

A Preparation of Spherical Calcium Carbonate and Application to Paper

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Abstract

Silica is generally used for ink-jet paper as a coating pigment for high print quality. As a substitute of expensive silica, calcium carbonate having a crystal form of vaterite was examined in terms of the preparation method for high purity and surface wetting behavior of its coated paper. Pure vaterite synthesis was successfully achieved by the modified interfacial reaction method, i.e., at a temperature of 25°C of all the reacting liquids and high shear rate during mixture. Spherical vaterite aggregates developed so is around 1 μm diameter and consists of primary particle less than 100 nm diameter. As for vaterite-coated paper, comparatively adequate surface wetting behavior for ink-jet printing was obtained. Contact angle between a water droplet and a paper surface decreased with time by absorption for vaterite while it decreased by lateral spreading for silica. These phenomena suggest that vaterite is potential to absorb water very quickly. Thus, the potential of vaterite as a coating pigment was suggested.

Introduction

Demanded quality of printed matter has been becoming higher and higher even for home use with the rapid spread and advancement of digital cameras. Printers used at home for outputting photo-like pictures are mainly compact ink-jet printers. However, characteristics of pictures printed with an ink-jet printer are greatly influenced by characteristics of paper used compared with Laser beam printers.

Silica is generally used for ink-jet paper as a coating pigment because of fast ink absorption and resultant high print quality. Although it is costly to produce coated paper using only silica because of its high production cost, there has been no cheap substitute.

One of key factors for a suitable pigment for ink-jet is considered to be fineness of pigment particles. Vaterite, a crystal form of calcium carbonate, tends to form aggregate structure consisting of very small primary particles as Figure 1 shows just like silica. A lot of calcium carbonate is conventionally used in paper industry as a filler or a coating pigment because it exists a lot in nature and harmless to a human body. But, vaterite has been hardly used in industry because of rarity in nature. So, in this study, calcium carbonate in the form of vaterite was evaluated as a coating pigment for ink-jet.

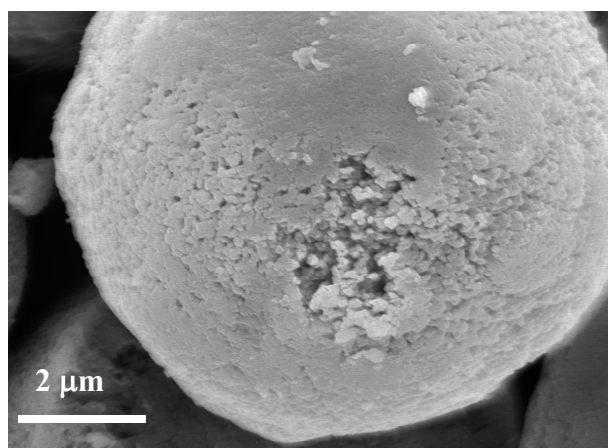


Figure 1. SEM image of vaterite prepared by interfacial reaction

Experimental Interfacial Reaction

Vaterite was synthesized in the method as illustrated in Figure 2. A water-in-oil emulsion with a water (calcium chloride, 1.0 M)/oil (toluene + Tween 80, 5% m/m) volume ratio of 7/3 was prepared. It was stirred by homogenizer for one minute and poured into a potassium carbonate aqueous solution (1.0 M) as quickly as possible. The precipitate generated immediately was separated from this mixture by centrifugation at 3500 rpm for 5 minutes. Then, the liquid phase was removed. The precipitate was washed with deionized water. This procedure was repeated a number of times until complete removal of toluene. Then, it was washed by acetone two times and dried at room temperature for 12 hours.

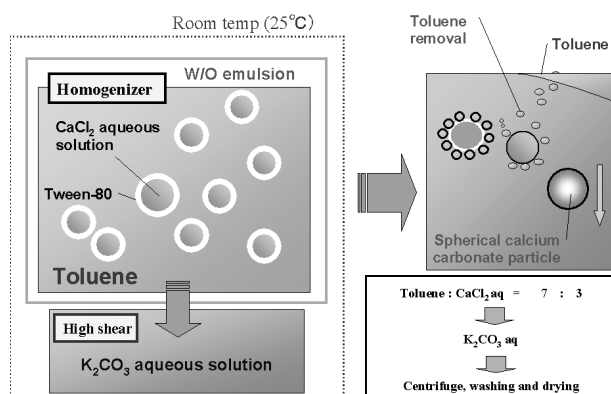


Figure 2. A model of interfacial reaction

In the modified methods, the two aqueous solutions of both calcium chloride and potassium carbonate were exchanged, temperature of all of the reacting liquids was altered to 0 or 25°C, and the stirring intensity of the calcium chloride aqueous solution was raised when the emulsion was poured.

