Toner Charge Control with Externally-Added CCA Particles

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Abstract

Externally-added charge control agents (EA-CCA) 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 is a polymer type P-1 and the other is a low molecular weight type P-2. Both of them make a remarkable contribution to toner charge. In a concentration range from 1 to $1x10^3$ ppm of CCA on toner, toner charge increased. From the relationship between the amount of EA-CCA in the toner and the tribocharge, P-2 was found more effective than P-1. It is estimated that 0.7 % of P-1 repeating units and 1.2 % of P-2 molecules contribute to toner charge, respectively.

Calculation of the surface coverage of P-2 on spherical silica particles shows that the efficient concentration region of charge agreed with the surface coverage. The P-2 concentration was 50 ppm based on toner. This means that the CCA molecule has great effect on tribocharge in small concentration.

Introduction

Charge control agents (CCAs) are widely used for both pulverized and chemical prepared toners. In the pulverized toner, CCA is applied as microcrystalline powder. After kneading 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 known that only a negative CCA has a large anion and a positive CCA has a large cation, when they are ionic molecules.

Suka et al. [1] has reported that even a small amount of CCA is very effective on toner charge control when the CCA is added into the two-component developer. Their work suggests that, although the CCA molecule has high chargeability, toner does not make use of CCA capability.

In this report, the authors attempt to clarify the effect of CCA on toner charge in molecular level by using two kinds of CCAs.

Experimental

Preparation of EA-CCA

Two kinds of positively chargeable CCA shown in Fig. 1 were applied to experiments. The CCA P-1 was an alternating copolymer of styrene and 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% judged from an amine value which was determined by titration. The charging site was the quarternary ammonium salt. The CCA P-2 is a well-known sulfonic acid salt with a molecular weight of 499. Spherical hydrophobic silica particles (SS100, from Shin-Etsu Chemical Co., Ltd.) were applied to experiments as the core for CCA. They have an average particle size of 100 nm and a very narrow particle size distribution. Therefore, they are very suitable for investigating the charging mechanism. The shape and particle size distribution of SS100 are shown in Figs. 2 and 3, respectively. Model toner was prepared from a pulverized styrene-butyl acrylate copolymer without using wax and pigment. Its shape is irregular as shown in Fig.4. The particle size distribution shows that of typical pulverized toner, as shown in Fig. 5. The average diameter is 8.6 µm.

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

Suka et al. [1] reported toner tribocharge properties applying CCA directly to model toner and a carrier. Iimura et al. [2] reported that of CCA-coated toner. In this report, we have adopted an approach to add CCA-coated silica as an external additive (EA-CCA). Tribocharge properties were investigated by using blow-off charge measurement.

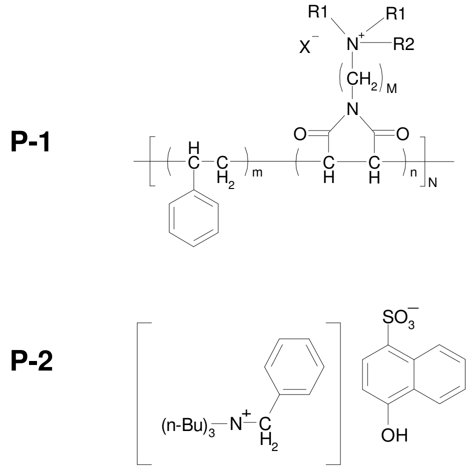

Figure 1 Structure of Applied CCAs

Tribocharge Measurement

Toner tribocharge (Charge/toner weight ratio, Q/M) was measured by a using blow-off charge measurement apparatus, complying with the standard measurement procedure stipulated by ISJ[3]. One gram of model toner and 19 g of a standard carrier (#L from ISJ) were weighed and placed in 50 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 minutes with a 6 cycles/s shaker. As shown in Fig. 6, carrier is coated with model toner uniformly. Sample preparation and charge measurement were carried out under controlled room temperature (23±3℃) and humidity (55±15 %RH).

