PEER-REVIEWED PAPER COATING

Application of spherical hollow calcium carbonate particles as filler and coating pigment

Toshiharu Enomae and Koji Tsujino

ABSTRACT

Spherical hollow particles of calcium carbonate were successfully obtained by the interfacial reaction method at high yields. Primary particles of 50 nm in diameter in mixed crystal forms of calcite and vaterite were found to comprise the spherical hollow particles as the secondary structure. As filler for internal loading to paper, the spherical hollow particles maintained sheet density of handsheets with only minimal density reduction and increased specific light scattering coefficient effectively probably because of their porous structure. This optical effect was higher than conventional ground calcium carbonate, but lower than the commercial coagulated scalenohedral particles with a large surface area. In the print quality evaluation of coated paper containing the spherical hollow particles, more addition of the particles provided higher ratios of wax ink transfer from ribbon to paper in thermal wax-transfer printing. The efficient thermal insulation due to the porous structure was expected to maintain the temperature of the heated head high as well as the effect of higher smoothness with more addition of the spherical hollow particles.

Application: Spherical hollow PCC, a novel pigment, produced by the interfacial reaction method gives high specific light scattering coefficient and thermal insulation advantageously when used as a filler or coating pigment.

Recently, there have been emerging new technologies for producing precipitated calcium carbonate (PCC) and their effective usage as filler or coating for papermaking has been sought to take advantage of its functionality. Production of PCC at satellite or on-site plants started in North America in 1985 in conjunction with the shift from acid to alkaline papermaking [1, 2]. The cost of producing PCC at satellite plants can be reduced by sharing paper mill resources, such as energy, water and carbon dioxide which mills normally vent. There is a further potential to reduce costs as the process eliminates certain transportation and drying expenses. Regarding qualitative characteristics of PCC by on-site production, Gill [3] reported that it provides improved optical properties, such as brightness and opacity, in paper over other forms of calcium carbonate and that it enhances filler retention due to the cationic surface charge.

In light of paper recycling and environmental protection, new on-site PCC processes have been created. A large amount of inorganic components emitted from recycling processes originates mainly from coating pigments and internal loading fillers. As an extension of on-site technology, a technique for producing calcium carbonate filler, including recycled deinking residues at 30 % of the product, has been realized in Germany in 1998. The satellite plant was producing about 60,000 ton of PCC annually. The product showed a relatively high opacity but a poor brightness when compared to regular PCC. Nanri [4, 5] reported about a new process to produce high quality calcium carbonate as a paper filler using the causticization step from green liquor to white liquor in the kraft pulping process. The author reported as a main advantage that the lime-kiln cycle can potentially become shortened, or even eliminated, and the separation of slaking of quick lime from causticizing of the slaked lime enables to control PCC particle shape. As a result, one can expect contributions to saving fuel oil and reducing the discharge of carbon dioxide gas.

One of the disadvantages of recycled paper when compared to paper from virgin pulp is the difficulty to gain high brightness. To improve brightness, papermakers introduce strong surfactants in floatation, increase intensive bleaching and so on. But, these processes demand more water and energy, adversely affecting the environment.

Another possible idea proposed here is to hide gray appearance with an efficient coating or internal loading by utilizing high-opacity PCC pigment. Hollow spheres made of calcium carbonate could be suitable for this purpose because hollow structure scatters more light, resulting in high brightness and opacity. Our work aimed at this approach. We compared spherical hollow particles of calcium carbonate with different types of calcium carbonate, considering both their fundamental properties and their application to internal loading and pigmented coating. In paper loading application, brightness and opacity were examined, while in the coating application, we investigated printing properties for thermal wax-transfer printing, as well as optical properties.

For the interfacial reaction method to make spherical hollow particles of calcium carbonate, Nakahara [6] originally gave the associated process dynamics. Basically, the experimental processes Nakahara created is just the same with the method we adopted except that Nakahara used benzene, seen as cancer-causing, for dispersing medium instead of toluene we adopted. **Figure 1** represents the mechanism predicted by that author. At surfaces of emulsified droplets, potassium carbonate and calcium chloride react to form a sphere with a hollow structure. Spherical morphology of on-site PCC and its properties was reported [7] as a high-surface-area scalenohedral type, but the spherical hollow PCC we adopted is advantageously lightweight due its hollow structure. When compared to organic hollow latex pigment [8 -10], the spherical hollow PCC gives higher light scattering due to its higher refractive index, while it has a naturally decomposition property. These are the reasons why we adopted the Nakahara method.

EXPERIMENTAL

Preparation of Spherical Hollow Particles of Precipitated Calcium Carbonate

We prepared precipitated calcium carbonate by the interfacial reaction method described by Nakahara. First, a surfactant (polyoxyethylene sorbitan monoolate, Tween-80) was dissolved in toluene at 0.5 wt. %. Second, a potassium carbonate solution of 1 mol/L was added to the toluene solution in a Water/Oil volume ratio of 3:7. Then, this mixture was emulsified by ultrasonic irradiation (Ultrasonic generator U0300FB, 26 kHz / 300 W, Kokusai Electric, Japan) for 10 min and then homogenizing with a homogenizer (Physcotron NS-20, Nihon Seimitsu, Japan) for 10 min at 15,000 min^{-1}. Last, the emulsion was poured into a stirred calcium chloride solution of 0.2 mol/L that contained twice as many calcium as carbonate ions. The amount of prepared calcium carbonate in one batch was 0.62 g, but when more pigment is necessary like for paper loading experiment, the scale was enlarged. Solid pigment was recovered by centrifugal separation. The mean yield was about 80 percent.

Commercially Available Calcium Carbonate

The prepared spherical hollow particles of calcium carbonate were compared to several types of commercially available calcium carbonate listed in **Table I**. Calcium carbonates A, B, C and D were Softon 1500, Whiton P-50, Whiton H and PCX-850, respectively; all manufactured by Shiraishi Kogyo Kaisha, Ltd., Japan. Calcium carbonate D was a coagulated type of scalenohedral particles, as can be seen in the picture of the loaded sheet, Fig. 4(D). Mean particle diameter was estimated approximately based on visual inspection of scanning electron microscopy (Hitachi S-4000, Japan) images. The specific surface area was measured by the nitrogen adsorption method (Coulter Omnisorp 100CX, USA). Brightness was measured according to the TAPPI Standard Test Method T-534.

