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# Toner Charge Control With Externally Added Charge Control Agent Particles

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**Abstract.** *Externally added charge control agents (EA-CCAs) were prepared by means of a coacervation process. Spherical silica particles of 100 nm average diameter were coated with two kinds of charge control agents (CCAs); one was a polymer type P-1 and the other was a low molecular weight type P-2. Both of CCAs made remarkable contribution to toner charge. In a concentration range up to 0.2 $\mu$mol/g of CCA on toner, toner charge increased. From the relationship between the amount of EA-CCA on the toner and the tribocharge, P-2 was found more effective than P-1. It was estimated that 0.7 mol% of P-1 repeating units and 1.3 mol% of P-2 molecules contributed to toner charge, respectively. Calculation of the surface coverage of P-2 on spherical silica particles showed that the efficient concentration region of charge agreed with the 100% of surface coverage. The P-2 concentration was 0.02 $\mu$mol/g based on toner. This means that the CCA molecule has a great effect on tribocharge in small concentration. © 2011 Society for Imaging Science and Technology.*
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## INTRODUCTION

Charge control agents (CCAs) are widely used for both pulverized and chemical prepared electrophotographic toners. In the pulverized toner, CCA is applied as microcrystalline powder. After kneading together the resin, CCA powder and other ingredients, their mixture is pulverized into powder of a suitable diameter. Neither the amount of CCA particles nor the number of molecules on the toner surface is known in such a manufacturing method. The influences of the resin and other ingredients on charge are also unknown. Furthermore, since external additives exist on the toner surface, contact probability between carrier and CCA is not clear in two-component developer. It is only known that a negative CCA has a large anion and a positive CCA has a large cation, when they are ionic molecules.

Suka et al.[1] have reported that even a small amount of CCA is very effective for toner charge control when the CCA is added into the two-component developer. Their work suggests that, although the CCA molecule has high chargeability, the toner may not make sufficient use of this CCA capability. Iimura et al.[2] have reported tribocharge properties of CCA-coated toner. In this report, the authors attempt to clarify the effect of CCA on toner charge in molecular level by using CCA-coated core particles with hydrophobic surface as external additive (EA-CCA).

## EXPERIMENTAL

### *Preparation of EA-CCA*

Two kinds of positively chargeable CCA shown in Figure 1 were used in these experiments. The CCA P-1 was an alternating copolymer of styrene and a maleic anhydride derivative. The average unit molecular weight was 535 and the average degree of polymerization was 53. The quarternarization ratio of P-1 was about 40 mol% determined from an amine value, which was obtained by titration. The charging site was the quaternary ammonium salt. The CCA P-2 was a well-known sulfonic acid salt with a molecular weight of 499. Spherical hydrophobic silica particles (SS100, from Shin-Etsu Chemical Co., Ltd.) were used in these experiments as cores for EA-CCA. The shape and particle size distribution of SS100 are shown in Figures 2 and 3, as obtained from scanning electron microscopy (SEM). They have an average particle sizes were 100 nm and a very narrow particle size distribution. Therefore, they are very suitable for investigating the charging mechanism.

Model toner was prepared from a pulverized styrene-butyl acrylate copolymer without using wax and pigment. Its shape was irregular as shown in Figure 4. The particle size distribution was typical of pulverized toner, as shown in Figure 5; average diameter was 8.6 $\mu$m.

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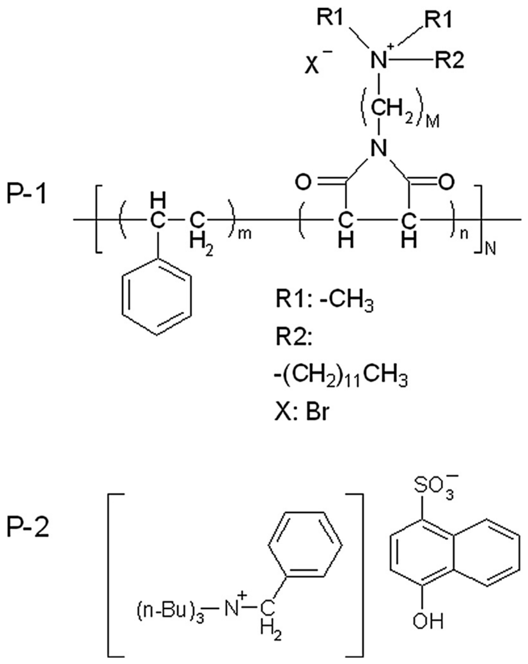

Figure 1. Structure of CCAs.

