

Influence of Charge Control Agent and Development Roller Surface on Toner Charging

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The effects of charge control agents (CCAs), especially for monocomponent nonmagnetic toner, were assessed in terms of their surface energies. The solid surface energy was calculated by the extended Fowkes equation. The energy value varied with CCA species and their content. The increase in surface energy created by adding excess CCA was one of the reasons for an observed increase in background density of print image. From infrared spectroscopy and viscosity measurements, it became apparent certain types of positive CCAs interact with polyester toner resin. It was also clarified that the material of the development roller could influence toner charge and print image quality. High-quality image prints were obtained by using a suitable combination of a chargeable toner and suitable roller material as tribocharge donor. To obtain high-quality image prints by monocomponent nonmagnetic development with positive toner, it is important to select a polyester resin and a CCA that keep toner surface energy low and a suitable combination of toner having high chargeability and development roller material suitable as tribocharge donor.

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Introduction

It is well known that a charge control agent (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 materials in the developer unit, such as the development roller, the blade, and the photoreceptor, all of which 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.^{1–9}

In general, styrene-acrylate copolymers are tribochargeable both positively and negatively when a suitable CCA is selected. However, polyesters are mainly negatively chargeable because of residual groups such as $-\text{COOH}$ and $-\text{COO}-$. 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, because the chance of toner charging is less than in dual-component development, the

charging rate of the toner affects the quality of the print image. Monocomponent toners accept charge mainly from the development roller surface, and the contact time between toners and the development roller surface is very short. Therefore, monocomponent toner is used in the charge rising region, which is unstable in the toner charging process. It has already been found that the total charge of toners is one of the dominant factors affecting the quality of the print image.^{10,11} Therefore, it is important to understand the charging functions of the CCA and the development roller surface. In this study, we have investigated the effects of CCA on toner surface energy and the effect of the development roller surface on toner charging and the quality of the print image.

Experimental

Materials. Three kinds of polyester were tested in this study. Polyester 1 (PE1) has a low acid value (AV), ~1.0 mg KOH/g polymer, and branched chains; PE2 has a low AV (~1.0) and linear chains; and PE3 has a medium AV (~5.0) and branched chains. Two types of CCA for positive toner were employed; one was tetraalkylammonium perchlorate (CCA1, low-molecular-weight type) and the other was modified styrene-acrylate-methacrylate terpolymer partially substituted by electrolyte (CCA2, polymer type). All toners were composed of polyester, CCA, pigment (quinacridone-type pigment), and modified polypropylene wax. All of them were compounded in a kneader and pulverized to 10- μm -diameter powder by a conventional method. For surface energy evaluation, the toner was melted on a glass plate and shaped into a 0.5-mm-thick plate and less than 0.3-s roughness.

Measurement of Polymer Solution Viscosity. The viscosity of the polymer solution was measured using a modified Uddelohde-type capillary viscometer in tetrahydrofuran (THF) at 30°C. The intrinsic 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 intrinsic 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 result of electrostatic forces.

Measurement of Contact Angle and Calculation of Surface Energy. The contact angle θ toners and model toners was measured using a CA-DTA-type contact-angle meter (Kyowa Interface Science Co., Ltd., Tokyo). The liquids shown in Table I¹² were used for this measurement. Zisman plots were obtained from plots of liquid surface

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TABLE I. Surface Tension and Its Constituents

	γ_L mN/m	γ_L^a mN/m	γ_L^b mN/m	γ_L^c mN/m
Water	72.8	29.1	1.3	42.4
GL ¹	63.4	37.4	0.2	25.8
EG ²	47.7	30.1	0	17.6
DEG ³	44.4	31.7	0	12.7
PPG ⁴	43.5	29.9	0.1	13.5
DPG ⁵	33.9	29.4	0	4.5
TOL ⁶	28.4	28.4	0	0

γ_L , surface tension of liquid; γ_L^a , its nonpolar constituent; γ_L^b , its polar constituent; γ_L^c , its hydrogen bonding constituent.

