

# Toner Charging Effect by CCA particles at the interface between Toner and Carrier

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## Abstract

Three toner-carrier combinations were prepared by using a styrene-acryl (St-Ac) model toner and three types of ferrite carriers (having an electron accepting, a neutral, or an electron donating coating on its surface). Six types of CCAs (Charge control agent) were externally added to the interface between the toner and carrier. The amount of toner charge  $q/m$  generated in each combination that contained the same amount of CCA was measured by a blow-off method and compared with the amount of toner charge  $q_0/m$  generated in the same combination that contained no CCA. By adding six types of CCA, the difference of the amount of toner charge  $\Delta q/m (= q/m - q_0/m)$  increases linearly with the increase of the Electron-donating Coordinate (EDC) that is determined by the amount of blow-off charge  $q_0/m$ . Six  $\Delta q/m$ -EDC characteristic curves obtained by the addition of six types of CCA shift toward the positive charging region with the increase of the positive charge impartation capability of the added CCA. The zero-point-of-charge-shift (zpcs) value, which is defined as the EDC value at  $\Delta q/m = 0$  in the  $\Delta q/m$ -EDC characteristic curve, decreased with the increase of positive charge impartation capability of the CCA. Using the above results, the role of CCA particles in the toner/carrier interface was correlated to the EDC value of the carrier from a viewpoint of electron-donating (or electron-accepting) characteristics between toner/carrier, toner/CCA and carrier/CCA interfaces.

## Introduction

It is said that, among CCA particles that contribute as a charge controlling agent to toner particles, those CCA particles that exist on the toner surface are particularly effective. In other words, the CCA particles exposed on or adhered to the pulverized toner surface act as a charging site when they are brought into contact with the carrier surface; when the CCA particles on the toner surfaces and the carrier particles are separated after the contact, the CCA particles and the carrier particles acquire the same amount of charge of opposite polarity<sup>[1]</sup>.

The authors of the present paper previously investigated a charge controlling capability of CCA particles that were added to the interface between the toner surface and carrier surface. They found that a large amount of toner charge was imparted by an extremely small quantity of CCA particles that were externally added to the interface<sup>[2]</sup>. The authors suggested the following toner charging mechanism. In agitation of toner/CCA/carrier mixture, a large number of charged CCA particles having a size of 10 to 100 nm are generated, part of the charged particles adhere to the toner surface, and finally a large amount of toner charge is obtained. The toner charging mechanism mentioned above functions by charged

particle transfer at the interface between the toner surface and carrier surface.

In this paper, six types of CCAs were externally added to three types of toner/carrier combinations which contained three types of ferrite carriers having different electron donating (or electron accepting) properties, and the charge impartation capability of each type of CCA was investigated. An interesting phenomenon in which the charge impartation capability of CCA particles to toner particles is determined by the level of electron donation of the carrier surface was observed. The precise experiments and results are mentioned below.

## Experimental

### Sample preparation

As a model toner, pulverized styrene-acryl (St-Ac) copolymer particles having an average particle size of  $8.5 \pm 0.5 \mu\text{m}$  and an acid value of 1.0 were prepared.

Spherical ferrite particles having an average particle diameter ranging from 44 to 125  $\mu\text{m}$  were used as the core for the preparation of carrier particles. The surface of the core particles was coated with three different types of silicon resin that have different electron donating (or electron accepting) properties to

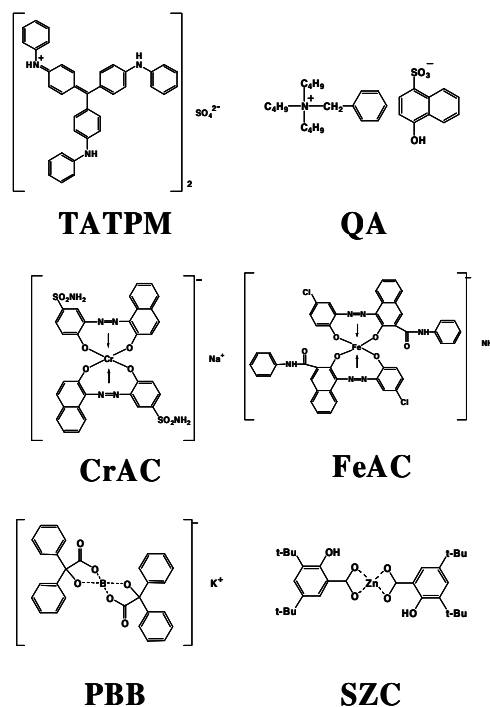


Fig. 1 Chemical structures of six types of CCAs.

obtain three types of carriers,  $C_A$  (electron accepting type),  $C_I$  (intermediate type), and  $C_D$  (electron donor type).