In preparation of the two-component developer, it is usual that a carrier is mixed with toner which is already admixed with external additives. Tribocharge was very similar between usual mixed developer (square plots in Fig. 7) and that of mixed carrier, toner and external additive at the same time (triangle plots in Fig. 7), as shown in Fig. 7. Therefore, developers were prepared by using the method as described above.

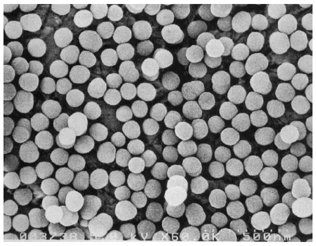

Figure 2 SEM photograph of SS100

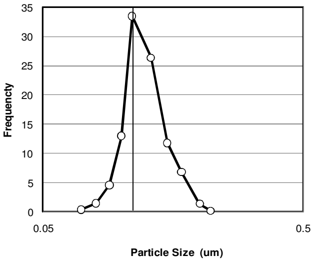

Figure 3 Particle Size Distribution of SS100

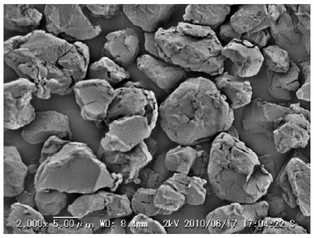

Figure 4 SEM photograph of Model toner

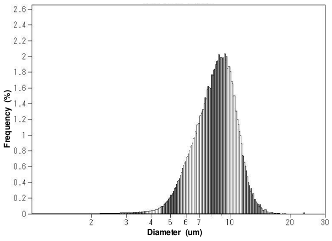

Figure 5 Particle Size Distribution of model toner

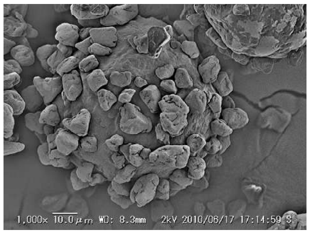

Figure 6 SEM photograph of developer (Carrier is coating by toner)

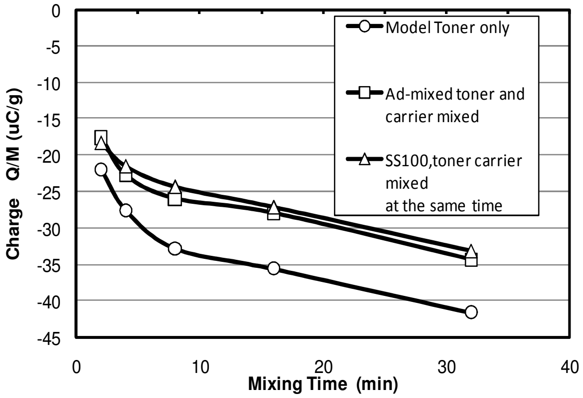

Figure 7 Influence of developer preparation method on toner charge

Results and Discussion

Effect of EA(P-1)

SS100 without CCA coating was used as a negatively chargeable external additive. The original contribution of SS100 to tribocharge was －4 μC/g from Q/M at 2 min mixing in Fig. 7.

Carrier was spent by toner, and external additive and other damages affected tribocharge in longer vigorous mixing. Therefore, ΔQ/M at 2 min mixing was adopted.

Fig. 8 shows the relationship between Q/M and mixing time of developer prepared from carrier, model toner and EA(P-1) which is coated with P-1 of different concentration. The value of Q/M increases with mixing time, and saturates at around 16 min mixing for higher P-1 concentration systems (more than 200 ppm relative to toner). SS100 without P-1 coating is very negative and Q/M is in the range of about －30 to －45 μC/g. The Q/M value increases with the increasing amount of P-1. Even when only 10 ppm of P-1 is added to toner, the Q/M value is higher than that of no P-1 addition. This means that P-1 is effective on charging greatly even in a very small amount.