Loading to Paper

Handsheets of paper were prepared according to TAPPI Standard Test Method T-205. The prepared spherical hollow particles of calcium carbonate were added to a pulp stock of bleached kraft hardwood at 30 m/m % on dry pulp. Calcium carbonate D was also added to another stock for comparison. As well, unloaded handsheets were prepared. In advance, cationic polymer, polyamideamine-epichlorohydrin resin (WS-570, Japan PMC Co., Japan) was added at 0.1 m/m % on dry pulp to increase the retention of calcium carbonate during stirring the slurry at 800 rpm with a three rotor blade mixer.

Loaded Handsheet Properties

The samples were conditioned at 20 °C and 65 % RH for more than 24 hours. The apparent sheet density was calculated from basis weight and thickness with 5 sheets of every sample. Optical properties, namely, brightness and specific light scattering coefficient were determined according to TAPPI Standard Test Method T-452. Two separate trials were made and in either trial a blank sample was prepared without calcium carbonate from hardwood bleached kraft pulp beaten with a PFI mill to 450 ml CSF.

Paper Coating

The spherical particles were applied to coating. Fine paper of 63 g/m^2 in basis weight was coated at about 28 g/m^2 in coat weight with three of coating colors at 55 % solids formulated as listed in **Table II**. The coatings were applied with a motor-driven drawdown type, YOA-B, Yoshimitsu Seiki Co. Ltd., Japan at a speed of 3 m/min, followed by hot air drying for one minute. The samples were all uncalendered. Calcium carbonate A is originally designed for internal loading. However, it was also used as base pigment for coating so that differences in smoothness would be minimal, as much as possible.

Coated Paper Properties

The samples were conditioned at 20 °C and 65 % RH for more than 24 hours. The Bekk smoothness of the coated papers was measured. Brightness and opacity were calculated only with the coating layers according to the equation derived by Robinson [11] and Hamada [12] on the basis of the Kubelka-Munk equation. To evaluate print quality by thermal wax-transfer printing, isolated dots were printed for single dot characterization and halftone dots (i.e., a checkered pattern of every other dot) were printed at several electric powers for heating the printer head to measure optical print density. A printer, MD-5500, Alps Electric Co. Ltd., Japan, was used with a black-ink ribbon in the wax-transfer mode. The dots were observed with a stereomicroscope, SZH10, Olympus Optical Co., Ltd., Japan.

RESULTS AND DISCUSSION

Characterization of Spherical Hollow Particles of Calcium Carbonate

Figure 2-a is a scanning electron micrograph of the spherical particles of calcium carbonate prepared in this work. The mean particle diameter was a little less than 2 μm in appearance including many small particles around 0.5 μm. **Figure 2-b** shows a close-up of the particle surface. The surface appears to be closely packed with primary scalenohedral (spin-shaped) and rhombohedral (cubic) particles both 50 to 100 nm in diameter, as well as bent-string-shaped particles ca 50 nm in diameter and ca 300 nm long (not in this picture).

To obtain spherical particles at high yields, the concentration of surfactant (Tween-80) was the most important factor because it is related to the stability of a potassium carbonate / toluene emulsion. At 1.5 wt. %, an excess of the surfactant caused stability of the emulsion to be lost, manifested by large drops of separate phases of toluene and potassium carbonate solution. Under this condition, fine primary particles were not observed. Instead, much large squared platelets as primary particles comprised sphere-like aggregates 3 to 5 μm in diameter. Surfactant added at 1.0 % and at between 0.5 and 0.8 % gave about 30 % and 95 % of spherical particles, respectively.

Agitation intensity during emulsification had important effects on particle size distribution of spherical particles. Homogenization at 15,000 min^{-1} increased the ratio of the spherical particles less than 1 μm in diameter up to about 20 %. Ultrasonic irradiation cannot render the particle diameter any more, but rather relatively large particles to 3 μm or less.

There are three crystal forms for calcium carbonate; calcite, aragonite and vaterite. Vaterite is not usually synthesized in reactions of aqueous solutions at room temperature and at atmospheric pressure. The interfacial reaction method, however, provided appreciably high percentage of vaterite, the rest of which was calcite as shown in **Figure 3**. In this X-ray diffraction pattern, some peaks correspond to pure calcite, but other peaks are all attributed to those of vaterite. According to Nakahara [13], the vaterite-to-calcite ratio can be about 50 %, but it depends on the concentrations of calcium chloride and potassium carbonate with their optimum concentrations to obtain the maximum ratio. These concentrations have been reported to affect also the synthesis ratio of spherical particles. Nakahara[3)] predicted that the surface energy of spherical particles was associated with the mechanism. External surfaces were hydrophobic and internal surfaces were hydrophilic, as indicated in terms of immersion heat. This is probably because the two-sidedness of the interfaces aligns calcium carbonate particles. The surface energy is considered to affect paper properties, such as wettability and water or oil penetration.

Properties of Handsheets Loaded with Spherical Hollow Particles of Calcium Carbonate

Table III shows the basis weight, density, brightness and light scattering coefficient of handsheets loaded with calcium carbonate; one loaded with the spherical particles; the next with commercial calcium carbonates; and the rest are unloaded. The density of paper loaded with the spherical particles was lower than that of the unloaded paper. This is often the case with filler loading because of acting as obstruction to interfiber bonding, but was higher than that for calcium carbonate D. Optical properties vary so easily among pulps from batch to batch that it is difficult to distinguish small difference in specific light scattering coefficient from separate trials, even between unloaded pulps. Therefore, we compared the specific light scattering coefficients among samples form the same pulp to evaluate the effect of calcium carbonate on optical properties. Uncalendered handsheets, in particular, become bulky with increasing loading though fillers have higher density than fiber. Bulkier sheets with smaller area of interfiber bonding inevitably scatter more light and give higher scattering coefficients. **Table IV** shows a decrease in density and an increase in specific light scattering coefficient for the calcium carbonate loaded handsheets. The spherical particles kept sheet density high and increased specific light scattering coefficient. Among ground calcium carbonates A, B and C, carbonate A decreased sheet density only slightly and increased light scattering coefficient, presumably due to its small particle size. Carbonates B and C showed moderate effect on light scattering coefficient. Calcium carbonate D not only reduced density the most, but it also increased light scattering coefficient. It is probably because its bulky structure caused loose interfiber bonding considering the particle shape like a sea urchin (see **Fig. 4(D)**) .**Figure 4** shows scanning electron micrographs of sheet surfaces loaded with calcium carbonate of the spherical particles and A to D. Spherical particles (S) were observed to distribute evenly in the sheet on the whole though this micrograph shows an aggregate. The spherical particles, as seen in the micrograph, included cubic particles that were generated in the synthesis reaction perhaps due to an unpredicted deviation from the optimum condition. Fine particles of A were attached to fiber surfaces, but there were, though rarely, large particles 10 μm in diameter at fiber crossings. Even larger particles of B and C were observed settled as surrounded by fibers. More particles of D were attached on fiber surfaces than at fiber crossings. The characteristic shape of the secondary aggregate like a sea urchin gives the ease with which the particles stick to fiber surfaces mechanically.

