 

# Tribocharging Mechanism of Polymers with CCA

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## Abstract

To understand tribocharging characteristic of polymers containing CCA, influence of the amount of surface CCA on the toner charging was investigated for various CCA's. The charging behavior of the toners with CCA was strongly related to the crystal form and solubility into resin of CCA particles. The amount of surface CCA influenced the tribochaging rate of toners. TSC measurements indicate that the interface between CCA and resin works as charging sites for tribocharging of toners.


## Introduction

Tribocharge of toners is a major factor in electrophotographic process, and CCA's (charge control agents) are used for toners to improve their tribocharging characteristics. To understand the role of CCA in toner charging, tribocharging behavior of toners containing CCA was studied, and influence of size and crystal form of CCA particles was discussed [1,2]. It was reported that the charging behavior of the toners with CCA was strongly related to the crystal form of CCA particles[3]. The amount of CCA on the toner surface, which is determined by the breaking behavior of the CCA particles during the melt mixing process and their affinity with the toner resin, mostly defines the toner charging characteristics. This suggests a possibility for optimization of toner charging by controlling the CCA crystal form.

This paper describes the influence of the amount of CCA on the toner surface on their charging characteristics. Thermally stimulated current (TSC) measurements were also carried out on CCA/resin layers to investigate the charging mechanism of resin with CCA. The role of the interface between CCA and resin on the toner charging will be discussed.

## Experimental

Toners used in this study were consisted of styrene-acrylic resin (Himer TB-1000; Sanyo Chemical Co., Ltd.), 5 % of carbon black (MA-100; Mitsubishi Chemical Co., Ltd.), and azo-iron complex compound CCA (T-77; Hodogaya Chemical Co., Ltd.) or salicylic acid metal complex (laboratory made). Several types of toners differing in kinds and amount of CCA's were prepared by the conventional sequence of kneeding, pulverizing and classification. The mean particle size of all the toners was 10 μm. Using a non-coated or silicone-coated ferrite carrier, having a mean particle size of 100 μm, a dual-component developer was prepared, in which the toner concentration was 4 wt%. An appropriate amount of the developer was charged in a polypropylene tube and was rotated at the rate of 110 rpm. The tribocharge of toner was measured as a function of agitation time by blow-off method. All the measurements were carried out at 25 °C and 50 %RH.

The amount of CCA existing on the toner surface (surface CCA) was determined as follows: first CCA on the toner surface was extracted with an alcoholic solvent, and then its amount was measured by a visible-spectrometer, while the CCA existing in the bulk of the toner particle (internal CCA) was entirely extracted with a polar solvent, and its amount was also measured by the visible-spectrometer after filtering out carbon black.

A CCA-resin layer 2 mm in thickness was sandwiched by a pair of metal electrodes and TSC[4] measurements were performed in the temperature range of –70 to 80 ºC by TSC Spectrometer TSC3000 (Rigaku Electric Co., Ltd.) .

## Results and Discussion

**Determination Factors of Amount of Surface CCA**

Generally speaking, both the saturation tribocharge and charging up rate are very important in the toner charging. The amount of surface CCA is considered to influence the toner charging characteristics, such as saturation, strongly. Determination factors of the amount of surface CCA are the functions of amount, crystal form and affinity with resins of CCA's added. Each factor is discussed in this paper.

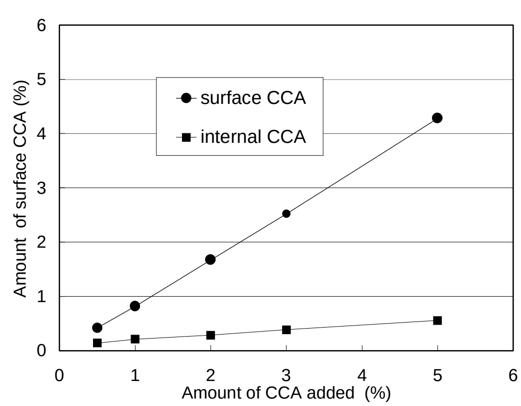



*Figure 1. The influence of amount of CCA added*

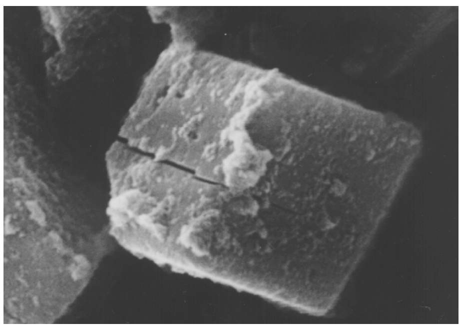
 

**(1) CCA Concentration in the Resin**

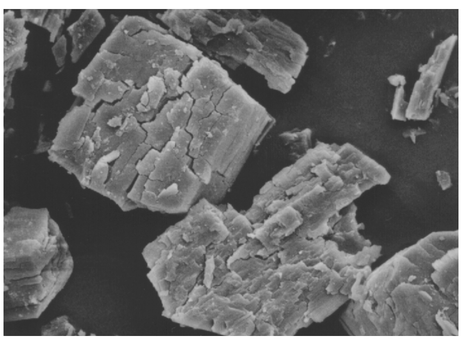
Figure 1 shows that the CCA amount on the toner surface increases proportionally with an increase in the amount of CCA added. More than 80% of incorporated CCA appears on the toner surface due to selective breaking behavior at the CCA/resin interface during pulverizing process.

