Preparation of Colored Core-Shell Particles by Coacervation Process in Organic Solvent

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Abstract

Core-shell (C-S) particles with a colored shell layer are prepared in an organic solvent system by a coacervation process. As the core-particles, a toner size polyethylene-norbornene copolymer particles are used. A dye molecules dissolved in acetone are precipitated onto the core particles from an acetone/water mixed solvent to form the colored C-S particles. The C-S particles are obtained without surfactant, need no washing process, and show sufficient color strength as well as good color reproduction. The colored shell layer also shows an excellent charge controlling capability, but the dye particles abraded from the colored shell layer function as a charge reducing agent. A resinous protecting layer deposited on the colored shell layer realizes colored particles with excellent durability and charge controlling capability.

Introduction

In general, the chemical toner has an advantage to give high quality core-shell (C-S) toner. In the C-S toner, several important functions are shared between the core part and shell part. The shell part has such functions as fluidity, tribo-charging, durability, anti-coherent or anti-blocking properties, etc.

Among the functions of the shell part, the tribo-charging characteristics are most essential. In our previous paper, the charge impartation capability of ultra-thin shell layers formed of nm size negatively or positively chargeable particles were investigated. [1,2] Interesting results in which the amount of negatively or positively chargeable shell particles determines the amount of charge on the C-S particles were obtained. The results suggest that the nanometer-sized particles on the shell surface can be regarded as the most effective charge imparting particles for the tribo-charging of the C-S particles.

In this paper, preparation of C-S particles with a colored shell layer having both the coloring and charge controlling functions was attempted. By selection of appropriate oil soluble type dyes and adoption of the coacervation process, a possibility to obtain the colored shell layers with sufficient color strength and color reproducibility was confirmed. The colored shells also show the charge controlling capability but the abrasion of the colored layer by mixing with carrier particles degraded the charging characteristics. The effect of a resinous protecting top shell that covers the colored shell layer was also investigated, and its excellent contribution to the protecting and charge controlling capabilities was confirmed. Detailed results are mentioned below.

Experimental

Starting materials for the colored C-S particles

Materials used to prepare the colored C-S particles are shown in Fig. 1. For the core particles, a negatively chargeable, pulverized polyethylene-norbornene copolymer (N core) was used. A SEM photograph of the N-core particles and its particle size distribution are shown in Fig. 2. For the colored shell material, three types of oil soluble type dye particles (Cy particles: Phthalocyanine dye, M and Y particles: Chromium azo complex dye), each dissolved in acetone, were used. For preparation of a top shell layer with the protecting and charge controlling functions, an aqueous solution of cationically modified styrene-maleimide copolymer (P particles) was used.

