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Application of Vaterite-Type Calcium Carbonate Prepared by Ultrasound for Ink Jet Paper

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Abstract. *Vaterite is a crystal polymorph of calcium carbonate that is widely used in various industries, but rarely occurs in nature. This article presents an effective method for application of vaterite-type calcium carbonate as a coating pigment for ink jet paper instead of silica. Vaterite was prepared by mixing and agitating* K_2CO_3 *and* $CaCl_2$ *solutions with an ultrasonic homogenizer. The vaterite crystal stability was examined to achieve vaterite properties appropriate for ink jet application. A high* pH *reduced transformation from vaterite to calcite because of the low solubility constant. Experiments revealed a low water contact angle on our vaterite-coated paper, suggesting high ink jet print quality. Furthermore, although our test calcite-coated and silica-coated samples exhibited bleeding, our vaterite-coated samples matched commercial silica-coated samples in quality, probably, because the large hydrophilicity of vaterite promoted quick inward absorption of inks before they could spread laterally on the surface.* © *2010 Society for Imaging Science and Technology.*
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INTRODUCTION

The quality demanded for printed matter has continued to increase even for home use, with the rapid spread and advancement of digital cameras. The main type of home-use printers for outputting photo-like pictures are compact ink jet printers. However, the characteristics of pictures printed with an ink jet printer are greatly influenced by the characteristics of the paper used. Silica is generally used for ink jet paper as a coating pigment because of its fast ink absorption and resultant high print quality. However, it is costly to produce paper coated with only silica because of its high production cost. Therefore, other kinds of pigments, such as calcium carbonate, have been tried as substitutes.

In some articles, the functionality of calcite-type precipitated calcium carbonate (PCC), as coating pigments for ink-receptive layers, has been discussed in comparison with silica. Trial applications of needle-shaped calcium carbonate to an undercoat layer for higher image densities go back to the late 1980s.[1] PCC generally decreases the ink absorption rate compared to hydrophilic silica pigment for aqueous ink jet inks but not for nonaqueous pigment ink. PCC provides high Bristow absorption coefficients between 0.5 and $5\ \mathrm{ml}/(\mathrm{m}^2\,\mathrm{s}^{1/2})$ for nonaqueous solvents, resulting in good quality for ink jet-recording media.[2] Calcium carbonate has been reported to work well with ink jet print media, even for printing on photograph paper.[3] A coating structure with fine pores prepared from highly porous precipitated silica was compared to a novel deformable PCC structure with relatively high surface area, consisting of porous spherical aggregates covered with small platelike crystals. The dissolved ink dye readily entered the silica interstitial structure but not the PCC structure, suggesting enhanced color density with a reduction in ink demand for the PCC structure.[4]

The effects of amorphous silica and PCC on the print quality of the ink jet paper have been compared as well. The type and mixture proportion of the pigments significantly influenced print characteristics such as wicking, mottling, and strike-through. However, the water absorption characteristics were related to the hydrophobicity/hydrophilicity of the base paper.[5] Through thin layer chromatography, silica-based and specialty PCC coatings were found to fix ink jet dyes through different mechanisms; this was due to different interactions between each pigment's surface and the carboxylic and sulfonic acid groups on the dyes.[6] A new ink fixative, styrene maleic anhydride imide (SMAI), was applied to PCC and polyvinyl alcohol-based ink jet paper as an alternative to the commonly used poly-(diallyldimethyl ammonium chloride) (poly-DADMAC). SMAI showed better print quality, water fastness, and gloss.[7] When comparing PCC and silica, PCC had a better coating color rheology, higher coated paper opacity, and higher optical print density.[8] Ink jet-printed samples exposed to elevated temperatures and humidity maintained a higher ink density with a PCC coating than with a silica coating for dye-based inks. However, the opposite was true for black pigment-based ink.[9]

Improvements in ink jet paper quality have been attempted not only through total pigment replacement, as mentioned so far, but also through pigment substitution or combination, layered structures, and internal loading to base paper. Trial ink jet papers with 50% replacement of silica with PCC or ground calcium carbonate (GCC) have been reported to achieve performances equivalent to commercial products.[10] Pigment particles comprised of an amorphous mixture of calcium carbonate and silica were prepared using an alkali metal silicate solution containing calcium hydroxide particles that react with carbon dioxide. These particles