Analysis of Calcium Carbonate

Prepared calcium carbonate was characterized in terms of crystal form by X-ray diffraction and its second particle structure was observed by SEM. BET specific surface area was measured by the nitrogen absorption method.

Preparation of Vaterite-Coated Paper

Figure 3 shows how coating colors were prepared from vaterite as a pigment before coating them on paper for copy use with a motor-driven wire bar coater. Calcite (conventional precipitated calcium carbonate = PCC) PZ, Shiraiishi Kogyo Kaisha and silica, an aggregate type, were also used for coating to prepare reference coated papers. For vaterite, enough coat weight was not obtained by single coating, so double coating was performed.

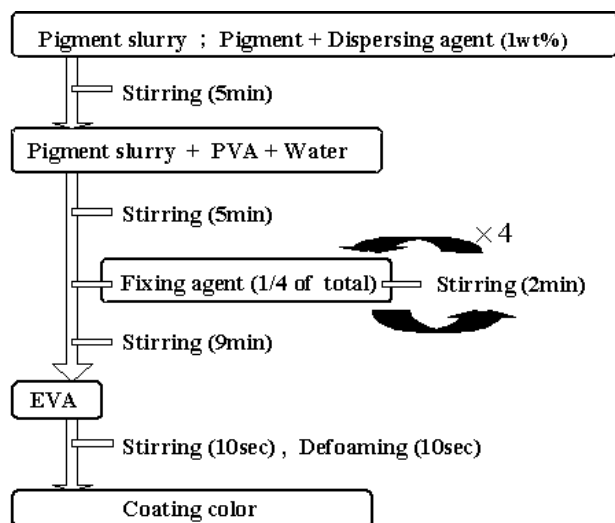


Figure 3. Preparation scheme of coating color

Printing Test

Some letters and small dots were printed on each sample with Pixus iP7100, Canon, and observed with naked eyes and with an optical microscope, Olympus, respectively. Area and perimeter length per dot were measured by image processing. Scion Image Beta 4.02, Scion Corporation was used to calculate these parameters as an image processing application.

Contact Angle Change with Time

Contact angle changing with time was measured with an automatic solid/liquid interface analyzing system Dropmaster 700, Kyowa Interface Science Co. Ltd. The water droplet volume was set constantly at 0.5 μ L. Images of a droplet on paper started to be recorded automatically 100 ms after contact with a paper surface and continued to be recorded every 33 ms. Contact angle

calculation was based on the $\theta/2$ method, i.e., circular interpolation.

Results and Discussion

Polymorphism of Synthesized Calcium Carbonate

Calcium carbonate, which had been prepared by the interfacial reaction method, was a mixture of vaterite and calcite. But the vaterite ratio was considerably increased under some conditions. It was understood in particular that the ratio changed with temperature and stirring intensity. Figure 4 is SEM images of synthesized calcium carbonate at different temperatures of the two reacting liquids and different shear rates. It was found that the vaterite ratio increased with a rise in temperature in comparison between A and B images. Sample A includes more cubic particles than Sample B. On the cubic particles, smooth platy surfaces are observed and those seem to be calcite, i.e., a part of the rhombohedral crystal. By comparison between Samples B and C, the vaterite ratio was found to become higher at a higher shear rate. Additionally, intense stirring was found to reduce the diameter of secondary particles remarkably. Size reduction of emulsified particles caused by intense stirring seems to enhance the efficiency of vaterite growth.

Figure 5 shows X-ray diffraction patterns of the synthesized calcium carbonate at three different conditions. The peak of calcite around 26 degrees became low as the reaction condition changed from A to C. So, sample C could be regarded as pure vaterite. And this pure vaterite was used for further analyses of pigment and coated paper properties. About reaction temperature, the vaterite ratio decreased again over 25°C.

Table 1 shows BET specific surface area and mean particle diameter judged roughly from SEM images for conventional PCC available commercially, vaterite and vaterite milled with a planetary ball-mill. The mean diameter of a spherical particle of vaterite was about 1 μ m. But, vaterite has a form of aggregate consisting of nano-sized particles. So, vaterite is expected to have a large specific surface area.

Table 1: Specific Surface Area (BET) and Particle Diameter

	Specific surface area (m^2/g)	Primary particle diameter (μm)	Secondary particle diameter (μm)
Pure calcite	9	0.3	3~5
Vaterite	22	0.1	1~2
Vaterite milled*	39	0.1	n.a.

