Effect of Negative Externally-Added CCA Particles on Toner Charge

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Abstract

Particles of externally-additive-charge-control-agent (EA-CCA) were prepared by means of coacervation process and their effects on toner charge were investigated. EA-CCA particles comprised with metal oxide core particles of 110nm diameter and CCA molecules adhered on the core surface. Four kinds of negative charge control agent (CCA), which were boron complex (N-1), zinc complex (N-2), iron complex (N-3) and styrene-acrylate copolymer with sulfonic acid (N-4), were applied to EA-CCA, respectively. Tribo-charge of the mixture of model toner and EA-CCA was measured in the CCA concentration range up to 1,000ppm against model toner by using blow off method. In both N-2 and N-4 added systems, tribo-charges were increased with increasing CCA concentration up to 1000ppm, in the range of these experiments. In other two CCA added systems, maximum region appeared in tribo-charge around 50ppm of CCA concentration. Relationships between tribo-charge and CCA concentration in all CCA show linear in smaller CCA concentration range, less than 20ppm. The former two kinds of CCA added system have slope value of one fifth smaller than latter two kinds of CCA system. It means that efficiency of CCA molecules was different among CCAs on tribo-charge. The difference considered to be dissociation energy and/or interaction between each CCA molecule on the core surface.

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 such as hydrophobic silica 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, conventional toner does not make use of CCA capability. The author et al. [2] has already reported effect of positively chargeable EA-CCA on toner charge.

In this report, the authors attempt to clarify the effect of negatively chargeable CCA on toner charge in molecular level by using four kinds of commercialized CCA.

Experimental

Preparation of EA-CCA

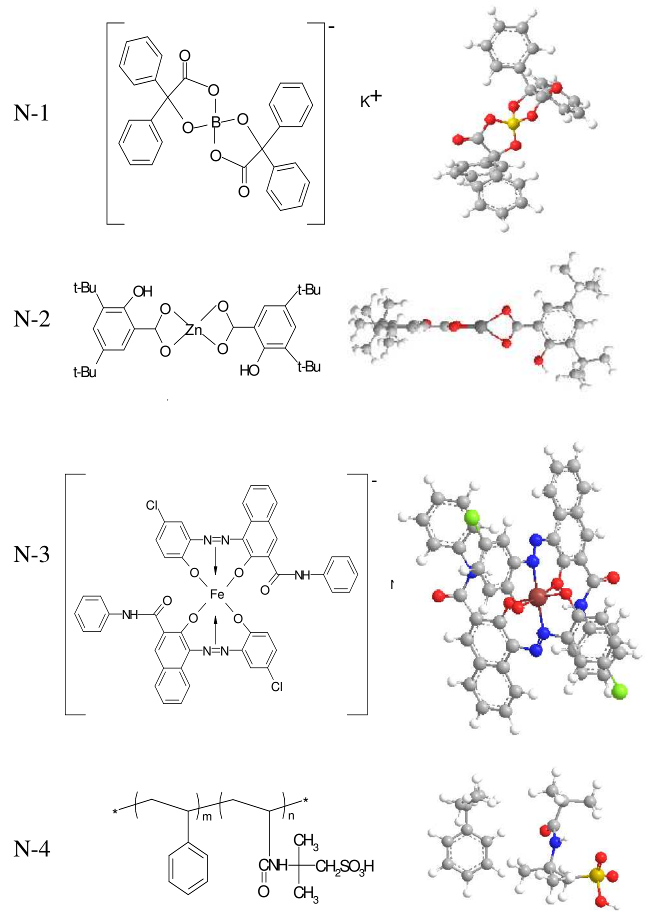

Fig.1 Applied Negative CCAs

Table 1 Molecular weight and projection area of applied CCAs

	MW	Projection area (nm^2)
N-1	502	1.30
N-2	563	1.61
N-3	905	1.37
N-4	155	0.72

Four kinds of well-known negatively chargeable CCA were applied to experiments as shown in Fig. 1. CCA N-1 was a boron complex, N-2 was zinc complex, N-3 was iron complex and N-4 was styrene-acrylate copolymer with sulfonic acid. Molecular weight or average molecular weight and projection area of each CCA were shown in Table 1. Molecular structure and projection area of each CCA were calculated by using MOPAC2009 application, PM6 method [3].