Properties of Paper Coated with Spherical Calcium Carbonate Particles

Figure 5 shows a scanning electron micrograph of a surface of paper coated with Color 3 containing the spherical particles at one third of the total pigment by weight. The particles are observed to keep their shape after application and drying. **Table V** shows properties of the coated paper. ISO 85 degree gloss is different from TAPPI gloss on the point that the former adopts a parallel beam, the smaller receptor window, and so on. However, an angle of 85 degrees is useful to distinguish low-gloss paper because it gives higher gloss values than conventional 75 degrees. Coated papers 1, 2 and 3 were prepared with Colors 1, 2 and 3 as shown in Table II, respectively. The particles of the spherical PCC were larger, by visual inspection of SEM picture, than common PCCs for coating in the diameter range of about 0.5 μm, but the spherical particle increased surface smoothness presumably because the spherical particles tended to align with a flat surface formed due to their shape and no irregularly large particles protruding above the surface contained, more easily than ground calcium carbonate A with a similar mean diameter. Brightness of both the coated paper and the coatings was increased by addition of the spherical particles. **Figure 6** shows that brightness of the spherical particles was much higher than calcium carbonate A because they were synthesized from pure chemicals with an infinitesimal impurity that looks gray. This is considered to be the main reason for the coating brightness enhancement. The specific light scattering coefficient also increased with the spherical particles due to their porous structure. This finding suggests that the spherical particles are promising for coating use although attention must be paid also to coating rheology.

While considering application of the coated paper to printing, paper for a variety of printing methods are worth investigating. The possible thermal insulation due to the hollow structure is a unique feature to potentially enhance thermal wax-transfer printing. In a thermal wax-transfer printer, isolated single dots were printed on the coated paper in black. **Figure 7** shows magnified single dots photographed by a stereomicroscope. A hundred dots were randomly chosen for coating made from each spherical particles ratio to conduct dot quality analysis. **Figure 8** shows the mean values of area, perimeter and degree of circularity per dot. Increased area and perimeter with increasing spherical particles ratio mean that larger amounts of wax ink transferred to paper when more spherical particles were formulated into the coating. Degree of circularity, calculated according to Equation (1), represents how close to a perfect circle the dot is. The value ranges from 0 to 1, and a value of 1 stands for a perfect circle. As can be seen in **Fig. 7**, the dot shape was always longer in the sub-scan (paper feed) direction. The degree of circularity was not dependent on the spherical particles ratio.

$$DC = \frac{4\pi A}{P^2} \qquad \cdots\cdots \quad (1),$$

where DC is the degree of circularity, A is the dot area and P is the dot perimeter.

Figure 9 shows images of half-tone dots printed on the coated papers by the thermal wax-transfer printer at the maximum electric power output of 0.29 W for heating the thermal head. It was found that more addition of spherical hollow particles provided a larger area of wax ink transfer. **Figure 10** shows the optical density of the printed surfaces as a function of electric power output. The optical density increased with an increase in formulated amount of the spherical particles. This can be because efficient thermal insulation due to the porous structure maintained the temperature of the heated head and gave high ratios of wax ink transfer from the ribbon to paper. The ink transfer ratio typically improves, primarily by high thermal conductivity and secondarily by high surface smoothness. With regard to smoothness, coated 1 was a little rougher, but coated 2 and coated 3 was not different significantly at the 95 % confidence level. Measuring exact values of thermal conductivity to distinguish the three sorts of coated paper was very difficult, and no significant difference was detected even in the quantitative test. However, the tendency for the optical density to increase with spherical particles addition is likely to be due to thermal insulating property typical of spherical particles. Furthermore, lipophilic surfaces of the spherical hollow particles might permit diffused wax ink spread over well.

CONCLUSIONS

Spherical hollow particles of precipitated calcium carbonate were successfully obtained by the interfacial reaction method at high yields. Primary particles of 50 nm in diameter in mixed crystal forms of calcite and vaterite were found to comprise the spherical hollow particles. As a filler for internal loading to paper, spherical hollow particles maintained sheet density of handsheets with only minimal density reduction and increased the specific light scattering coefficient probably because of their porous structure. The contribution to optical sheet properties was greater than with conventional ground calcium carbonate, but lower than the commercially coagulated scalenohedral PCC particles with a large surface area. In the print quality evaluation of coated paper containing spherical hollow particles in its coating, more addition of the particles provided higher ratios of wax ink transfer from ribbon to paper in thermal wax-transfer printing. The efficient thermal insulation due to the porous structure was expected to maintain the temperature of the heated head high, as well as provide higher smoothness with more addition of the spherical hollow particles. **TJ**

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REFERENCES

1) Duncan, P., *Pulp Paper Intl.*, 37(5): 29(1995)

2) Patrick, K. L, *Pulp and Paper*, 69(5): 141(1995)

3) Gill, R. A., *Pulp Paper Can.*, 91(9):T342(1990)

4) Nanri, Y., , *Proceedings of 2000 JAPAN TAPPI Annual meeting*, Japan TAPPI, Tokyo, Japan, p. 607

5) Goto, H., Kanai, K., Konno, H. Nanri, Y. and Takahashi, K., *Proceedings of the 68th pulp and paper research conference*, Japan TAPPI, 80(2001)

6) Nakahara, Y., Tazawa, T. and Miyata, K., Nippon Kagaku kaishi, *Chemical Society of Japan* 1976(5): 732 (in Japanese)

7) Passaretti, J. D., Young, T. D., Herman, M. J., Duane, K. S. and Evans, D. B., *TAPPI J.* 76(12): 135 (1993)

8) Hamada, H., Enomae, T., Onabe F. and Saito Y., *Japan TAPPI J.*, 55(11): 79(2001)

9) Rennel C. and Rigdahl M., *Colloid and Polymer Science*, 272 (9): 1111 (1994)

10) Lepoutre P. and Alince B., *TAPPI J.* 64 (5): 67(1981)

11) Robinson, J. V., *TAPPI J.* 58(10): 152(1975)

12) Hamada, H., Enomae, T., Onabe, F. and Saito, Y., *Proceedings of Pre-symposium of the 10th ISWPC*, Korea TAPPI, Seoul, Korea, p. 309(1999)

13) Nakahara, Y., Funtai Kogaku kai-hi *Journal of the Society of Powder Technology*, Japan, 32(2): 97(1995) (in Japanese)

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INSIGHTS FROM THE AUTHORS

Why did you choose this topic to research? ***Because lightweight pigment with a high light scattering coefficient allows low brightness pulps and saves weight of coated paper.***

How does this research either complement and support previous research you (or others) have done, or how does it differ from previous research? ***A new crystal form of calcium carbonate was applied for paper coating to expect new surface properties.***

What was the most difficult aspect of this research and how did you address that? ***Production cost is the most difficult problem and partial formulation was tried to evaluate its effect.***

What did you personally discover from this research? What was most interesting or surprising about your findings? Thermal insulation of the spherical hollow pigment can be utilized for thermal-transfer printing.