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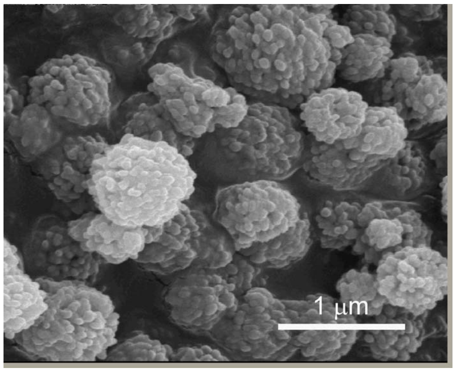

Figure 1. Scanning electron microscopy image of vaterite-type calcium carbonate.

provided a sizing effect, i.e., water repellency, to paper or board and improved the printability for a black ink.[11] A mixture of amorphous silica with calcium carbonate or kaolin with a specific surface area of 60–85 m^2/g has been used for glossy coating.[12] A double-layered coating structure was reported to increase the ink jet paper gloss by more than 60% by applying a plastic pigment to the top coating despite the calcium carbonate and clay in the precoating layer.[13] A top coating layer for ink absorption and fixation functioned well if the undercoat layer contained calcium carbonate of the aragonite or calcite type.[14] Internal loading of PCC to the base paper as well as an appropriate Stöckigt sizing degree adjusted to a less than 3 s on 60 g/m^2 basis also provided excellent ink jet printing properties while improving conveyability without jamming.[15] GCC loading to paper manufactured from recycled pulp containing mechanical pulp showed good ink absorption and high density images.[16]

Synthesis methods for PCC and other pigment complexes have been investigated. A new PCC synthesis method was developed by mixing organophosphonate and aluminum sulfate in a calcium oxide slurry to reduce ink feathering.[17] To stabilize the ink jet printability of the produced PCC agglomerates for matte paper, the carbon dioxide gas flow rate was kept below 30 L/min during the carbonation process.[18] To increase the specific surface area of PCC pigment to more than 60 m^2/g, surface active agents, such as organophosphate, were added to the carbonation process;[19] nanosized PCC that was 15–40 nm in size was produced.[20] Even GCC that was 0.1–1 μm in diameter was cationized in an effort to prevent bleeding.[21] It has been proposed to apply PCC to the manufacture of hollow silica for good ink absorption to take advantage of the reaction process, where a mixture of alkali silicate and PCC aggregates, that is, neutralized to a pH of 7–9 forms silica-PCC complexes, after which the PCC is dissolved by adding an acid.[22]

One of the key factors in developing a suitable ink jet pigment is the fineness of pigment particles; this is because the resultant large surface area adsorbs the ink dyes. Vaterite tends to form aggregate structures consisting of very small primary particles, as shown in Figure 1, which is similar to a silica structure. However, vaterite-type calcium carbonate is rarely used in industry because of its rarity in nature and poor crystal stability. In our previous study, a new method to prepare stable vaterite through simple mechanical agitation was proposed.[23] In this study, vaterite was evaluated as a coating pigment for ink jet in terms of hydrophilicity and control of metastability.

Some articles have focused on vaterite characteristics in terms of its application to ink jet paper. A synthesis method for vaterite from calcium nitrate, urea, and sodium alkylethersulfonate has been reported for coating with poly-(vinyl alcohol).[24] Another method that blows carbon dioxide gas into lime milk for the reaction between carbonate salts and calcium chloride was proposed to manufacture vaterite for ink jet paper.[25] Vaterite can be loaded internally to paper as hollow particles to maintain its high strength and ink absorption capacity.[26] A method has been proposed to develop high vaterite stability during crystal transformation by forming a complex with starch.[27] Our previous report[28] described a new method to stably prepare vaterite through simple mechanical agitation using a double cylinder-type or ultrasonic homogenizer.

EXPERIMENT

Vaterite Preparation in Water

Calcium carbonate was synthesized by quickly pouring a potassium carbonate solution into a calcium chloride solution; the mixture was then agitated in a glass beaker using an ultrasonic homogenizer at 19.5 kHz and 300 W output power (26 mm probe tip diameter, US-300T, Nihonseiki, Japan). The concentration and volume of the salt solutions before mixing were set at 1.0 M and 20 ml, respectively. No surfactants or additives were formulated in those solutions.