Spherical hydrophobic silica particles (SS-100, from Shin-Etsu Chemical Co., Ltd.) were applied to experiments as the core for CCA. They have an average particle size of 110 nm and a very narrow particle size distribution. Density and surface area of SS-100 were 1.8g/cm^2 and 28m^2/g, respectively. Model toner was prepared from a pulverized styrene-butyl acrylate copolymer without using wax and pigment. Its shape was irregular and the particle size distribution was that of typical pulverized toner. The average particle size was 8.2μm.

The applied CCAs were dissolved in a desired concentration into THF. Then SS-100 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, SS-100 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 was called 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 further drying, white powder was obtained. After pulverization of the powder, EA-CCA was obtained. The SS-100 coated with each CCA was described as EA(N-1), EA(N-2), EA(N-3) and EA(N-4), respectively. The coating amount of CCA was in the range of from 0.01 to 5% based on silica weight.

Coating method was similar as described above. Same polymer for model toner was used for binder resin. Both CCA and binder resin were dissolved into THF and coated on SS-100. Ratio of SS-100/resin was 10/1 in weight and ratio of resin/CCA was from 10/0.01 to 10/5.

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[4]. One gram of model toner and 19 g of a standard carrier (#N-02 from ISJ) were weighed and placed in 100ml 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. It was confirmed that carrier was coated with model toner uniformly by SEM observation. Sample preparation and charge measurement were carried out under controlled room temperature (23±3°C) 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. It has been already confirmed that tribocharge is very similar between usual mixed developer and that of mixed carrier, toner and external additive at the same time [2]. Therefore, developers were prepared by using the method as described above.

Results and Discussion

Blank Test

Firstly, Q/M of model toner and that of model toner added 1% of SS-100 (without CCA coating) were measured as shown in Fig.2. Q/M of model toner was around -10μC/g and that of model toner added SS-100 was around -20μC/g.

EA(N-1) System

Fig. 3 shows the relationship between Q/M and mixing time of developer prepared from carrier, model toner and EA(N-1) which is coated with N-1 of different concentration. The value of Q/M increased slightly with increasing N-1 content up to 50ppm and it slightly decreased with increasing of N-1 content over 50ppm. SS-100 without CCA coating was also negative and Q/M was around -20μC/g and increased with mixing time. Even when only 2 ppm of N-1 was added to toner, the Q/M value was higher than that of no N-1 added system. This means that N-1 is effective on toner charge even in a very small amount. Q/M values of 32 min shaking (square solid plots in Fig.3) are specific because of carrier and toner surface change due to long time vigorous shaking, Q/M values of 32min shaking were neglected in following discussion. Q/M values of EA(N-1) added system were almost constant up to 100ppm of N-1 content and slightly decreased over 100 ppm as shown in Fig.4. In Fig.4, mixing time dependence of Q/M was small and Q/M was almost constant over than 100ppm of N-1 content, independent of mixing time. It means that N-1 has two effects on Q/M, one is increasing Q/M itself and another is to stabilize Q/M against mixing time.

Fig.5 shows Q/M dependence on N-1 content in another EA(N-1) system. SS-100 particles were coated by N-1 with binder

