Optimization of vaterite synthesis for application to coating pigment of ink-jet paper

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Abstract

Calcium carbonate in the crystal form of vaterite can be expected as a coating pigment because of fineness of primary particles and the spherical secondary structure. So far, the interfacial reaction method has been applied to prepare vaterite particles. However, to avoid using volatile organic solvents, an aqueous system with no organic solvent was developed in this study. Consequently, vaterite was successfully synthesized from only two aqueous solutions of potassium carbonate and calcium chloride with no additive. As parameters of the reaction condition, temperature, agitation rate and effects of surfactants were examined. The optimum temperature of the reacting liquids was around 40 ºC. Reduced volumes of the reacting liquids to intensify the agitation effect increased the vaterite ratio for a given homogenizer at a constantly rotating speed. Among surfactants used, there was no difference observed in the effect on vaterite generation. At a suitable condition about other parameters, pure vaterite was obtained even under no surfactant condition. In summary, it was speculated that the vaterite form was generated at an early stage of the reaction. At insufficient levels of shear stress, vaterite growth is not promoted and generated vaterite transfers spontaneously to calcite. Surfactants are assumed to adsorb onto surfaces of primary particles and trigger an orderly aggregation.

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 ink-jet printers 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 shown by Figure 1, 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.

Experimental

Vaterite preparation in aqueous system

Vaterite was synthesized in the very simple method as illustrated in Figure 2. A potassium carbonate aqueous solution (1.0 M) was poured as slowly as possible into a calcium chloride aqueous solution (1.0 M), which was agitated by homogenizer at 5000 min^{-1}. In prior to the mixture, a surfactant of Tween series, referred-to in the later sections, was dissolved in the calcium chloride aqueous solution. The precipitate generated immediately was separated from this mixture by centrifugation at 3000 min^{-1} for 5 minutes. Then, the liquid phase was removed. The precipitate was washed with deionized water. This

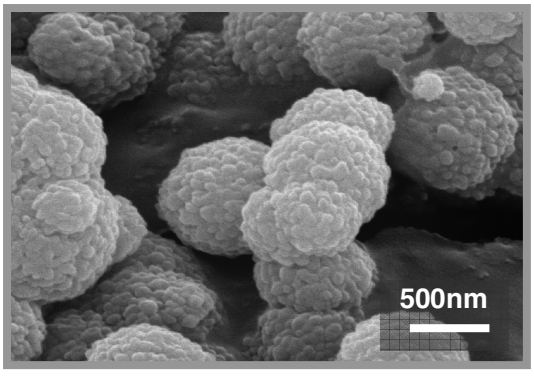

Fig. 1 SEM image of vaterite form of calcium carbonate.

procedure was repeated a few times to remove ions. Then, it was additionally washed with ethanol then acetone and dried at room temperature for 12 hours.

In the modified methods to synthesize pure vaterite, the temperature of all of the reacting liquids was altered to 25, 40 and 70 ºC. The reaction volume of the two each aqueous solutions of calcium chloride and potassium carbonate were changed. And some surfactants, such as Tween-80 (poly-oxyethylene sorbitan monooleate) were applied to examine the secondary particle size and shape of the precipitates.

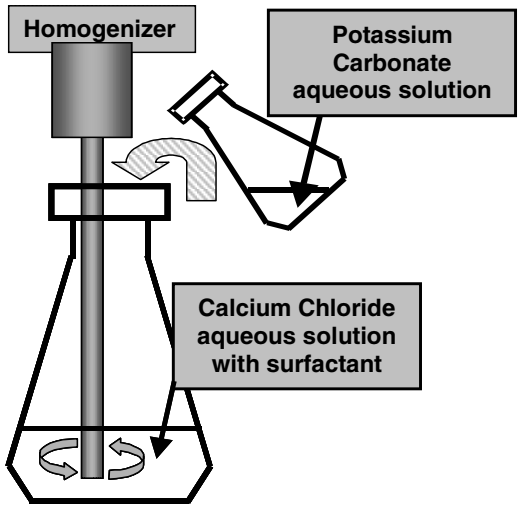

Fig. 2 Aqueous system for vaterite synthesis.

Analysis of calcium carbonate

Prepared calcium carbonate was characterized in terms of crystal form by X-ray diffraction patterns as Figure 3 shows. Vaterite has peaks at around 24.8, 27.1, 32.8 and 50.1 º. Calcite has peaks at around 29.4, 39.3 and 43.1 º. Aragonite has peaks at around 26.2 and 33.2 º. But, these peaks of aragonite are too close to the peaks of vaterite to distinguish of vaterite from calcite.

