

# Influence of CCA on Toner Surface Obtaining High-Quality Images in Monocomponent Non-Magnetic Development

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## Abstract

The effects of charge control agent (CCA) were assessed in terms of surface energy of toners. The critical surface tension of toner plates, prepared from molten toners, was estimated by Zisman's plots, and their solid surface energy was calculated by the extended Fowkes' equation. Surface energy was 38.9 mN/m when the toner was free of CCA. The energy value varied with CCA species and their content. In normal atmosphere, the increase in background density was due to the increase in surface energy by adding excess CCA. From IR and viscosity measurements, it became apparent that a kind of positive CCA interacts with carbonyl groups of polyester. Moreover, it was demonstrated that this interaction increases the background density on a photoreceptor in the presence of high room temperature and high room humidity. To obtain high-quality prints by monocomponent nonmagnetic development with positive toner, it is important to select a polyester and CCA which keep toner surface energy low.

## Introduction

It is well known that CCA is necessary when designing not only a dual component toner but also a monocomponent toner. The charging mechanism of a toner, especially a monocomponent one, is difficult to study because toner composition is complicated. Each constituent has many functional groups, and toner particles come into contact with many kinds of material in the developer unit, such as the development roller, the blade, and the photoreceptor. All of these materials are associated with tribocharging. In spite of the complexity, the effects of CCA in the mechanism of tribocharging and its intrinsic role have gradually become clear.<sup>1-6</sup>

In general, styrene-acrylate copolymers are tribochargeable (both positively and negatively when a suitable CCA is selected). However, polyesters are mainly negatively chargeable due to residual groups such as -COOH and -COO-. If the effect of CCA on toner charging could be clarified, its charging polarity could easily be controlled for toners composed of any polymer. In monocomponent nonmagnetic development, since the chance of toner charging is less than that in dual component development, the charging rate of the toner affects the quality of the print image. It has already been found that total charge is one of the dominant factors affecting the quality of the print im-

age.<sup>7,8</sup> Therefore, it is important to understand the function of CCA. In this study we investigated the effects of CCA on toner surface energy to obtain guiding principles for CCA selection or its suitable combination with polymer.

## Experimental Design

### Materials

Three kinds of polyester were selected in this study. Polyester 1 (PE1) has a low acid value (AV, approx. 1.0 mg KOH/g polymer) and branched chains, PE2 has a low AV (approx. 1.0) and linear chains, and PE3 has a medium AV (approx. 5.0) and branched chains. Two types of CCA for positive toner were employed, one was tetraalkylammonium perchlorate (low molecular weight type) and the other was modified styrene-acrylate-methacrylate copolymer partially substituted by electrolyte. All toners were composed of polyester, CCA, pigment (quinacridone-type pigment was selected), and wax. Model toners were also produced by using two toner constituents. All of them were compounded in a kneader and crushed to powder of 10  $\mu\text{m}$  diameter. The toner was melted on a glass plate and shaped into a plate of 0.5 mm thickness and less than 0.3s roughness.

### Measurement of Polymer Solution Viscosity

Viscosity of the polymer solution was measured using a modified Ubbelohde-type capillary viscometer in THF at 30°C. The limiting viscosity of a polymer solution  $[\eta]$  is defined as

$$[\eta] = \lim_{c \rightarrow 0} (t - t_0) / t_0 c \quad (1)$$

in terms of solvent viscosity  $t_0$ , polymer solution viscosity  $t$ , and solute concentration  $c$ . The limiting viscosity reflects the conformation of the polymer chain in a solution. When it is large, the polymer chain spreads in the solution due to repulsion between polymer chains mainly as the results of electrostatic forces.