Fig. 9 shows the relationship between Q/M and P-1 concentration on toner. The Q/M value increases dramatically with the increasing amount of P-1 in the range of less than 50 ppm. In the range larger than 50 ppm, Q/Ms still increases significantly and have no saturation point. The tendency is almost similar for various lengths of mixing time. This suggests that P-1 contributes to Q/M effectively in a lower concentration region and less effectively in a higher concentration region. Fig. 10 shows the linear part of Fig. 9 in a P-1 concentration range of less than 50 ppm. The slope represents CCA contribution to Q/M. Table 1 shows the slopes in Fig. 10 obtained by linear regression calculation. P-1 contribution to tribocharge estimated from the slope is 0.51 μC/ppm

The unit average molecular weight of P-1 was 535, and 1 μg ($1x10^{-6}$ grams, equal to ppm in this discussion) of P-1 has $1.12x10^{15}$ unit molecules. As described in the Experimental part, it is considered that the charging site is the quarternary ammonium salt and P-1 has 40 % of charging sites based on unit molecular number. An electron has a charge of $1.6x10^{-19}$ C. It is estimated that charging sites of P-1 contribute to tribocharge of 72 μC/ppm if all of P-1 charging sites contribute to toner charge. However, the actual contribution rate was 0.51 μC/g. This suggests that only 0.7 mol% of charging sites contributes to tribocharge.

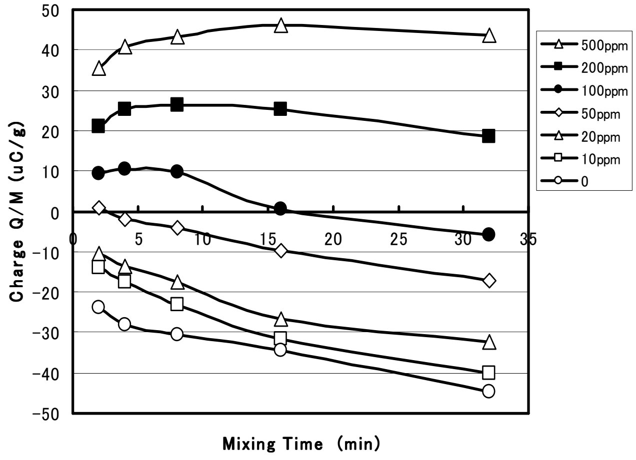

Figure 8 Dependence of charge on mixing time in model toners mixed with various concentrations of EA(P-1)

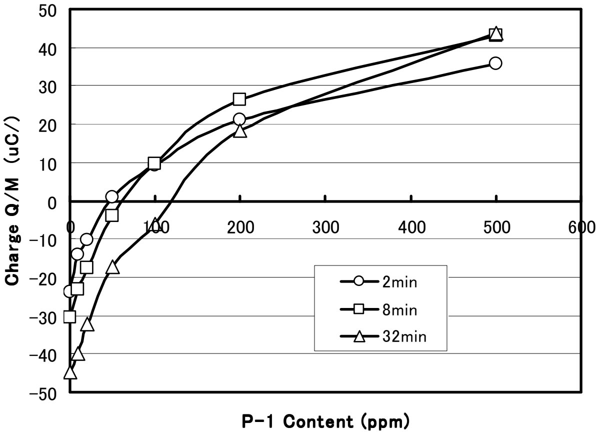

Figure 9 Relation between charge and P-1 content in toner for various mixing time