¹ Glycerol; ² Ethylene glycol; ³ Diethylene glycol; ⁴ Polypropylene glycol (molecular weight 200); ⁵ Dipropylene glycol; and ⁶ toluene.

tension versus $\cos\theta$. Surface energy values were calculated as follows: Solid surface energy γ_s is defined by Young's equation, Eq. 2, and by the extended Fowkes equation,¹² Eq. 4:

$$\gamma_s = \gamma_L(1 + \cos\theta) \quad (2)$$

$$= \gamma_s^a + \gamma_s^b + \gamma_s^c \quad (3)$$

$$= 2(\gamma_L^a \gamma_s^a)^{1/2} + 2(\gamma_L^b \gamma_s^b)^{1/2} + 2(\gamma_L^c \gamma_s^c)^{1/2} \quad (4)$$

and

$$\gamma_L = \gamma_L^a + \gamma_L^b + \gamma_L^c \quad (5)$$

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

Print Image. The 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,¹⁰ and a modified laser printer (LB1305, TEC Corp.). Toner particles in the background of developed images on the photoreceptor were transferred by adhesion to a piece of transparent adhesive tape (Scotch, 3M, USA) and the tape was then applied to a piece of plain white paper. The reflectivity of the tape was measured, using a reflectometer (CR-121, Minolta Corp. Ltd., Osaka). Background density is defined as the difference between the reflectivity value of the tape with toner and that of blank tape.

Charge Distribution Measurement and Relation between Developing Bias and Background Density. To clarify the contribution of the material of the development roller surface to toner charge, two kinds of material were applied to the development roller. The surface of Roller A was made of conductive polyurethane, and the surface of Roller B was made of perfluoroelastomer. Their surface resistance was around $10^6 \Omega \text{ cm}$. Toner A was based on PE 1 and CCA2. Toner B was based on PE 1 and CCA1.

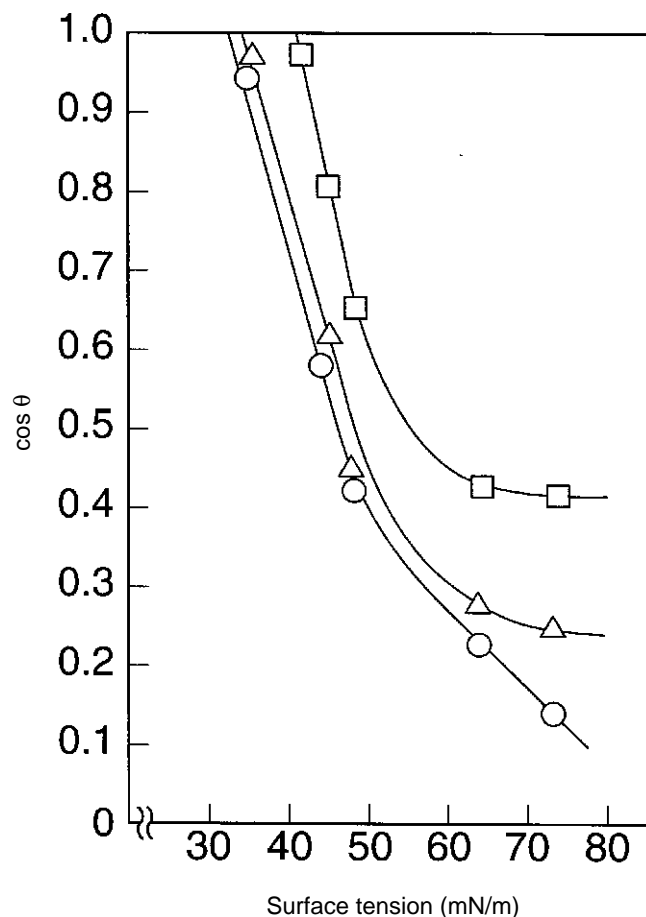


Figure 1. Zisman plots of polymers. \circ , polyester 1 (PE1); Δ polyester 2 (PE2); \square polyester 3 (PE3).

