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New White Pigment Ink - Correlation between Structure of Inorganic Hollow Particles and White Opacity -

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Abstract

We have developed a new white ink which features less sedimentation and high white opacity even upon non-permeable media. Titanium dioxide has been used in the white ink in order to obtain high opacity, but it has the problem of sedimentation. Hollow resin particles have also been used for white ink. Sedimentation is drastically reduced, however, white opacity is limited when heating and drying especially on non-permeable media. In order to solve these problems, we focused on characteristics of hollow silica particles with low density in addition to heat resistance and solvent resistance. We developed new white pigment of hollow silica particles which lead to less sedimentation and high white opacity by optimizing primary particle size and wall thickness size.

Introduction

White ink for inkjet has already been put to practical use, such as sign graphics, labels and packages, which enables high quality printing on transparent or semitransparent media [1-3].

One of the characteristics required for white inkjet ink is white opacity which sufficiently hides the printing media. Pigments with high refractive index, such as titanium dioxide, have been used in white ink [4]. However, titanium dioxide easily sediments in a low viscosity fluid like inkjet ink due to its large specific gravity. It causes issues such as poor storage stability of the ink and clogging of inkjet printhead nozzles due to the difference in specific gravity between pigment particles and vehicle of the ink.

Previous Approach for Issues

A variety of approaches have been trying to solve these problems. One approach is the adaption of the hardware involving an agitating device for reducing sedimentation. Recently, inkjet heads capable of constantly stirring ink up to the vicinity of nozzles have been released [5]. However, it requires complex or costly adaption of the printer.

As another approach for material, it is known to use hollow particles as white pigments [6]. Hollow particles contain voids inside the particles and therefore have low specific gravity. In the hollow particles, white opacity can be obtained by scattering utilizing the difference in refractive index between the outer shell and the inner void, as shown in Figure 1. In recent years, inkjet ink printers equipped with aqueous white ink containing hollow resin particles have already been released [7]. However, it needs to use permeable printing media in combination. Figure 2 shows the image of media dependency on which white ink containing hollow resin particles was printed. In non-permeable media, the solvent component can be removed to the atmosphere side. Therefore, it is necessary to heat at high temperature in order to dry the coating quickly. However, there are problems that hollow resin particles are softened and collapse by heat to dry on non-permeable media. Once hollow resin particles collapse, a favorable white opacity cannot be obtained as shown in Figure 3. On the other hand, in permeable media, the solvent component in the coating film can be removed by evaporation to the atmosphere side and penetration into the media side upon drying. Owing to maintain the hollow structure in the coating film, high white opacity is obtained.

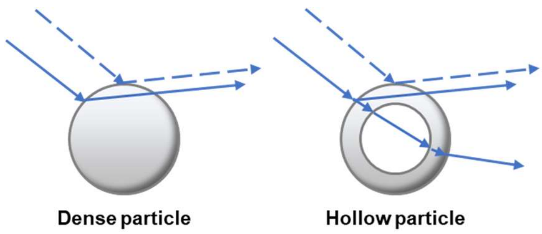

Figure 1. *Image of light scattering from dense particle and hollow particle.*

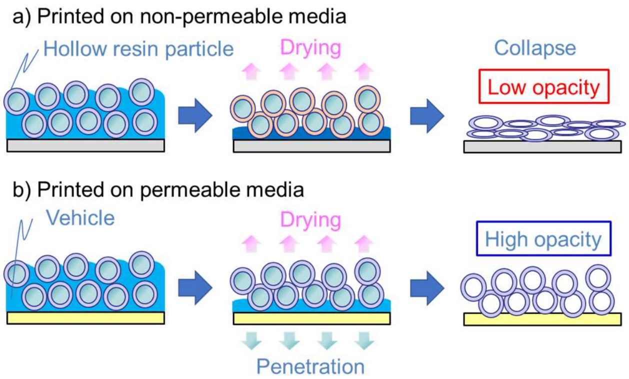

Figure 2. *Image of media dependency on which white ink containing hollow resin particles was printed a) on non-permeable media and b) on permeable media.*

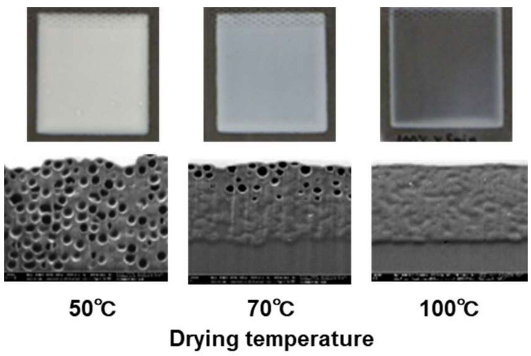

Figure 3. *Printed white ink containing hollow resin particles on PET.*

Inorganic Hollow Particles

In order to solve the problems described above, we focused on characteristics of inorganic hollow particles, especially hollow silica particles. Inorganic materials have heat resistance and solvent resistance. The specific gravity of silica is 2.2 g/cm^3, which is lower than that of titanium dioxide of 4.0 g/cm^3. Therefore, hollow silica particles are expected to be less sedimentation compared to titanium dioxide.