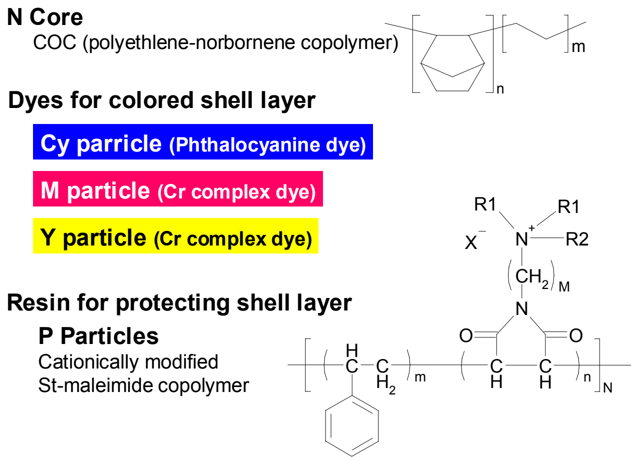

Fig.1 Starting materials for preparing colored C-S particles

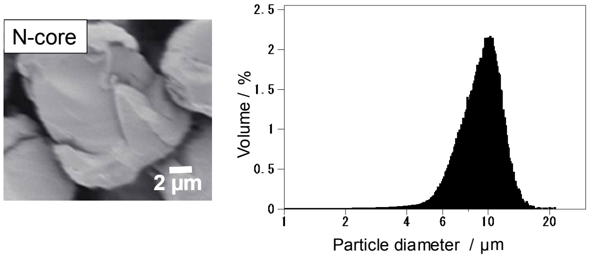

Fig.2 Morphology and particle size distribution of N-core particle

Colored C-S particles prepared

Four series of core-shell particles schematically shown in Fig. 3 were prepared. Three of them are colored single-shell particles NCy, NM, and NY, where the N core is covered with the colored shell layer of the Cy, M or Y dye of the amounts from 1 k to 30 kppm. The name of the colored C-S particles represents the composition of core particles, shell particles, and the amount of shell particles, respectively. For example, NCy 1k represents the colored single shell C-S particles with the N shell core covered with 1000 (1 k) ppm of Cy shell particles, and NCyP 10k represents the colored double shell C-S particles with the NCy 10k colored shell core covered with 10,000 (10 k) ppm of P shell particles.

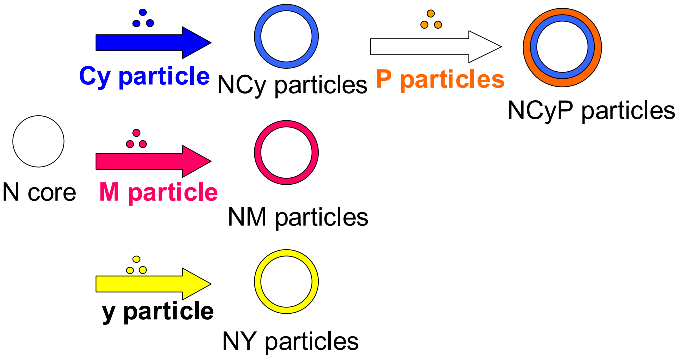

Fig.3 Colored C-S particles parepared

Preparation of colored C-S particles

The process for preparing the colored C-S particles is shown in Fig. 4. A prescribed amount of Cy, M or Y dye was dissolved in 50 g of acetone, and 10 g of N particles were added to the solution. The mixture was agitated vigorously, and 200 g of de-ionized water was added dropwise. While continuing the agitation and maintaining the temperature at 50ºC, acetone evaporated. The dissolved dye particles gradually precipitated onto the N core surface to yield colored C-S particles. The C-S particles were filtered and kept in a 50ºC oven to obtain a dried C-S particle sample

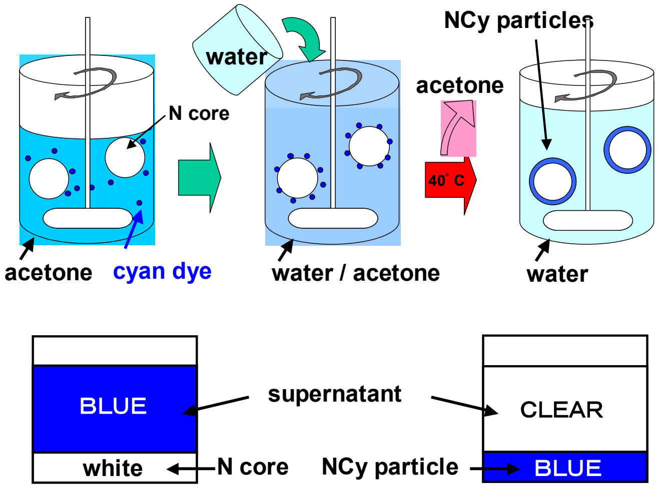

Fig.4 Process for preparing colored C-S particle

Tribo-charge measurement

The amount of tribo-charge q/m was measured by the blow-off method complying with the standard measurement procedure stipulated by ISJ.3) For the carrier particles, the standard carrier N-2 issued by ISJ was used. 4)

Results and Discussion

Observation of colored C-S particles with microscope and SEM

Fig. 5 shows the SEM photographs of four types of C-S particles that are coverd with 10 kppm of colored and P shell particles. The surface of all the C-S particles is as smooth as the surface of the N core (Fig. 2) even after the colored and/or P shell layers cover the core surface.

On the other hand, the particles were also observed with a microscope of high magnification (Keyence NHX-1000, x5000). For NCy 10k and NM 10k particles, a uniform and transparent colored shell layer was observed, but for the NY 10k particles, a mixture of transparent uncolored cores and yellow dye crystals (diameter • 10 μm) was observed.

The results show that, in the case of NCy 10k and NM 10k particles, uniform and transparent colored shell layers were obtained by the steady precipitation of the Cy and/or M dye molecules onto the core surface. However, in the case of NY 10k particles the colored shell layer was not obtained because of the rapid crystallization of yellow dye molecules in the coacervation process.

