Preparation of vaterite type calcium carbonate by using ultrasound and application to ink-jet paper

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Abstract

Calcium carbonate is used widely in various industries because it is costless and harmless. Vaterite is one type of crystal form of calcium carbonate and occurs rarely in nature. This study aims at safe synthesis method to prepare vaterite and its application to ink-jet paper. A new method for preparing pure vaterite has been established by using ultrasonic homogenizer to mix and agitate K_2CO_3 and $CaCl_2$ solutions. Shapes and sizes of vaterite particles formed are controllable by selecting a surfactant present in the mixing solution. Vaterite type calcium carbonate is easily transformed into calcite type in water. However, high pH, addition of surfactant SDBS (Sodium Dodecyl Benzene Sulfonate) and immersion in ethanol lowered or prevented crystal transformation because of low solubility constants. Ink-jet printing test was performed with vaterite-coated paper and resulted in high print quality. Bleeding problem did not occur as well as commercial silica coated ink-jet paper, although calcite coated and trial silica coated papers exhibited worse bleeding probably because high hydrophilicity of vaterite promoted quick absorption of inks inward before spreading laterally on the surface.

Introduction

Ink-Jet printing

Printers used at home for outputting photo-like pictures are mainly compact ink-jet printers, and high quality has been demanded for ink-jet printed matters. The quality of those matters is more greatly influenced by characteristics of paper used for printing than that by electrophotography.

Silica is generally used for ink-jet paper as a coating pigment because of fast ink absorption, color density and resultant high print quality. Although it is costly to produce ink-jet paper coated with 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.

In industry, a large amount of calcium carbonate is consumed because it is harmless to a human body and produced at low cost easily by grinding limestone that exists widely in nature. As well as in various industries, a lot of calcium carbonate is conventionally used in paper industry as a loading filler or a coating pigment to improve optical properties. Vaterite, a crystal form of calcium carbonate, tends to form aggregate structure consisting of very small primary particles, as shown in Figure 1, like silica. However, vaterite has been hardly used in industry because of rarity in nature. So, in this study, manufacturing processes, stability of crystal type in water and ink-jet applicability of vaterite type calcium carbonate was developed and evaluated.

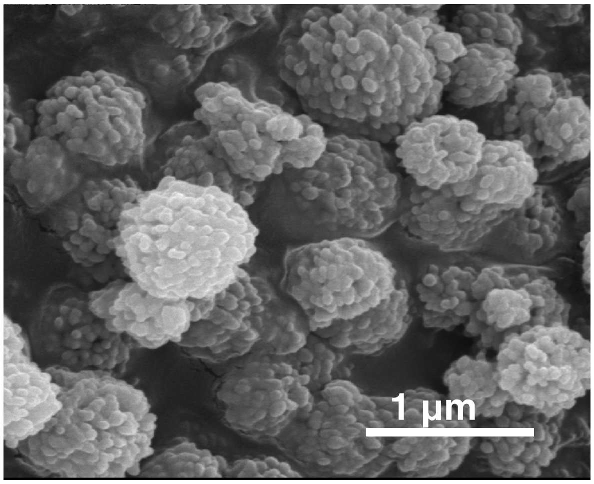

Fig. 1 SEM image of vaterite form calcium carbonate.

Calcium Carbonate

Calcium carbonate has three crystal forms. They are calcite, aragonite and vaterite. Calcite is the most common form for almost all calcium carbonate in nature with the X-ray-CuKα major peaks at 29.4°, 39.3°, and 43.1° as shown in Figure 2. Aragonite exists in nature as well although the amount is much less than calcite. It has a typical form like a needle and X-ray major peaks at 26.2° and 33.2°. In contrast, vaterite hardly occurs in nature, but according to

