Thermally Stimulated Current and Thermally Stimulated Charge Decay Measurements in Toner Layers

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Abstract

The influence of charge control agent (CCA) on tribocharging characteristics of toner particles was examined by thermally stimulated current (TSC) measurements. Thermally stimulated charge decay (TSCD) measurements, similar technique to TSC were also carried out on the same specimens for the TSC measurements. Four kinds of toner, differing in chemical composition and an acrylic spherical powder were used in this study. It was confirmed that the CCA increased the charge to mass ratio of the toner. The peak height of TSC spectrum was larger in the toner with CCA than in those without CCA. However, the CCA did not introduced new traps in toners. These results suggest that the CCA captures charge carriers and/or promotes charge exchange between toner and carrier, but does not store charge carriers in itself. The TSC spectrum did not depend on the chemical composition of toners for corona charging. This result supports the idea, in which the CCA does not store charge carriers in itself. It was confirmed that TSCD measurements give similar results concerning charge traps in toners as TSC measurements.

Introduction

It is well known that the tribocharging characteristics of a toner play an important role in the electrophotographic processes.¹ Since the tribocharging of toner is a complicated phenomenon, which is affected by many factors, such as particle size, resistivity, process condition, environmental condition, etc., the tribocharging mechanism of toners has not perfectly been clarified yet. It is obvious that charge carrier traps play an important role in tribocharging as well as corona charging of toners.

Carrier traps can be investigated by thermally stimulated current (TSC) measurements, in which trapped charge carriers are released thermally from traps and observed as a current. However, application of TSC measurements to particulate materials is very limited.²⁴

Thermally stimulated charge decay (TSCD) measurement is a similar technique to TSC, in which the thermally stimulated decay of surface potential of the specimen layer, instead of current, is observed. If a TSCD curve is differentiated with time, a curve that corresponds to a TSC spectrum will be obtained. The TSCD technique is more easily applicable to particulate materials. We applied both the TSC and TSCD techniques to study the charging mechanism of toners, especially the role of a CCA for toner charging.⁵⁶

Experimental TSC Measurements

Thermally stimulated current (TSC) measurements were carried out with a home-made-equipment by the following procedure. The TSC measuring system is shown in Fig. 1. Suitable amount of the sample toner was charged into a well-shaped (0.5 mm depth and 32 mm diameter) aluminum sample holder. Then, this toner layer was corona charged in the ambient air. The corona voltage was -5 kV or +5 kV. Another charging method for the toners was tribocharing. A certain amount of the toner was put into a polymer tube, the inner surface of which was coated with a carrier completely, and was tribocharged by rotating the tube. Then, suitable amount of the tribocharged toner was sampled from the tube and was charged into the sample holder of the TSC measuring system. Open-circuit TSC spectra of toners were measured by a collecting electrode placed about 2 mm above the upper surface of the sample toner layer on the aluminum substrate. The heating rate was 3°C/min and the measurements ranged from room temperature to about 160°C. For the TSC measurements, the aluminum sample holder was used as a grounded electrode.



Figure 1. Experimental setup for TSC measurements.

TSCD Measurements

The experimental apparatus for the TSCD measurements is shown in Fig. 2. A toner layer was formed in a metal sample holder (0.5 mm in depth and 33mm in diameter), and its surface was corona charged (positive, negative), or tribocharged polymer powder layer was formed in the metal sample holder. The probe of a surface potential meter (Trek: Model 344) was set 1cm above the toner layer. The temperature of toner layer was increased by a heater lineally with time, and the decay of the surface potential was recorded by a PC. A copper-constantan thermocouple was used to measure the temperature. The heating rate was 0.10° C/s. It should be noted that both the TSC and TSCD measurements can be applied to toners whose isothermal decay is negligible slow.



Figure 2. Experimental setup for TSCD measurements.

Toner Samples

Four kinds of toner and two kinds of carrier were used in this study, whose fundamental characteristics are given in Table 1. The charge to mass ratio of the toners was measured by a suction type blow-off method. A dual-component developer was prepared by using a toner and a carrier. The toner concentration of the developer was 5 wt%. An appropriate amount of the developer was charged into a polystyrene tube and was rotated at the rotation rate of 209 rpm. The apparent resistivity of the toners was measured by a dielectric constant auto-measuring unit (Ando Denki Co., Ltd., TR-1100). The ionization potentials were measured by observing electron emission from the toner and carrier particles associated with UV-light irradiation.

An acrylic spherical powder (diameter: $5\mu m)$ was also used for the TSC and TSCD measurements.