The total toner charge on the roller was measured by a Keithley 610C electrometer with a Faraday vacuum cell to suck toner from the roller.

The charge distribution of toner particles on the development roller was measured with an E-spart analyzer (Hosokawa Micron, Osaka).

Results and Discussion

Critical Surface Energy of Toner. Typical Zisman plots are shown in Figs. 1, 2, and 3. Using one of the liquids shown in Table I, the contact angle was measured and the solid surface energy was defined from Eq. 3, which is the extended Fowkes equation. In Fig. 1, of the three kinds of polyester studied, Polyester 1 (PE1) with the lowest acid value indicated the lowest $\cos\theta$ throughout the range, and PE1 was used for further investigation. The plots shown in Fig. 1 deviate from a linear relationship in the higher surface tension range because of hydrogen bonding between the toner surface and the applied liquid. This phenomenon is reflected in the toner surface energy, especially in the hydrogen bonding constituent, γ_s^c . Zisman plots of PE1 and the low-molecular-weight type CCA1 toner system are shown in Fig. 2. Because the toner surface energy became high, $\cos\theta$ rose with addition of CCA1, especially in the liquid surface tension range above 50 mN/m. This indicates that the toner surface became hydrophilic with CCA1. In contrast to CCA1, Zisman plots of PE1 and polymer type CCA2 toner system, Fig. 3 shows a decrease in $\cos\theta$ with addition of CCA2. Here the linearity is maintained up to a surface tension range of ~ 60 mN/m. This indicates that

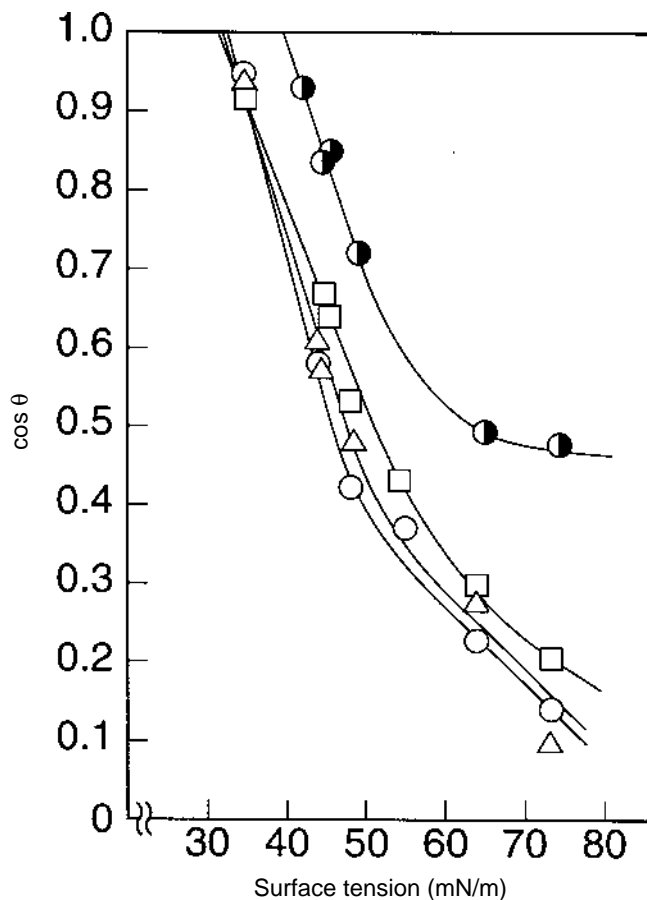


Figure 2. Zisman plots of polyester 1 + CCA1 toner systems. ○, CCA1 free; △, CCA1 0.5 wt% added; □, CCA1 1.0 wt% added; ●, CCA1 2.0 wt% added.

the hydrogen bonding energy between the toner and the test liquid is decreased by CCA2, indicating a reduced concentration of functional groups available for hydrogen bonding on the toner surface.