**(2) CCA Crystal Form**

Crystal forms of CCA have a complicated influence on the tribocharging behavior. For instance, some scientists reported that CCA particles with many cracks selectively appear on the toner surface because of their brittle tendency, which enhances tribocharging of toners[3]. While others considered that cracks in CCA particles themselves have a strong driving force in generating tribocharge in toners[5]. Figure 2 shows SEM photographs of CCA particles. Both CCA's have exactly the same chemical composition (azo-iron complex), but were treated differently depending on the preparation methods, resulting in different crystal forms.



*Crystal form A*



*Crystal form B*

*Figure 2. SEM photographs of CCA particles*

These two types of CCA's were incorporated into the toners prepared in this study, and their charging performances were measured. The results are shown in Fig. 3. The CCA with cracks (crystal form B) apparently enhances the tribocharging rate. The amount of surface and internal CCA's in the toners containing the CCA of crystal forms A and B were measured by the procedure described above. The results are given in Table 1. The amount of CCA on the toner surface is about the same for either case. However, the amount of internal CCA of crystal form B is less than that of crystal form A. This result indicates that the CCA of crystal form B is more brittle than that of form A. Therefore, the CCA of crystal form B breaks more easily than that of form A during the pulverizing process.

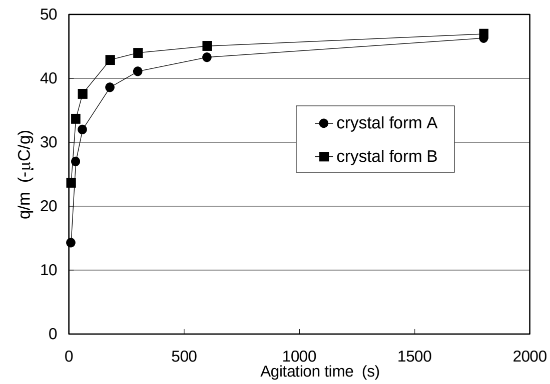



*Figure 3. Tribocharging characteristics for the two kinds of toners differing in the crystal form of the CCA*

**Table 1. Amount of Surface/Internal CCA's in the Toner**

| | CCA added(%) | Surface CCA (%) | Internal CCA (%) | Total CCA(%) |
|---|---|---|---|---|
| Form A | 1.00 | 0.612 | 0.338 | 0.950 |
| Form B | 1.00 | 0.615 | 0.119 | 0.734 |

Next, the amount of CCA in every toner size was measured by Particle Analyzer PT1000 (Yokogawa Electric Corp.,). Figures 4 and 5 show the relationship between relative size of the iron distribution region in a toner particle, and relative particle size of toner for the toners with the CCA of crystal forms A and B, respectively. The toner with CCA of crystal form A shows homogeneous CCA distribution within the toner particle, while CCA of crystal form B was heterogeneously distributed. This result also indicates that the CCA of crystal form B is more brittle than A. Some free CCA isolated from toner particles may increase the charging up rate.

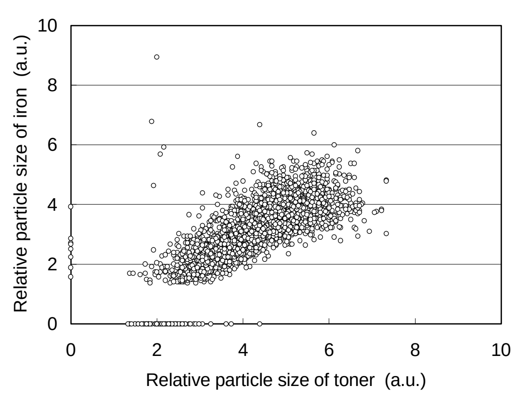



*Figure 4. Relationship between relative particle size of iron and relative particle size of toner*