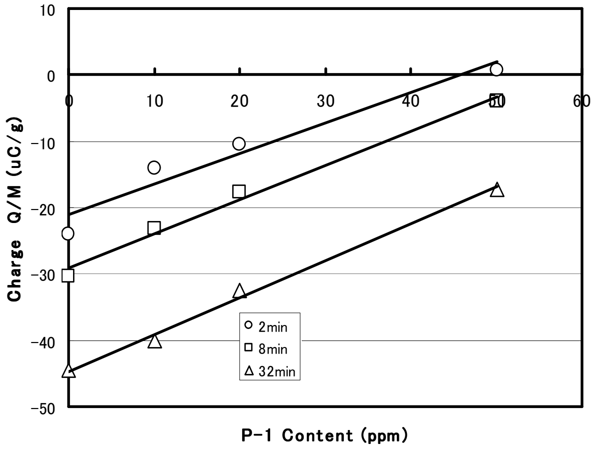

Figure 10 Relation between charge and P-1 content in toner (lower content region) for various mixing time

Table 1 CCA Contribution to Charge from Fig. 10

Mixing Time (min)	Slope (uC/ppm)
2	0.46
8	0.51
32	0.55
Average	0.51

Effect of EA(P-2)

Next, the contribution of P-2 to charging was investigated. Fig. 11 shows the relationship between Q/M and mixing time of developer prepared from carrier, model toner and EA(P-2) which is coated with P-2 in different concentration. In contrast to Fig. 9, Q/M increases within 2 minute mixing. After 2 min, Q/Ms slightly decreases with mixing time. The Q/M values increase with the amount of P-2 in a similar way to the case of EA(P-1). The Q/M increases when 10 ppm of P-2 was added to toner and P-2 has a higher efficiency than P-1 because Q/M increases by even 1 ppm addition of P-2.

Fig. 12 shows the relationship between charge and P-2 concentration on toner. The Q/M value increases more dramatically with the increasing amount of P-2 than in the case of P-1 in the concentration range of less than 50 ppm.

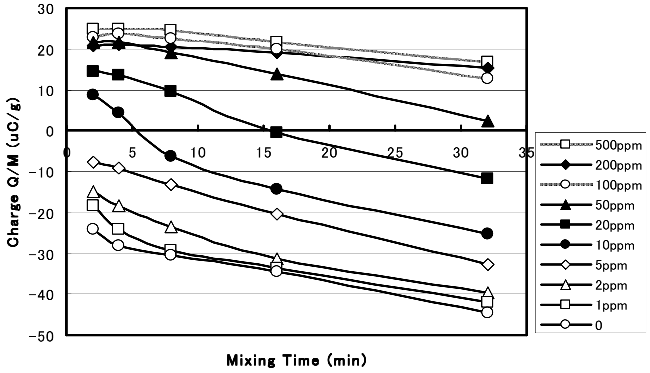

Figure 11 Dependence of charge on mixing time in model toners mixed with various concentration of EA(P-2)

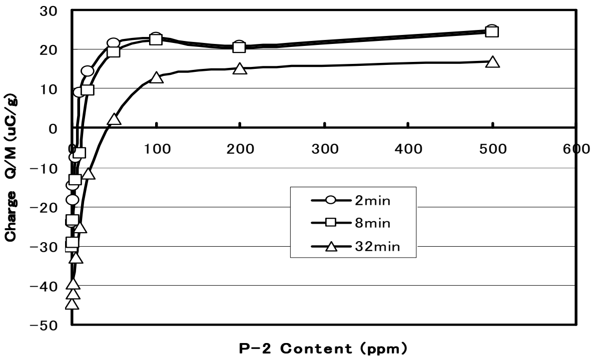

Figure 12 Relationship between charge and P-2 content in toner for various mixing time

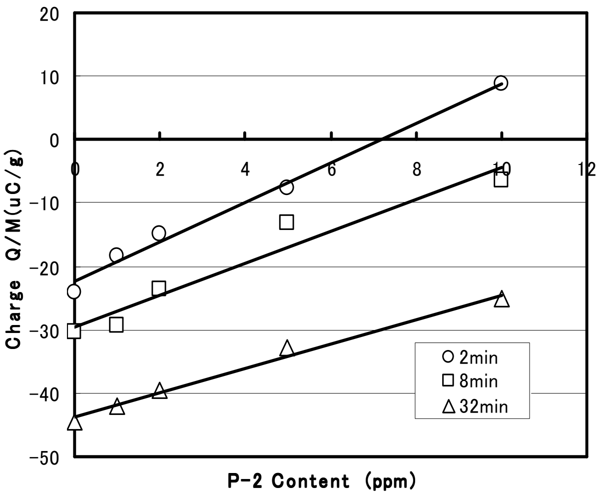

Figure 13 Relationship between charge and P-2 content in toner(lower content region) for various mixing time