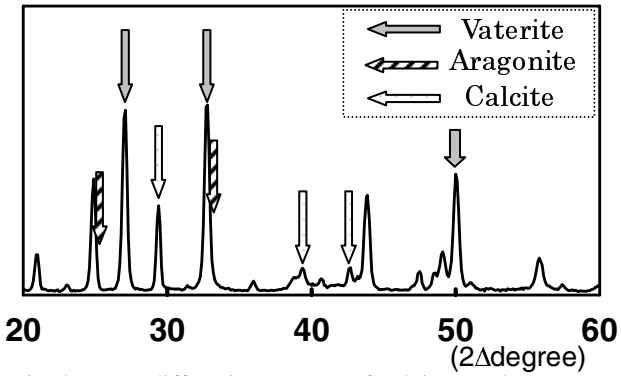

Fig. 3 X-ray diffraction pattern of calcium carbonate. (Mixed sample of vaterite, calcite and aragonite)

Secondary particle structure and size of vaterite were observed by Scanning Electron Microscope (hereinafter referred to as SEM).

Results and Discussion

1) Effect of temperature

The effect of temperature on the crystal form was examined in the aqueous system. A procedure of reaction is schematically shown in Figure 2. actually, this method was adopted for the purpose of observing a tendency depending on the temperature, but the temperature control was not so precise, the influence of frictional heat by the homogenizer was not considered in this method.

When the system temperature was at around 25 ºC (room temperature), intense peaks of calcite were observed, and many rhombohedral particles of the calcite form were observed in SEM images as shown by Figure 4.

When the system temperature was at around 40 ºC, generation of the calcite form seemed to be suppressed.

When the system temperature was at around 70 ºC, against expectation, there were many particles of the calcite form were synthesized. Furthermore, the relatively higher peak at around 33 º than at 27.1 º means that the generation of the aragonite form was promoted. It is known widely that the crystal form of aragonite was synthesized at high temperatures and this result agrees well to this knowledge. In addition, there was no systematic relationship between temperature and vaterite generation. But it is assumed that there was a suitable temperature of around 40 ºC for vaterite generation.

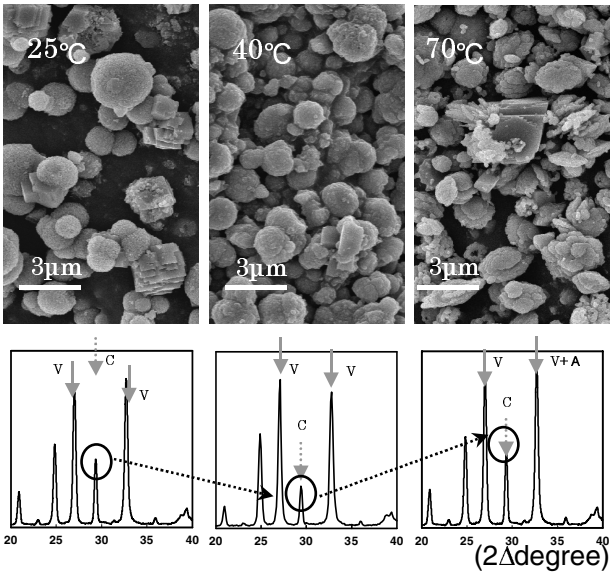

Fig. 4 Influence of temperature on crystal forms.

2) Effect of agitation rate (reaction volume)

The effect of agitation rate, which had much influence on preparation of vaterite form in the interfacial reaction[1], was examined. The literature has already shown that higher agitation rates promote more selective generation of the vaterite form. So, it was suggested that the agitation condition would be important in the aqueous system as well as in the interfacial reaction. From the past experiments, it was considered that given shear force by agitation promotes growth of the vaterite form.

Generation of the vaterite form was promoted by reducing reaction volume. Furthermore, comparing X-ray diffraction patterns between at 25ºC and 40 ºC, there were weaker peaks of calcite, and it was confirmed that almost all precipitates were of the vaterite form as shown by Figure 5. It was found that agitation was an important condition in the aqueous system from these results.