### Measurement of Contact Angle and Calculation of Surface Energy

The contact angle  $\theta$  of toners and model toners was measured using a CA-DTA-type contact anglemeter (Kyowa Interface Science Co., Ltd., Tokyo). The solvents shown in Table 1<sup>9</sup> were applied to this measurement. Zisman's plots were obtained from plots of solvent surface tension vs  $\cos\theta$ . Critical surface tension  $\gamma_c$  was obtained by

extrapolation to  $\cos\theta = 1$ . Surface energy values were calculated as follows. Solid surface energy  $\gamma_s$ , is defined by the extended Fowkes' equation<sup>9</sup> as

$$\gamma_s = \gamma_L(1 + \cos\theta) = 2(\gamma_L^a \gamma_s^a)^{1/2} + 2(\gamma_L^b \gamma_s^b)^{1/2} + 2(\gamma_L^c \gamma_s^c)^{1/2} \quad (2)$$

in terms of surface tension of solvent  $\gamma_L$  and contact angle  $\theta$  or  $\gamma_L^a$ ,  $\gamma_L^b$ , and  $\gamma_L^c$ , the nonpolar constituent, the polar constituent, and the hydrogen bonding constituent, respectively, and  $\gamma_s^a$ ,  $\gamma_s^b$ , and  $\gamma_s^c$  the nonpolar, polar, and hydrogen bonding constituents contributing to solid surface energy, respectively,  $\gamma_s^a$  was calculated from  $\gamma_L$ ,  $\gamma_L^a$  and  $\cos\theta$  measured for a solvent with only a  $\gamma_L^a$  constituent, such as hydrocarbon or toluene. In this study, toluene was used to determine  $\gamma_s^a$ . Next,  $\gamma_s^c$  was determined using  $\gamma_s^a$  from the data for toluene and  $\cos\theta$  measured by a solvent with  $\gamma_L^a$  and  $\gamma_L^c$  constituents, such as ethylene glycol, diethylene glycol and dipropylene glycol, as shown in Table 1. Finally,  $\gamma_s^b$  was determined for these data and  $\cos\theta$  measured for a solvent with  $\gamma_L^a$ ,  $\gamma_L^b$  and  $\gamma_L^c$  constituents, such as water, glycerol, and polyethylene glycol 200. Total surface energy  $\gamma_s$  was determined as the sum of  $\gamma_s^a$ ,  $\gamma_s^b$ , and  $\gamma_s^c$ .

### Print Images

Background density on a photoreceptor was determined as follows. Print images were obtained using the toner samples described above, a contact-type monocomponent nonmagnetic development unit with an elastic/conductive development roller<sup>7</sup> and a modified laser printer (LB1305, Tokyo Electric Co. Ltd.). Toner particles on the background of developed images on the photoreceptor were adhered to a piece of transparent adhesive tape (Scotch, 3M, U.S.A.) and then the tape was adhered to a piece of plain white paper. Reflectivity of the tape was measured using a reflectometer (CR-121, Minolta Corp. Ltd., Osaka). Back-

ground density is defined as the difference between the reflectivity value of the tape with toner and that of a blank tape.

**Table 1. Surface tension and its constituent**

Solvent	$\gamma_{La}$ (mN/m)	$\gamma_{Lb}$ (mN/m)	$\gamma_{Lc}$ (mN/m)	$\gamma_L$ (mN/m)
Water	29.1	1.3	42.4	72.8
Glycerol	37.4	0.2	25.8	63.4
Ethylene glycol	30.1	0	17.6	47.7
Diethylene glycol	31.7	0	12.7	44.4
Polyethylene glycol 200	29.9	0.1	13.5	43.5
Dipropylene glycol	29.4	0	4.5	33.9
Toluene	28.4	0	0	28.4

## Results and Discussion

### Critical Surface Tension and Surface Energy of Toner

Critical surface tensions  $\gamma_c$  of toners and model toners were determined by Zisman's plots. Typical Zisman's plots are shown in Figs. 1-3 and surface tension values are shown in Table 2. In the solvent surface tension range below 50 mN/m, plots of surface tension vs  $\cos\theta$  show a linear relationship. Critical surface tensions  $\gamma_c$  shown in Table 2 are around 30 mN/m except for three kinds of toners. In Zisman's plots, differences in each toner surface appeared not in the critical surface tension but in the solvent surface tension range above 50 mN/m. In that range, hydrogen bonding occurred between the solid surface and the solvent. This phenomenon is reflected in the surface energy  $\gamma_s$ , determined from eq. (2), as shown in Table 2. However, it is difficult to separate  $\gamma_s^c$  from  $\gamma_s^b$  because the solvents used for determination of  $\gamma_s^c$  also include  $\gamma_s^b$ . All samples show  $\gamma_s^a$  values near 27 mN/m, which are almost constant.