The thickness of the colored shell layer for the NCy 10k, NM 10k, and NCyP 10k particles was estimated to be about 10 nm.

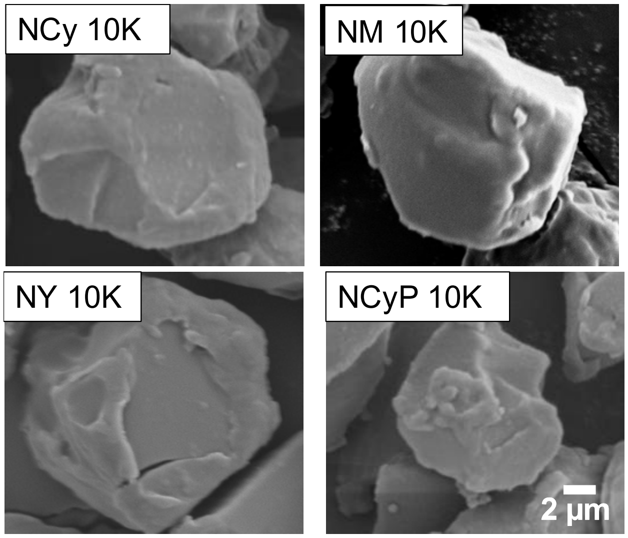

Fig.5 SEM Photographs of four types of colored C-S particles

Tribo-charging characteristics in NCy colored C-S particles

Fig. 6 shows the tribo-charging characteristic curves for the NCy particle series, indicating the amount of tribo-charge q/m as a function of mixing time. When the characteristic curves are compared with the reference curve, which was obtained from the N core particles, the change of q/m for the curves of the different amount of NCy particles is very small in the mixing time range of from 2 to 32 min. The curves obtained with NCy particles shift toward the positive charge region with the increasing amount of Cy particles (m_{Cy}) on the N core surface.

Fig. 7 shows the relationship between the q/m and m_{Cy}. The q/m increases with the increase of m_{Cy}. The results clearly show that the Cy molecules impart the positive charge to the N core particles. However, the data in the previous paper show that the q/m imparted by the nanometer-size shell particles (m) reaches a saturation value when the m exceeds 1 kppm.[5] Therefore, it is reasonable to infer that the Cy molecules on the N core surface are imparting the negative charge to make the negative q/m saturate at about 1 kppm of m_{Cy}, and, the positive q/m starts to increase when the m_{Cy} exceeds 1 kppm. From this point of view, the positive q/m increase seen in the m_{Cy} range of 1k to 20k ppm is caused by the abrasion and transfer of Cy molecules to the carrier surface. In this tribo-charging model, the Cy molecules on the carrier surface increase with the increase of m_{Cy}, and act as a negative charge reducing agent (or positive charge imparting agent) for the colored NCy particles.

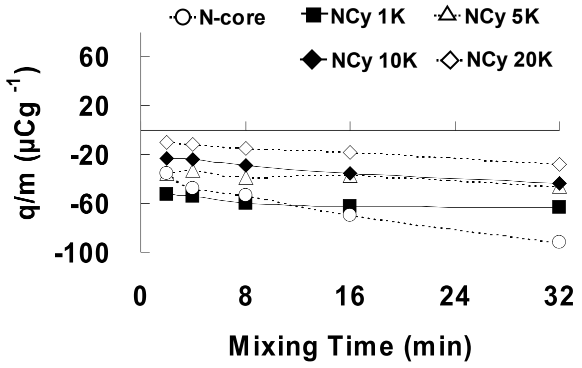

Fig.6 Tribo-charging characteristics for NCy colored shell particles

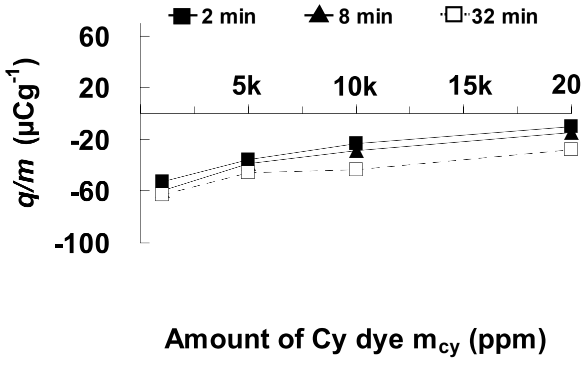

Fig.7 Relationship between $\Delta q/m$ and amount of Cy dye (m_{cy}) on core N

Tribo-charging characteristics in NM colored C-S particles

Fig. 8 shows the tribo-charging characteristic curves for the NM particle series. When the characteristic curves are compared with the reference curve, the change of q/m as a function of ixing time in each curve is negligible even the mixing time is prolonged for 32 min. The curves obtained with the NM particles shift towards the positive charge region with the increasing amount of M particles (m_M) on the N core surface.