Two positive charging type CCA particles, namely trianilino - triphenylmethane sulfate (TATPM) and a quaternary ammonium salt (QA), and four negative charging type CCA particles, namely chrome-azo complex (CrAC), a ferrous-azo complex (FeAC), potassium borobenzyrate (PBB) and the zinc complex of *t*-butyl salicylic acid (SZC), were used as CCA particles. The chemical structures of all types of CCAs mentioned above are shown in Fig. 1.

### Measurement of toner charge

A mixture of 19 g of carrier, 1 g of model toner and a prescribed amount of CCA (2000, 4000, 8000 and 16000 ppm of toner weight) was put into a 100 ml wide-mouth polyethylene bottle and maintained for 24 hr under an atmosphere of 20 to 25°C and 50 to 60%RH to adjust the moisture content. The bottle was set to a paint shake type blender and the bottle content was mixed for 2, 4, 8, 16, and 32 min. The toner charge  $q/m$  at each mixing time was measured by the blow-off method according to the standard measurement procedure stipulated by ISJ<sup>[3]</sup>.

For comparison, the toner charge  $q_0/m$  obtained from the same model-toner/carrier combination that contains no CCA particles was measured through the same procedure.

## Results and discussion

### Values of $q_0/m$ and definition of EDC

Variation of the  $q_0/m$  values with mixing time in (St-Ac model toner) / (three types of carrier:  $C_A$ ,  $C_I$  or  $C_D$ ) combinations are shown in Fig. 2. The absolute value of the  $q_0/m$  in each toner/carrier combination increases gradually with the increase of the mixing time and reaches a saturation value. When the three  $q_0/m$  values at the mixing time of 32 minutes are compared, it is clear that the negative amount of charge is increases by changing the carrier from  $C_A$  to  $C_D$ ; the negative charge increasing by 60  $\mu\text{C/g}$  by changing the carrier from  $C_A$  to  $C_I$ , and by 30  $\mu\text{C/g}$  by changing the carrier from  $C_I$  to  $C_D$ . The  $q_0/m$  value is proportional to the number of electrons transferred from the carrier surface to toner surface. Therefore, the fact that the increase of negative toner charge by changing the carrier from  $C_A$  to  $C_D$  means that the electron donating capability of the carrier surface increases by changing the carrier from  $C_A$  to  $C_D$ .

From the above consideration, it is reasonable to determine the Electron-donating Coordinate (EDC) values for each carrier using a certain amount of charge shift as a measure. In this paper, we define the 30  $\mu\text{C/g}$  of charge shift as one EDC unit, and the

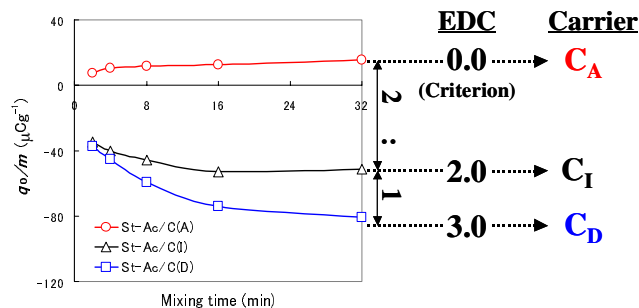


Fig. 2 Relationship between  $q_0/m$  and mixing time. EDC values are defined for each carrier by using the  $q_0/m$ .

EDC value of carrier  $C_A$  to 0.0. Considering the amount of charge shift by changing the carrier from  $C_A$  to  $C_I$  and  $C_I$  to  $C_D$ , the EDC values of  $C_I$  and  $C_D$  are found to be 2.0 and 3.0, respectively. The EDC value can be related to the position of the carrier in the tribo-electric series; the carrier that has the largest (smallest) EDC value occupies the highest (lowest) positively (negatively) charging position in the tribo-electric series.

### Effect of addition of positive type CCA (TATPM) to the toner/carrier interface on toner charging

The effect of the addition of a positive type CCA (TATPM) into the interface between the St-Ac model-toner and three types of carrier ( $C_A$ ,  $C_I$  or  $C_D$ ) are shown in Figures 3, 4 and 5. The

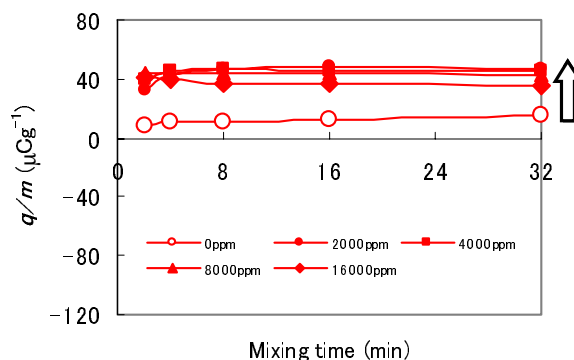


Fig. 3 Charge impartation effect by addition of TATPM into interface between St-Ac model toner and carrier  $C_A$ .