In the concentration range of larger than 50 ppm, Q/Ms saturates at around +20 µC/g. The tendency was almost similar for various mixing time. However, the Q/M values of 32 min mixing are smaller than those of shorter mixing time. This means that the carrier is spent in long time mixing as pointed above. Fig. 13 shows the linear part of Fig. 12. The slope represents the contribution of P-2 to Q/M. The contribution is found to be 2.82 µC/ppm from the slope, after neglecting the date of 32 min mixing. Estimation on P-2, which is analogous to that of P-1, carried out using P-2 molecular weight of 499. Contribution to toner charge is 240 µC/ppm when all of P-2 molecules contribute to tribocharge. However, the experimental value suggests that only 1.2 mol% of charging sites contribute to the charge.

Comparison of the charge contribution rate of P-1 and P-2 shows that P-2 has efficiency about twice of that of P-1. The sulfonic salt with low molecular weight is more effective than the polymeric quarternary ammonium salt.

The coverage ratio of each CCA on SS100 surface can be calculated from the projection area of CCA molecules by assuming that each molecule adsorbs on SS100 with the maximum projection area. In rough estimation, P-1 monomer unit has a projection area of $1x10^{-14}$ cm^2 of projection area and a P-2 molecule has $5.6x10^{-15}$ cm^2, respectively. Since 1% of EA-CCA is added to toner, 50 ppm of CCA based on toner weight means 0.5% CCA based on silica. However, in P-1 system, the estimation can not explain the experimental results. Adopting these assumptions, all the surface area of a 100 nm diameter spherical silica particle is covered by 0.3% of P-1 and 0.5% of P-2, respectively. In EA(P-2) shown in Fig. 12, the estimation is very reasonable because Q/M saturates at a CCA concentration of less than 50 ppm. In EA(P-1) system, however Q/M increases to some extent with the increasing amount of P-1 beyond 100% coverage at 30 ppm, as shown in Fig. 9. It is thought that the polymer type P-1 has long main chain and its molecules adsorbed on SS100 is not spread and part of chargeable sites exist on SS100 surface. The assumption of projection area is not suitable for the polymer type CCA. These reasons are the causes that the chargeable sites of P-1 are less effective than P-2.

Table 2 CCA Contribution to Charge from Fig. 13

Mixing Time (min)	Slope (uC/ppm)
2	3.12
8	2.51
32	1.93 (neglected)
Average	2.82

Conclusion

(1) Two kinds of CCA, the polymer type P-1 and the low molecular weight type P-2, were coated on spherical silica particle by using a coacervation method.
(2) Both of CCAs affect on toner tribocharge in a small concentration range of less than 50 ppm.
(3) It was clarified that 0.7 mol% of charging sites in P-1 and 1.2 mol% of those in P-2 contribute to toner tribocharge.
(4) Tribocharge saturates by adding excess P-2 in the concentration range of around 50 ppm based on toner and this concentration agreed with 100% coverage ratio of P-2 on spherical silica particle.
(5) The CCA P-1 has different efficiency on tribocharge from the CCA P-2 due to the shape they take on the silica surface.

References

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Author Biography

Koichi Tsunemi received his BS and MS in polymer chemistry from Waseda University in 1981 and 1983 respectively. Thereafter he worked in electronics companies in Japan and Korea. He joined R&D Division of Morimura Chemicals in 2010. He has focusing on the development of new toner additives for charge control.