As shown in Fig. 4, in toners with a CCA1 content around 1 wt%, the surface energy γ_s is the lowest and background density is low enough to obtain high image quality prints when a suitable development process condition is selected. Surface energy and background density increased dramatically at 2 wt% addition of CCA1. This means that a toner with a high surface energy γ_s results in a high background density. As shown in Fig. 5, in contrast to CCA1, γ_s of the toner containing CCA2 is constant and the background density is nearly zero up to 5 wt% of CCA2. These differences in toner properties between CCA1 and CCA2 are due to the difference in the concentration of functional groups and in interaction between CCA and polar groups of polymer in the toner. Because low-molecular-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, polymer type 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.

Figure 6 shows the relationship between CCA content and charge per toner mass (mC/kg) on the polyurethane development roller, measured by an electrometer with a vacuum Faraday cell. It is clear that CCA2 has a greater

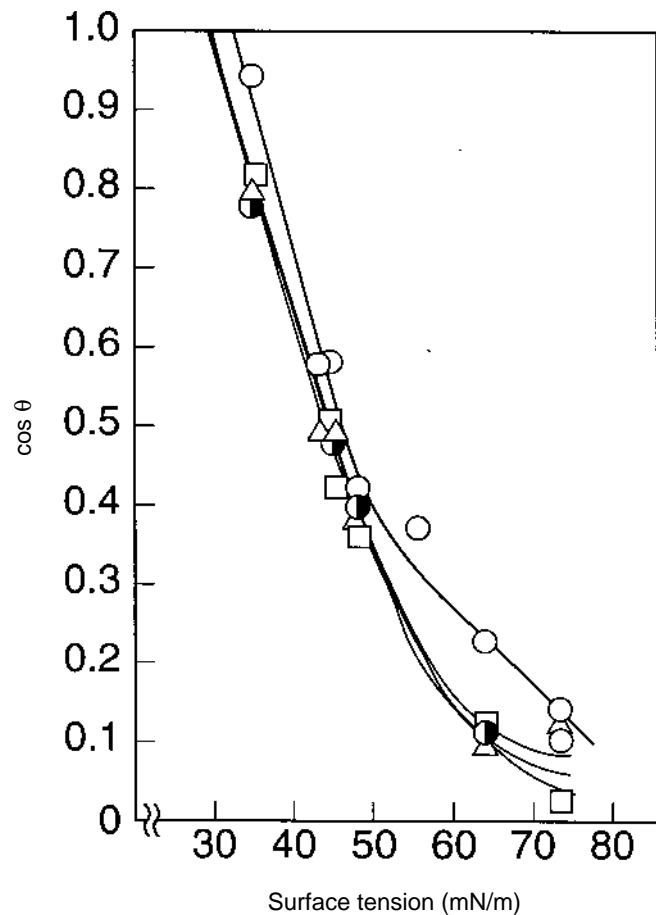


Figure 3. Zisman plots of polyester 1 + CCA2 toner systems. ○, CCA2 free; △, CCA2 1.0 wt% added; □, CCA2 3.0 wt% added; ●, CCA2 5.0 wt% added.