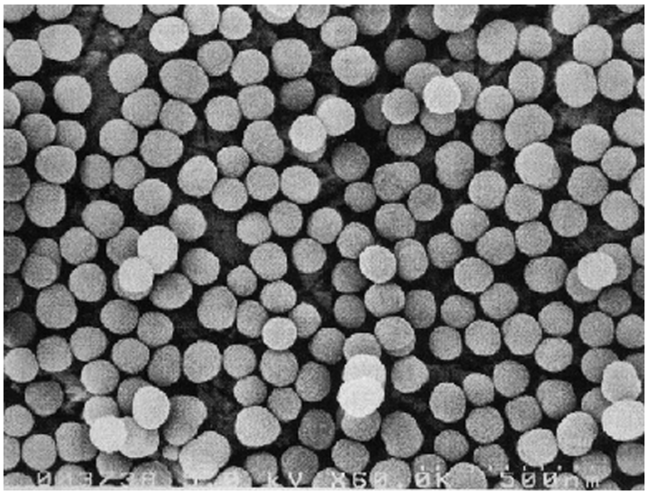

Figure 2. SEM photograph of SS100.

The CCAs were dissolved in a desired concentration into an ethanol/methanol 9/1 mixed solvent. Then, core particles were dispersed into the CCA solution. The mixture was stirred vigorously for a few minutes and the excess solvent was evaporated. In the evaporation process, core particles were coated with the CCA, because the CCA was insoluble at a high concentration in the solvent, and core particles played the role of nuclei for CCA recrystallization, which was a coacervation process. The CCA molecules could be adsorbed onto core particles because of interaction between their hydrophobic surface and CCA molecules. After evaporation of the solvent and drying, white powder was obtained. After pulverization of the powder, EA-CCA was obtained. SS100 coated with P-1 was described as SS100(P-1) and that coated with P-2 as SS100(P-2). The coating amount of CCA was in the range from 0.01 to 5% based on core particle weight, and those amounts were converted into molar number for discussion of charging mechanism.

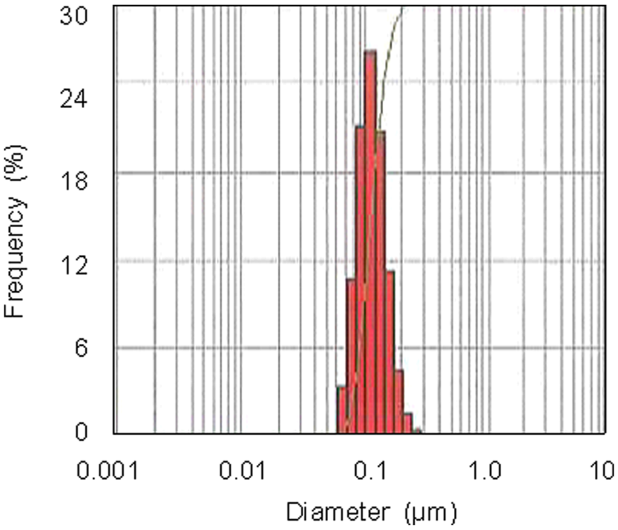

Figure 3. Particle size distribution of SS100.