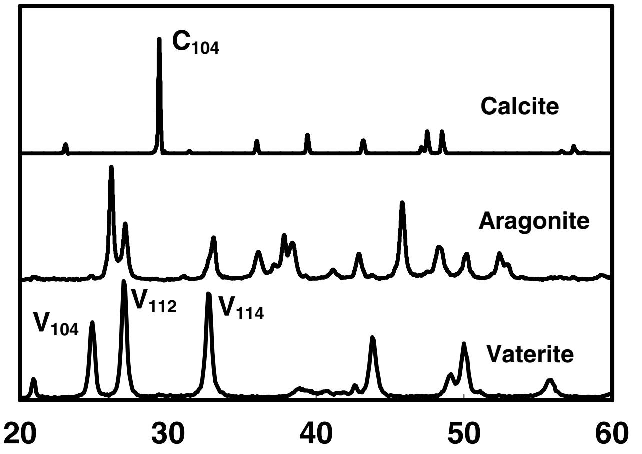

Fig.2 XRD patterns of calcium carbonate

SEM observation, the size of primary particles was only around 100 nm in diameter as shown in Figure 1. Therefore, vaterite is expected to have large surface area and advantageous properties which would not be attained by the other crystal forms. It has X-ray major peaks at 24.8°, 27.1°, and 32.8°. X-ray diffraction (XRD) patterns are shown in Figure 2. From this stand point, in this study, vaterite was tried to be prepared by a new method and applied to ink-jet paper.

Although vaterite was already applied to ink-jet paper in the previous research, vaterite was prepared by the interfacial reaction method [1] or developmentally by the water system using a rotor homogenizer with a double cylinder [2]. The interfacial reaction method needed some kind of volatile organic solvent. The double cylinder type homogenizer only gave shear stress heterogeneously; mixing two reactant solutions formed white gel because energy transfer was different from adjacent tip to flask wall. This heterogeneous condition did not always achieve the highest vaterite preparation ratio. Although those preparation methods formed pure vaterite, they need a large amount of energy such as high temperature, high pressure and long reaction time.

In this study, an ultrasonic homogenizer was introduced to agitate the two reactant aqueous solutions. In addition, the reaction condition to synthesize vaterite was modified to make spherical calcium carbonate with pure vaterite to control its properties. This simple and mild reaction method has been established as an aqueous system also for the energy-saving reason. Vaterite is generally known to transform spontaneously to calcite type for a few tens of hours to a few days in water. To examine the conditions to increase or decrease the rate of crystal transformation is another purpose of this study. In addition, prepared vaterite particles were coated on paper to evaluate ink-jet print quality.

Experimental

Vaterite preparation in water system

Calcium carbonate was synthesized by quickly pouring a potassium carbonate solution into a calcium chloride solution with or without 0.5% surfactant, which was agitated in an Erlenmeyer flask using an ultrasonic homogenizer at 19.5 kHz and 300W output power (26 mm in the probe tip diameter, US-300T, Nihonseiki, Japan). The concentration and volume of the salt solutions before mixing was set to be 1.0 M and 20 mL. Tween 20, 40, 60 or 80 was dissolved in the 1.0 M $CaCl_2$ solutions. Tween 20, 40, 60 and 80 have chemical structures of polyoxyethylene sorbitan mono-fatty acid ester, and the fatty acid components are lauric, palmitic, stearic and oleic acid, respectively.

White fine powder of $CaCO_3$ was formed as the precipitate immediately after mixing the two salt solutions. The flask was appropriately moved by hand to agitate the mixture homogeneously. After agitation for 2-3 min, the $CaCO_3$ precipitate was separated from the mixture by centrifugation at 1,000G for 5 min. The supernatant was removed by decantation, and the precipitate was washed thoroughly with water by repeated centrifugation. The $CaCO_3$ precipitate was washed with ethanol and then acetone by centrifugation, and dried in air at room temperature for 12 h. The powder-like $CaCO_3$ was stored at room temperature in a sample bottle with a screw cap before use. Yields of $CaCO_3$ were in the range of 90-95%, and the yield losses were mostly caused by handling during the recovery and washing processes.