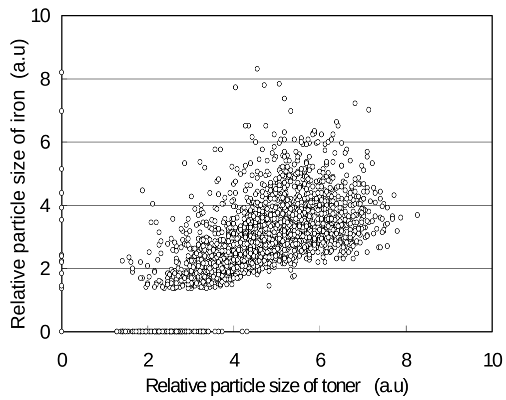



*Figure 5. Relationship between relative size of iron and relative particle size of toner*

### (3) CCA Affinity with Resin

Affinity of CCA's with resin is also considered to be very important in the toner charging, since the amount of CCA on the toner surface is determined by its affinity. Solubility parameter (SP) is generally used to indicate the affinity between two substances, the affinity of CCA with resin in this case.

Other types of CCA's were prepared, actually four types of salicylic acid metal complexes, which work as n-type CCA's, and whose solubility into toluene was measured. Figure 6 shows the relationship between CCA amount on the toner surface and CCA solubility into toluene. The amount of CCA on the toner surface was measured by fluorescence-spectrometer after extracting CCA from the surface with organic solvent in this case. The amount of CCA on the toner surface decreases with an increase in solubility into toluene. It should be noted that the SP of CCA into styrene is very similar to that into toluene. These results indicate that CCA affinity with resin is one of the most important factors in tribocharging.

### Relationship between CCA Amount on the Toner Surface and Tribocharging Behavior

To understand the influence that the CCA amount on the toner surface has on the tribocharging behavior, various toners were prepared using the salicylic acid metal complex derivatives as CCA's. The amount of surface CCA was affected by changing the kneading condition and amount of CCA added. Figure 7 shows the relationship between CCA amount on the toner surface and tribocharge value after agitation of the toner with the silicone-coated carrier for 30min.

The tribocharge increases proportionally with CCA amount on the toner surface in the low CCA amount region, and saturates at high CCA amounts.

Next, three samples which had different surface CCA amounts (1.92 mg, 3.62 mg, 8.19 mg) were picked up, and their tribocharging behavior was measured for an extended period of agitation. The results are shown in Fig. 8.

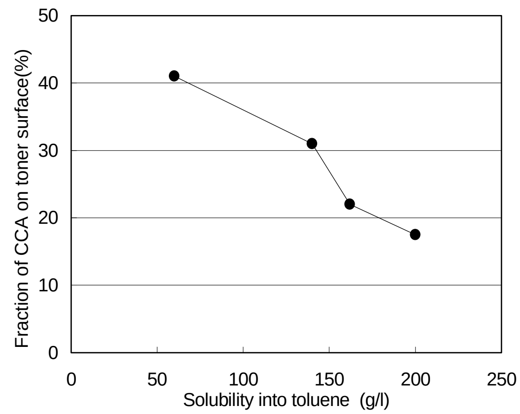



*Figure 6. CCA solubility into toluene versus CCA amount on the toner surface*

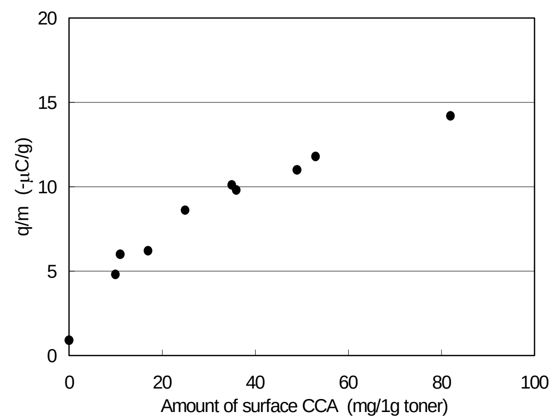



*Figure 7. Relationship between tribocharge value and CCA amount on the toner surface*

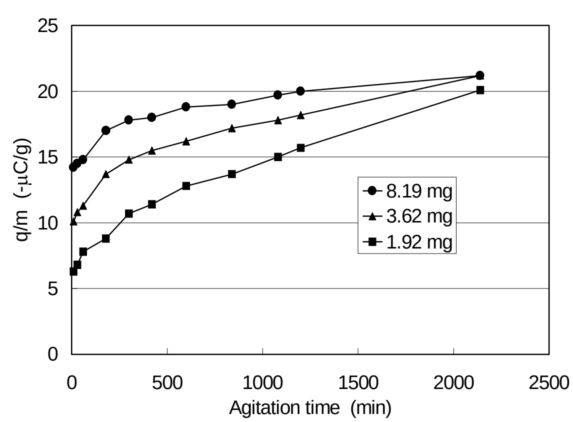



*Figure 8. Tribocharging behavior of toners at various surface CCA amounts*

Each sample shows almost same level of saturated tribocharge values after a long period of agitation. That result leads to the important conclusion that the amount of surface CCA does not determine the saturated tribocharge, but only influences charging up rate. Localization of CCA at the toner surface does not change the well saturated tribocharge level. The surface CCA enables high rate charging, while the internal CCA makes the saturation time longer. This result is similar to those on the crystal forms of CCA's described above.