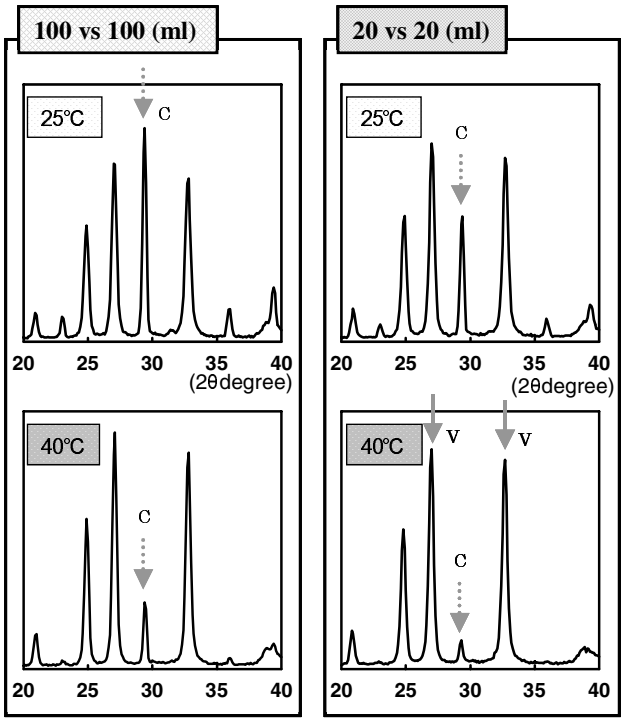

Fig.5 Effect of reaction volume and temperature on crystal forms as changes of X-ray diffraction patterns.

3) Effect of surfactant

It was found that there was no relationship between the generation of the vaterite form and the kind of surfactants used, from X-ray diffraction patterns shown in Figure 6. However, regardless of the kind of surfactants, there was no difference in the primary particle size (around 100nm). In addition, no clear difference in the size of the secondary aggregated particle was observed, excluding the Tween 20 added sample, in the SEM images, as well as in the case of the interfacial reaction method. The particle size distribution of the sample prepared with Tween 20 was exceptionally broad with very small particles included.

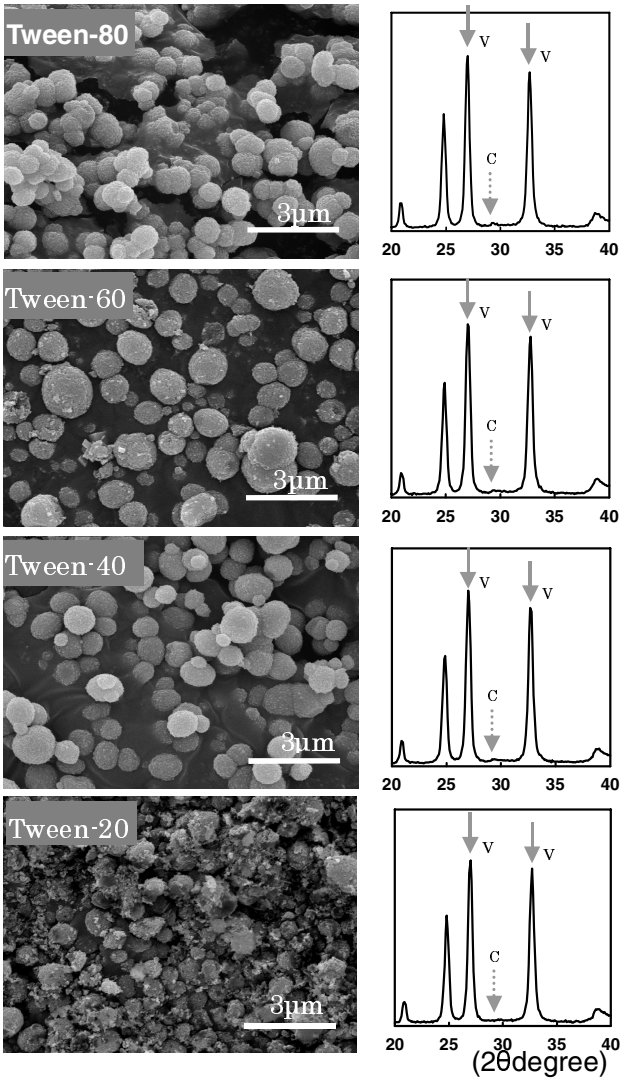

Fig. 6 Effect of surfactants on particle shape and crystal forms

Having no influence on the crystal form of calcium carbonate, surfactants were expected to control secondary particle size and shape effectively. Therefore, it was tried to clarify the synthesis mechanism of vaterite generation in the aqueous system with no surfactant.