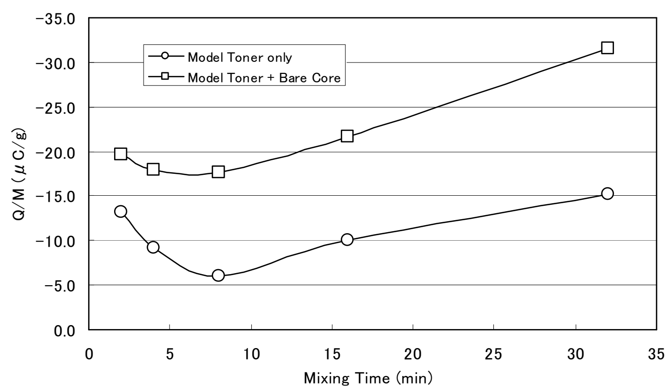

Fig. 2 Q/M dependence on mixing time of model toner and bare SS-100 added system

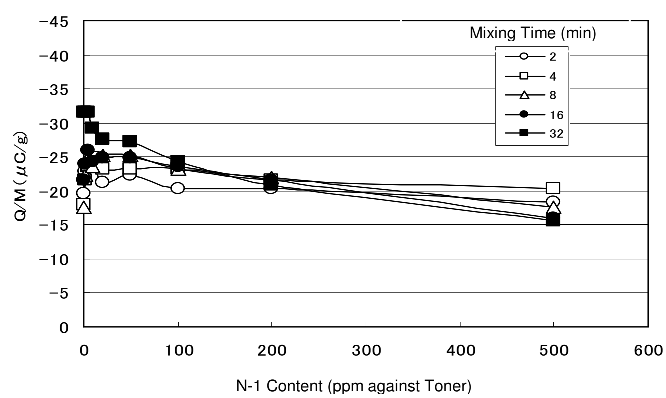

Fig. 3 Relationship between N-1 content and Q/M in various mixing time

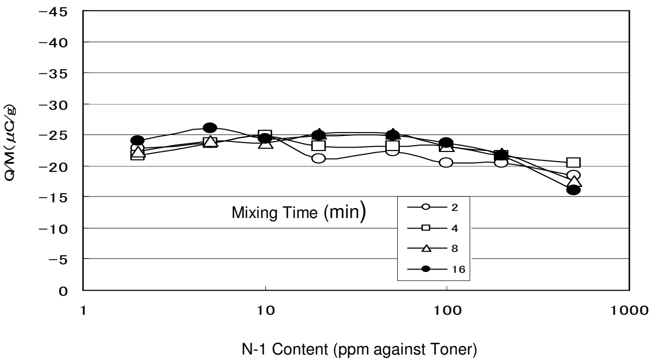

Fig. 4 Relationship between N-1 Content and Q/M (Log Scale)

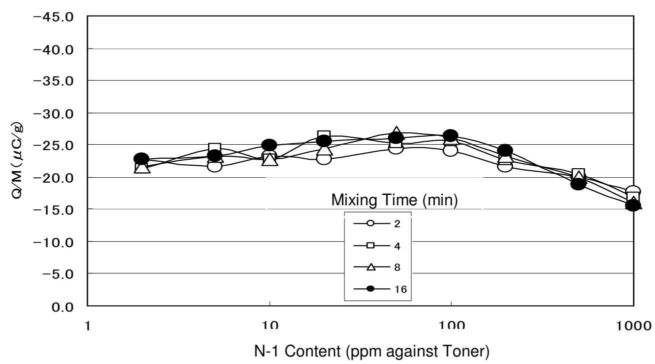

Fig.5 Relationship between N-1 Content and Q/M (Log scale) (Polymer +N-1 coating)

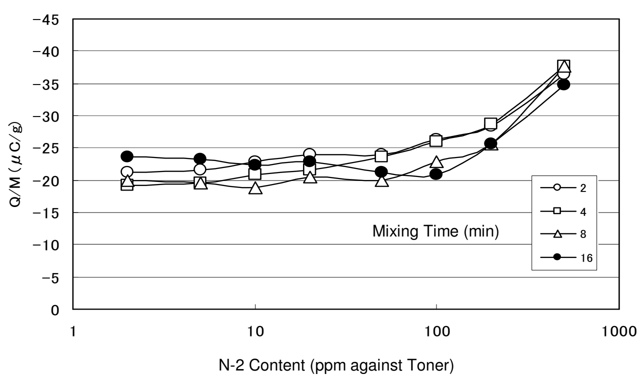

Fig.6 Relationship between N-2 Content and Q/M (Log Scale)

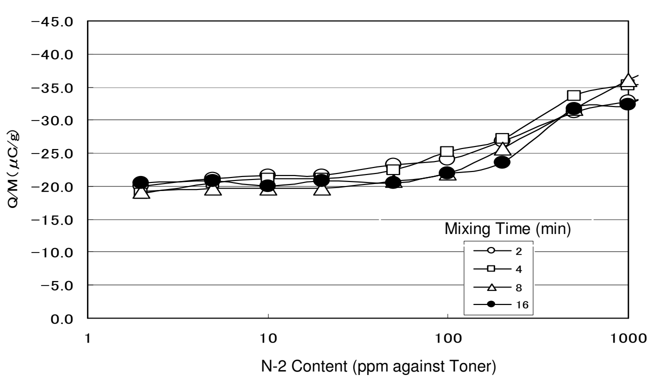

Fig.7 Relationship between N-2 Content and Q/M (Log scale) (Polymer +N-2 coating)

resin. Both Q/M values and their N-1 content dependence were similar to Fig.4. Thickness of binder resin on SS-100 particle was estimated to 33nm from amount of resin and SS-100 surface area. It means that thin binder resin has no influence on toner charge and it plays a role of CCA binder.