The $CaCO_3$ powders thus obtained were subjected to XRD measurement by the reflection mode using a Rigaku RINT 2000 with monochromatic CuKα radiation at 40 kV and 40 mA. The weight ratios of vaterite in the $CaCO_3$ powders were calculated from the XRD intensities due to vaterite and calcite according to the equation proposed by Rao [3]. Morphologies of $CaCO_3$ powders were observed by means of a field-emission-type scanning electron microscope at 10 kV (SEM; S-4000, Hitachi Co., Japan) after platinum-spattering for 120 s.

Stability of Vaterite type

Stability of vaterite type in hot water was examined. Calcium carbonate easily dissolves in an acidic solution. The solubility is considered to be important for transformation from vaterite type to calcite type. Therefore, stability test was carried out at high pH conditions, that is, pH 9, 10 and 11 by using sodium hydroxide or conditions of high surfactant concentration with sodium dodecyl benzene sulfonate (SDBS), that is, 5%. Prepared vaterite samples were incubated in oven at 40 and 80 ºC for 1, 3, 6 and 12 hours. These samples were analyzed by XRD and observed by SEM. Calcite ratio was calculated by Rao's equation.

$$f_c = \frac{I_{104(C)}}{I_{104(V)} + I_{112(V)} + I_{104(c)} + I_{114(V)}}$$

f_c : Calcite fraction

$I_{104(C)} \sim I_{114(V)}$:Intensity of XRD peaks

Fig.3 Rao's equation

Preparation of calcium carbonate-coated papers

Figure 4 shows a scheme for preparing coating colors from calcium carbonate as a pigment. The coating colors were applied on coated paper for offset rinting to prevent rippling with a motor-driven wire bar coater [2]. Vaterite type calcium carbonate was prepared by the ultrasonic homogenizer method without surfactant. Calcite type calcium carbonate (conventional precipitated calcium carbonate = PCC), reagent grade, Wako pure chemical industries, Japan and aggregate type silica, Aerosil 200, Nippon Aerosil, Japan, were also used for coating to prepare coated papers for reference. For vaterite, enough coat weight was not obtained by single coating, so double coating was performed.

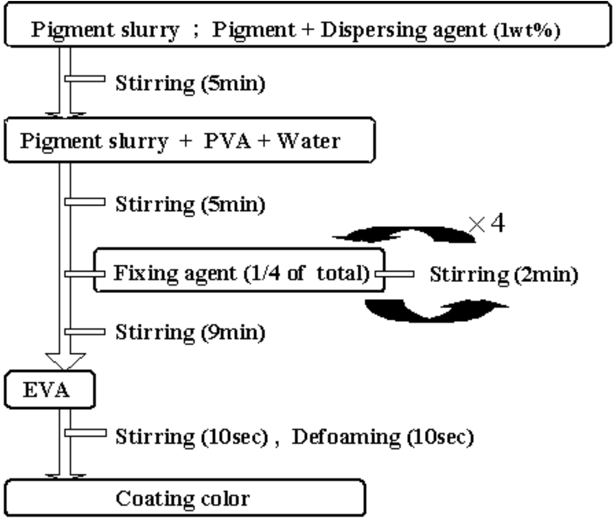

Fig.4 Preparation scheme of coating color

Printing test

Some letters, small dots and test patterns were printed on each sample of the coated papers prepared following the procedure described in the previous section with Pixus iP7500, Canon, and observed with naked eyes and with an optical microscope, SZH10, Olympus, Japan, 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.

Results and Discussion

Vaterite preparation

By using ultrasonic homogenizer, pure vaterite can be prepared as precipitates by mixing simply K_2CO_3 and $CaCl_2$ solutions at room temperature without any surfactant. Homogeneous, high-shear and constant agitation for mixing solutions of around 1 M salt concentration are necessary to prepare pure vaterite, while the temperature control of the solutions or the presence of surfactant is not necessarily required. Vaterite type calcium carbonate can be prepared mostly as typical spherical particles 0.1-1 μm in diameter by this method. However, the shapes and sizes of the vaterite particles formed are controllable by selecting a surfactant present in the mixing solution. Especially, when Tween 20 was used, vaterite aggregates of collapsed shapes were obtained. And, when Tween 80 was used, surface of obtained particles was smooth. Surface morphologies or shapes of primary particles comprising spherical aggregates also vary, depending on the surfactant used as shown in Figure 5. It was confirmed that all the prepared calcium carbonate samples were vaterite according to XRD analysis.