Fig. 9 shows the relationship between q/m and m_M. The q/m increases with the increase of m_M. This result shows that, the tribo-charging mechanism for NM colored particles with the m_M of 5 k to 10 kppm is the same as that of the NCy colored particles mentioned above.

As shown in Figs. 7 and 9, the negative q/m values for NCy and NM particles gradually approach the zero line with the increase of m_{Cy} or m_M. The result means that thicker colored layers formed with more than 5 kppm of colored particles are easily abraded by the mixing with carrier. Therefore, some protective layer seems necessary to retain anti-abrasion strength for both colored shell layers.

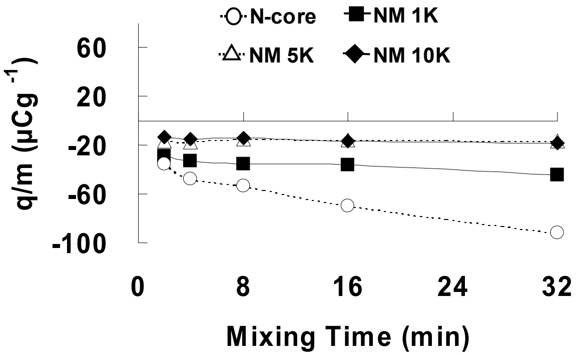

Fig.8 Tribo-charging characteristics for NM colored shell particles

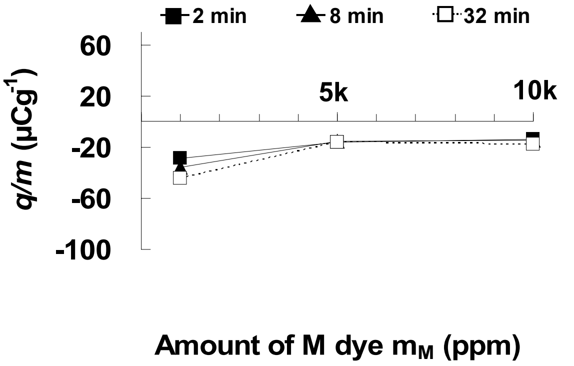

Fig.9 Relationship between $\Delta q/m$ and amount of M dye (m_M) on core N

Tribo-charging characteristics in NY colored C-S particles

The tribo-charging characteristic curves obtained for the NY particles with the m_Y range of from 1 k to 20 kppm were nearly the same as the reference curve. As mentioned in the microscopic observation, the NY particles were the mixture of the toner-sized crystal of the Y dye and the N core. The result shows that a uniformly covered Y molecule layer on the N core surface is needed to obtain the same tribo-charging characteristics as those of the NCy or NM particles.

Tribo-charging characteristics in NCP colored double shell C-S particles

Fig. 10 shows the tribo-charging characteristics curves for NCyP double shell particle series. When the curves are compared with the reference curve obtained by NCy 10k core, the curves obtained with NCyP particles shift towards the positive charge region with the increase of the amount of P particles (m_P) on the NC 10k core surface.

Fig. 11 shows the relationship between the q/m and m_P. The q/m value steadily increases with the increase of m_P, and the increase profiles for 2 to 32 min mixing are maintained almost the same. The result shows that the resinous P shell layer is serving not only as the protecting layer but also as the charge controlling layer. The charge controlling capability of the P shell layer originates from the quaternary anmonium groups in the P resin molecules.