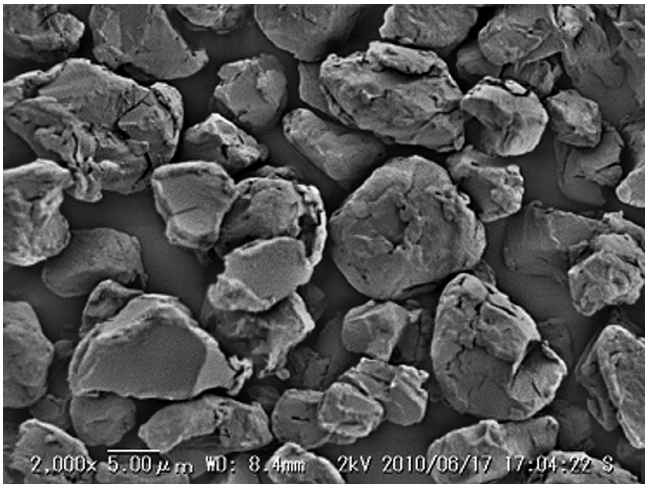

Figure 4. SEM photograph of model toner.

### *Tribocharge Measurement*

Toner tribocharge (charge/toner weight ratio, Q/M) was measured using a blow-off charge measurement apparatus, complying with the standard measurement procedure stipulated by the Imaging Society of Japan (ISJ).[3] One gram of model toner and 19 g of a standard carrier #L from ISJ were weighed and placed in 100 ml polyethylene bottle. One percent of EA-CCA based on model toner was added into the bottle. The content was mixed for 2 to 32 min with a 6 cycles/s shaker. Sample preparation and charge measurement were carried out under controlled room temperature (23 ± 3°C) and humidity (55 ± 15% RH).

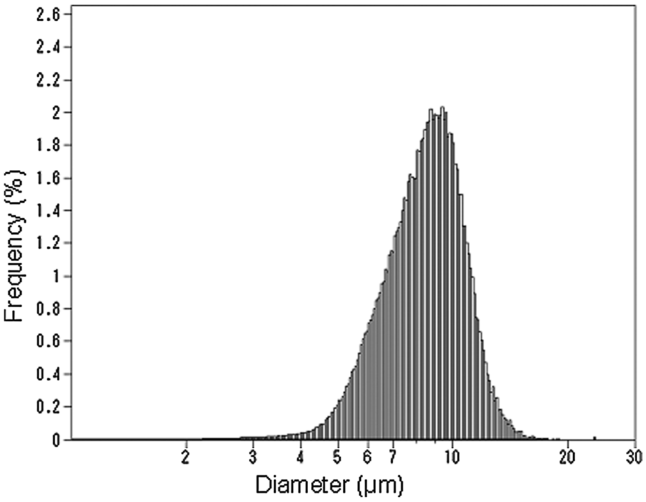

Figure 5. Particle size distribution of model toner.

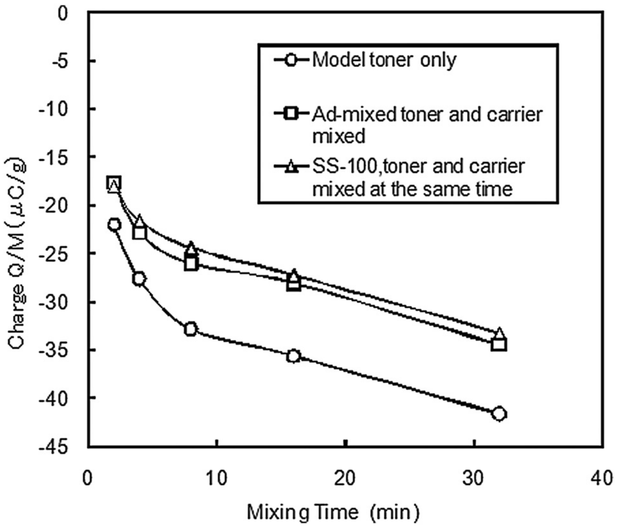

Figure 6. Influence of developer preparation method on toner charge.

### *Calculation of Molecular Size*

Molecular size of each CCA was calculated by using MOPAC2009 application, PM6 method.[4]

## RESULTS AND DISCUSSION

### *Influence of Developer Preparation Method on Toner Charge*

In preparation of the two-component developer, it is usual that a carrier is mixed with toner, which has already been admixed with external additives. Tribocharge was very similar between usual mixed developer (square plots in Figure 6) and that of carrier, toner and external additive mixed at the same time (triangle plots in Fig. 6), as shown in Fig. 6. Therefore, developers were prepared by using the method as described above.