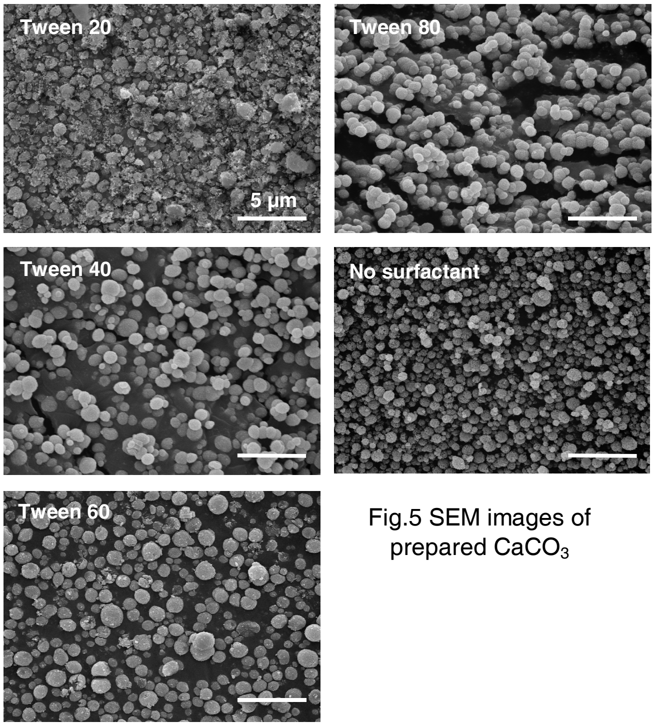

Fig.5 SEM images of prepared $CaCO_3$

Stability of Vaterite type

Physical energy such as shear stress or ultrasonic vibration supplied from the ultrasonic homogenizer seems to make vaterite type stably. Aragonite form calcium carbonate was synthesized at a high temperature, over 90 ºC, in this method. To determine the stability of the synthesized vaterite, the ratio of calcite fraction was

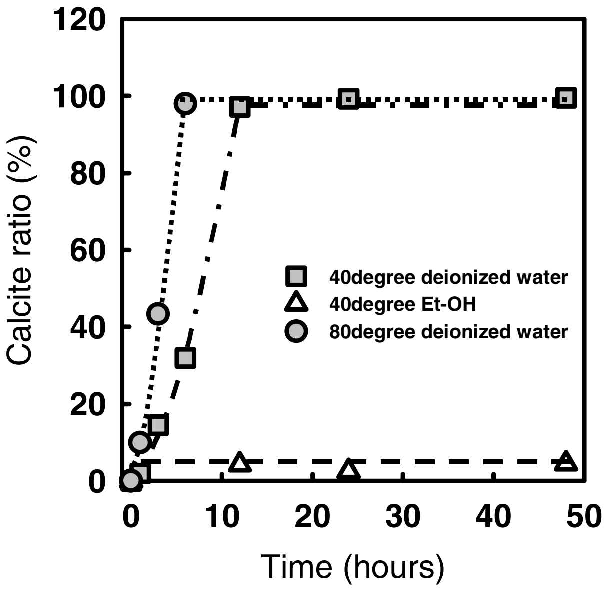

Fig.6 Crystal transformation rate at different temperatures and dispersion media.

calculated by Rao's equation. At the higher temperature, 80 ºC, vaterite type transformed more easily into calcite type as shown in Figure 6.

At the highest pH, pH 11, vaterite was slightly more stable than the other two pH as shown in Figure 7 probably because the solubility constant of vaterite vary depending on temperature and pH. Therefore, vaterite was remarkably stable in ethanol as shown in Figure 6. Thus, existence of H_2O is necessary for the transformation behavior of vaterite type calcium carbonate.