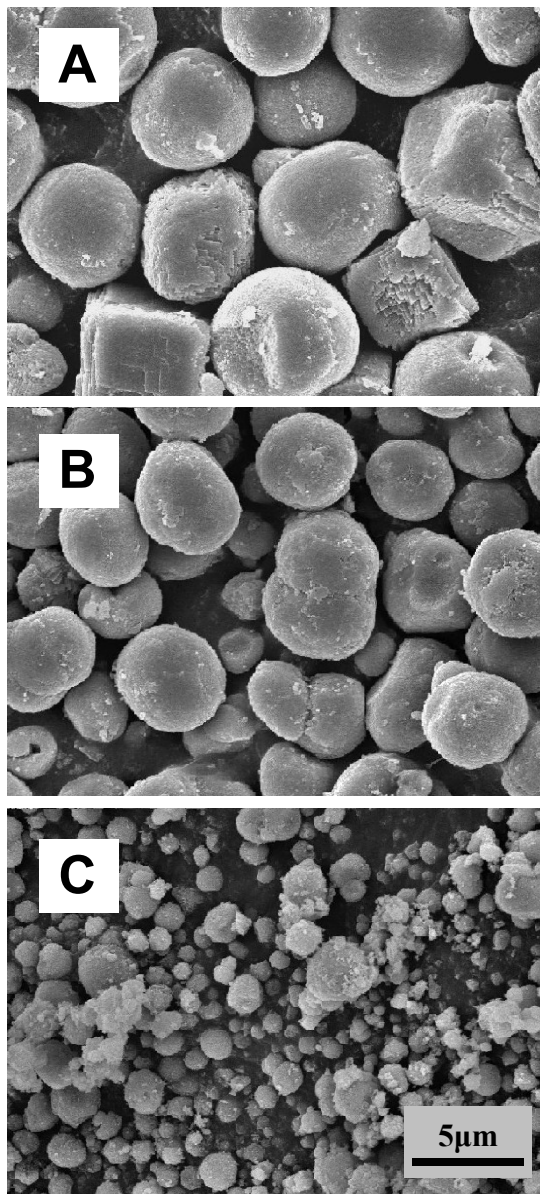


Figure 4. SEM images of synthesized calcium carbonate. Reaction conditions were 0°C at low shear(A), 25°C at low shear (B) and 25°C at high shear(C).

From the result of the BET method, vaterite was found to have a specific surface area of as large as 20 m²/g due to unique structure of secondary spherical particles packed with primary nano-sized particles. To check whether this aggregate structure is formed by firm chemical bonding between primary particles or just loose physical adsorption, spherical secondary particle structure was broken down with the ball mill into individual primary particle of around 100 nm. Consequently, the specific surface area of this ground vaterite attained 40 m²/g, which is equivalent to twice as large as that before grinding. This increasing rate is likely to suggest that secondary particles are formed by at least some degree of chemical bonding considering that the increasing rate for the conventional calcite PZ was about 50% by similar grinding.¹

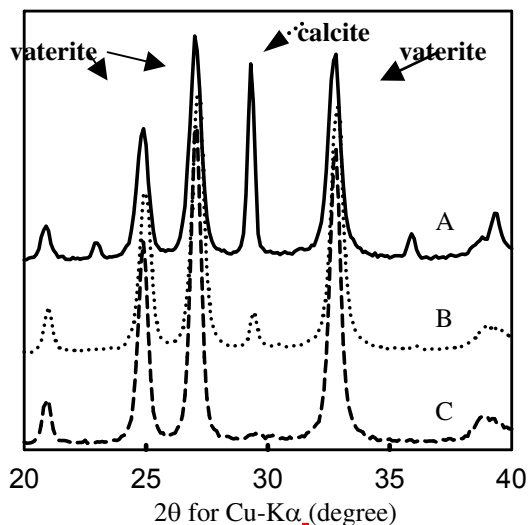


Figure 5. X-ray diffraction patterns of synthesized calcium carbonates. The reaction conditions are same with those in Fig. 4 caption.

Wetting Property of Vaterite-Coated Paper

Vaterite-coated papers were evaluated from a standpoint of ink-jet printability. Surface wetting behavior was examined by measuring contact angle between deionized water and surfaces of the papers coated with the three kinds of pigment. Figure 6 shows changes in contact angle. Among the carbonates, vaterite becomes wetted with water easily than calcite PZ because the contact angle is lower for vaterite. Silica shows a very similar change with the double coating vaterite [vaterite(2)] for initial one second, but decreased continuously for a long time.