**Table 2. Surface energy and surface tension of toner**

	$\gamma_{sa}$ (mN/m)	$\gamma_{sb}$ (mN/m)	$\gamma_{sc}$ (mN/m)	$\gamma_s$ (mN/m)	$\gamma_c$ (mN/m)	Background density (%)
<b>Model</b>						
PE1	27.4	1.2	3.0	31.6	32.5	
PE2	27.9	7.0	3.3	38.2	33.5	
PE3	27.7	7.4	7.7	46.6	40.5	
PE1 + Pigment	27.5	6.6	3.0	37.1	32.0	
PE1 + CCA1 1%	26.7	9.4	4.3	40.4	33.6	
PE1 + CCA2 3%	27.4	4.3	4.0	35.7	33.6	
<b>Toner</b>						
PEI Base CCA-free	27.1	8.7	3.1	38.9	31.5	*
CCA1 0.5%	27.3	0.1	3.3	30.7	32.5	2.5
CCA1 1.0%	26.3	0.9	3.4	30.6	31.0	3.0
CCA1 2.0%	26.8	24.7	9.0	60.5	40.0	50
CCA2 1.0%	26.8	7.2	1.3	35.3	27.4	0.0
CCA2 3.0%	26.9	6.4	1.0	34.3	27.6	0.0
CCA2 5.0%	26.9	7.2	1.2	35.3	27.4	0.0
PE2 Base CCA1 1.0%	27.5	79.5	3.9	110.9	—	30
PE3 Base CCA-free	27.4	15.1	3.9	46.4	36.5	*

\* Toner layer poorly formed

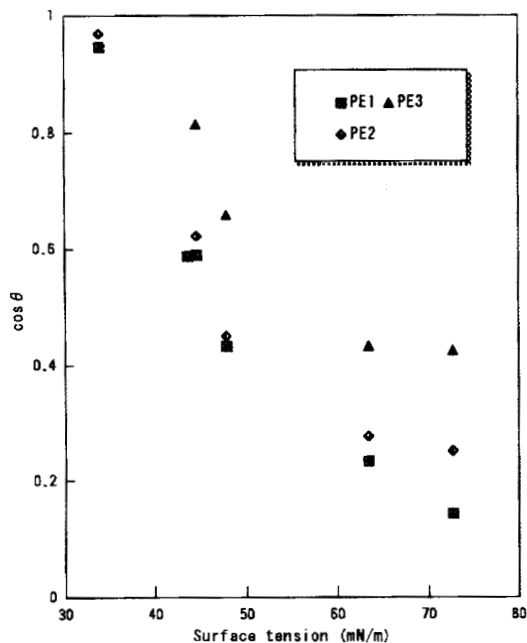


Figure 1. Zisman's plots of polymers.

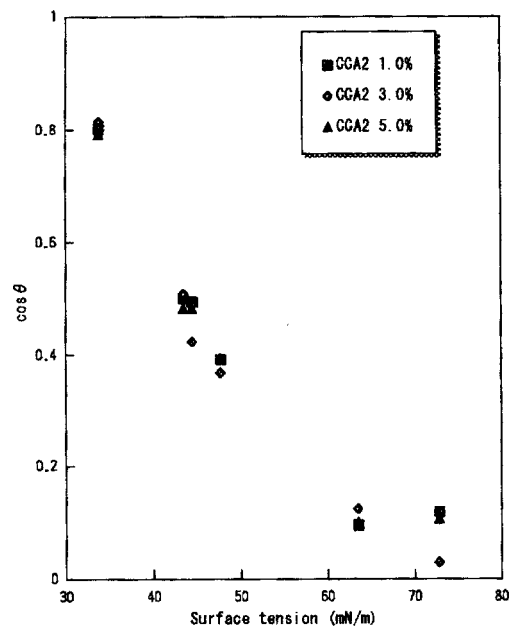


Figure 3. Zisman's plots of PE1 + CCA2 toners.