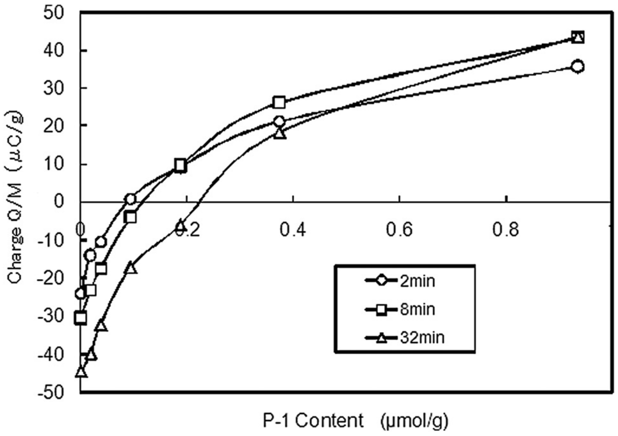

Figure 7. Relation between charge and P-1 content in toner for various mixing times in SS100(P-1) system.

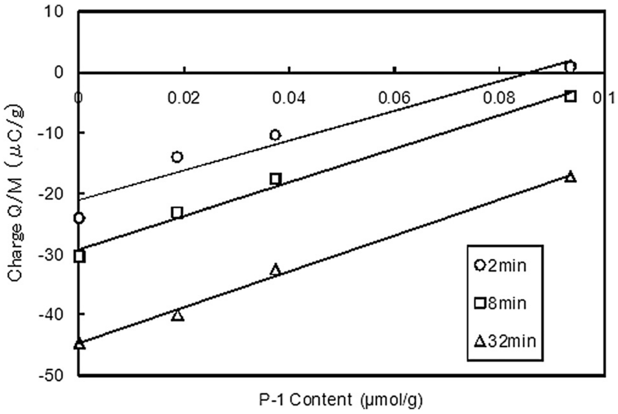

Figure 8. Relation between charge and P-1 content in toner (lower content region) for various mixing times in SS100(P-1) system.

### *Effect of SS100(P-1)*

Figure 7 shows the relationship between charge (Q/M) and P-1 content on toner, for various mixing times. The Q/M value increased dramatically with the increasing amount of P-1 in the range of up to 0.2 μmol/g. In the range above 0.2 μmol/g, Q/Ms still increased slightly with no saturation point. The tendencies were similar for the various mixing times. This suggests that P-1 contributes to Q/M effectively in the lower concentration region and less effectively in the higher concentration region. Figure 8 shows the linear part of Fig. 7 in a P-1 concentration range of less than 0.1 μmol/g. The slope represents CCA contribution to Q/M. Table I shows the slopes in Fig. 8 obtained by linear regression. P-1 contribution to tribocharge estimated from the slope was 0.27 kC/mol.

Since an electron has a charge of $1.6 \times 10^{-19}$ C, 1 mol CCA can theoretically yield 96.3 kC/mol. However, P-1 gives only 0.27 kC/mol. The value was 0.7 mol% of the ideal value, on the assumption that only the quaternary ammonium salt in P-1, which was 40 mol% as shown in Fig. 1, contributed to toner charge. This analysis suggests that only 0.7 mol% of charging sites contributes to tribocharge.

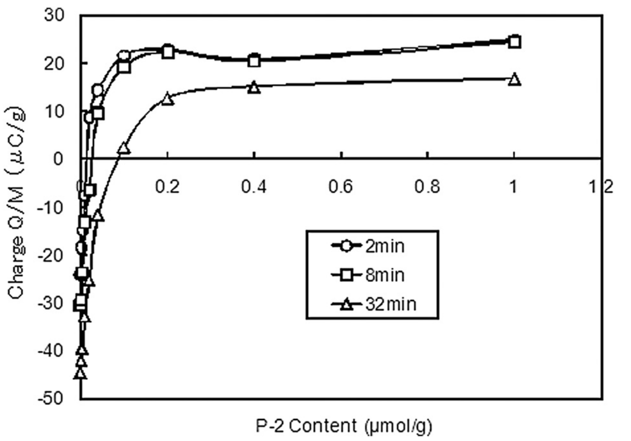

Figure 9. Relation between charge and P-2 (over SS-100) content in toner for various mixing times in SS100(P-2) system.