EA(N-2),EA(N-3) and EA(N-4) System

Effects of N-2 CCA in EA(N-2) system on Q/M were investigated by same method applied to EA(N-1) system. Fig.6 shows the relationship between Q/M and mixing time of developer prepared from carrier, model toner and EA(N-2) which is coated with N-2 of different concentration. The Q/M values were almost constant up to 100ppm of N-2 content and increased with increasing of N-2 content. In contrast to EA(N-1) system, N-2 contributed to Q/M in higher concentration in toner and it seemed that more N-2 addition was more effective on Q/M.

Fig.7 shows Q/M dependence on N-2 content in EA(N-2) system, which was coated N-2 with binder resin. Both Q/M values and their N-2 content dependence were similar to Fig.6. These results supported that thin binder resin has no influence on toner charge.

Fig.8 shows Q/M dependence on N-3 content in EA(N-3) system. Q/M value saturated around 100ppm of N-3 content and it decreased over 100ppm. The tendency was similar to that of EA(N-1) system. Fig.9 shows Q/M dependence on N-4 content in EA(N-4) system. The tendency was similar to that of EA(N-2) system.

It is suggested that there are two kinds of negatively chargeable CCA. One is a CCA which has suitable concentration to contribute to toner charge such as N-1 and N-3. The other one is more effective on toner charge with more addition into toner.

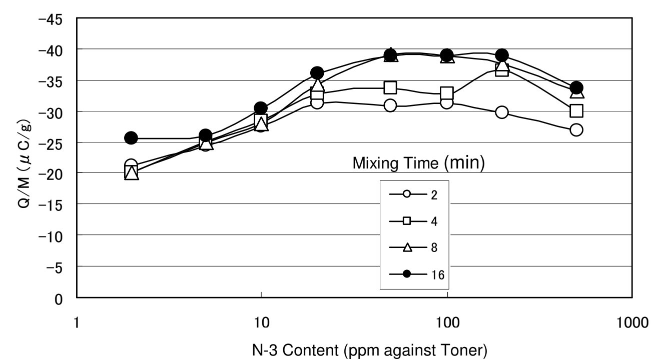

Fig.8 Relationship between N-3 Content and Q/M (Log Scale)

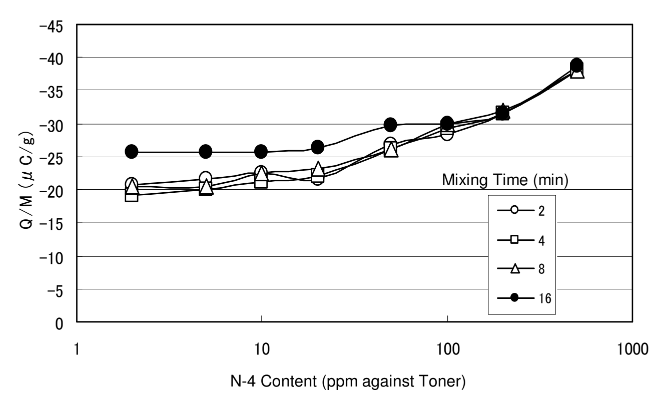

Fig.9 Relationship between N-4 Content and Q/M (Log Scale)

It is known that there are such two kinds of CCA in actual pulverized toner. CCA content is usually around 1% in pulverized toner. When the relationship between Q/M and CCA content in this study reflects actual pulverized toner system, effective CCA amount in actual pulverized toner is 1/100 in added CCA amount.