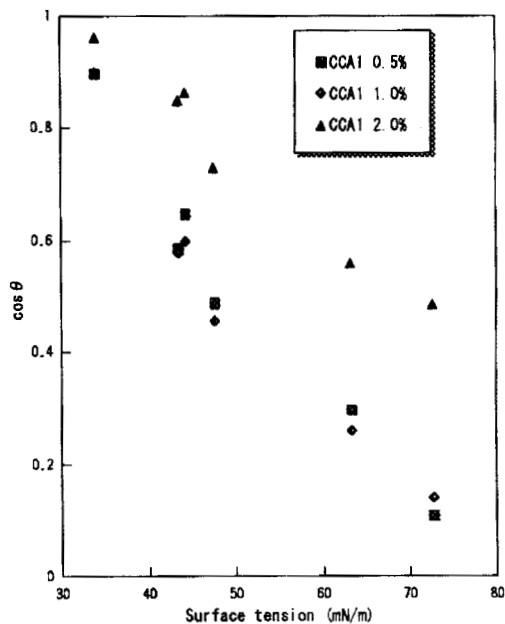


Figure 2. Zisman's plots of PE1 + CCA1 toners.

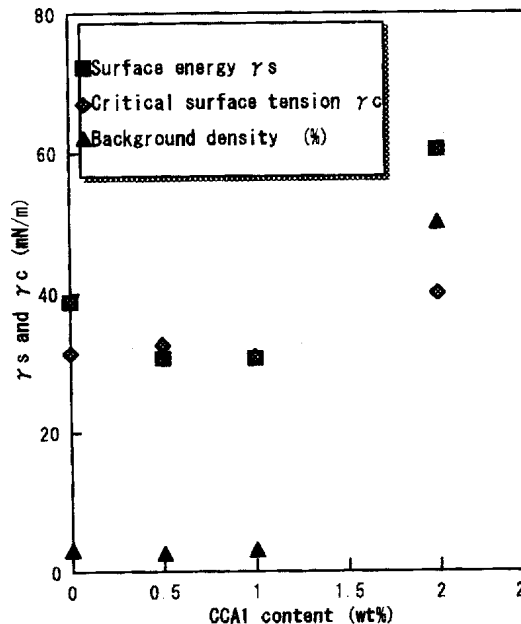


Figure 4. CCA1 content dependence on surface energy.

Therefore, since variation in the  $\gamma_s$  value of toners is due to variation in  $\gamma_s^b + \gamma_s^c$ , we can discuss the relationship between the total surface energy  $\gamma_s$ , and print image quality. As shown in Fig. 4, in toners with a CCA1 content up to 1 wt%, surface energy  $\gamma_s$  is constant and background density on the photoreceptor is low. However,  $\gamma_s$  and the background density increased dramatically at 2 wt% addition. This means that a toner with a high  $\gamma_s$  results in a high background density. In contrast to CCA1,  $\gamma_s$  of the toner containing CCA2 is constant and the background density is nearly zero up to its 5 wt% addition, as shown in Fig. 5. This difference in toner properties between CCA1 and CCA2 is thought to be due to differences in the concentrations of functional groups in the toner. Since low molecu-

lar weight CCA1 has a high concentration of functional groups, it is more effective than the same weight of CCA2. However, its functional groups are hydrophilic and interact with polyester. Therefore, it is thought that CCA1 increases surface energy and the background density precipitously when it is added beyond the critical point. In contrast, CCA2 has a low concentration of functional groups, surface energy is kept almost constant, and the background density is low in the range from 1 to 5 wt% content. Fig. 6 shows the relationship between CCA content and charge per mass (mC/kg). The charge of toner containing CCA1 decreased with CCA content and that of toner containing CCA2 increased. The reason for this phenomenon is thought to be that CCA2 has a greater charging ability than CCA1, and

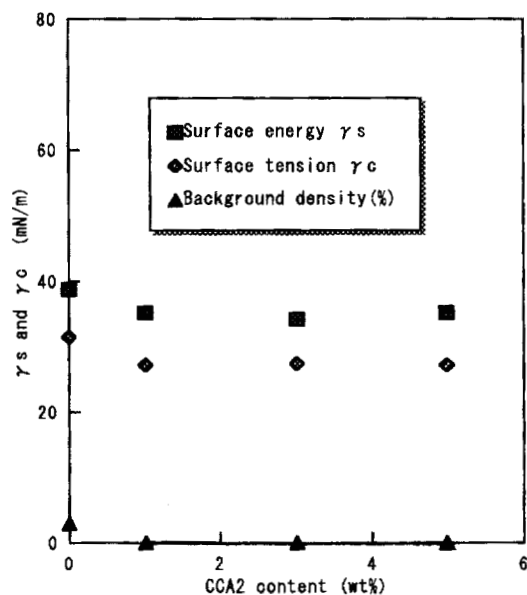


Figure 5. CCA2 content dependence on surface energy.