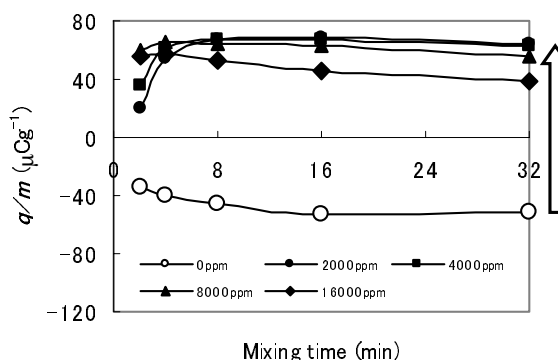


Fig. 4 Charge impartation effect by addition of TATPM into interface between St-Ac model toner and carrier  $C_I$ .

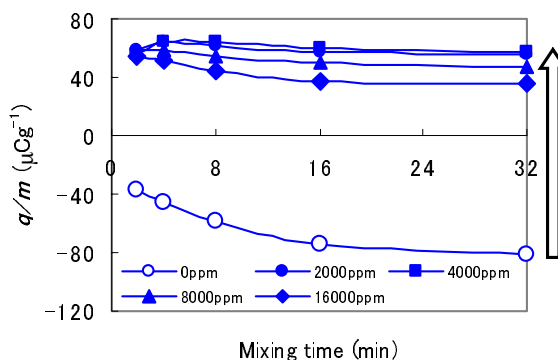


Fig. 5 The charge impartation effect by addition of TATPM into interface between St-Ac model toner and carrier  $C_D$ .

white circles show the values of  $q_0/m$ , and the black symbols show the values of  $q/m$  for different amounts of TATPM addition.

The variation of  $q_0/m$  and  $q/m$  values for the mixing time from 2 to 32 minutes are relatively small and reaches a saturation value at 32 minutes of mixing. As shown in Fig. 3, the  $q_0/m$  value obtained by using the carrier  $C_A$  (EDC = 0) shows positive polarity. In other two combinations in Fig. 4 and Fig. 5, the  $q_0/m$  value obtained by using the carrier  $C_1$  (EDC = 2.0) and carrier  $C_D$  (EDC = 3.0) show negative polarity. On the other hand, the  $q/m$  values in all combinations are larger than  $q_0/m$  values and show positive polarity.

With the  $q_0/m$  and  $q/m$  values at 32 minutes mixing time, an amount of charge shift  $\Delta q/m (= q/m - q_0/m)$  were estimated and shown with an arrow in each figure. The arrow length is equivalent to the amount of charge shift by the addition of TATPM for each toner/carrier combination. All of the arrows in the three figures are directed toward an upper positive charging region regardless of the polarity of  $q_0/m$ . The results show that the TATPM particles which were added to the three toner/carrier combinations act as a positive charge imparting agent to the St-Ac model toner.

The arrow length in the three figures, which is an equivalent to the amount of charge shift  $\Delta q/m$  by the addition of TATPM to each toner/carrier combination, seems to be increasing with the increase of the EDC value of carrier.

Fig. 6 shows the  $\Delta q/m$ -EDC characteristic relationship for different amounts of TATPM addition to the toner/carrier interface. The figure shows that the  $\Delta q/m$  values obtained by the addition of the same amount of TATPM linearly increase with the increase of EDC. The variation of  $\Delta q/m$  values by the different amounts of TATPM addition is very small except the case of 16000 ppm (highest amount) in which  $\Delta q/m$  values are slightly smaller than those of other cases.

The effects of the addition of another positive charging type CCA (QA) on the toner charging for the three types of toner/carrier combinations showed nearly the same results as TATPM addition, giving also a linear  $\Delta q/m$ -EDC characteristic relationship. The result will be shown and discussed in another section.

