

# Charge Impartation Capability of CCA Nano-particles Deposited on the Surface of Core-shell Type Chemical Toner

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## Abstract

For the purpose of controlling the amount of tribo-charge on core-shell type toner, the charge impartation capability of a charge control agent (CCA) particles in the shell layer was investigated. Spherical acryl cores (Ac-core) having a particle size of 10  $\mu\text{m}$  or Ac-cores having a styrene-acryl particle shell on their surface (St-Ac/Ac-cores) were used as core particles. As the CCA particles, Trianilino-triphenyl methane sulfate (TATPM, positive type CCA) particles were used. Nanometer sized TATPM particles and St-Ac particles were coprecipitated onto a core particle surface to form a positive charge imparting shell. The amount of tribo-charge  $q/m$  generated between the core-shell type particles and carrier particles was measured by the blow-off method. It was confirmed that a shell which contained an extremely small number of CCA particles shows remarkable positive charge impartation capability. The result suggests a promising manufacturing process for new types of chemical toners that realizes control of the amount of tribo-charge easily and accurately.

## Introduction

The tribo-charging phenomenon of electrophotographic toner is regarded as a charging phenomenon on the particle surface. Usually, a charge control agent (CCA) is added to obtain a required level of a toner charge. In the case of pulverized toner, CCA particles that are exposed on a toner particle surface act as charging sites, and the tribo-charge obtained by the CCA particles is imparted to the toner particles. In this toner charging mechanism, the number of CCA particles that exist on the toner surface determines the amount of toner charge. Suka *et al.* confirmed that an extremely small number of CCA particles externally added to the toner-carrier interface impart a large amount of charge to the toner particles. They suggested that, during the mixing operation of toner and carrier, fine mobile CCA particles are generated and acquire a tribo-charge. Part of CCA particles that deposited on the toner surface impart the acquired charge to the toner.<sup>1)</sup> An extremely thin CCA layer on the toner surface can also serve as an effective charge imparting layer. During the mixing operation, the thin CCA layer is easily peeled off to generate fine CCA particles. Through the same mechanism as mentioned above, parts of the charged fine CCA particles impart its charge to the toner.<sup>2)</sup>

In this report, the charge impartation capability of CCA particles that form a shell layer of core-shell type particles is studied. An interesting result was found that the composition and structure of the shell that contains the CCA particles determine the charge impartation capability for core-shell particles. It was confirmed that the CCA particles that exist on the top surface of the shell can be regarded as the most effective charge imparting

particles for the tribo-charging of core-shell particles. Detailed results are mentioned below.

## Experimental

### Component Materials

Ac-core: Spherical mono-disperse polymethyl-methacrylate particles (Ac-cores) having a diameter of about 10  $\mu\text{m}$  (glass transition temperature  $T_g = 100^\circ\text{C}$ ) were used as core particles. A SEM photograph of the Ac-core particles is shown in Figure 1.

St-Ac dispersion: Styrene-acryl (85:15) copolymer particles St-Ac (average particle size = 50 nm,  $T_g = 40^\circ\text{C}$ ) were used as binder particles for shell formation on Ac-core surfaces. The particles were dispersed in water (pH = 8.0) in a concentration of 1.0 wt%.

TATPM dispersion: Trianilino-triphenyl methane sulfate particles (TATPM: positive type CCA, average particle size = 500 nm) were used as CCA particles for the shell formation on the Ac-core surface. The particles were dispersed in ethanol in a concentration of 1.0 wt%.

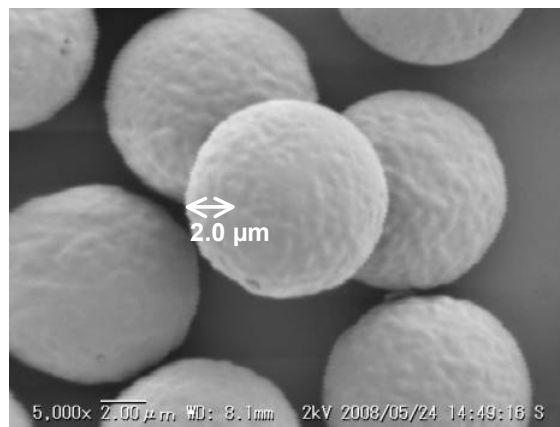


Figure 1. SEM photograph of Ac-core particles.