How might mills benefit from or use this information? ***Alternation of surface property of coated paper is potential to extend products to applications other than conventional printing.***

What's the next step? ***Printability for ink-jet recording is the next target of this pigment and the evaluation is now underway.***

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I. Properties of spherical hollow particles and commercially available calcium carbonate used

Kind of calcium carbonate	Type	Mean particle diameter, μm	Specific surface area, m^2/g	Brightness, %
Spherical hollow particles	PCC [a]	3.0	10.4	98
A	GCC [b]	1.5	3.0	96
B	GCC	3.2	1.6	96
C	GCC	5.0	1.2	96
D	PCC	3.5	8.9	98

[a] Precipitated Calcium Carbonate [b] Ground Calcium Carbonate

II. Formulation of coating colors

Ingredient	Formulated amount, pph		
	Color 1	Color 2	Color 3
Calcium carbonate A	100	83.3	66.7
Spherical hollow particles	0	16.7	33.3
Dispersant	0.4	0.4	0.4
SB-latex	15	15	15

III. Physical and optical properties of calcium carbonate loaded handsheets

Kind of calcium carbonate	Basis weight, g/m^2	Density, g/cm^3	Retention, %	Brightness, %	Specific scattering coefficient, m^2/kg
------Trial 1 ------					
Spherical hollow particles	69.4(0.8)	0.622(0.005)	20(5)	78.4*(1.0)	37.4(1.2)
A	70.7(1.2)	0.623(0.003)	25(1)	81.2(1.2)	41.1(0.7)
B	74.0(0.9)	0.617(0.002)	38(2)	83.2(1.4)	36.8(1.5)
C	76.0(1.1)	0.620(0.003)	49(3)	81.1(2.0)	35.8(1.5)
Unloaded	68.0(1.2)	0.633(0.012)	-	80.3(1.4)	35.7(1.5)
------Trial 2 ------					
Spherical hollow particles	65.9(2.8)	0.675(0.005)	23(3)	87.0(1.0)	35.1(1.2)
D	65.6(1.3)	0.659(0.003)	19(1)	82.5(1.7)	43.9(2.4)
Unloaded	62.0(0.5)	0.684(0.005)	-	79.0(1.1)	32.6(1.9)

(Values in parentheses indicate 95 % confidence level.)

* Irregularly low due to mixed-in iron rust

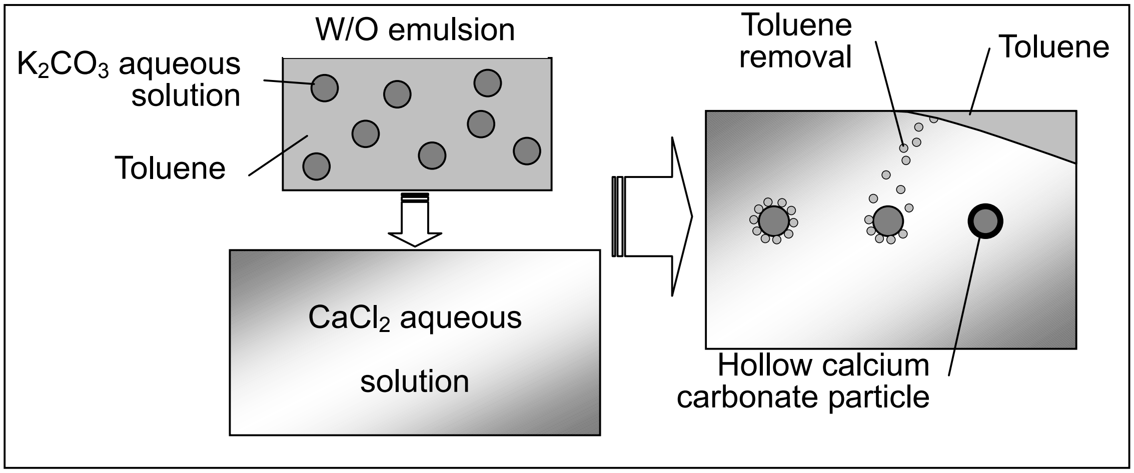
IV. Filling effect of calcium carbonate

Filler type	Decrease in sheet density, g/cm^3	Increase in specific scattering coefficient, m^2/kg
Spherical hollow particles	0.010	2.1
A	0.010	5.4
B	0.016	1.1
C	0.013	0.1
D	0.025	11.3

