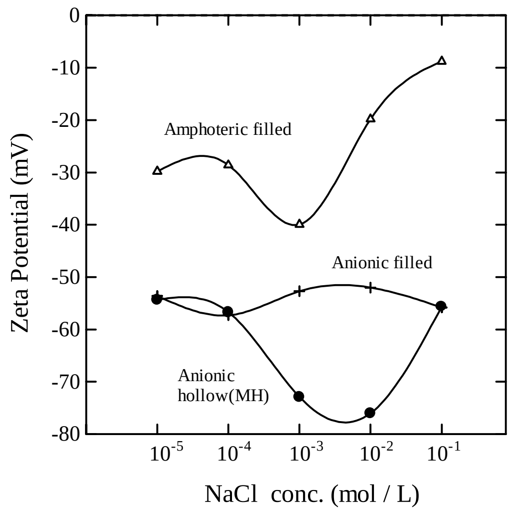


Fig. 5 Effect of ionic strength on the value of zeta potential.

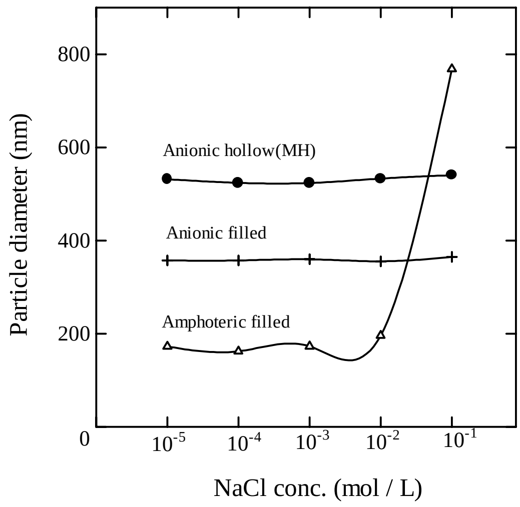


Fig 6. Effect of ionic strength on the average value of particle diameter.

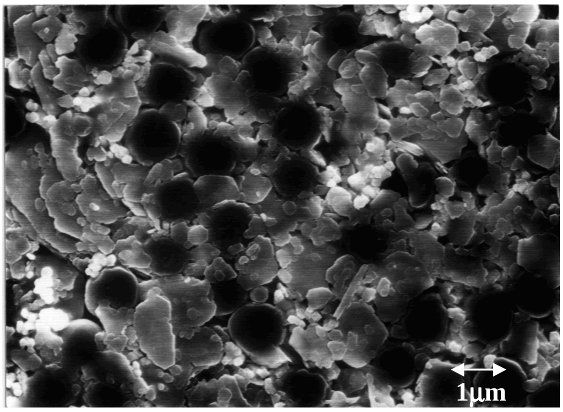


Fig. 7 Coated paper surface containing 20 pph of anionic hollow sphere pigment (HP).

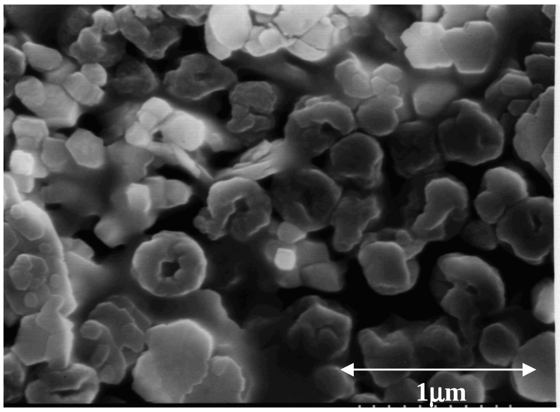


Fig. 8 Coated paper surface containing 20 pph of anionic filled sphere pigment.

potential. The negative values of zeta potential of both of the anionic latices and the amphoteric latex decrease with increasing ionic strength at concentrations of NaCl higher than $10^{-3}$ mol/L. However, reversal of the polarity of the zeta potential was not observed even at the highest concentrations of NaCl (e.g., $10^{-1}$mol/L). Effects of the increasing ionic strength on the zeta potential of the latices may shield the charges of the ionic groups on the surface, changes in distribution of the counterions and the coions in the electric double layer, and a decrease in thickness of the electric double layer adjacent to the surface. It is normally accepted in colloidal systems that the charge reversal phenomena occur at higher concentrations of inorganic electrolyte when the polarization energy of counterions for the interaction with the fixed charged species is sufficiently high.[13] In view of this, the polarization energy of the counterions from NaCl (i.e., $Na^+$ or $Cl^-$) was not high enough to reverse the polarity of the charge of the latices even at the highest concentration of NaCl.