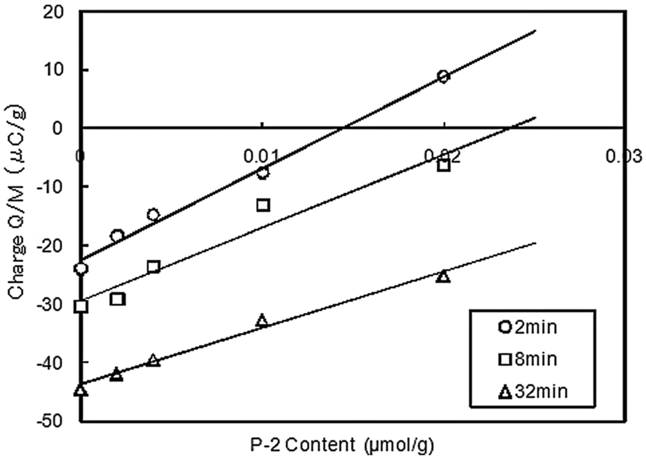

Figure 10. Relation between charge and P-2 content in toner (lower content region) for various mixing times in SS100(P-2) system.

### Effect of SS100(P-2)

The contribution of P-2 to charging was also investigated. Figure 9 shows the relationship between charge and P-2 concentration on toner in various mixing times. The Q/M value increased more dramatically with the increasing amount of P-2 than in the case of P-1 over the concentration range of up to 0.1 μmol/g on toner.

In the concentration range above 0.1 μmol/g toner, Q/M values saturated around +20 μC/g. The tendencies were similar for various mixing times. However, the Q/M values at 32 min mixing were smaller than those of shorter mixing time. The cause of this phenomenon is thought to be that carrier ability decreases with time spent on carrier particles over long mixing times. Figure 10 shows the linear part of Fig. 9. The slope represents the contribution of P-2 to Q/M. The contribution was found to be 1.26 kC/mol, as shown in Table I.

Analysis analogous to that applied to the P-1 data was carried out. Contribution to toner charge would be 96.3 kC/mol, if all of P-2 molecules contributed to tribocharge. However, the experimental value suggests that only 1.31 mol% of charging sites contribute to the charge.

**Table I.** CCA contribution to charge from Figs. 8 and 10 (unit; kC/mol).

| | SS100 (P-1) | SS100 (P-2) |
|---|---|---|
| 2min | 0.25 | 1.56 |
| 8min | 0.28 | 1.26 |
| 32min | 0.29 | 0.97 |
| Average | 0.27 | 1.26 |

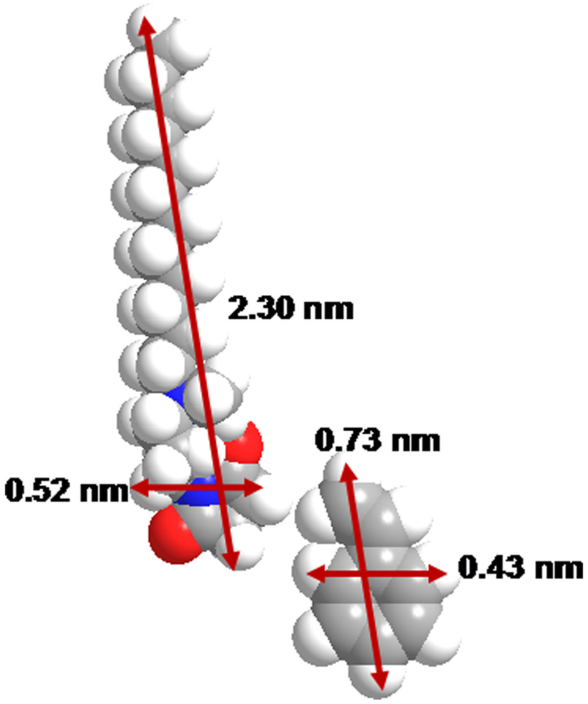

Figure 11. Molecular size of P-1.

