

# Evaluation of Charging Characteristics of CCA by the Cascade Method

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## Abstract

The amount of charges generated by cascading spherical ferrite beads onto a CCA/binder matrix layer was measured using an apparatus newly developed by us. It was confirmed that the cascade measurement is a useful technique for evaluating the charging characteristics of the CCA/Binder matrix layer.

## Introduction

Charging characteristics evaluation of the charge control agent (CCA) is a key technology for developing the color toner for electrophotography. Many kinds of charging evaluation method have been proposed to select a proper CCA, which yields a toner matching to the developing system.

Measurement of the charge amount has been a popular method for the evaluation of CCA contained inside the toner. Much time is needed for the preparation of the toner, however, and the amount of charge varies with preparation processes.<sup>1-5</sup>

Measurement of the charge amount of toners or toner like particles which have a CCA as a coated layer on it was also attempted. In this case, evaluation is simple, but it needs a well defined particles for coating by CCAs. In the case of a low molecular weight (Mw) and mobile CCA, moreover, the reference material surface which comes in contact with the toner to generate the charge is easily contaminated through CCA molecule transfer. As a result, the amount of charge of the CCA coated toners decrease.<sup>6</sup>

A direct measurement of the charge amount of CCA particles themselves versus a reference powder by the blow-off method was also attempted. This evaluation is convenient to study the charging tendency of a CCA. However, it is difficult to estimate the amount of the charge of a toner CCA system from the obtained charge amount of CCA alone.<sup>7</sup>

In this paper, we report an attempt to evaluate several kinds of CCAs using the cascade equipment which the author has newly developed.<sup>8</sup> This equipment enables to measure the charge amount of a CCA/binder matrix layer with high reproducibility, and the measuring operation is rapid and simple.

## Equipment Construction

Figure 1 shows the principle of cascade charge measurement. As the reference powder, spherical ferrite beads (74~147 $\mu$ m) were used. The beads were loaded in a hopper and then cascaded onto an inclined CCA/binder matrix

layer. The charge generated on the layer, which is the same amount of, but has the opposite polarity to, the ferrite beads, was measured by an electrometer. The whole parts of the measurement system were placed in a closed box, and atmospheres (nitrogen gas or vacuum), temperature and humidity could be selected. A pneumatic reciprocal shutter was attached to the hopper tip. The shutter was operated by signals from an outside timer. The inner diameter of the orifice of the hopper tip was 1 mm. Fluctuation of the feeding amount per 1 g of ferrite beads in each measurement was less than 10mg. The charge drift was less than  $1 \times 10^{-12}$  C per hr. Five hopper positions to the matrix layer could be selected from the outside, so that measurement could be repeated without breaking a predetermined atmosphere. The deviation of the measured charge amount from the average value was less than 3%.

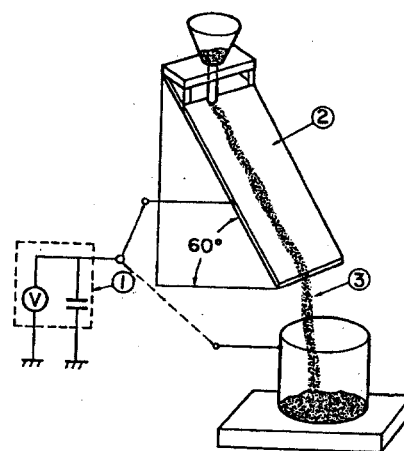


Figure 1. Principle of the cascade charge measurement. (1): Electrometer, (2): CCA/binder matrix layer, (3): Reference ferrite powder.