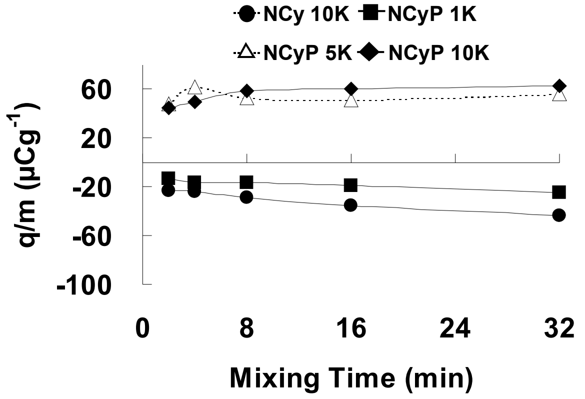

Fig.10 Tribo-charging characteristics for NCyP colored shell particles

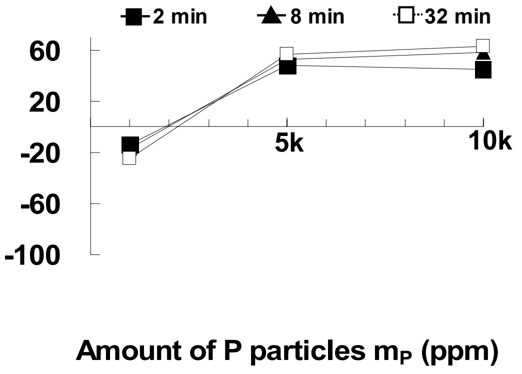

Fig.11 Relationship between Δq/m and amount of P particles (m_P) on the NCy 10k.

Color Gamut

The color gamut for the colored C-S particles is unclear because of the imperfect colored shell layer for the NY particles. However, an estimation can be made for the color gamut obtained for solid ink jet ink films containing the same Cy, M and Y dyes as those of the present paper in poly-amide resin and coated on the same proof paper as that for toner tests. As shown in Fig. 12, a slightly narrower color gamut would be realized assuming that the same color reproduction obtained by Y ink could be obtained for the NY particles with a smoothly colored shell. The reason for the slightly narrower color gamut for the C-S particles shows the limit of color reproduction capability by the dye layer on the core surface. Therefore, some appropriate resin binder as the poly-amide resin would be needed to obtain higher color reproduction capability. The colored shell layer using a resin binder together with the dye molecules might be able to provide an ideal layer not only for enlarging the color gamut but also improving the tribo-charging stability for the colored shell layer for the colored C-S particles.

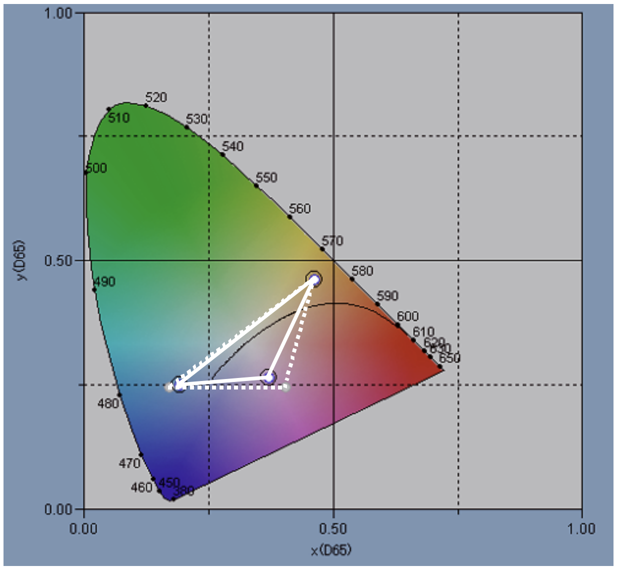

Fig.12 Color gamut obtained with the colored C-S particles
Solid line : obtained for ideally colored C-S particles.
Dotted line: obtained for solid IJ inks using the same dyes as those for C-S particles.

Conclusion

The C-S particles with an ultra-thin colored shell layer having a thickness of about 10 nm were prepared. The C-S particles show a sufficient color strength and good color reproducibility. Howener, in the case of C-S particles with the yellow dye, the same coloring performance was not obtained as those for the cyan and magenta dye because of the rapid crystallization of Y dye particles in the coacervation process. The colored shell layer shows the strong charge controlling capability. However, because of the lack of abrasion resistance, the colored layers also served as a tribo-charge reducing layer. The resinous protecting layer P on the colored shell layer showed excellent durability and stable charging capability. The resin binder or resinous protecting layer for the colored shell layer will be needed to realize high performance colored C-S particles.

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