### Preparation of core-shell particles

Six types of core-shell particles were prepared. Table 1 shows the shell structure and shell composition of each of the core-shell particles. In this table, the amount of 1 ppm of TATPM or St-Ac particles correspond to  $10^{-4}$ wt% of each particles for the unit weight of Ac-core.

A batch of 10 g of Ac-core particles were mixed with 20 g of de-ionized water (DIW) that contained 15 mg of sodium dodecylbenzensulfonate. Further 170 g of DIW was added to the mixture. The temperature of the mixture was adjusted to  $40^\circ\text{C}$ . The

mixture was mixed vigorously, and prescribed amounts of St-Ac dispersion, TATPM dispersion and precipitator shown in Table 1 were added to the mixture. The temperature was maintained at 40°C, and mixing was continued for 30 min to form a shell 1 on the Ac-core particle surface. Then, the temperature was raised to 60°C, prescribed amounts of St-Ac dispersion, TATPM dispersion and precipitator were added, and the mixing was continued for another 30 min to form a shell 2 on the shell 1 surface. The mixture was then cooled to room temperature and obtained core-shell particles were washed with DIW by means of decantation. The wet cake of the core-shell particles that was obtained through filtration of the mixture was left in a 50°C oven for 24 h to obtain a dried core-shell particle sample.

**Table 1. Structure and chemical composition of Core-Shell particles.**

core-shell particle type	core	shell 1	shell 2	precipitator
Type 1	Ac-core	St-Ac 500 ~ 50000 ppm	-	CaCl <sub>2</sub> , HCL
Type 2-1	Ac-core	TATPM: St-Ac 1000: 1000 ppm	-	CH <sub>3</sub> COOH
Type 2-2	Ac-core	TATPM: St-Ac 1000: 1000 ppm	-	CaCl <sub>2</sub> , HCL
Type 3-1	Ac-core	St-Ac 10000 ppm	TATPM: St-Ac = 1: 1 500: 500 ppm ~ 5000: 5000 ppm	CaCl <sub>2</sub> , HCL
Type 3-2	Ac-core	St-Ac 10000 ppm	TATPM 2000 ppm constant St-Ac 200 ~ 1000 ppm	CaCl <sub>2</sub> , HCL
Type 3-3	Ac-core	St-Ac 50000 ppm	TATPM: St-Ac = 1: 1 500: 500 ppm ~ 5000: 5000 ppm	CaCl <sub>2</sub> , HCL

### Tribo-charge measurement

Measurement samples were prepared by putting 19 g of carrier and 1 g of core-shell particles into a 100 ml wide-mouth polyethylene bottle, and bottle contents were left for 24 h under a 20 to 25°C, 50 to 60%RH atmosphere to adjust the moisture content of the components. The sample-containing bottles were set to a paint shake type blender and the contents were mixed for 2, 4, 8, 16, or 32 min. The toner  $q/m$  at each mixing time was measured by the blow-off method complying with the standard measurement procedure stipulated by ISJ.<sup>3)</sup>

## Results and discussion

### Tribo-charge on Ac-core and St-Ac/Ac-core (Type 1) particles

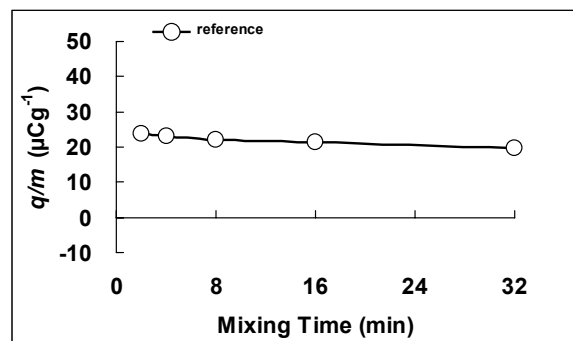
Figure 2 shows a characteristic curve of  $q/m$  vs. mixing time obtained for the Ac-core particles. The  $q/m$  value maintained an almost constant value while the mixing time increased from 1 min to 32 min. The  $q/m$  value at 32 min is defined as the charging level of Ac-core particles.