## Sample Preparation and Charge Measurements

Six types of CCAs were selected. Three types of CCAs were for preparing positive charge toners (P-type CCA). They were a styrene-butyl-methacrylate copolymer having a quaternary ammonium salt group and a high Mw (P-1), an alkyl ammonium salt compound having a low Mw (P-2), and a zinc complex of imidazole (P-3). P-1 and P-2 were soluble and P-3 was insoluble in methyl-ethyl-ketone

(MEK). Three types of CCAs were for negative charge toners (N-type CCA). They were a styrene-butyl-methacrylate copolymer having a sodium sulfonate salt group and a high Mw (N-1), a zinc complex salt of alkylsalicylic acid (N-2), and a calixarene (N-3). N-1 was soluble, N-2 was slightly soluble and N-3 was insoluble in MEK.

A styrene-butyl-methacrylate copolymer (Sty • Acry, softening point  $S_p = 100^\circ\text{C}$ ) and two types of polyesters having carboxyl groups (PET-1 and PET-2, Acid value = 1 and 5,  $S_p = 109^\circ\text{C}$  and  $127^\circ\text{C}$ ) were used as binders, as these binders are common for the commercial toners.

A batch of 2.5g of CCA/binder mixtures in which CCA concentration was adjusted to 0, 0.5, 1.0, 2.0, 4.0 and 8.0 wt% and 25 g of MEK were shaken for 20 minutes in a polyethylene bottle. Then, the dispersions were coated on the surface of a stainless steel plate ( $80 \times 100\text{mm}$ ), and dried in a  $80^\circ\text{C}$  oven for 15 minutes. Obtained CCA/binder matrix layers were used as samples for charge measurements.

The sample plate was attached to the inclined Teflon bed with two fixing pins which were connected to the electrometer. The cascading time was set to 5.0 seconds. The generated charge was measured by the electrometer. Measurements were repeated three times for each sample by shifting hopper positions. The ambient temperature was kept at  $25^\circ\text{C}$  and relative humidity at 50~60%. All experiments were carried out in air.

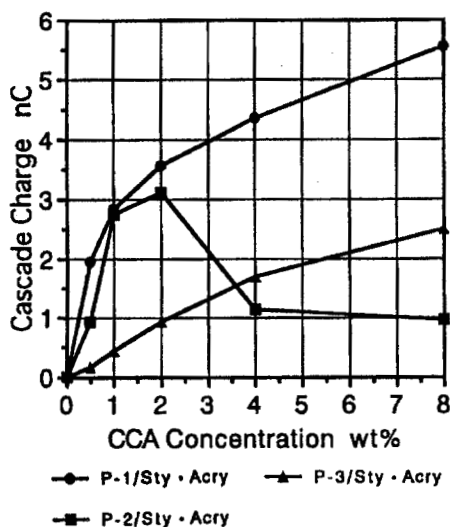


Figure 2. Cascade charge on (P-type CCA)/Sty • Acry matrix layer.

### Relation Between the Types of CCA and Charging Characteristics

The cascade charge amounts on the (P-type CCA)/Sty • Acry layers are shown in Figure 2. Within the CCA concentration of 0 ~ 2 wt%, the positive charge amounts increase with the increase of CCA concentration. At the same CCA concentration, the two types of layers which contain MEK-soluble CCAs (P-1/Sty • Acry and P-2/Sty/Acry) are charged more than the layer containing a MEK insoluble CCA (P-3/Sty • Acry). The most possible explanation is that the number of the ammonium- or amino-functional groups on the matrix layer surface that contains a MEK

soluble CCA is larger than that contains a MEK insoluble CCA, and this number of the functional group determines the positive charge amount.

In the CCA concentration range of more than 2 wt%, the charge amount of the P-2/Sty • Acry layer decreases with the CCA concentration increase. This phenomena is due probably to the surface contamination of the ferrite beads which is caused by the transfer of the P-2 molecules bleeding out on the matrix layer surface.

The cascade charge on the (N-type CCA)/Sty • Acry layers are shown in Figure 3. Similarly to the P-type CCA layers, charging is enhanced with the increase of CCA concentration, and the charge amounts of the two types of the layers which contain MEK soluble CCAs (N-1/Sty • Acry and N-2/Sty • Acry) are larger than that of the layer containing MEK insoluble CCA (N-3/Sty • Acry).