Figure 6 shows the particle size distribution for both the anionic latices was very stable to the increased ionic strength. However, the amphoteric latex, the particle size distribution showed an extraordinarily high value at a concentration of $10^{-1}$mol/L, where the diameter increased over time. pH of the latex emulsion with NaCl solution at this concentration is ca.5, which is equivalent to that at the isoelectric point. So, it seems that the latex proceeded to be aggregated at this point.

**SEM observation of coated papers**

Figures 7 and 8 are SEM photographs showing the particle shape in coated papers. The particle diameter of the hollow sphere pigment of latex (HP) and the filled one was apparently about 1 μm and 350 nm, respectively. These values agreed with the results measured by ZETA SIZER. For the filled sphere pigment, many concave particles were observed. The particles of the hollow sphere pigment appeares to be circular and black. This finding assumes that hollow sphere pigment particles tend to become collapsed and flat during calendering, as generally seen on coated paper surfaces.

**Optical properties of coated papers**

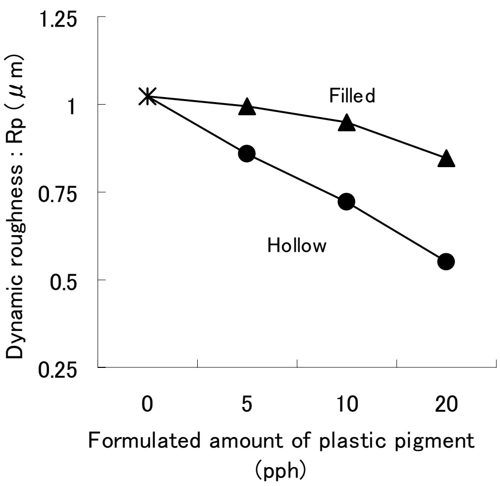


Fig. 9 Dynamic roughness (Rp) vs formulated amount of plastic pigment

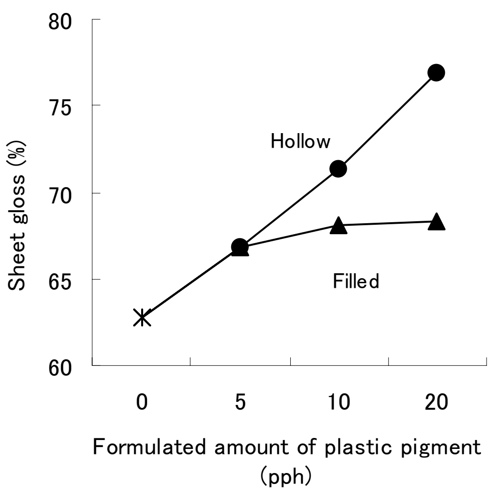


Fig. 10 Sheet gloss vs formulated amount of plastic pigment

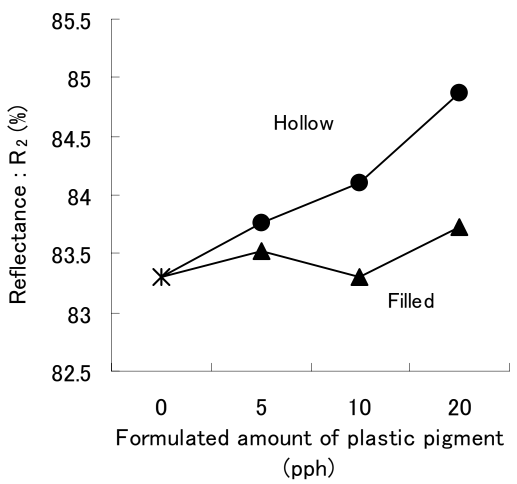


Fig. 11 Reflectance of coated paper backed by sufficient number of sheets of base paper ($R_2$) vs formulated amount of plastic pigment