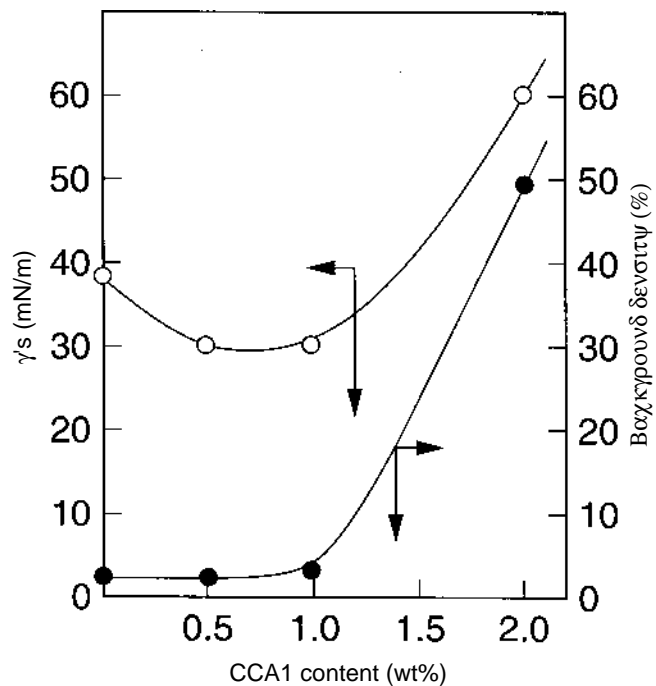


Figure 4. CCA1 content dependence on surface energy and background density. ○, surface energy; ●, background density.

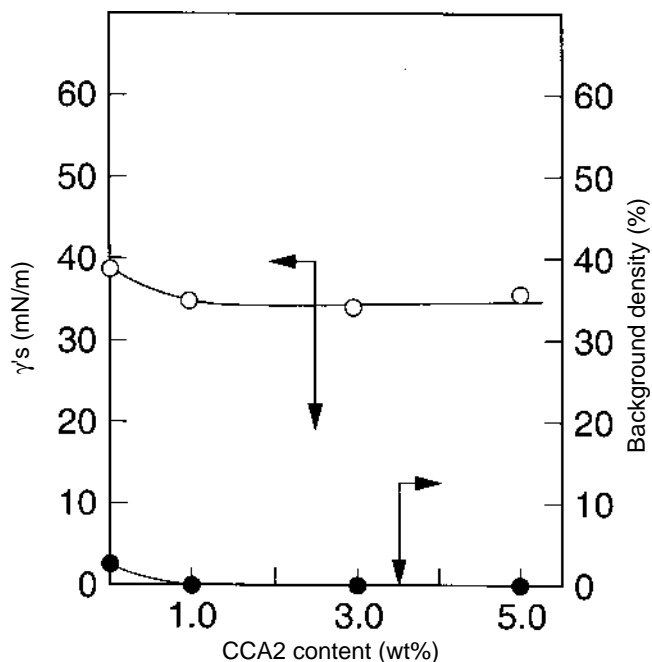


Figure 5. CCA2 content dependence on surface energy and background density. ○, surface energy; ●, background density.

TABLE II. The Intrinsic Viscosity $[\eta]$ of Polymer Solutions

	CCA content	$[\eta]$ (l/g)
PE1, CCA	free	0.0360
PE1 + CCA1	1%	0.0358
PE1 + CCA1	5%	0.0374
PE1 + CCA2	5%	0.0356

charging ability than CCA1. In CCA1 added toner (circle plots in Fig. 6), charge is constant in the region 1 to 2 wt% CCA1, but only 2 wt% CCA1 produced high background density, as shown in Fig. 4. This result supports the view that the background density is related to surface energy, as well as toner charge. The toner with high surface energy produces high background density, even though it has enough charge to be developed. By contrast, CCA2 has a greater charging ability than CCA1, and influences the toner surface energy less than CCA1. While CCA1 could give the toner chargeability, it also increased the surface energy of the toner.

Measurements of Viscosity and IR Spectra. Typical reduced viscosity dependences on polymer concentration are shown in Fig. 7, and the intrinsic viscosities are shown in Table II. The intrinsic viscosity of PE1 in THF solution is 0.0360 l/g. When CCA1 content was 1 wt% relative to polymer, the intrinsic viscosity was almost unchanged because no interaction took place between polymer and CCA1. However, when the CCA1 content was 5 wt%, the intrinsic viscosity increased to 0.0374 l/g. This means that CCA1 interacted with the polyester, causing the polymer chains to spread in the solution because inter- and intramolecular repulsion occurred due to electrostatic forces. In contrast, when the CCA2 content was 5 wt% relative to polymer, the intrinsic viscosity was lower than that of the CCA-free solution. It is suggested that CCA2 made the polymer chains compact.