In preceding study, application of hollow titanium particles and hollow silica particles to inkjet ink has been reported [8, 9]. The former has a concern of pigment sedimentation due to particle specific gravity. The latter has small particle size of 30-50 nm and therefore high white opacity cannot be obtained. Although there are commercially available hollow silica particles, there is a problem that it cannot be dispersed while maintaining the hollow structure. If the hollow structure cannot be maintained in the coating film, white opacity cannot be obtained.

To goal of this work is to obtain a new white ink which features less sedimentation and high white opacity even upon non-permeable media. Furthermore, regarding white opacity, we aimed at achieving Hunter whiteness degree of 76 or more under one pass condition. One pass condition is ink volume 9.6 g/m^2 with pezo head made by Ricoh. Hunter whiteness degree 76 is a very high target equivalent to twice coating of offset printing.

Preparation of Hollow Silica Particles

We synthesized hollow silica particles by the method shown in Figure 4. Although commercially available hollow silica particles have problems in dispersibility, our synthetic material has the following features. It can be controlled to have primary particle size of 100-500 nm and wall thickness size of 10-40 nm. It also can be dispersed while maintaining the hollow structure in the ink. Figure 5 shows synthetic hollow silica particles with different primary particle size and wall thickness size.

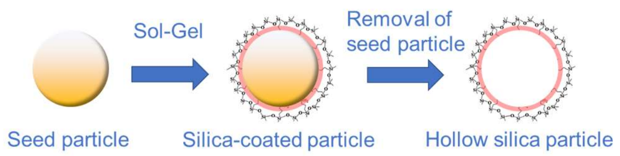

Figure 4. *Synthetic method of hollow silica particle.*

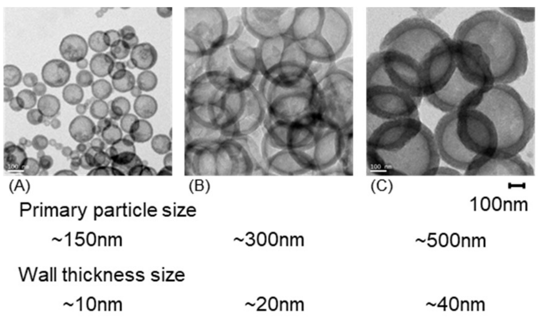

Figure 5. *TEM images of synthesized hollow silica particles.*

Influence of Primary Particle Size on White Opacity and Sedimentation Velocity

In order to confirm the effect of primary particle size, inks were prepared using hollow silica particles having different particle characteristics as described above. Experimental conditions 1 are as shown in Table 1. White opacity was evaluated using Hunter whiteness degree shown in Equation 1, and sedimentation velocity was calculated using Stokes`s low shown in Equation 2. Figure 6 shows the influence of primary particle size on white opacity and sedimentation velocity. As primary particle size of hollow silica particles and titanium dioxide increases, white opacity increases and sedimentation velocity also increases. Sedimentation velocity of hollow silica particles having primary particle size of 500 nm is about half that of titanium dioxide having that of 200 nm. This suggests that using hollow silica particles reduce pigment sedimentation problems.

Table 1. Experimental conditions 1.

Ink	Water-based resin ink
Media	Non-permeable media (OPP)
Print	Wire bar (winding diameter 0.15mm)
Drying	80℃ (Natural convection oven)

$$W = 100 - \{(100 - L)^2 + a^2 + b^2\}^{1/2}$$

W : Hunter whiteness　　a : redness-greenness
L : Lightness　　b : yellowness-blueness

Equation 1. *Hunter whiteness.*

$$V = \frac{D^2 (\rho_p - \rho_f)\, g}{18\, \eta}$$

V : Sedimentation velocity (m/s)　　ρ_f : Density of fluid (kg/m^3)
D : Diameter of particle (m)　　g : Gravitational acceleration (m/s^2)
ρ_p : Density of particle (kg/m^3)　　η : Viscosity (kg/m s)

Equation 2. *Stokes`s low.*

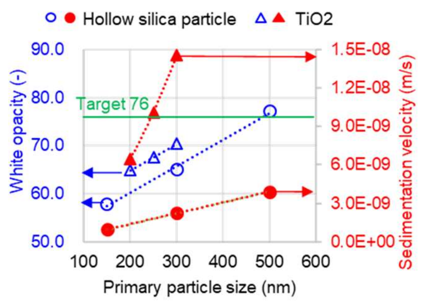

Figure 6. *Influence of primary particle size on white opacity and sedimentation velocity.*

Correlation between Pigment Volume and White Opacity

In order to confirm correlation between pigment volume and white opacity, an ink was prepared using hollow silica particles having primary particle size of 500 nm. Similarly, another ink was prepared using titanium dioxide having that of 300 nm. Printed coating films were fabricated by Ricoh printer GX e5500. Experimental conditions 2 are as shown in Table 2. Figure 7 shows the correlation between pigment volume of hollow silica particle and titanium dioxide and white opacity. As pigment volume increases, white opacity tends to increase. White opacity of coating film containing hollow silica particles is larger than that of titanium dioxide. With hollow silica particles, Hunter whiteness degree 76 is reached by setting pigment volume to about 0.50 g/m^2 or more. In the conventional white inkjet ink, it is necessary to repeat the printing times in order to sufficiently hide the substrate. In white inkjet ink containing hollow silica particles, it is expected that coating film with high white opacity can be formed with less number of printing times.