There were no changes for preparation conditions or procedure except surfactant addition to a calcium chloride aqueous solution. The temperature of this reaction was 25 ºC. As a result, the X-ray diffraction pattern showed that there were no peaks of calcite and that pure vaterite was prepared dominantly. Consequently, surfactants were not always necessary to promote vaterite generation selectively. However, from SEM observation, the secondary aggregated structure was found to have a collapsed shape in comparison with that prepared with the surfactants. From this result, it is

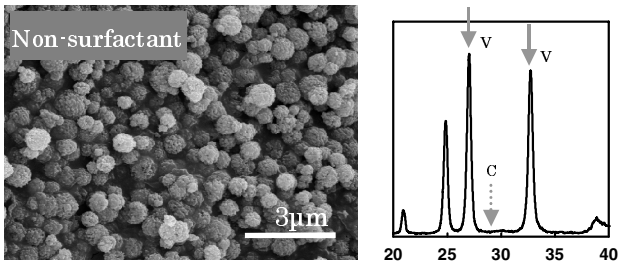

Fig. 7 Shape and crystal forms of particles prepared with no surfactant.

expected that some surfactants work effectively to control the secondary particle structure and size.

Conclusion

Temperature and agitation rate (shear stress) conditions were the most important to synthesize the vaterite form of calcium carbonate. Actually, the vaterite form of calcium carbonate was generated without surfactant even in the aqueous system. Therefore, it was clarified that existence of a surfactant in the reaction system is not an essential condition to promote vaterite generation selectively. From observations of SEM images, the primary particle size was not influenced by any conditions, whatever methods were used. But surfactants had a great influence on the secondary particle size and shape. Samples prepared with surfactants gained smooth surfaces of the secondary particle, and the sample with no surfactant had rough surfaces.

It was considered that the vaterite form was generated at an early stage of the reaction because the primary particle size was not influenced by any conditions, whatever methods were used. In the case of low or no shear stress in the reaction system, generation of the vaterite form is not promoted. Therefore, vaterite transfers spontaneously to calcite, which is the most stable form of calcium carbonate thermodynamically. When surfactants exist, it is assumed that they adsorb onto surfaces of primary particles and trigger an orderly aggregation from the primary particles. The aggregation by virtue of the surfactant affects surface smoothness of the secondary particle.

Results of application to paper measured in the microscopic high-speed video camera system[2] will be shown in the poster session.

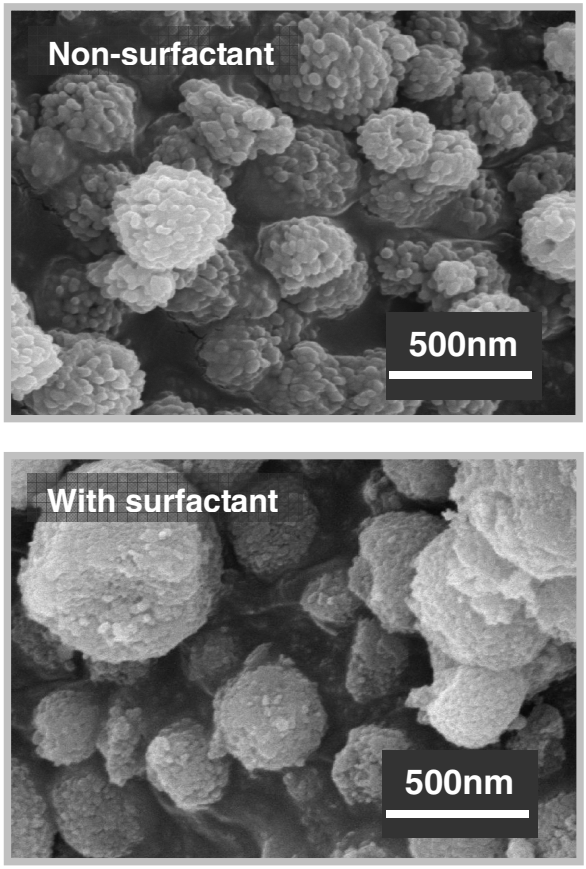

Fig8. Effect of surfactant. (SEM images)

Reference

[1]Yohta, M. Enomae, T. and Isogai, A., Proc. of IS&T's NIP21, No.20 (2005)

[2] Ivutin, D. Enomae, T. and Isogai, A., Proc. of IS&T's NIP21, No.20 (2005)

Biography

Yohta Mori was born in1979. He received B.E. degrees in Information and Image Sciences from Chiba University, Chiba, Japan in 2003 and received MSc in Graduate School of Agricultural and Life Sciences, The University of Tokyo in March, 2006. His research interests are functional pigments for ink-jet paper and its printability.