As shown in Table III, the interaction between CCA and the functional groups of the polyester was also detected by a shift in IR absorption around 1720 cm^{-1} due to stretching of the carbonyl group. Following addition of CCA1, the peak wavenumber shifted from 1728.4 to 1720.7 cm^{-1} .

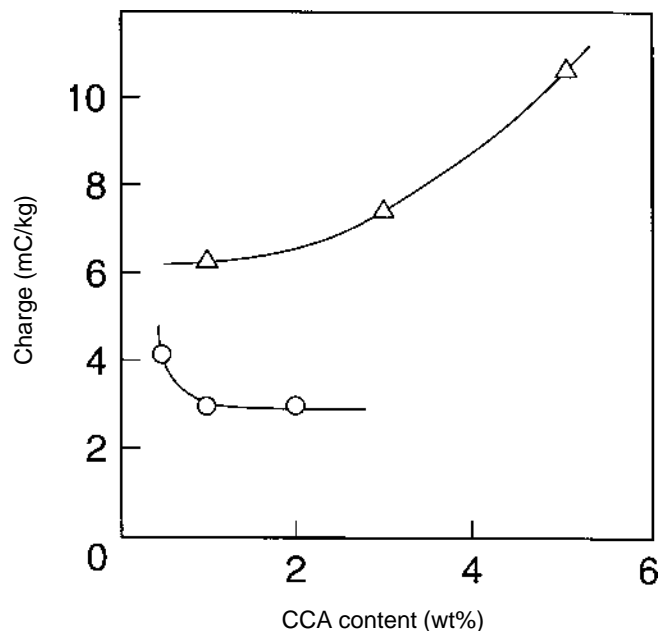


Figure 6. CCA content dependence on total toner charge on the development roller. ○, polyester 1 + CCA1 toner system; Δ, polyester 1 + CCA2 toner system.

TABLE III. Wavenumber of Carbonyl Group of Polyester In Toner

	CCA content	Wavenumber (cm^{-1})
PE1		1728.4
PE1 + CCA1	1%	1720.7
PE1 + CCA2	3%	1723.6

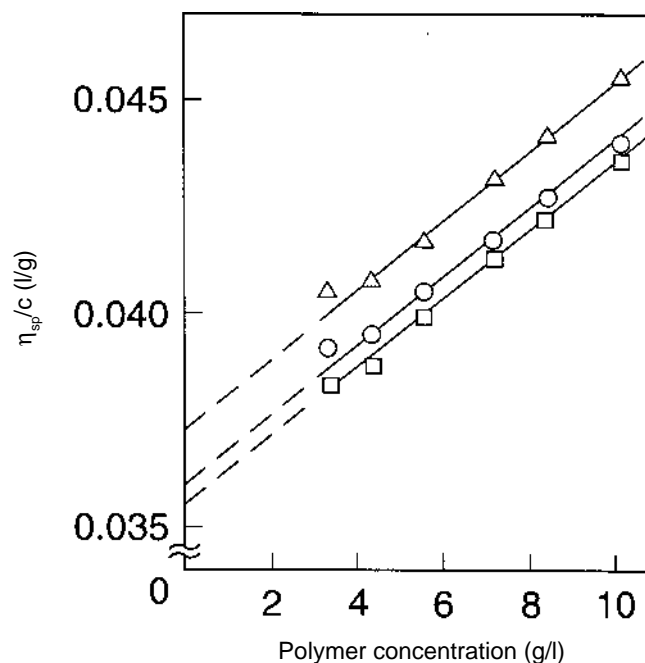


Figure 7. Relation between CCA concentration polymer and reduced viscosity. ○, polyester 1 (CCA free); Δ, polyester 1 + CCA1 5.0 wt% added; □, polyester 1 + CCA2 5.0 wt% added.