**Trap Sites in Toner with CCA**

Thermally stimulated current (TSC) measurements were also carried out on the toners, which were incorporated with 1% of salicylic acid metal complex type CCA, in order to study trapping sites in the toners containing CCA. Figures 9 and 10 show the TSC curves for four choices of poling fields for the CCA-free resin and resin with 1 % of CCA, respectively. A new peak was observed at around 30 ºC for the resin with CCA.

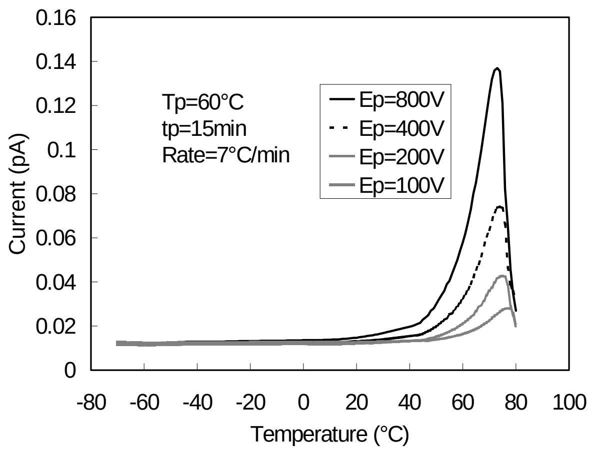



*Figure 9. TSC curves (resin only)*

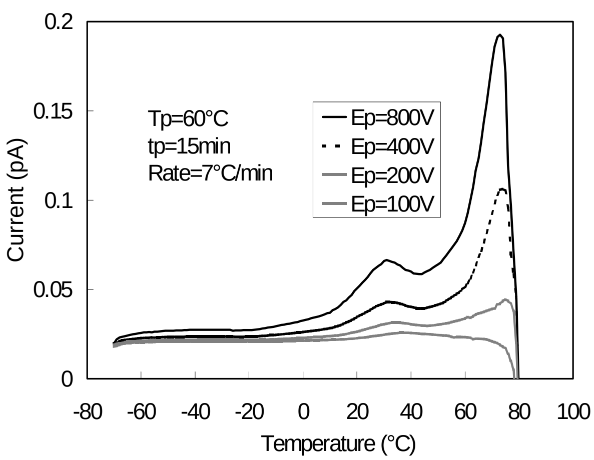



*Figure 10. TSC curves for the toner with CCA of 1.0 (%)*

Thermally stimulated current (TSC) measurements were also carried out on CCA/resin stacked layers to investigate the charging mechanism of resin with CCA, and a similar peak was observed as shown in Fig. 11. Since the peak centered at around 30 ºC did not appear in a packed layer of CCA, the trapping sites in the CCA-resin system can be assigned to the interface between CCA and resin.

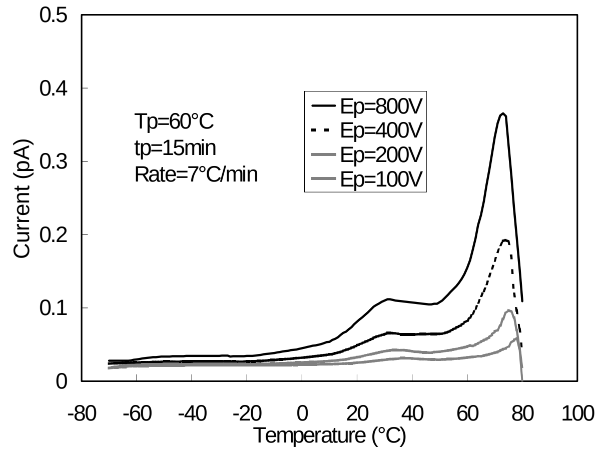



*Figure 11. TSC curves for CCA/resin layer*

## Conclusions

The charging behavior of the toners with CCA is strongly related to the crystal form, and solubility into resin, of CCA particles, because these factors change the amount of the surface CCA. The amount of surface CCA influences the tribochaging rate of toners. TSC measurements indicate that the interface between CCA and resin works as charging sites for tribocharging.

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## Biography

Graduated in 1989 from the Ehime University, Japan and joined Hodogaya Chemical Co., Ltd. Since then, I have been working on R&D of CCA in toner materials. I am currently a doctor course student at the Ibaraki University. I am a member of the Society of Electrophotography of Japan and the Japan Society of Applied Physics.