The SEM photographs of the St-Ac/Ac-core (Type 1) particles are shown in Figure 3. The particles in Figure 3a have a shell with 10,000 ppm St-Ac particles and the particles in Figure 3b have a shell with 50,000 ppm St-Ac particles. Compared to the Ac-core surface shown in Figure 1, both surfaces of the Type 1 particles are slightly rougher because of the coagulation of St-Ac particles which were formed during the precipitation process.

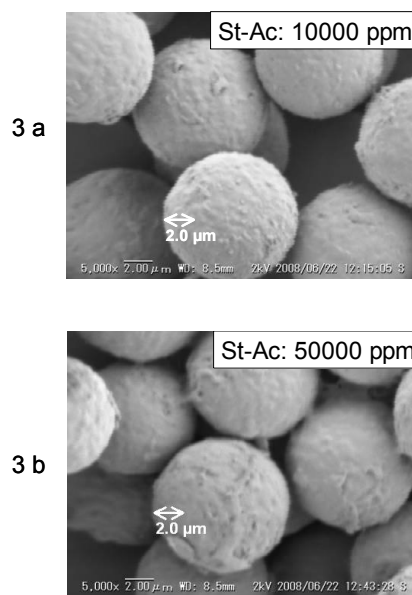
Figure 4 shows the characteristic curves of  $q/m$  vs. mixing time obtained for the Type 1 particles. When the characteristic curves are compared with the reference characteristic curve, which was obtained for the Ac-core particles, all the curves shift towards the negative charging region. The amount of negative charge shift

of the curves increases with the increase of the number of St-Ac particles on the core surface. Moreover, the curves almost converge to a single curve when the number of St-Ac particles on the core surface exceeds 3,000 ppm.

The results show that the St-Ac shell is behaving as a negative charge imparting layer; the negative charging properties of St-Ac particles is so strong that even the shell formed only of 500 ppm St-Ac particles can be regarded as a negative charge imparting layer. Probably, the number of St-Ac particles less than 3,000 ppm is insufficient to form a continuous shell layer on the Ac-core surface. However, as shown in Figure 4, the shells formed of 500 ppm or 1,000 ppm St-Ac particles are behaving as if continuous St-Ac shell layers were formed on the Ac-core surface. From the standpoint of tribo-electric charging, the shell formed of more than 3,000 ppm St-Ac particles can be regarded as a complete shell layer.



**Figure 2.** Relationship between  $q/m$  and mixing time obtained for Ac-core and carrier mixture.



**Figure 3.** SEM photographs of St-Ac/Ac-core particles.

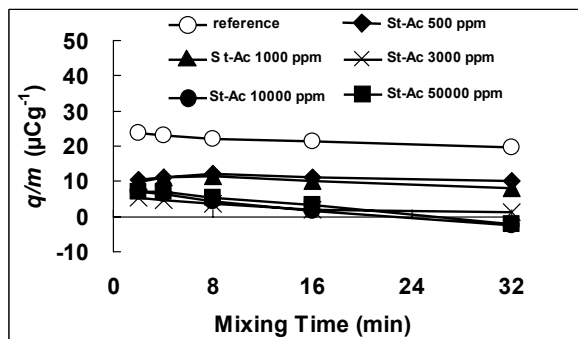


Figure 4. Relationship between  $q/m$  and mixing time obtained for St-Ac/Ac-core (Type 1) particle-carrier mixture.