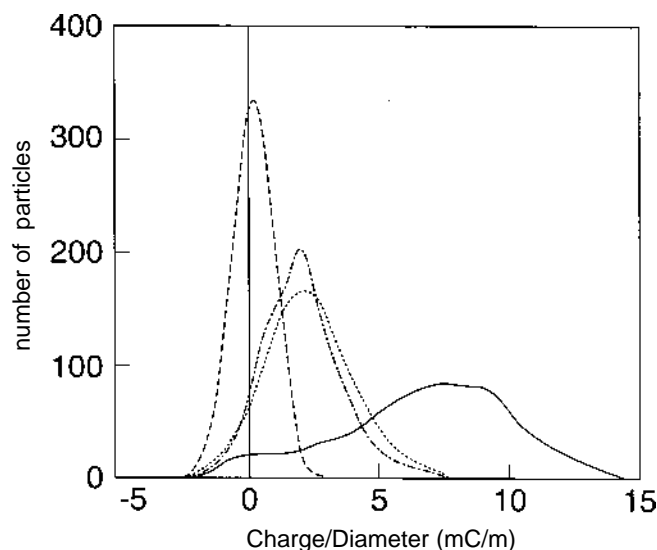


Figure 8. Charge distribution of toners on various types of development rollers. . . . (dotted line), toner A / roller A; — (solid line), toner A / roller B; - - - (dashed line), toner B / roller A; - . . . (dotted chain), toner B / roller B.

This means that the bond energy was less than that in the toner with CCA1. These results also indicate that CCA1 interacts with polyester, especially with the carbonyl groups, and that interaction caused increases in surface energy and background density.

Charge Distribution and Relation between Developing Bias and Background Density. To apply charge to a toner, the material of the development roller is also important as a tribocharge donor. Two kinds of material were applied to the development roller and two kinds of toner were used for measurement of toner charge distribution. The surface of Roller A was made of conductive polyurethane, and the surface of Roller B was made of conductive perfluoroelastomer. Toner A was based on PE1 added CCA2 3 wt%, which had higher chargeability. Toner B was based on PE1 added CCA1 1 wt%, which had lower chargeability. As shown in Fig. 8, when Toner A and Roller B were combined, (indicated by solid line), the charge of the toner was too high to develop, and prints with low image density were obtained. On the other hand, when Toner B and Roller A were combined (indicated by dashed line), the total charge of the toner was too low because of the large amount of oppositely charged toner, and prints with high background density were obtained. It is obvious that Toner A accepted too much charge from Roller B and the toner remained on the roller, in spite of the potential gap between developing bias and photoreceptor surface potential of light-irradiated part, as shown schematically in Fig. 9. In the case of Toner B on Roller A, oppositely charged toner developed on the unexposed part of the photoreceptor and resulted in a high density background.

As shown in Fig. 8, charge distribution is almost the same for the combination of Toner A and Roller A (indicated by dotted line), and for that of Toner B and Roller B (indicated by dashed-dotted line). However, a high quality print was obtained only for the combination of Toner A and Roller A.

To clarify the reason for these different results, the relation between background density and the development potential, the potential between the photoreceptor surface and developing bias on the roller was measured in each of these combinations. As shown in Fig. 10, the dependence is quite different for these combinations. In the combina-

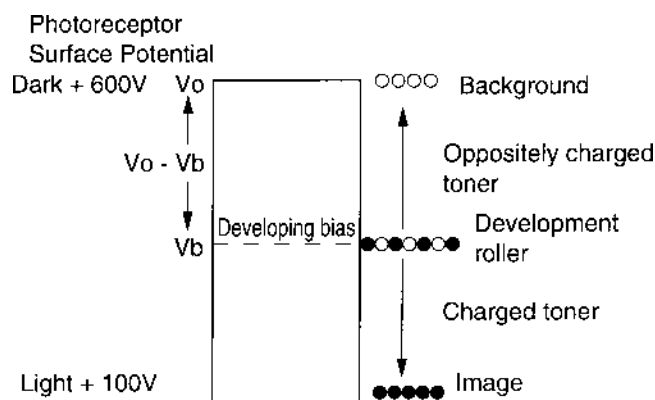


Figure 9. Potential diagram of photoreceptor surface and development roller.