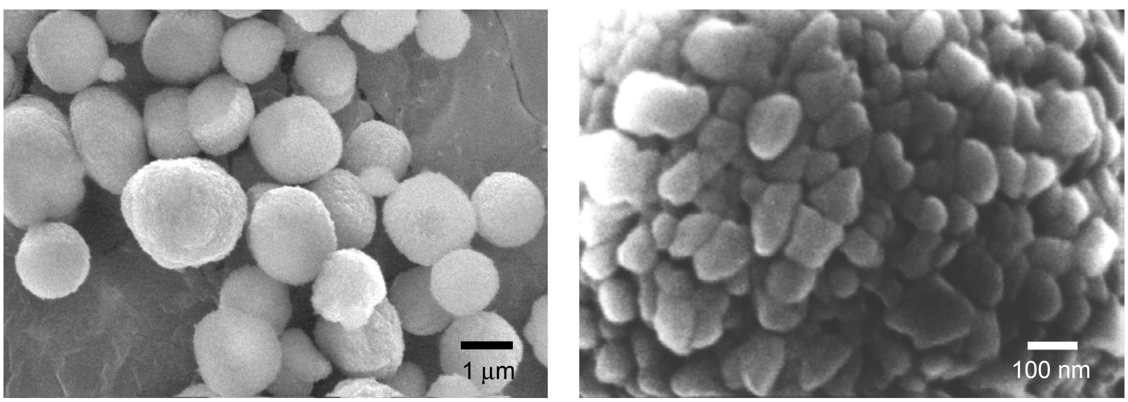
V. Physical properties of coated paper

Property	Kind of coated paper		
	Coated 1	Coated 2	Coated 3
Mean coat weight, g/m^2	29.5(6.0)	27.9(3.7)	29.23.9 ()
Bekk smoothness, s	42(10)	63 (12)	68 (12)
Optical properties of coated paper			
- Brightness, %	80.7(0.0)	81.3(0.0)	82.3(0.0)
- Opacity, %	90.4(0.0)	90.0(0.0)	90.4(0.0)
- ISO 85º gloss, %	8.3(0.4)	9.8(0.7)	8.8(0.5)
Optical properties of only coating layer			
- Brightness, %	80.6 (2.4)	83.8(2.1)	86.8(1.7)
- Specific light scattering coefficient, m^2/kg	24.8(6.2)	25.6(4.4)	33.8(4.6)
Thermal conductivity, W/(m・k)	0.58	0.68	0.58

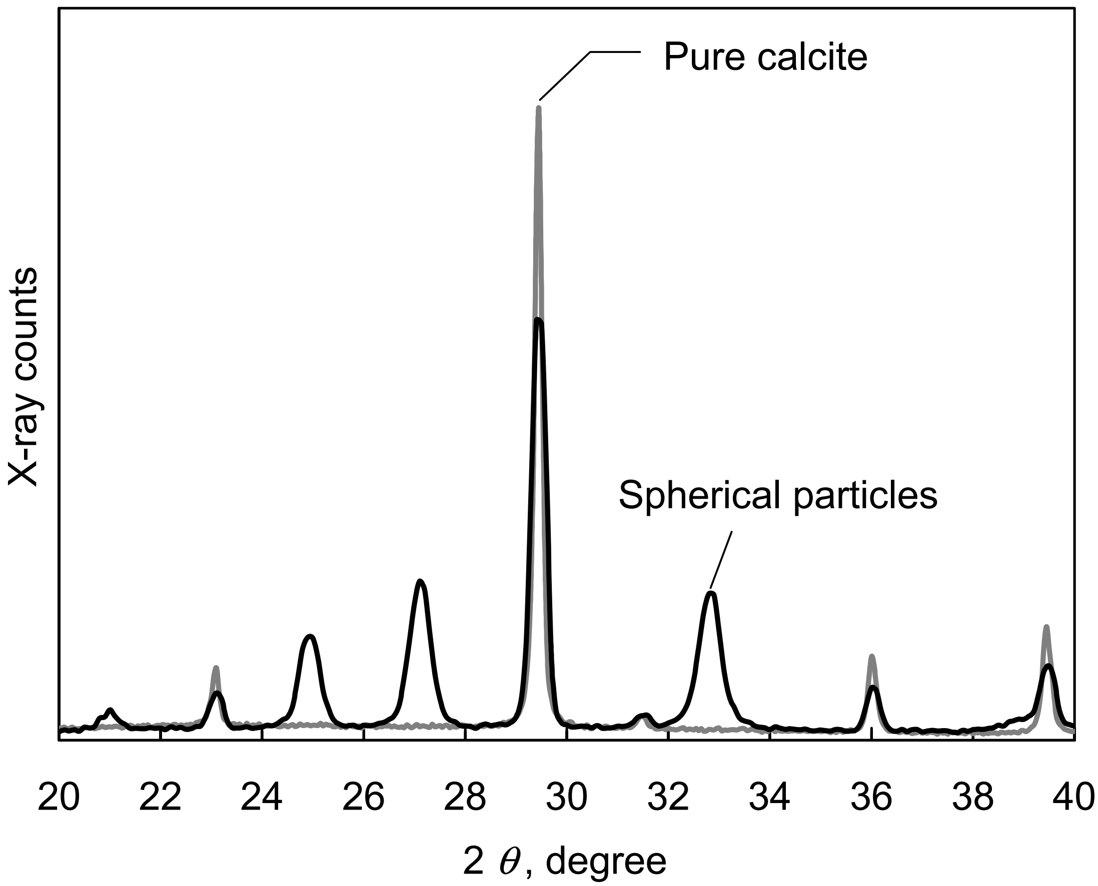
(Values in parentheses indicate 95 % confidence level.)



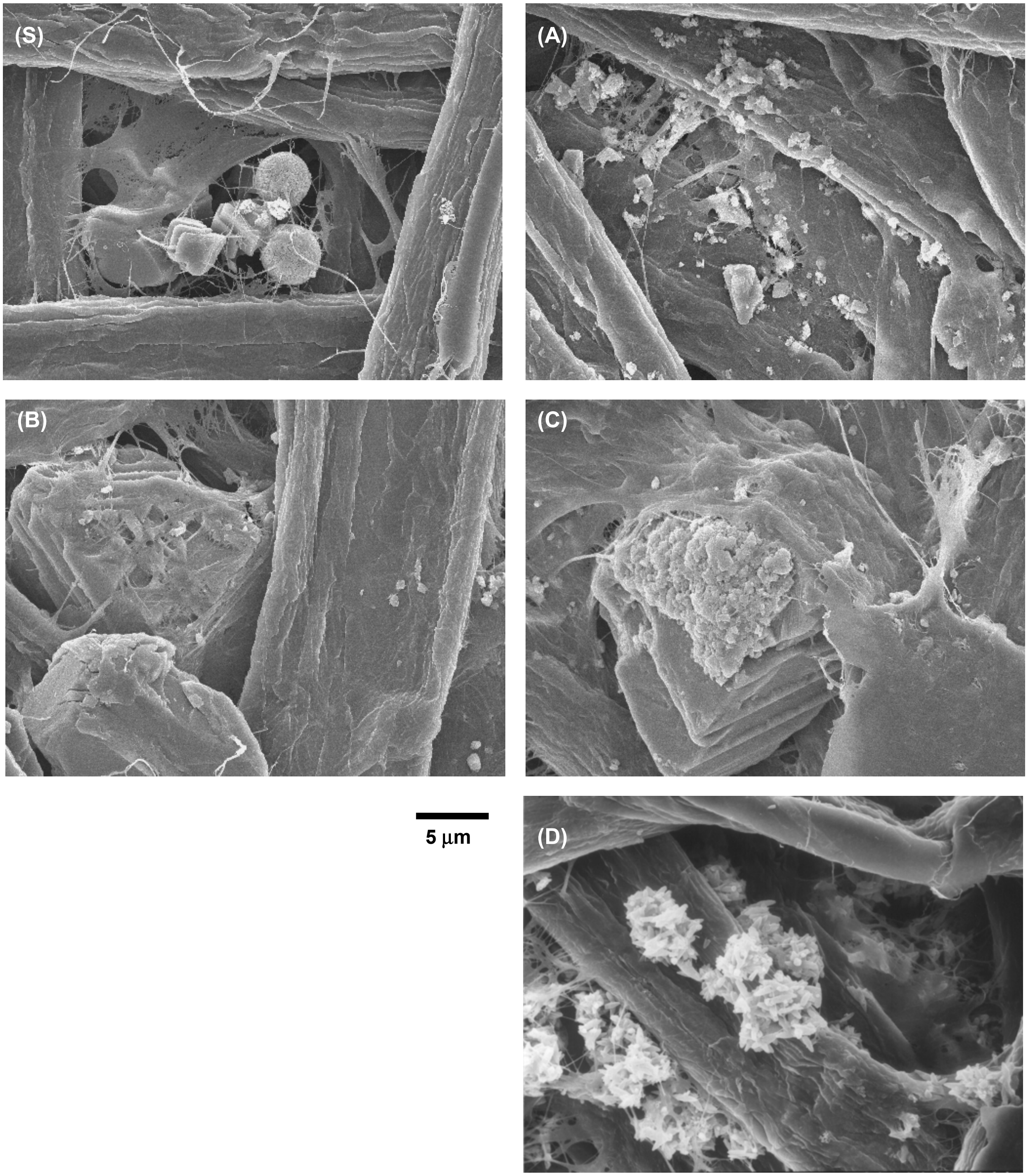
1. Predicted mechanism to produce hollow calcium carbonate particles by the interfacial reaction method.