### Tribo-charge on TATPM: St-Ac/Ac-core (Type 2) particles

The TATPM: St-Ac shell was formed by coprecipitation of TATPM and St-Ac particles. Acetic acid and a mixture of calcium chloride and hydrochloric acid was used as a precipitator to obtain the Type 2-1 and Type 2-2 core-shell particles, respectively. In almost all the shell formation processes, the color of a supernatant which was observed in the coprecipitation process turned from blue to clear. However in the case of shell formation of two kinds of Type 2-1 particles, which have the TATPM: St-Ac shell composition of 1,000 ppm: 300 ppm and 1,000 ppm: 1,000 ppm, respectively, a thin bluish color remained. The result shows that, in the case of two kinds of Type 2-1 particles, the number of St-Ac particles, which act as a binder to form the coprecipitated shell by the effect of weak precipitator as acetic acid, is insufficient to precipitate a the whole TATPM particles.

Figure 5 shows the characteristic curves of  $q/m$  vs. mixing time obtained for the Type 2-1 particles. It is remarkable that, compared to the reference curve, which was obtained for the Ac-core particles, the characteristic curves shift in a direction of stronger positive charge. It is also remarkable that the amount of positive charge shift is increasing with increase of the ratio of TATPM in TATPM: St-Ac shell layer. The results suggest that, in the shell structure of Type 2-1 particles, the TATPM particles have a tendency to occupy the top surface of the shell; as mentioned above, by the effect of weak precipitator as acetic acid, the TATPM particles probably precipitate more slowly on the St-Ac particle layer which precipitate first on the core surface. The thin bluish color of the supernatant that was seen in the coprecipitation of two kinds of Type 2-1 particles preparation supports the suggested shell structure.

Figure 6 shows the characteristic curves of  $q/m$  vs. mixing time obtained for the Type 2-2 particles. For the Type 2-2 particles, the ratio of the TATPM: St-Ac in the shell is kept constant at 1:1, and the amount of TATPM particles and St-Ac particles are 500 ppm: 500 ppm, 1,000 ppm: 1,000 ppm, 2,000 ppm: 2,000 ppm and 5,000 ppm: 5,000 ppm.

The  $q/m$  characteristic curves are different from the curves obtained for the Type 2-1 particles; comparison of the two curves in Figure 5 and Figure 6 obtained for the particles having the same 1,000 ppm: 1,000 ppm shell composition shows that the amount of shift toward the stronger positive charge obtained for the Type 2-2 particles is negligibly small. Moreover, all the curves obtained for

Type2-2 particles nearly coincide with the curve in Figure 5 obtained for the Type2-1 particle having 1,000 ppm: 50,000 ppm shell composition. The results show that, in the case of Type 2-2 particles, the positive charge imparting capability of TATPM particles is weakened by the uniformly mixed negatively charging St-Ac nano-particles.

Figure 7 schematically shows the structure of TATPM: St-Ac shell layers for the Type 2-1 particles (7a) and for the Type 2-2 particles (7b). The difference of the shell structures of the two types of particles is considered to originate from the difference of shell compositions and difference of precipitators in the shell formation process.

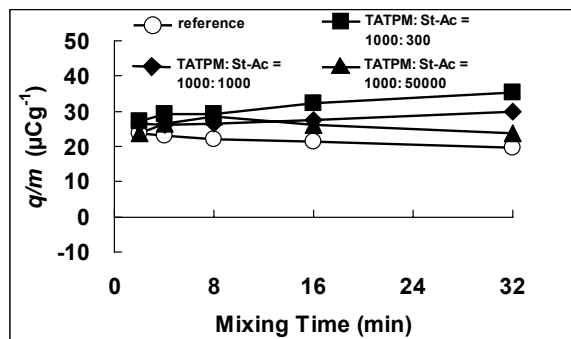


Figure 5. Relationship between  $q/m$  and mixing time obtained for TATPM: St-Ac/Ac-core (Type 2-1) particle-carrier mixture.