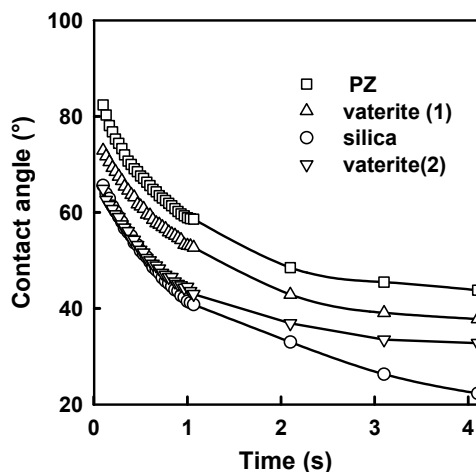


Figure 6. Changes in contact angle with time

Figure 7 shows that the radius of the contact circle for silica increased greatly while those of the carbonates leveled off much earlier. This means that, on silica coating surfaces, a water droplet tends to spread laterally along the surface. If this hypothetical mechanism is correct, the height of the water droplet must decrease quickly for silica coating surfaces.

Accordingly, Figure 8 shows that the height of the water droplet on the silica-coated paper decreased quickly, but that on the vaterite-coated paper by double coating was lower, in particular, for initial five seconds. To interpret this behavior, it seems to be natural to consider that the vaterite coatings absorbed water quickly.

The water droplet volume for double coating vaterite decreased quickly to a very low value initially. This result suggests high water absorbency of vaterite-coated paper.

Conclusion

By optimizing the reaction condition regarding stirring intensity and temperature, pure vaterite synthesis by the interfacial reaction method was successfully achieved. Spherical vaterite aggregates developed so is around 1 μm diameter and consists of primary particle less than 100 nm diameter. So, vaterite was found to be very porous as implied by the large specific surface area. Furthermore, vaterite can gain a larger specific surface area by ball-mill grinding. As for vaterite-coated paper, comparatively adequate surface wetting behavior for ink-jet printing was suggested. Contact angle between a water droplet and a paper surface decreased by absorption for vaterite while it decreased by lateral spreading for silica coating. These phenomena suggest that vaterite is potential to absorb water very quickly. Thus, the potential of vaterite as a coating pigment was suggested from these findings.

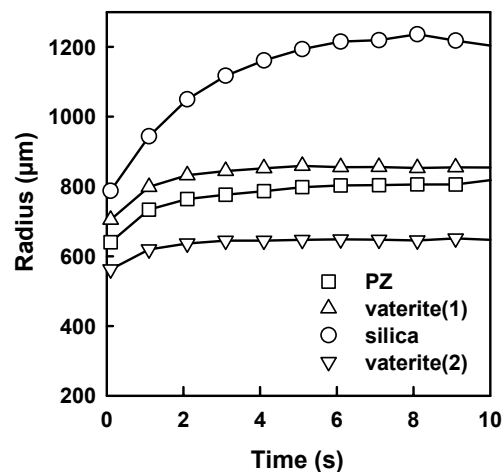


Figure 7. Changes in droplet radius

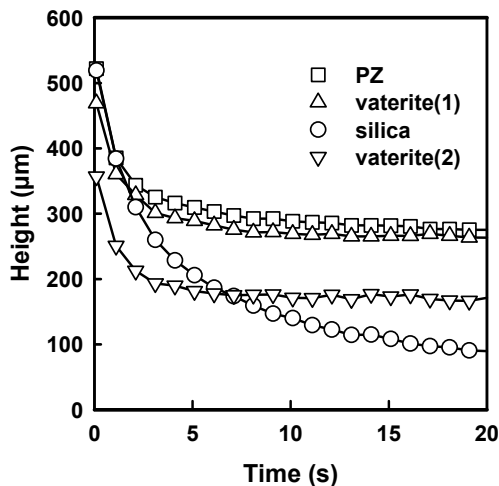


Figure 8. Changes in droplet height

	Coat weight (m^2/g)
□ PZ (Pure calcite)	5.4
△ vaterite (1)	4.0
○ silica	5.5
▽ vaterite (2)	8.2

References

1. D. Ivutin, T. Enomae, and A. Isogai., Proc. of IS&T's NIP21, No.20 in press (2005)

Author Biography

Yohta Mori was born in 1979, received B.E. degrees in Information and Image Sciences from Chiba University, Chiba, Japan in 2003. He became master course student of Agricultural and Life Sciences, The University of Tokyo from April, 1, 2004. His research interests are preparation of pigment for ink-jet paper and its printability.