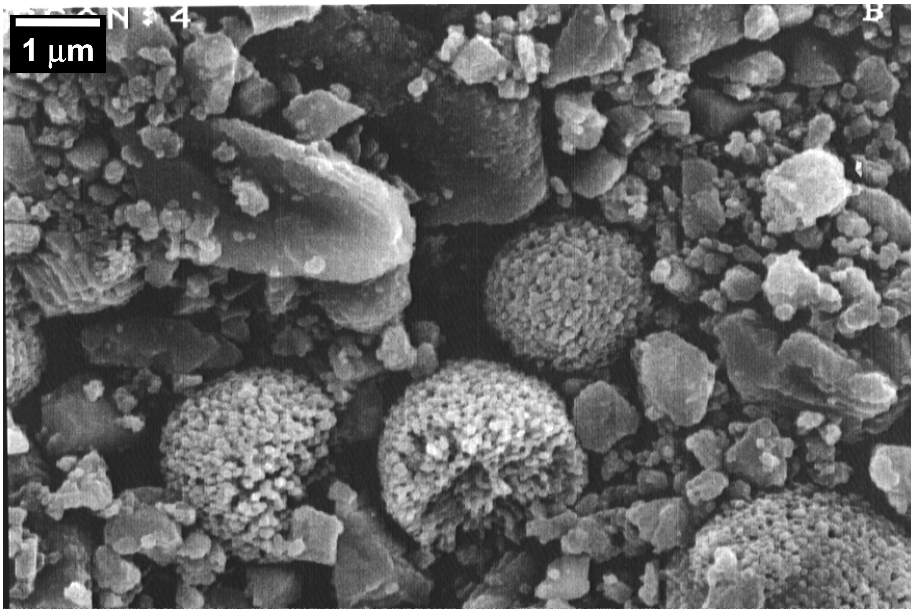
2. Scanning electron micrographs of spherical particles of calcium carbonate prepared by the interfacial reaction method (a) and a close-up of the particle surface (b).



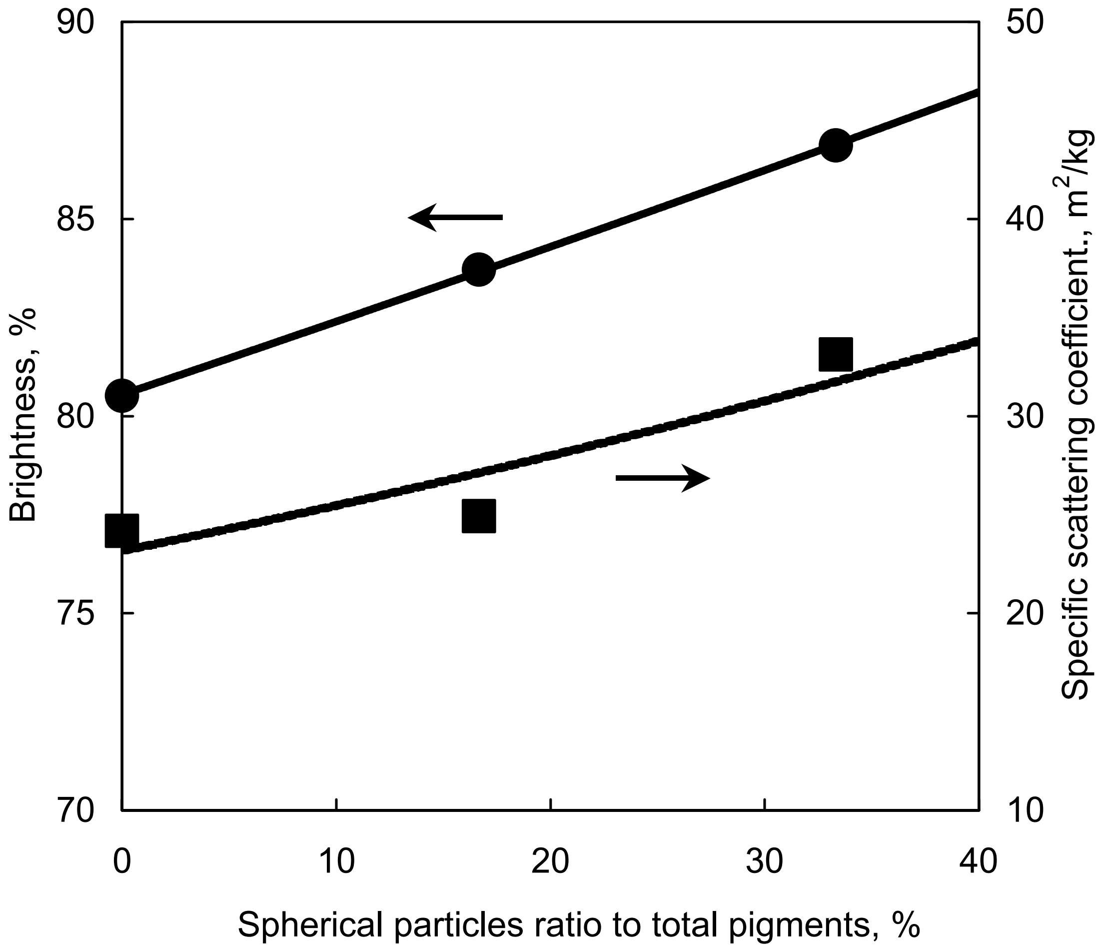
3. X-ray diffraction patterns of the spherical particles of calcium carbonate and pure calcite.