Low CCA Content Region

Relationship between Q/M and CCA content shows linear in low CCA concentration region in every EA-CCA added system. Figs.10 and 11 show typical relationship of between Q/M and CCA content in lower concentration region. The slope of the linear plots shows contribution rate of CCA molecules as shown in Table 2. The contribution rate was around -1.0μC/ppm in N-1 and N-3. The values in N-2 and N-4 were around -0.18μC/ppm, which was one fifth of that of N-1 and N-3. Number of molecules in 1ppm of each CCA was also shown in Table 2. By considering $1.6x10^{-19}$ C of an electron charge, it is estimated that 0.56% of added CCA molecules contribute to toner charge. The values are 0.10% for N-2, 1.0% for N-3 and 0.06% for N-4, respectively. These values are similar to that of positive chargeable CCA which reported by authors before [2].

Table 3 shows contribution rate on tribo-charge in N-2 and N-4, whose Q/M increased with increasing of those content even in higher concentration region. The values were less that 20% of those in lower concentration region. In N-1 and N-3, Q/M decreased with increasing of CCA content in this region.

Each CCA covers SS-100 in 100% coverage in the concentration range from 100 to 300ppm against toner calculated by projection area of each CCA in Table 1. These results mean that CCA becomes ineffective before reaching 100% coverage.

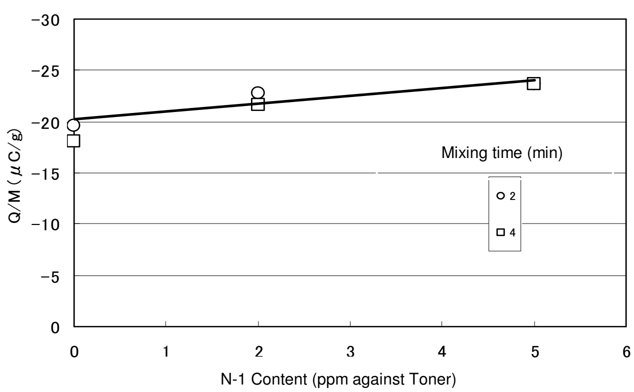

Fig.10 Relationship between N-1 Content and Q/M (Lower Content region)

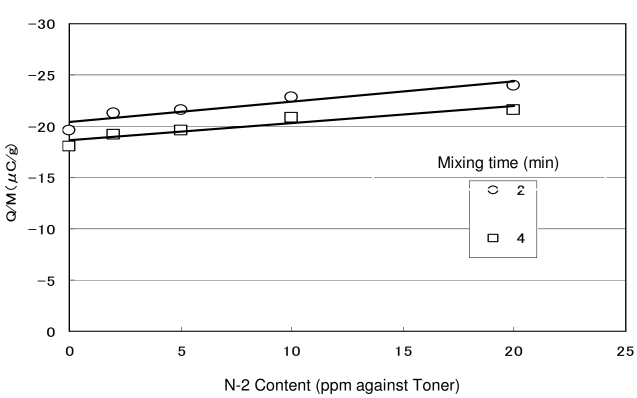

Fig.11 Relationship between N-2 content and Q/M (Lower Content Region)

Table 2 Slopes of Q/M against CCA Content (Lower Content Region)

CCA	Slope (μC/ppm)	Region	Number of molecules in 1ppm	Contribution Rate (%)
N-1	-1.08	<5ppm	$1.2x10^{15}$	0.56
N-2	-0.17	<20ppm	$1.1x10^{15}$	0.10
N-3	-1.07	<10ppm	$0.66x10^{15}$	1.00
N-4	-0.19	<20ppm	$3.9x10^{15}$	0.06

Table 3 Slopes of Q/M against CCA Content (Higher Content Region)

CCA	Slope (μC/ppm)	Region	Contribution Rate (%)
N-1	+0.014	100-500ppm	-
N-2	-0.029	100-500ppm	0.016
N-3	+0.013	100-500ppm	-
N-4	-0.022	100-500ppm	0.007

Conclusion

(1) Contribution rates of four kinds of negatively chargeable CCA to tribo-charge were investigated. Their values were from 0.17 to 1.0μC/ppm.

(2) The values were almost similar to those of positively chargeable CCAs. It was estimated that around 1% of added CCA molecules contributed to tribo-charge.

(3) Q/M saturation was observed in both EA(N-1) and EA(N-3) system in a certain concentration of CCA. The tendency was similar to actual pulverized toner applied N-1 and N-3 CCA.

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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 Limited in 2010. He has also been studying at graduate school of Chiba university. He has been focusing on the development of new toner additives for charge control.