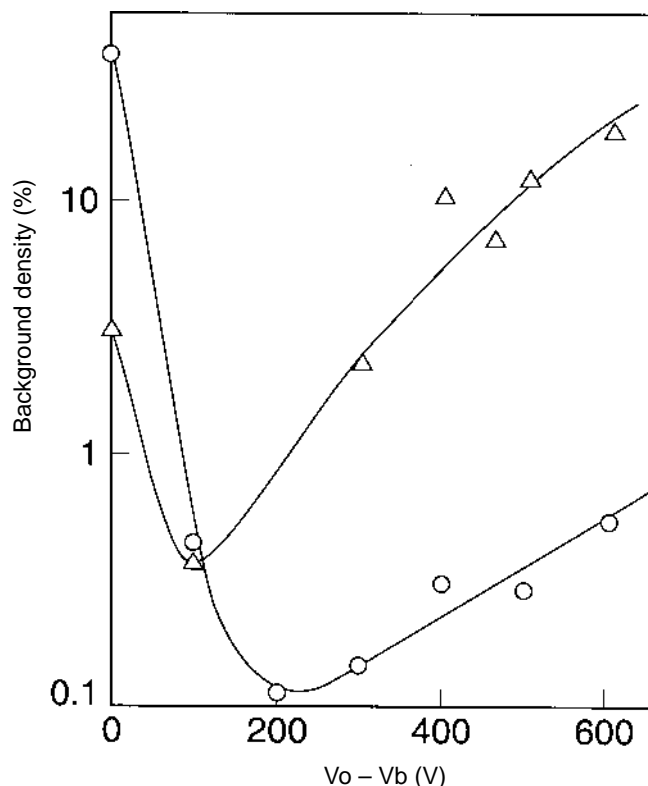


Figure 10. Background density versus potential difference between photoreceptor and development roller in various combinations of toner and surface of development roller material. ○, combination of toner A (polyester 1 + CCA2 3.0 wt% added) and roller A (polyurethane); △, combination of toner B (polyester 1 + CCA1 1.0 wt% added) and roller B (perfluoroelastomer).

tion of Toner A and Roller A, the area of background density lower than 1% is obtained in the $(V_0 - V_b)$ range from 100 to 600 V, where V_0 refers to the surface potential of photoreceptor in the dark part and V_b refers to the developing bias potential on the development roller. On the other hand, for the combination of Toner B and Roller B, the range is very narrow, being only from 50 to 200 V. This difference indicates that the developing bias on the roller has a greater influence than the roller material on the toner charge and print image quality in this system. The effect of the roller as a tribocharge donor is small when the chargeability of the toner is small and the receivability of charge injected from the roller is high. Because Toner

B receives more charge injected from the roller than Toner A, a suitable developing bias range is thought to be narrow, even if a roller is applied that donates tribocharge well. It is suggested that the surface energy of toner relates to the charge injection.

Conclusion

CCAs interact with polar groups of polymer and influence toner surface energy. A low-molecular-weight type CCA1 makes toner surface energy high and induces a more hydrophilic surface. This is one of the reasons for the increase in background density in spite of the increase of CCA content. The optimum amount of CCA for polymer differs for various CCA species due to influence on surface energy and contribution to charging. Because most molecules are functional in low-molecular-weight type CCA1, the amount of addition is less than 2 wt%. In the range above 2 wt%, the CCA increases the toner surface energy and induces a more hydrophilic surface rather than functioning as a charge controller. The density of functional groups that increased the surface energy in the polymer type CCA2 is much lower than in the low-molecular-weight type. Therefore, the surface energy and background density did not increase, even with 5 wt% addition.

The development roller is also important because toner charge distribution depends on development roller material. The ability of the roller to donate tribocharging is different for various toners. It is suggested that a high

surface energy toner is more subject to charge injection than the low surface energy one.

From these facts, to obtain high quality image prints by monocomponent nonmagnetic development with positive toner, we must consider two important principles. The first is to combine a suitable polymer and an optimum CCA type and content. The second is to select readily chargeable toner and an optimum roller material as tribocharge donor. ▲

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