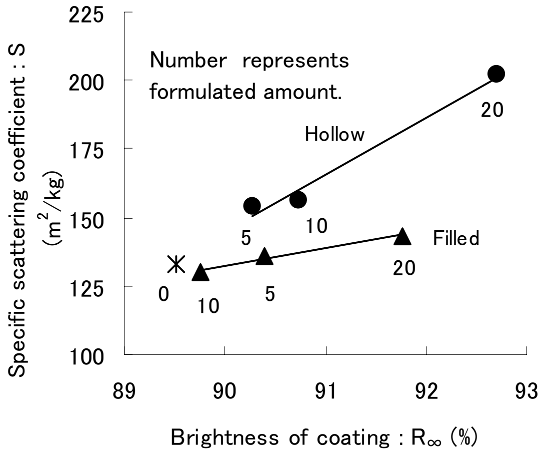


Fig. 12 Specific scattering coefficient (S) vs brightness of coating ($R_\infty$)

Figures 9, 10 and 11 show that the sheet gloss and the reflectance of the coated paper increased, and the dynamic roughness decreased with increasing the amount of pigment latex formulated. The hollow sphere pigment showed higher values for sheet gloss and reflectance, and lower values in dynamic roughness compared with the filled one. 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.

Figure 12 shows the relation between the brightness ($R_\infty$) and specific scattering coefficient (S) of the coating. Both of the parameters increased with increasing formulated amount of the pigment latices. The hollow sphere pigment showed higher values than the filled one in both of the parameters. Since the hollow sphere pigment has an air-filled core, even in the dry state, surrounded by a shell of hard polymer, light is scattered at the air-polymer interface. Therefore, the 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.

**Colorimetric parameters of printed papers**

Figure 13 shows that the lightness (L) increased slightly with increasing amount of both the sphere pigment latices formulated in the coating, but decreased slightly for the filled sphere pigment of latex. The chroma increased with increasing formulated amount for both of the latices. In comparison between the latices, these parameters were higher for the hollow sphere pigment than for the filled one. For the coated papers containing the hollow sphere pigment, the specific scattering coefficient increased with increasing formulated amount, thus inducing high lightness. So, this increase in lightness of the coated paper is considerd to help increase the lightness of the printed surface. In the case of the coated papers containing the filled sphere pigment, the smoothness

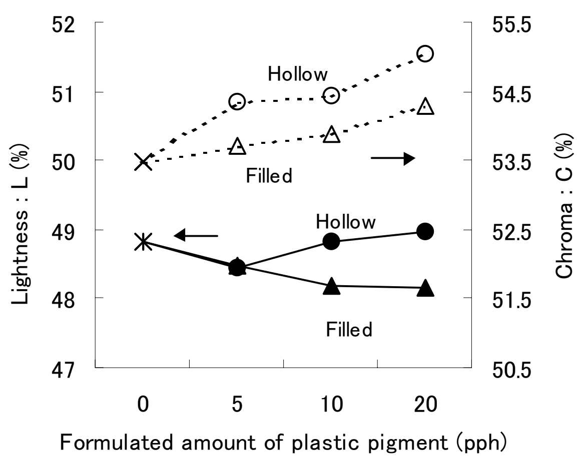


Fig. 13 Lightness (L) and Chroma (C) of printed surface of the coated paper

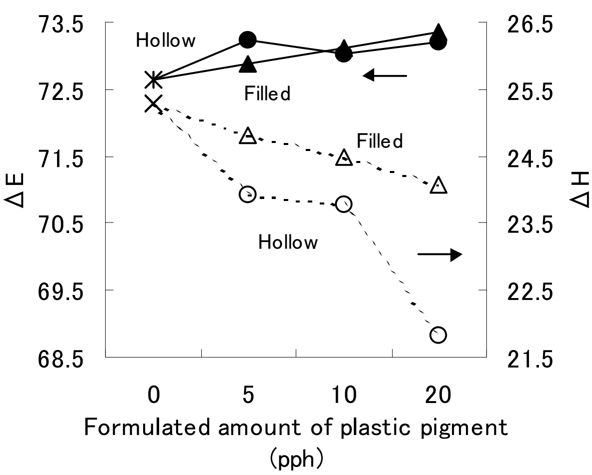


Fig. 14 Color difference (ΔE) and Hue difference (ΔH) (difference between printed paper and non-printed) of printed surface of the coated paper