In this process, calcium carbonate appeared as a white precipitate immediately after the two salt solutions were mixed. The flask was moved by hand to adequately agitate the mixture into a homogeneous state. After agitation for 2–3 min, the calcium carbonate precipitate was separated from the mixture by centrifugation at 1000 G for 5 min. The supernatant was removed by decantation, and the precipitate was washed thoroughly with water by repeated centrifugation. The precipitate was washed with ethanol and then acetone by centrifugation; it was then dried in an oven at 40°C for 12 h. The powdered calcium carbonate was stored at room temperature in a sample bottle with a screw cap before use. The calcium carbonate yield ranged from 90 to 95%; yield loss mostly occurred due to handling during the recovery and washing processes.

The calcium carbonate obtained was subjected to x-ray diffraction (XRD) measurements in reflection mode using a diffractometer (RINT 2000, Rigaku, Japan) with monochromatic Cu $K\alpha$ radiation at 40 kV and 40 mA. The mass ratios of vaterite to the total calcium carbonate were calculated from the intensity of the XRD peaks for vaterite and calcite according to the equation proposed by Rao.[29] The morphology of the calcium carbonate was observed with a field emission-type scanning electron microscope (SEM);

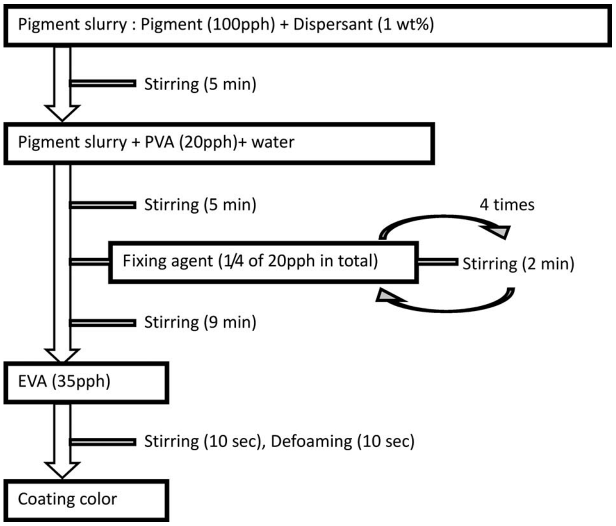

Figure 2. Preparation scheme of coating; "pph" denotes "parts per hundred of pigment."

(S-4000, Hitachi Co., Japan) at 10 kV after platinum sputtering for 120 s.

Stability Test for Vaterite

Because vaterite is thermodynamically unstable, crystal transformation may occur and particle diameter may change in aqueous dispersions when they are prepared for coating. The crystal transformation may also impair the ink jet print quality. The temperature of pigment dispersion during coating often becomes close to 40°C. Thus, it was necessary to examine the stability of vaterite at relatively high temperatures. An important factor that affects the transformation from vaterite to calcite is aqueous solubility. Therefore, stability tests were carried out at high pH conditions, i.e., pH 9, 10, and 11, obtained with sodium hydroxide. Aqueous dispersions of vaterite were incubated in an oven at 40° and 80°C for 1, 3, 6, 12, 24, and 48 h. These samples were analyzed with XRD and observed with SEM

Calcite ratios were calculated from Rao's equation,[29] which is shown as Eq. (1)

$$f_C = \frac{I_{104(C)}}{I_{104(V)} + I_{112(V)} + I_{104(C)} + I_{114(V)}}, \qquad (1)$$

where f_C is the calcite fraction and $I_{104(C)} - I_{114(V)}$ are the XRD peak intensities.