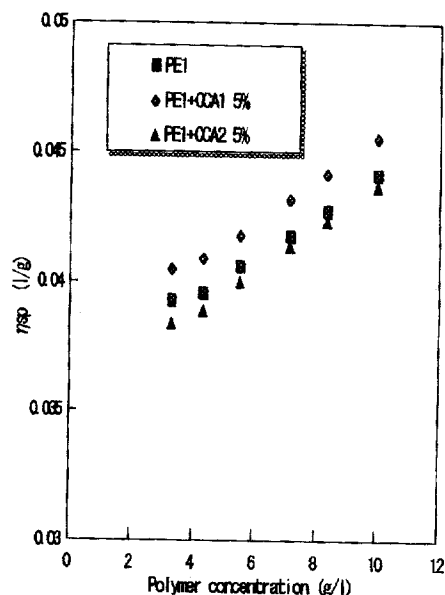


Figure 7. Relation between polymer conc. and reduced viscosity.

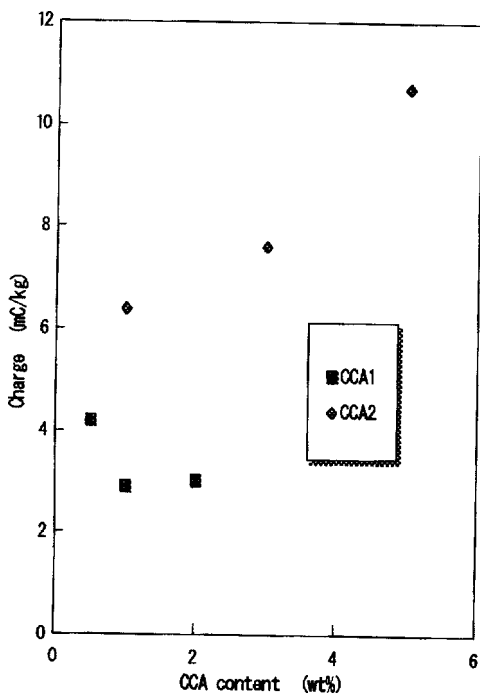


Figure 6. CCA content dependence on charge.

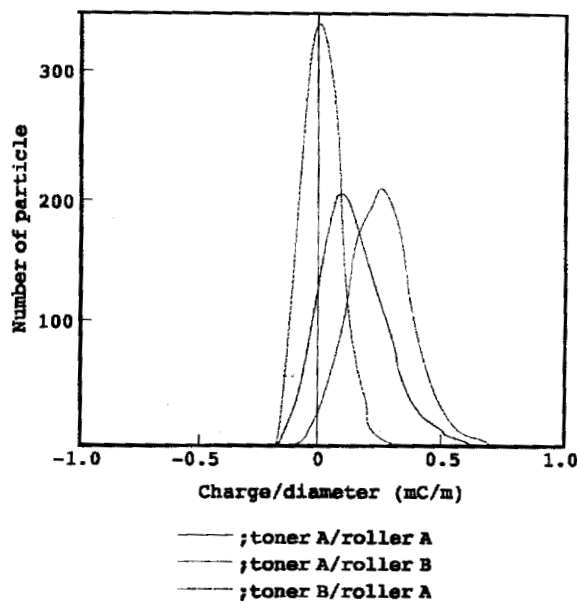


Figure 8. Charge distribution of toners.

influences the surface energy less than CCA1. While CCA1 could give the toner chargeability, it also made the surface energy of the toner low. This is one of the reasons for the increase in background density in spite of the increase in CCA content. As shown in Table 2, it was found that model toner consisting of PEI and CCA1 has a higher surface energy than the toner with the same CCA1 content. The reason is thought to be that, since other components in toner (such as pigment and wax), interact with PEI and CCA1, the surface energy of model toner is greater than that of toner. Moreover, CCA1 influenced PE2 and increased only surface energy to a great extent. From this fact, it is concluded that, to obtain toner with high performance, it is

necessary to combine polyester with appropriate acid value and a suitable CCA. These results show that the appropriate combination of polyester and CCA can be produced by determination of the surface energy of the toner or model toner.