increased with increasing formulated amount. Therefore, it seems that the transferred ink volume increased and the lightness decreased as a result. The rule of changes in the parameters (L, a, b, C, $\Delta E$ and $\Delta H$) with decreasing the ink amount found with the same coated paper holds with the case, although the exact volumes of the transferred ink are unknown with the samples in this work.

Those results conclude that the color of a printed surface is dominated by the brightness and smoothness of the coated paper as a printing medium and that the major factor out of the two properties, brightness and smoothness, is dependent on each level.

## CONCLUSION

The effects of the hollow sphere pigment of latex on properties of the coated papers and its prints were estimated and compared to the filled type.

Firstly, colloidal properties were measured. For the amphoteric filled sphere pigment of latex, the polarity was reversed at pH where the ionization degree of both the negatively and positively charged groups are balanced on the surfaces. For the effect of ionic strength, the reversal of the polarity of the zeta potential was not observed even at a concentration of NaCl solution as high as $10^{-1}$mol/L. The extraordinarily high particle diameter observed at the isoelectric point for the amphoteric filled suggests that the particle aggregation proceeded. The zeta potential and particle size distribution of both the anionic hollow and filled ones were very stable against changes in pH and ionic strength.

Addition of the hollow sphere pigment decreased roughness and increased gloss and light reflectance of the coated paper. This effect was more striking than that of the filled one. This is because the particles of the hollow sphere pigment in the coated paper surface are collapsed during calendering, as shown by the SEM photographs. The brightness solely of the coatings was calculated using the Kubelka-Munk theory. The hollow sphere pigment showed a higher value than the filled one in both brightness and specific scattering coefficient, which leads to higher brightness of the coated paper.

As for colorimetric parameters of the printed surfaces of the coated papers, lightness increased with increasing formulated amount for the hollow sphere pigment, but decreased for the filled one. The former behavior is explained by higher brightness of the coated paper; the latter by increased ink volume due to higher smoothness. The major factor out of the two properties, brightness and smoothness, is dependent on each level.

## REFERENCE


1. M. Okubo and H. Mori, Colloid and Polymer Science, 275(7): 634(1997)
2. M. Okubo and H. Minami, Colloid and Polymer Science, 275(10): 992(1997)
3. M. Okubo, Y. Konishi and H. Minami, Colloid and Polymer Science, 276(7): 638(1998)
4. H. Izawa, Y. Saito and J. Kasai, Japan Tappi Journal 53(4): 458(1999)
5. J. T. Brown, Tappi Coating Conference Proceedings, 113(1991)
6. T. Kaji, Japan Tappi Journal 46(2): 271(1992)
7. Y. Shimokawa, O. Ishizu and T. Shimazoe, Japan Tappi Journal 52(2): 171(1998)
8. H. Hamada, T. Enomae, F. Onabe and Y. Saito, Sen'I Gakkai Annual Meeting Preprints(1999)
9. P. Kubelka, Journal of the Optical Society of America 38(5): 448(1948)
10. J. V. Robinson, Tappi 58(10): 152(1975)
11. P. Lepoutre, Y. Potier and B. Alince, Pulp and Paper Magazine of Canada, (3): 9(1982)
12. T. Sugimura, Y. Kataoka, S. Suzuki and K. Kasahara, Application of Synthetic Latices (in Japanese; Gosei latex no oyo), Kobunshi kankokai, 1993, pp.119-124
13. F. Onabe, Journal of Applied Polymer Science, 23: 2909 (1979)