### Effect of addition of negative type CCA (CrAC) to the toner-carrier interface on toner charging

The effect of the addition of a negative charging type CCA

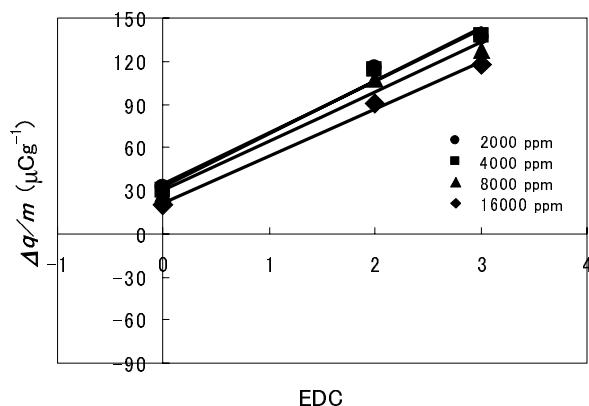


Fig. 6 Relationship between  $\Delta q/m$  and EDC for various mixing time.

(CrAC) into the St-Ac model-toner and three types of carrier ( $C_A$ ,  $C_1$  or  $C_D$ ) interfaces are shown in Figures 7, 8 and 9.

As shown in the three Figures, all  $q/m$  values show negative polarity of charge by the addition of CrAC. The amounts of toner charge shift ( $\Delta q/m$ : shown with arrow length) by the addition of CrAC to the three types of toner/carrier combinations are smaller than those obtained by the addition of positive charging type CCA (TATPM) (see Figures 3, 4 and 5).

The direction of charge shift by the addition of CrAC is different depending on the carrier species. The charge shift when the carrier  $C_A$  (EDC = 0) is used is shown in Fig. 7. In this case, the charge shift (shown by arrow) is directed toward a lower

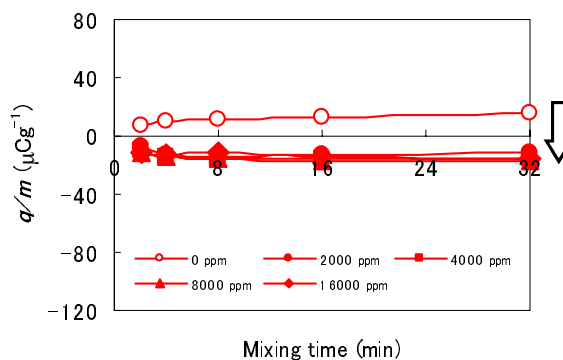


Fig.7 Charge impartation effect by addition of CrAC into interface between St-Ac model toner and carrier  $C_A$ .

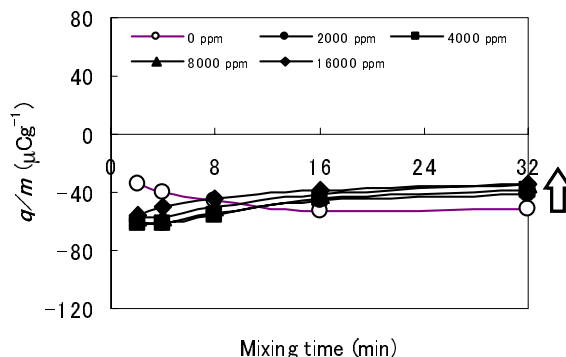


Fig.8 Charge impartation effect by addition of CrAC into interface between St-Ac model toner and carrier  $C_1$ .

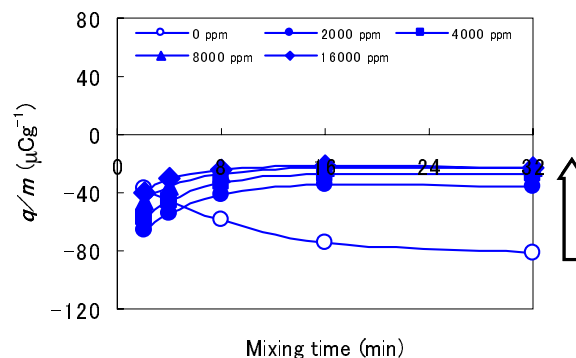


Fig.9 Charge impartation effect by addition of CrAC into interface between St-Ac model toner and carrier  $C_D$ .

negative charging region. The charge shift by using the carrier  $C_1$  (EDC = 2.0) and carrier  $C_D$  (EDC = 3.0) are shown in Fig. 8 and Fig. 9 respectively. In these cases, charge shifts are directed toward an upper positive charging region. The amount of toner charge shift and the direction of charge shift caused by the addition of negative type CCA (CrAC) are different from those obtained by the addition of positive type CCA (TATPM and QA).