In comparison to the charge contribution rate of P-1 and P-2, P-2 has an efficiency about 4.7 times higher than that of P-1, as shown Table I.

### Surface Coverage Ratio

Surface area per unit weight S of each particle was calculated from Eq. (1) assuming spherical shape.

$$S = 3/r\rho \tag{1}$$

where r is the radius and $\rho$ is the particle density, respectively. For SS100 S was 33.0 $m^2/g$, where r was 50 nm and $\rho$ was 1.80 $g/cm^3$. Projection area of each CCA was approximately calculated from molecular size, as shown in Figures 11 and 12, using the MOPAC2009 application, PM6 method.[4] K. Uta et al.[5,6] have reported the crystal structure of P-2. In this article, however, since CCA molecules could not disperse in the crystalline state but only in the molecular state, results from MOPAC2009 were adopted.

Projection area of P-1 in repeating unit was $1.63 \times 10^{-18}$ $m^2$ and that of P-2 was $2.72 \times 10^{-18}$ $m^2$,

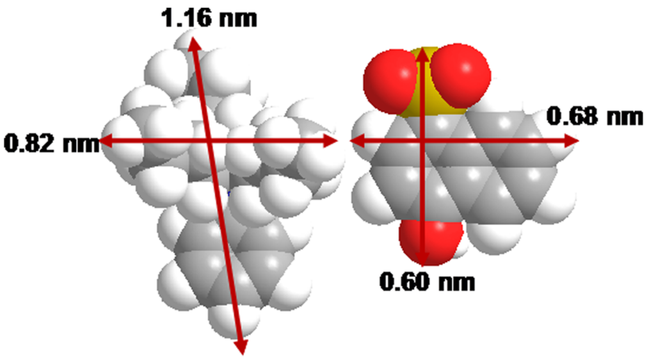

Figure 12. Molecular size of P-2.

respectively. Using these data, it was calculated that 1 g of SS100 surface was covered by 33 $\mu$mol of P-1 for 100% coverage rate, and that it was likewise covered by 20 $\mu$mol of P-2. When 1% of EA-CCA was added to toner, the CCA content of 100% coverage based on toner was 0.33 $\mu$mol/g in SS100(P-1) system, and 0.20 $\mu$mol/g in SS100(P-2) system, respectively.

Inflection points could be observed all plots in Figs. 7 and 9. In Fig. 7, inflection points were not so clear but could be seen around 0.2 $\mu$mol/g P-1 content. Inflection points were in the range from 0.1 to 0.2 $\mu$mol/g in Fig. 9. These CCA concentrations were in fair agreement with the estimates of 100% coverage. This correspondence means that CCA molecules on core particles contribute to toner charge effectively until coverage rate reaches 100%. Further, when coverage rate reaches 100%, excess CCA makes no contribution to charge. So, only the outermost surface CCA molecules are effective. The reason why no clear inflection points were observed in the SS100(P-1) system in Fig. 5 may be that the P-1 molecule, being a polymer, is able to have many conformations. Therefore, charging sites are not always on the exterior of the molecules as required to contribute effectively to charging.

## CONCLUSIONS

Two kinds of CCA, the polymer type P-1 and the low molecular weight type P-2, were coated on a core particle using a coacervation method. Both CCAs were effective in enabling toner tribocharge over a small concentration range of less than 0.2 $\mu$mol/g on toner. Next, it was clarified that 0.7 mol% of charging sites in P-1 and 1.3 mol% of those in P-2 contribute to tribocharge on hydrophobic silica. Tribocharge saturated on adding excess CCA in the concentration range from 0.1 to 0.2 $\mu$mol/g based on toner, and the saturation concentration agreed with 100% coverage of CCA molecules on the core particle. P-1 had a different efficiency for tribocharging from P-2, which we attribute to the conformations, the polymer molecules may take on the core surface.

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