Preparation of Calcium Carbonate-Coated Papers

Figure 2 shows the scheme for preparing coatings from calcium carbonate as a pigment. The coatings were applied with a motor-driven wire bar coater on coated paper to prevent rippling due to swelling from water absorption. The coated paper used as the base paper was for offset printing. The coating layer properties depend on the imperviousness of the base paper and are reflected in the print quality. Vaterite-type calcium carbonate was prepared through the ultrasonic homogenizer method mentioned previously. Calcite-type calcium carbonate (PZ, Shiraishi Kogyo, Japan; hereafter referred to as PCC) and reagent-grade (Wako Pure Chemical Industries, Japan) and aggregate-type (Aerosil 200, Nippon Aerosil, Japan) silicas were also used to prepare coated papers for comparison. Poly-vinyl alcohol and ethylene vinyl acetate emulsions were formulated as binders as well as poly-DADMAC as a fixing agent.

For vaterite, a single coating with 4.0 g/m^2 was not sufficient for complete coverage of fibers on base paper surfaces; consequently, a double coating was performed. The coating weights were 5.4, 8.2, and 5.5 g/m^2 for the calcite, vaterite, and silica coatings, respectively. The fiber coverage by the vaterite double coating was equivalent to that by the silica coating and better than that by the calcite coating according to the SEM observation, although the vaterite coating had a higher coat weight than the others.

Contact Angle Change with Time

The contact angle as it changed with time was measured with an automatic solid/liquid interface analyzing system (Dropmaster 500, Kyowa Interface Science Co. Ltd., Japan). The water droplet volume prior to contact was set to a constant of 0.5 μL. Images of a droplet on paper were automatically recorded 100 ms after contact with a paper surface and continued to be recorded once per second. The contact angle calculation was based on the $\theta/2$ method or circular interpolation. The measured samples were coated papers prepared from vaterite, calcite (PCC), and silica.

Printing Test

A color chart was printed on each prepared coated paper sample with a dye type ink jet printer (Pixus iP7500, Canon); the print was then observed with the naked eye and using an optical microscope (SZH10, Olympus, Japan). The clarity of interspaces between two adjacent solid areas was evaluated to evaluate bleeding and feathering occurrences, although objective quantitative determination could be made with edge acuity methods.

RESULTS AND DISCUSSION

Vaterite Preparation

By using the ultrasonic homogenizer, pure vaterite was prepared as a precipitate successfully by mixing and agitating K_2CO_3 and $CaCl_2$ solutions at room temperature. Homogeneous, high-shear, and constant agitation for mixing solutions of around 1M salt concentration was necessary to prepare pure vaterite, although it was not required to control solution temperature or add any surfactant. Vaterite-type calcium carbonate was prepared mostly as typical spherical aggregates, i.e., secondary particles 0.1–1 μm in diameter, with this method. Particle diameter was evaluated from SEM pictures. All the measured data, including BET specific surface area, are shown in Table I.

Vaterite Stability

Physical energy, such as shear stress or ultrasonic vibration supplied from the ultrasonic homogenizer, seems to stabilize vaterite crystals. Figure 3 shows that vaterite-type calcium carbonate particles were completely transformed into calcite

Table I. Particle diameter and specific surface area (BET) of pigments.

Pigment	Primary particle diameter (nm)	Secondary particle diameter (μm)	BET surface area (m^2/g)
Calcite	200	3–5	10.2
Vaterite	100	1–2	24.6
Silica	50		100

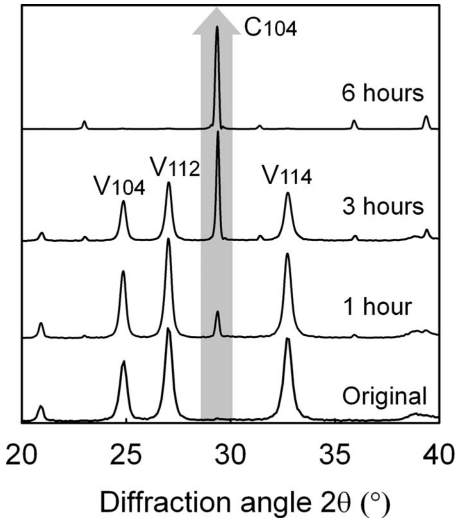

Figure 3. Changes in x-ray diffraction patterns for aqueous treatment at 80°C.