#### Measurement of Viscosity and IR Spectra

Typical reduced viscosity dependence on polymer concentration is shown in Fig. 7 and the limiting viscosity is shown in Table 3. The limiting viscosity of PEI in THF solution is 0.0360 (l/g). With 1 wt% addition of CCA1, the limiting viscosity was unchanged because no interaction took place between polymer and CCA1. However, when

CCA1 content was 5 wt% relative to polymer, the limiting viscosity increased to 0.0374 (l/g). This means that CCA1 interacted with polyester and the polymer chains spread in the solution because intermolecular and intramolecular repulsion occurred due to electrostatic forces. In contrast, since the limiting viscosity was not changed by its addition, it is suggested that CCA2 had little effect on the polymer chain. As shown in Table 4, the interaction between CCA and the functional groups of polyester was also detected by a shift in IR absorption around 1720 cm<sup>-1</sup> due to stretching of the carbonyl group. Following addition of CCA1, the peak wavenumber shifted from 1728.4 cm<sup>-1</sup> to 1720.7 cm<sup>-1</sup>. This means that the bond energy between carbon and oxygen atoms is decreased by CCA1. In the toner containing CCA2, the decrease in bond energy was less than that in the toner with CCA1. It was confirmed that pigment and wax did not affect IR absorption in model toner. These results indicate that CCA1 interacts with polyester, especially with the carbonyl groups and that the interaction causes increases in surface energy and background density.

**Table 3. Limiting viscosity of polymer.**

	[η] (l / g)
PE1	0.0360
PE1 + CCA1 1%	0.0358
PE1 + CCA1 5%	0.0374
PE1 + CCA2 5%	0.0356

**Table 4. Wavenumber of carbonyl group**

	Wavenumber (cm-1)
PE1	1728.4
PE1 + CCA1 toner	1720.7
PE1 + CCA1 toner	1723.6

### Charge Distribution

CCA in the toner plays an important role as a charge controller, related to polymer conformation and surface energy. To apply charge to the toner, the material of the development roller is also important as a tribocharge donor. Two kinds of material were used for measurement of toner charge distribution. The surface of roller A was made of conductive polyurethane and that of roller B was made of conductive perfluoroelastomer. Their surface resistance was around 10<sup>6</sup> (Ωcm). Two kinds of toner were used for measurement, one easily chargeable and the other poorly chargeable. The charge distribution of toner particles on the roller was measured by an Espart analyzer (Hosokawa Micron, Osaka). Fig. 8 show the charge distribution of toners. High-quality print images were obtained using toner A and roller A. When toner A and roller B were combined, since the charge of the toner was too high for development,

low-density prints were obtained. On the other hand, prints with high background density were obtained by the combination of toner B and roller A due to the large amount of oppositely charged toner. From these findings, it is concluded that it is necessary to apply a suitable charge to the toner, which depends on the combination of toner and roller material, to obtain high-quality print images, in agreement with the basic theory of nonmagnetic contact development.<sup>7,8</sup>

### Conclusion

CCAs interact with carbonyl groups of polyester and affect the toner surface energy. Both low molecular weight and polymer CCAs decrease surface energy of polyesters when adding a certain amount is added to toner. The optimum amount of CCA for polymer differs for various CCA species due to differences in the density of functional groups that contribute to charging. Since all the molecules are functional in low molecular weight CCA, the optimum amount of addition is less than 2 wt%. In the range above 2 wt%, the CCA makes the surface energy high and it induces a more hydrophilic surface rather than functioning as a charge controller. This is the reason for the increase in background density in spite of the increase in CCA content of the toner in contact monocomponent nonmagnetic development. In the polymer type, the density of functional groups is much lower than that in the low molecular weight type. Therefore, the surface energy and background density did not increase, even with 5 wt% addition.

The material of the development roller is also an important factor in obtaining high-quality images. When a roller with a perfluoropolymer surface is used for the development with an easily chargeable toner, the charge seems too high for development, and only low image density and low-quality prints are obtained. To obtain high-quality image prints, it is also necessary to select the optimum roller and a toner with high performance.

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