Table 2. Experimental conditions 2.

Ink	Water-based resin ink
Media	Non-permeable media (OPP)
Printer	GX e5500 (Ricoh)
Printhead	Piezo head (Ricoh)
Carriage speed	508 mm/sec (Main scanning direction)
Resolution	600×600dpi
Droplet size	2, 3, 4, 8, 9, 21 pL (Multi)
Drying	80℃ (Natural convection oven)

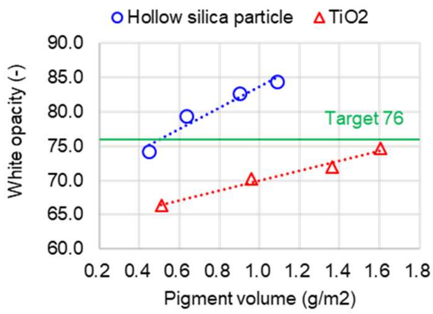

Figure 7. *Correlation between pigment volume and white opacity.*

Coating Film Cross-section Structure

Figure 8 shows the cross section of the print film of hollow silica particles and titanium dioxide observed by SEM. The print film of hollow silica particles in Fig. 8 (A) has pigment volume of 0.64 g/m^2 and an average film thickness of 4.9 ± 0.3 um. On the other hand, the print film of titanium dioxide in Fig. 8 (B) has pigment volume of 1.60 g/m^2 and an average film thickness of 2.9 ± 0.4 um. The print film of hollow silica particles is thicker than that of titanium dioxide, despite low pigment volume. One of the factors is that high white opacity is large in film thickness. In the printed film of hollow silica particles, the particles maintain a hollow structure in the coating film. It can also cope well with heating and drying on non-permeable media. It is expected to be applicable to high-speed production requiring high heat drying and also to solvent ink.

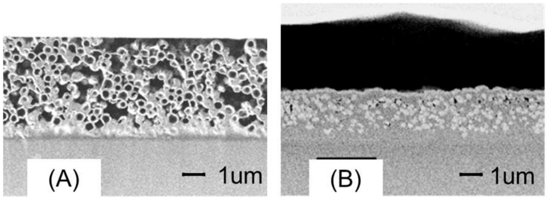

Figure 8. *SEM image of printing film of (A) hollow silica particle and (B) TiO_2.*

Sedimentation Evaluation

Sedimentation property of hollow silica particles and titanium dioxide was confirmed experimentally. Experimental conditions 3 are as shown in Table 3. The change amount of the backscattered light was evaluated. Figure 9 shows experimental data on sedimentation. Calculated similarly, the larger primary particle size, the more likely sedimentation occurs. We confirmed that hollow silica particles are less sedimentation compared with titanium dioxide.

Table 3. Experimental conditions 3.

Ink	Water-based resin ink
Viscosity	8 mPa·s
Instrument	TURBISCAN MA2000 (Formulaction)
Liquid volume	5 ml
Evaluation time	100 h
Evaluation position	Supernatant 10 mm

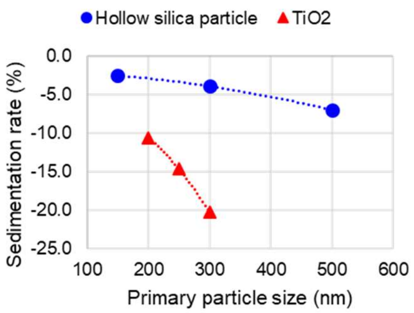

Figure 9. *Sedimentation rate.*

Conclusion

We have developed a new white ink which features less sedimentation and high white opacity even upon non-permeable media. It was made by developing a method for synthesizing dispersible hollow silica while maintaining a hollow structure. By optimizing primary particle size and wall thickness size of hollow silica particle, it was achieved to form coating film with Hunter whiteness degree of 77 under 1 pass condition. In addition, it is less sedimentation than titanium dioxide. White ink containing hollow silica particles can be expected to be applied to various inks and media.

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Author Biography

Tomohiro Hirade graduated from Tokyo University of Science in Japan in 2009 and obtained his masters in chemistry at Tokyo Institute of Technology in Japan in 2011. He entered Ricoh Company, Ltd. in 2011, and he specialized in aqueous white ink