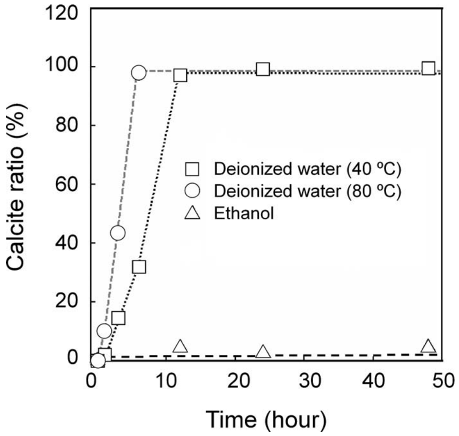

Figure 4. Crystal transformation rates for different temperatures and dispersion media.

after treatment in water for 6 h at 80°C. At higher temperatures, vaterite transformed more easily to calcite, as shown in Figure 4.

Figure 5 shows that vaterite was slightly more stable at the highest pH (pH 11) than at the other two pH levels; this was because the solubility constant of vaterite varies depending on temperature and pH. Therefore, vaterite was remarkably stable in ethanol, as shown in Fig. 4. Thus, the presence of water is necessary for the crystal transformation of vaterite-type calcium carbonate. However, it is known that ambient humidity conditions do not cause crystal transformation probably because aqueous dissolution of the crystal surfaces is necessary for the transformation.[30]

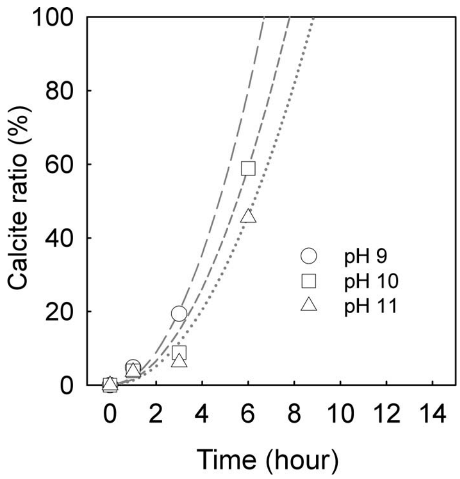

Figure 5. Crystal transformation rate for different pH.

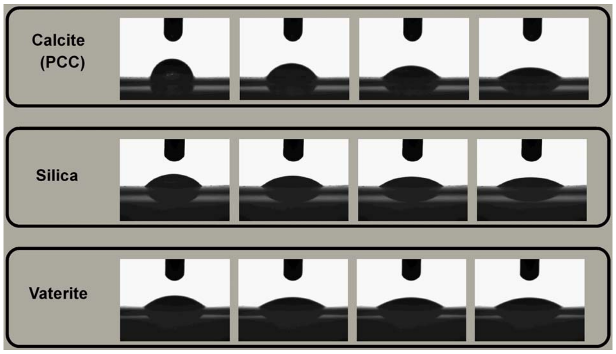

Figure 6. Images of contact angle every 1 s.

Wetting Property of Vaterite-Coated Paper

Vaterite-coated papers were evaluated in terms of ink jet printability. Surface wetting behavior was examined by measuring the contact angle between deionized water and the surface of the papers coated with the three kinds of pigment from the side view; pictures of the water droplets are in Figure 6. Figure 7 shows the changes in the contact angle. When comparing the two carbonates, the lower contact angle for vaterite suggests that vaterite becomes wetted with water easily, which might be due to it having more highly polar surfaces than calcite (PCC). Polarity cannot be evaluated from only the contact angle because porosity and surface roughness affect it.[31] However, all the coated surfaces were not calendered or processed with any smoothing finish; therefore, the surface roughness level is considered to be equivalent. The activation energy of an apparent diffusion coefficient, that is, the rate-determining process for dissolution of solids into water, is 24.38 kJ/mol for vaterite while it is 8–23 kJ/mol for calcite. This difference means that vaterite has a higher solubility than calcite,[32] suggesting a higher hydrophilicity for vaterite.

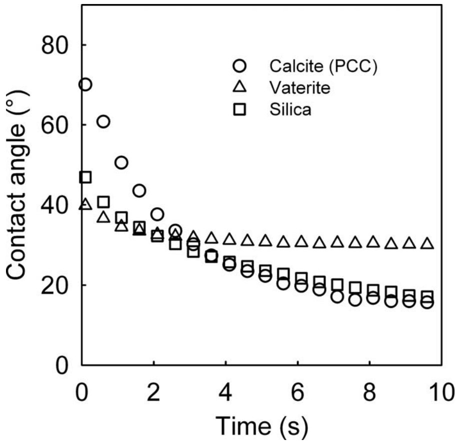

Figure 7. Contact angle change with time.