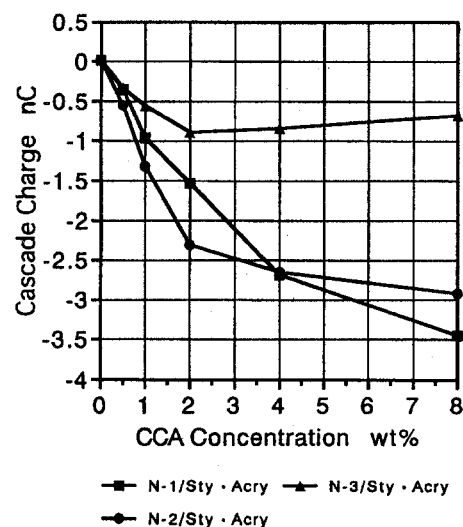


Figure 3. Cascade charge on (N-type CCA)/Sty • Acry matrix layer.

### Relation Between the Types of Binder Resin and Charging Characteristics

The cascade charge amounts on the (P-type CCA)/polyester layer (P-1/PET-1 and P-1/PET-2) and P-1/Sty • Acry layers are shown in Fig. 4. The cascade charge at 0% CCA indicates the charging characteristics of the binder layer itself. Both PET-1 and PET-2 layers show negative charges at 0% CCA, whereas the charge of Sty • Acry layer at this point is nearly zero. PET-2, which has the larger acid number, shows the larger negative charge than PET-1. These results suggest that the negative charge amount depends on the number of the carboxyl group on the binder layer.

The positive charge increases with increasing P-1 concentration. In the case of the two polyester matrix layers, the increase of positive charge for the same CCA concentration increase are very large. Because of the difference of the P-1 solubility into the polyester layers and the Sty • Acry layer, the number of P-1 molecules on the polyester matrix surfaces is considered to be larger than that of the Sty • Acry matrix surface.

The charge characteristic curves of the two polyester matrix layers are nearly the same. The curve shifts toward

to the negative direction with increase of the acid number of the polyester layers. Both the negative charge caused by the carboxyl group in the polyester molecules and the positive charge caused by the ammonium salt group in the CCA molecules determine the charge amount of the matrix layer.

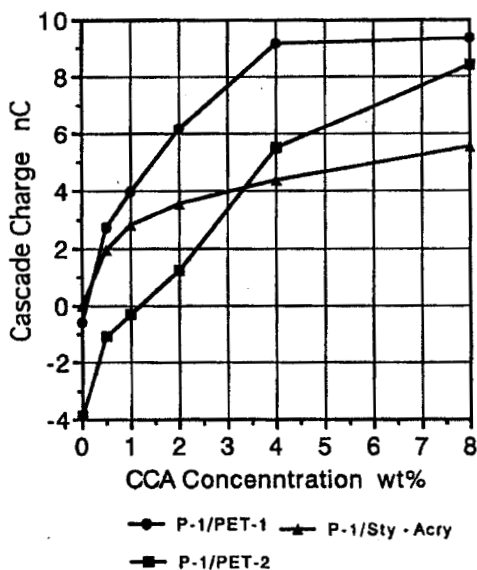


Figure 4. Cascade charge on P-1/Binder matrix layer.

The cascade charge on the (N-type CCA) /polyester layers (N-2/PET-1 and N-2/PET-2) and the N-2/Sty • Acry layer are shown in Figure 5. For all three binders, the charge increases with the increase of the CCA concentration. The charge characteristic curves shift toward the negative direction with increase the acid number of the binder. The negative charge caused by the carboxyl group in the polyester molecules and the negative charge caused by the CCA molecules determine the charge amount of the matrix layer.