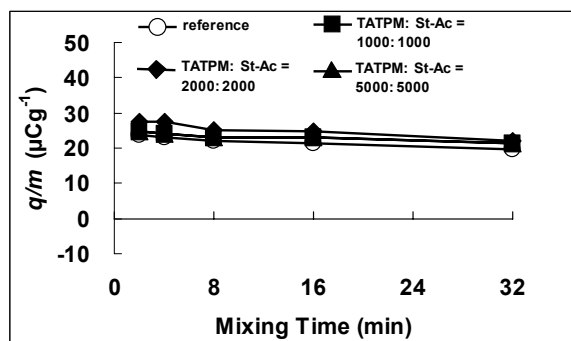


Figure 6. Relationship between  $q/m$  and mixing time obtained for TATPM: St-Ac/Ac-core (Type 2-2) particle-carrier mixture.

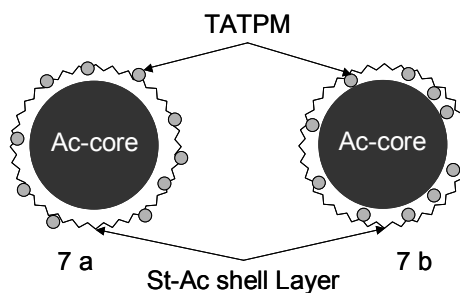


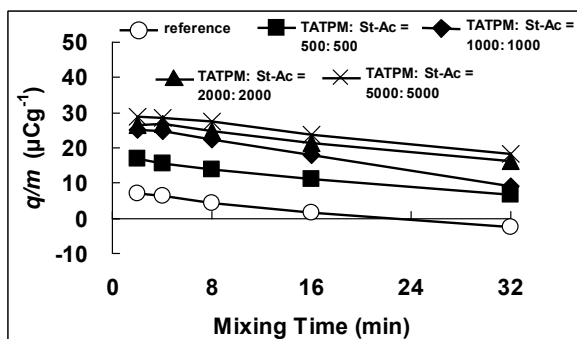
Figure 7. Schematic structure of Type2-1 and Type2-2 particle shells.

### ***Tribo-charge on TATPM:St-Ac/St-Ac/Ac-Core (Type 3) particles***

Figures 8, 9 and 10 show the characteristic curves of  $q/m$  vs. mixing time obtained for the Type 3 particles in which a double shell layer was formed on the Ac-Core surface; a TATPM: St-Ac top shell is formed on the St-Ac under shell.

Figure 8 shows the characteristic curves of  $q/m$  vs. mixing time obtained for the five kinds of Type 3-1 particles in which a TATPM: St-Ac top shell layer is formed on the 10,000 ppm St-Ac under shell layer. The TATPM: St-Ac particle ratio in the top shell layer is kept constant at 1:1 and the mixing amount of TATPM: St-Ac is in the range from 500 ppm: 500 ppm to 5,000 ppm: 5,000 ppm.

Compared to the reference characteristic curve, which was obtained for the Type 1 particle with the 10,000 ppm St-Ac shell layer on the Ac-Core surface, all the curves in Figure 8 are occupying the upper positive charge region. The results are supposed to originate from the strong positive charge imparting capability of TATPM. On the other hand, the amount of shift is increasing with increase of the total amount of the top shell material, and the  $q/m$  values in the curves decreases with increase of the mixing time. The results are ascribed to the negatively charging effect of St-Ac under shell and the negative charge imparting effect of the St-Ac particles in the top layer.