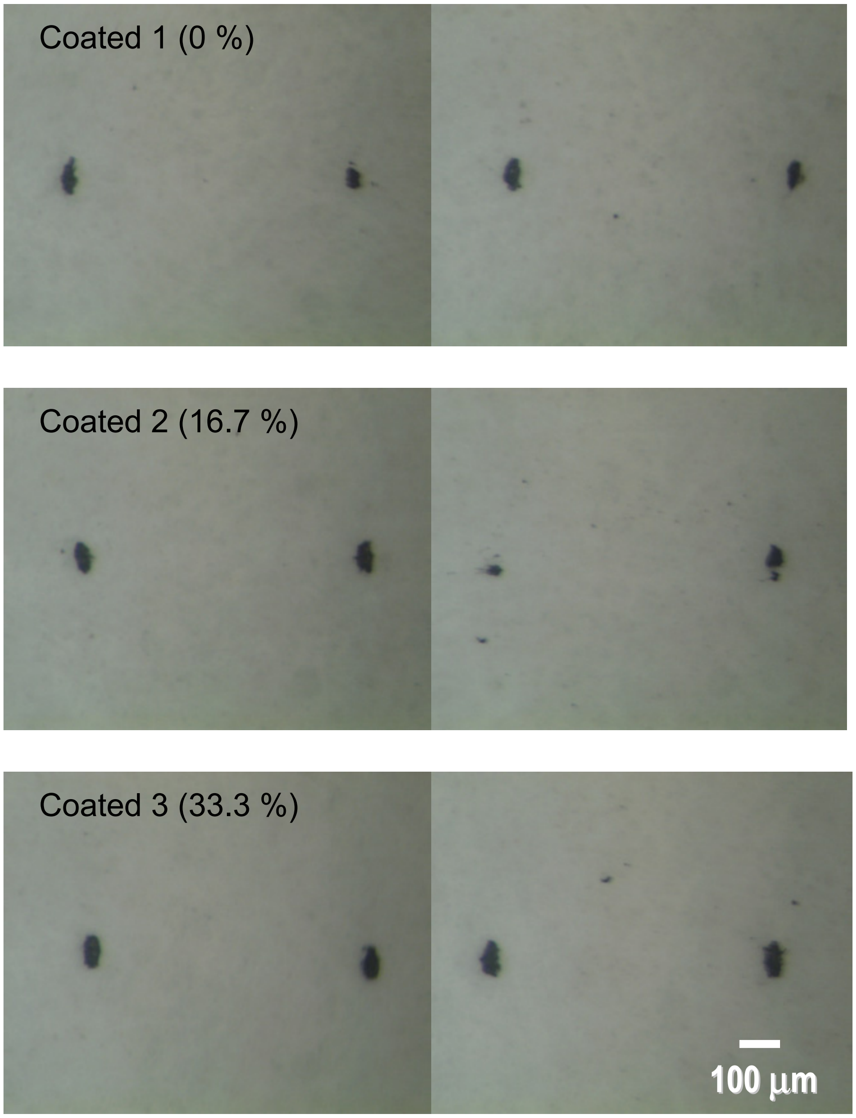
4. Scanning electron micrographs of a surface of a handsheet loaded with calcium carbonate. The loaded filler type is spherical particles S prepared in this work, ground calcium carbonates A, B and C, and coagulated type of precipitated calcium carbonate D.



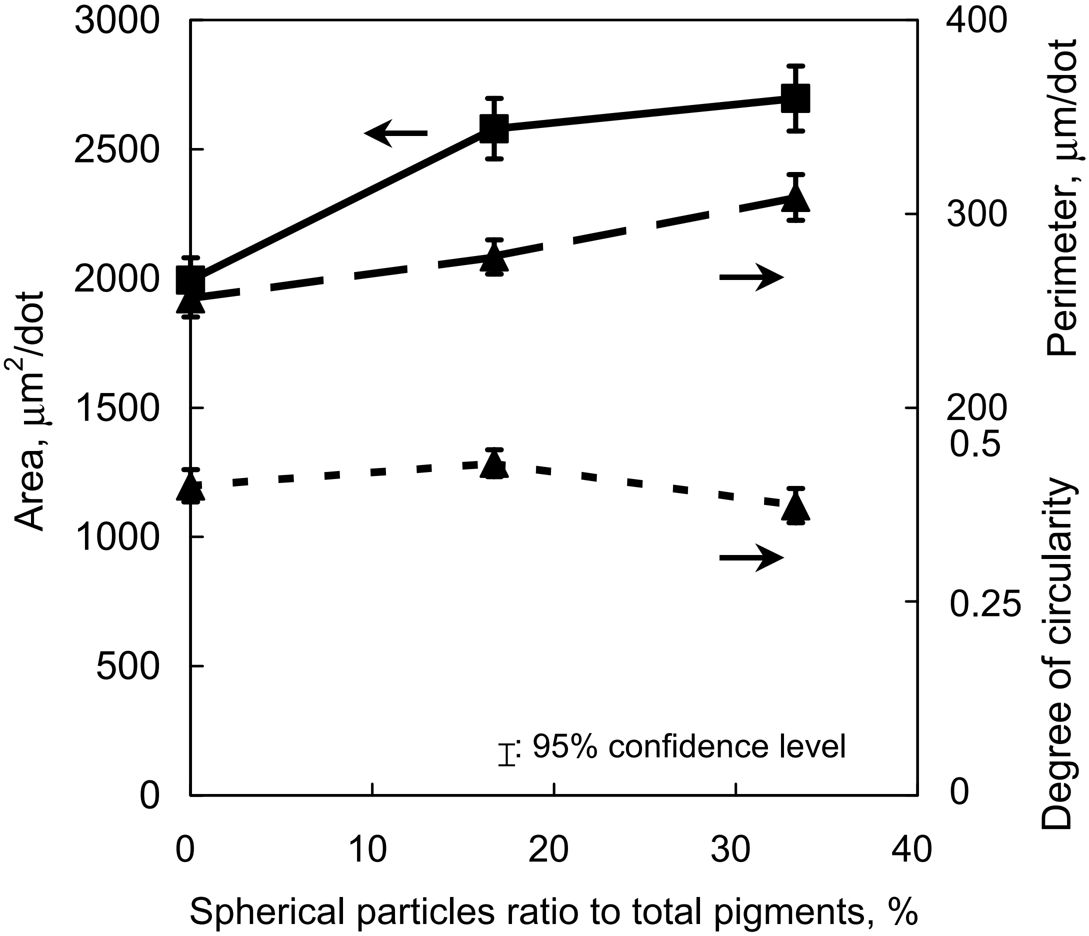
5. Scanning electron micrograph of a surface of Coated 3 containing 33.3 % of the spherical hollow particles to the total pigment