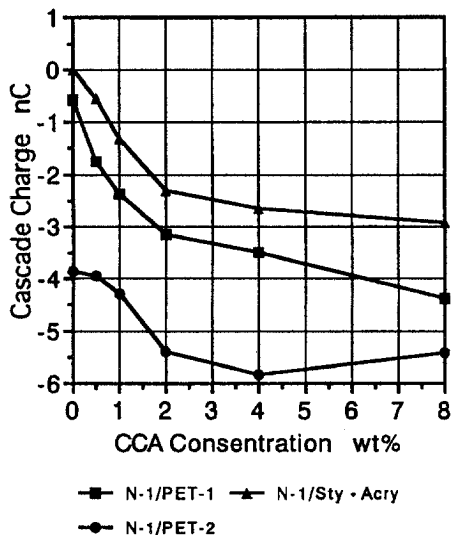


Figure 5. Cascade charge on N-2/Binder matrix layer.

## The Charging Characteristics of a Matrix Layer Containing Mixed CCA

It is expected that, instead of providing many different CCAs, a mixture of a N-type and a P-type CCA may cover a wide range of charge amount. Therefore, the CCAs P-1 and N-1 were blended in a various ratio, and their charging characteristics were measured. The molecular structure, Mw and the molar concentration of the functional groups in P-1 and in N-1 were estimated to be nearly the same. The mixture was added to the Sty • Acry binder. The CCA matrix layers were prepared by the process mentioned above. Concentration of the total amount of mixed CCA in the layer was kept to 4.0 wt%.

Figure 6 shows the relation between the N-1 mixing ratio ( $N-1/(N-1 + P-1)$ ) and the cascade charge. The negative charge increases with the N-1 ratio. The result is explained from the fact that the number of the sulfonic acid group, which contribute to the negative charge on the layer surface, increases with the N-1 ratio. Assuming that the cascade charge amount is proportional to the number of the sulfonic acid group on the layer, the measured charge values in the Figure 7 has to be found on the straight line which is obtained by connecting the charge amount at N-1 ratio = 0 (P-1 ratio = 1) and N-1 ratio = 1 (P-1 ratio = 0). The measured values, however, shows a small deviation to the positive charge side. There might exist a weak tendency in which P-1 molecules having ammonium salt group preferentially occupy the outer position in the CCA mixture layer.

Thus it was confirmed that, by using a P- and N-type CCA mixture, the charging polarity and charging amount of the CCA/Binder layer can be controlled in a wide range.

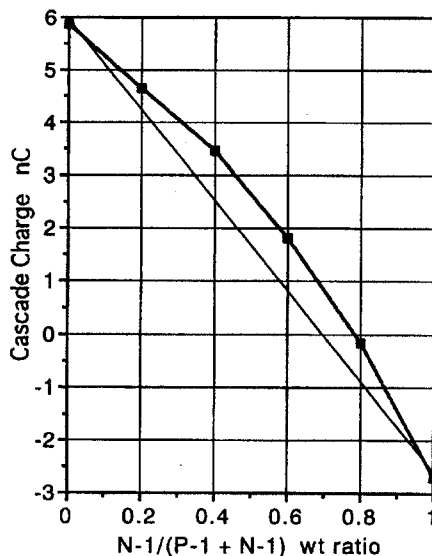


Figure 6. Cascade charge on (P-and N-type mixed CCA)/Sty • Acry matrix layer.

## Conclusion

Contact charges between CCA/Binder matrix layers and spherical ferrite beads were measured by the cascade

method using an equipment newly developed by us. The cascade measurement shows high reproducibility and detects a very small change of chemical composition on the layer surfaces. The charge amount increases with the number of the functional group which is introduced by CCA molecules to the layer surface. The charge controllability of a CCA on various CCA/binder layers is easily evaluated by the cascade measurement. Acid/base interaction between a CCA and a binder molecule that affects the toner charge amount can also be evaluated. By using a P- and N-type CCA mixture, the charging amount of the CCA/binder matrix layer can be controlled in a wide range.

## References

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