When vaterite type calcium carbonate in water with SDBS, the stability was remarkably increased as shown in Figure 7.

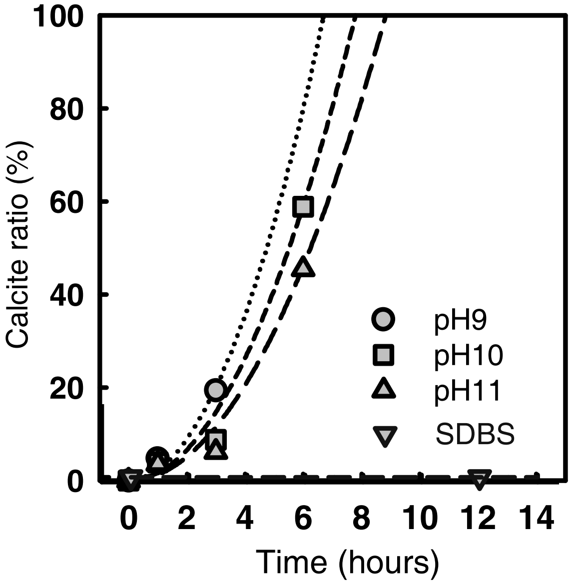

Fig.7 Crystal transformation rate at different pH

Printing test

Printed samples were scanned by scanner (GT-X900, EPSON, 1200 dpi in color mode). In this paper, only color chart images were shown in Figure 8.

The original data has white lines to separate each color boxes. These white lines were not completely reproduced on the base paper, calcite coated or silica coated samples. In contrast, those were clear on the vaterite coated and commercially-available papers. These two samples had good color optical density additionally. The non-coated sample was copy paper, on which white lines appeared. It was assumed that inks did not spread over the surfaces because of its water repellency. The upper left numbers were rank orders of white line sharpness by subjective evaluation. (1 = poor, 6 = good). Very high ink-jet print quality realized by vaterite seems to be due to high hydrophilicity that promotes quick absorption of inks inward before spreading laterally on the surface.

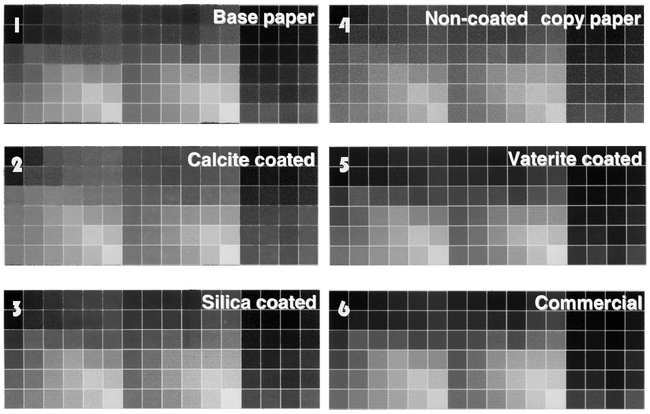

Fig.8 Printed color chart on each sample

Conclusion

A new method for preparing vaterite type calcium carbonate in an aqueous system has been established by using ultrasonic homogenizer. By this method, pure vaterite can be prepared by mixing simply K_2CO_3 and $CaCl_2$ solutions at room temperature without any surfactant. However, shapes and sizes of vaterite particles formed are controllable by selecting a surfactant present in the mixing solution.

Vaterite type calcium carbonate is unstable and easily transformed into calcite type in water. However, high pH of aqueous vaterite dispersion, addition of surfactant SDBS (Sodium Dodecyl Benzene Sulfonate) to the dispersion and immersion of vaterite particles in ethanol lowered or prevented crystal transformation because of low solubility constants of vaterite.

Ink-jet printing test was performed with vaterite-coated paper and resulted in high print quality. Bleeding problem did not occur as well as commercial silica coated ink-jet paper, although calcite coated and trial silica coated papers exhibited worse bleeding probably because vaterite has high hydrophilicity that promotes quick absorption of inks inward before spreading laterally on the surface.

References

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Author Biography

Yohta Mori was born in 1979. 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.