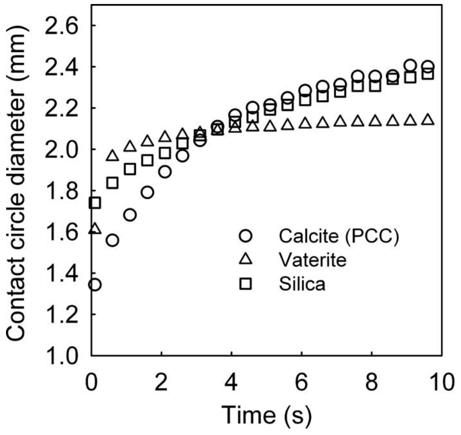

Figure 8. Contact circle diameter changes with time.

Figure 8 shows that the radius of the contact circle for silica increased greatly, while the radius for vaterite leveled off much earlier. This means that on silica coating surfaces, a water droplet tends to spread laterally along the surface more easily than on vaterite. The capacity of the vaterite coating layer to absorb water may be smaller than that of the silica coating layer.

Printing Test

Printed samples were scanned with an image scanner (GT-X900, EPSON, 1200 dpi color mode). Figure 9 shows the printed images of the color chart in order of bleeding severity, although the order of the print quality ranking may alter if color gamut and optical density are taken into account.

The original image data had white lines separating color squares. These white lines were not completely reproduced on the base, calcite-coated, or silica-coated papers. In contrast, the lines clearly showed on the vaterite-coated and commercial silica-coated papers. These two papers had good color optical density as well. White lines appeared clearly even on the copy paper. For this copy paper, the inks were assumed to not spread over the surfaces because of adequate water repellency and a polymer barrier film to avoid excessive pore penetration, which leads to bleeding. The very high ink jet print quality realized by vaterite seems to be due to its high hydrophilicity, which promotes the quick absorption of inks inward before it spreads laterally on the surface.

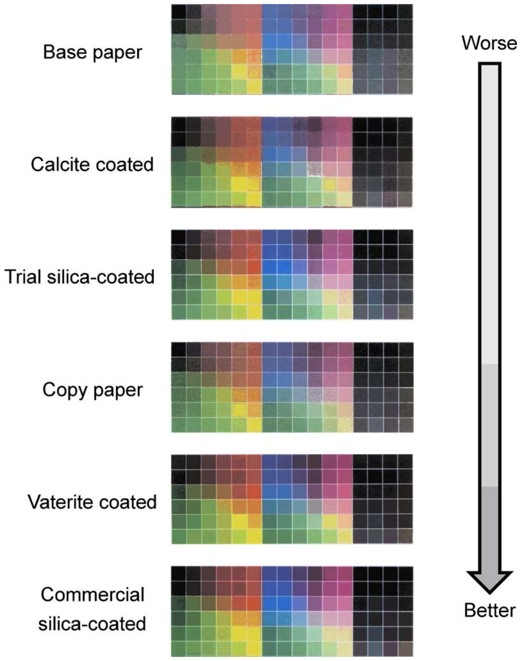

Figure 9. Test prints of color chart for different types of trial ink jet papers.

CONCLUSION

Although vaterite-type calcium carbonate is apt to transform gradually to calcite in water, a high *p*H for aqueous vaterite dispersions prevents crystal transformation because of the low solubility constants of vaterite under this *p*H condition. This suggests that vaterite can be applied as a coating pigment to ink jet paper when formulated in basic aqueous media.

Measurement of the contact angles between water and the trial ink jet paper surfaces showed that hydrophilicity was higher for vaterite than for calcite and was equivalent to that for silica. An ink jet printing test for the vaterite-coated paper resulted in high print quality. Neither bleeding nor feathering problem occurred, affording quality comparable with that of commercial silica-coated ink jet paper, although our calcite-coated and silica-coated samples exhibited bleeding. This result was probably because vaterite has high hydrophilicity, which promotes quick absorption of inks inward before they can spread laterally on the surface.

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