It is clear that the charge shifts by the addition of CrAC are different with the EDC value of carrier particles in the toner/carrier combination; in the case of toner-carrier combination using a carrier  $C_A$  (EDC = 0), the CrAC acts as a negative charge imparting agent, and in other toner-carrier combinations using the carrier  $C_1$  (EDC = 2.0) and the carrier  $C_D$  (EDC = 3.0), the CrAC acts as a positive charge imparting agent. The same results as those shown in Fig. 6, in which the  $\Delta q/m$  values obtained by the addition of TATPM increase linearly with the increase of EDC value, was also obtained by the addition of CrAC.

The charge shifts by the addition of other three types of negative charging type CCAs (PBB, FeAC and SZC) to the three types of toner/carrier combinations were also investigated. Nearly the same behavior as that obtained by the addition of CrAC was observed. The  $\Delta q/m$ -EDC characteristics curves obtained by the addition of these three negative charging types of CCAs will be discussed in the following section.

### Relationship between $\Delta q/m$ and EDC

Figure 10 shows the relationship between  $\Delta q/m$  and EDC for six types of CCAs (TATPM, QA, PBB, FeAC, CrAC and SZC). The  $\Delta q/m$  values obtained by the addition of each CCA increase linearly with increase of the EDC values of the carrier. Comparing the six  $\Delta q/m$ -EDC characteristic lines obtained by the addition of six types of CCAs, the  $\Delta q/m$  values of the two positive charging type CCAs (TATPM and QA) are located in the upper positive charging region while those of the four negative charging type CCAs (PBB, FeAC, CrAC and SZC) are situated in the lower, sometimes negative, charging region. From the order of six characteristic lines, six types of CCAs can be arranged to form the following tribo-electric series.

(-) SZC - CrAC - FeAC - PBB - QA - TATPM (+)

The order of  $\Delta q/m$  values at an arbitrary EDC value is identical with the order of the tribo-electric series because the six  $\Delta q/m$ -EDC characteristic lines do not cross each other.

The  $\Delta q/m$  values in each  $\Delta q/m$ -EDC characteristic lines increase with the increase of the value of EDC and become zero at a certain EDC value. That EDC value is defined as the zero point of charge shift (zpcs). The locations of zpcs for the two positive charging type CCAs are out of the present EDC scale, but they are roughly estimated by EDC value extrapolation.

It is interesting that the series of six types of CCAs that are arranged according to the zpcs values show an order reverse to the above tribo-electric series. The result shows that the zpcs value can be regarded to as expressing the negative charge impartation capability of each CCA to the toner particles. According to the above consideration, SZC is regarded as the strongest negative charge imparting agent and TATPM as the strongest positive charge imparting agent.

As shown in Fig. 10, each CCA changes from a negative charge imparting agent to a positive charge imparting agent by using the carrier that has a larger EDC value than that of zpcs. The

$\Delta q/m$ -EDC characteristic lines in Fig. 10 also suggests that, in the toner/carrier combinations which contain the carrier having the largest (smallest) EDC, all CCA particles added to the combination act as a positive (negative) charge imparting agent.

It was confirmed that, in the present system, the role of EDC value of the carrier surface is an important factor to determine the amount of tribo-charge on toner particles, CCAs and carrier particles themselves.

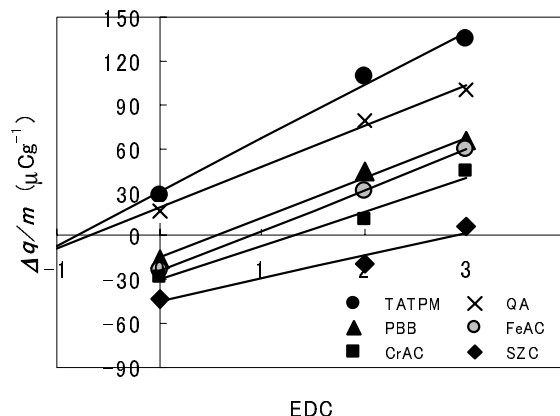


Fig.10 Relationship between  $\Delta q/m$  and EDC in six types of CCAs.

### Conclusion

Three types of toner-carrier combinations were prepared with a styrene-acryl (St-Ac) model toner and three types of ferrite carriers having a different EDC value. Six type of CCAs were externally added to the interface between the toner and carrier. The amount of toner charge  $q/m$  was measured by a blow-off method and compared with the amount of toner charge  $q_0/m$  that contained no CCA. By addition of six types of CCA, the toner charge shift  $\Delta q/m (= q_0/m - q/m)$  increases linearly with the increase of the EDC. Using the six  $\Delta q/m$ -EDC characteristic lines the charge impartation capabilities of six types of CCAs were discussed. It was concluded that, for the toner/carrier combination which contains a carrier having the largest (smallest) EDC, all types of CCA added to the combination act as a positive (negative) charge imparting agent.

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