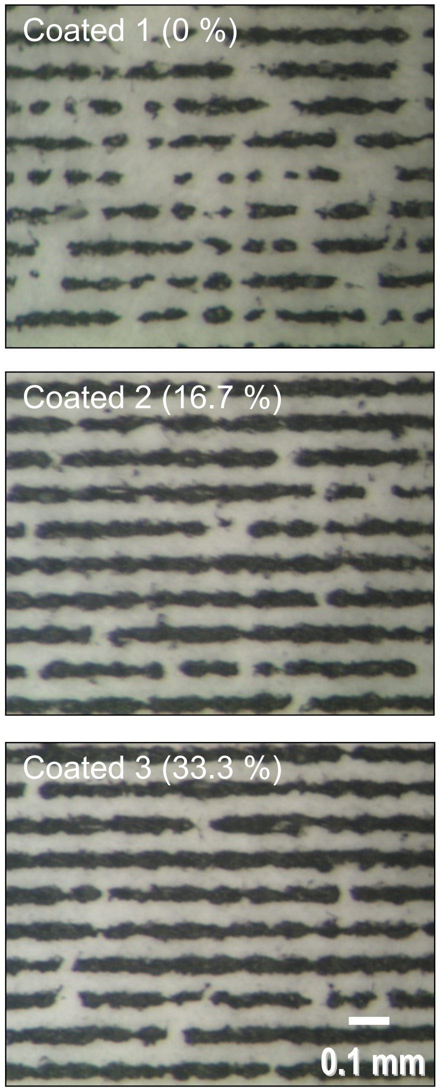
6. Change in optical properties of coatings with ratio of spherical particles formulated.



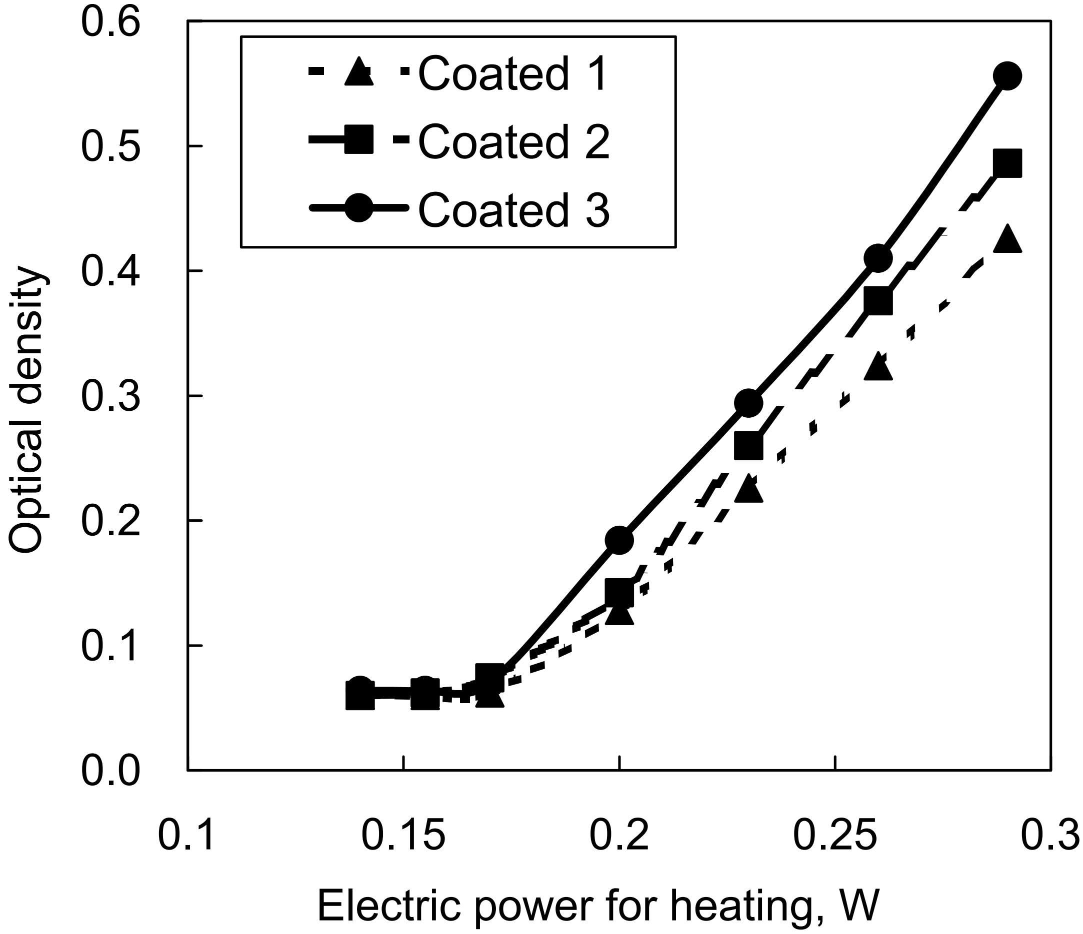
7. Stereomicroscope images of single dots printed by the thermal wax-transfer printer for coated papers containing spherical particles at different levels denoted in parentheses.



8. Characteristics of single dots printed by the thermal wax-transfer printer for coated papers containing spherical particles at different levels.



9. Stereomicroscope images of half-tone dots printed by the thermal wax-transfer printer at 0.29 W in electric power for heating the printer head for coated papers containing spherical particles at different levels.



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10. Optical density of half-tone dots printed by the thermal wax-transfer printer vs electric power supplied to the printer head for heating for coated papers containing spherical particles at different levels.