Table 1: Fundamental Characteristics of Toners Used in this Study

Composition	D _{mean} [µm]	ρ [Ωcm]	I. P. [eV]
R	8.30	2.44*10 ¹¹	5.54
R+CB(92/8)	8.02	1.79*10 ¹¹	4.46
R+CCA(98/2)	8.52	2.25*10 ¹¹	5.74
R+CB+CCA(90/8/2)	8.28	1.85*10 ¹¹	4.81
Carrier A (Ferrite)	42.17	3.27*10 ⁶	4.22
Carrier B (Ferrite)	71.62	3.78*10 ¹	4.74

R: styrene-acrylic, CB: carbon black, I.P.: ionization potential

Results and Discussion *Charge to Mass Ratios of Toners*

Four kinds of toner, differing in the chemical composition as shown in Table 1, were used in this study. The charge to mass ratio of the toners with carriers A and B are given in Table 2. The charge to mass ratio was different with each in the four kinds of toner. The toner R, consisting of only resin (styrene-acrylic), was tribocharged negatively with both the carriers A and B. This can be explained by the difference in the ionization potential between the toner and the carrier. The charge to mass ratio of the toner R+CB, consisting of resin and carbon black, was smaller than that of toner R with carrier A or was of opposite polarity with carrier B. This change is attributable to change in ionization potential, because the apparent resistivity scarcely depends on the chemical composition of toners. Incorporation of carbon black to the resin shifted the tribocharging tendency in positive direction. Incorporation of a charge control agent (CCA) of negative type into the resin increased the toner charge significantly, which proved that the CCA worked well for tribocharging of toners. Finally incorporation of carbon black to toner R+CCA decreased the toner charge, or shifted the toner charging in the positive direction. The change in charge to mass ratios in Table 2 can be explained by the change in the ionization potentials with chemical compositions.

Table 2: Charge to Mass Ratio of Toners After 30 min Tribocharging with a Carrier

Sample	Charge to mass ratio [μC/g]			
	with carrier A	with carrier B		
R	-4.53	-1.32		
R+CB(92/8)	-2.78	3.42		
R+CCA(98/2)	-49.23	-11.81		
R+CB+CCA(90/8/2)	-25.64	-4.54		

R: styrene-acrylic, CB: carbon black

TSC Measurements

The TSC spectra of the four kinds of toner are shown in Figs. 3-6, which were measured after tribocharging of the toner specimens by carrier A. Roughly speaking, the peak temperature and the peak height of a TSC spectrum correspond to the trap depth and the trap density of the toner, respectively. The peak temperatures were almost same for all the four kinds of toner, suggesting that the resin has a kind of trap in itself. The incorporation of carbon black into the resin increased the TSC peak height somewhat, which may be due to a decrease in apparent resistivity associated with incorporation of carbon black, although the decrease is not so large. The incorporation of CCA into the resin increased the peak height significantly, which proves that the CCA works well in the toner used in this study. It should be noted here, however, that the CCA does not generate a new trap in the toner. In other words, the CCA captures charge carriers and/or promotes charge exchange between toner and carrier, but does not store charge carriers in itself. The incorporation of carbon black into R+CCA decreased the TSC peak height a little bit, which may be due to the decrease in charge to mass ratio.







Figure 4. TSC spectrum for toner R+CB tribocharged.

60

90

Temperature [°C]

120

150

180

30

0.15

0.1

0.05

-0.05

-0.1

0

0

TSC [pA]



Figure 7. TSC spectrum for toner R corona charged (-5kV).





Figure 9. TSC spectrum for toner R+CCA corona charged(-5kV).



Figure 10. TSC spectrum for toner R+CB+CCA corona charged (-5kV).

The TSC spectra of the four kinds of toner are shown in Figs. 7-10, which were measured after corona charging (-5kV) of the toner specimens. All the TSC spectra seem similar and not to be affected by the chemical composition. Similar results were obtained for the positive corona charging. These results indicate that charge carriers supplied by the corona discharge are captured by a trap in resin, although the identity of the charge carriers is ambiguous.

TSCD Measurements

The TSCD measurements were carried out on an acrylic spherical powder. A TSCD curve, which was obtained by positive corona charging, is shown in Fig. 11. If the curve is differentiated with time, a curve corresponding to a usual TSC spectrum will be obtained as shown in Fig.12.



Figure 11. TSCD curve for acrylic powder corona charged (-1kV)



Figure 12. The differential of the TECS curve in Fig. 11 (TSCD spectrum).

The differentiated TSCD curves for the acrylic powder by tribocharging, positive and negative corona charging are shown in Figs. 13-15, respectively. The TSC spectra measured in the same specimens under the same charging conditions are also given in those figures. It can be confirmed that the TSCD measurements give the similar results concerning with traps to TSC measurements. The small low temperature shift of the TSCD peak from TSC can be reduced to the delay in heat conduction in the specimen layers in the TSCD measurements.



Figure 13. TSCD spectrum for acrylic powder tribocharged.



Figure 14. TSCD spectrum for acrylic powder corona charged (1kV).



Figure 15. TSCD spectrum for acrylic powder corona charged (-1kV).

Conclusions

We applied both the TSC and TSCD techniques to study the charging mechanism of toners, and obtained the following results.

- 1. The TSC and TSCD measurements give similar results concerning charge traps in toners with each other.
- 2. The styrene-acrylic resin, used in this study, has a kind of charge trap, but the CCA does not introduce new charge traps in toners.
- 3. The CCA captured charge carriers and/or promotes charge exchange between toner and carrier, but does not store charge carriers in itself.

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