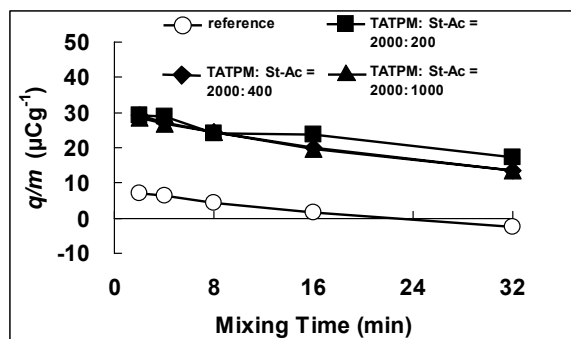


**Figure 8.** Relationship between  $q/m$  and mixing time obtained for TATPM: St-Ac/St-Ac/Ac-core (Type 3-1) particle-carrier mixture.

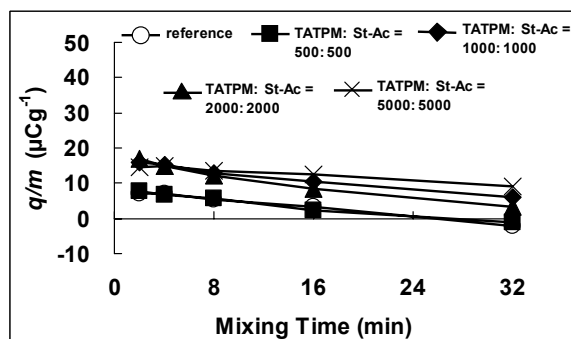
The characteristic curves of  $q/m$  vs. mixing time in Figure 9 were obtained for four kinds of Type 3-2 particles in which a TATPM: St-Ac top shell was formed on the 10,000 ppm St-Ac under shell. In the top shell, the amount of TATPM portion is kept constant at 2,000 ppm and the amount of St-Ac portion ranges from 200 ppm to 1,000 ppm. Compared to the reference curve, which was obtained for the Type 1 particle having 10,000 ppm St-Ac shell on the Ac-core surface, all the characteristic curves in Figure 9 are occupying the upper positive charge region. On the other hand, the amount of the positive charge shift from the reference curve is almost the same although the amount of St-Ac portion in the top shell differed from 200 ppm to 1,000 ppm.

The characteristic curves of  $q/m$  vs. mixing time in Figure 10 were obtained for three kinds of Type 3-3 particles in which TATPM: St-Ac top shell was formed on the 50,000 ppm St-Ac under shell. Compared to the reference curve, which was obtained for the Type 1 particles with 50,000 ppm St-Ac shell layer on the Ac-core surface, all the curves in Figure 10 are occupying the upper positive region but the amount of positive charge shift is very small. The authors postulate that the results come from the

effect of negatively charged St-Ac under layer. As shown in Figure 3b, the surface of the 50,000 ppm St-Ac shell on the Ac-core surface is so rough that the TATPM:St-Ac top shell layer could not cover the whole under shell surface; exposed or protruding St-Ac under shell portions on the top shell surface are probably imparting a negative charge to the Type 3-3 particles.



**Figure 9.** Relationship between  $q/m$  and mixing time obtained for TATPM: St-Ac/St-Ac/Ac-core (Type 3-2) particle-carrier mixture.



**Figure 10.** Relationship between  $q/m$  and mixing time obtained for TATPM: St-Ac/St-Ac/Ac-core (Type 3-3) particle-carrier mixture.

### **Conclusion**

The positive charge imparting capability of TATPM particles that were added to the shell layer of the core-shell type particles was investigated. The shell was formed by the coprecipitation of TATPM and St-Ac particles having a nano-meter size. It was confirmed that the key factors to determine the charge imparting capability are the shell structure, shell composition and smoothness of the core surface. In one case in which TATPM particles covered the top shell surface, the largest positive charge imparting capability was obtained by an extremely small number of TATPM particles. In the other case in which the TATPM and St-Ac coprecipitated layer formed a continuous and uniform layer, the obtained charge was determined by the TATPM: St-Ac ratio. The effect of the roughness of the core surface was not negligible especially when the shell thickness was so small to form a continuous shell layer on the core surface. It was concluded that the accurately charge-controlled core-shell particles can be

obtained by adjusting the structure and composition of the shell layer containing CCA particles in it.

## References

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## Author Biography

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