# Effects of an External Additive on Toner Adhesion

# Haruo limura, Hisao Kurosu and Takeo Yamaguchi

Imaging Technology Division, Ricoh Co. Ltd., Yokohama, Japan

We have studied the effects of an external additive on the non-electrostatic and electrostatic adhesion of toner. Toner samples with various concentrations of the additive were prepared. The additive surface coverage on the toner was evaluated with a scanning electron microscope. The adhesion to a photoconductor of non-tribocharged or tribocharged toner was measured by the centrifugal method. It was found that the non-electrostatic adhesion rapidly decreased with increasing surface coverage, and saturated at a certain coverage. The dependence of the non-electrostatic adhesion on the surface coverage can be explained as a change of the van der Waals force. The electrostatic adhesion increases in proportion to the square of toner charge to mass ratio, and the slope decreases exponentially with increasing surface coverage. A simple electrostatic image force model cannot explain an enhanced electrostatic adhesion. It is suggested that the enhanced adhesion is caused by a non-uniform charge distribution in the toner surface. The decrease in electrostatic adhesion with increasing surface additive is attributed to increasing total charged area on the toner particle.

Journal of Imaging Science and Technology 44: 457-461 (2000)

# Introduction

Various forces acting on toner particles control the particle motion in the electrophotographic process. For example, in transferring toner to paper, the properties are influenced by the balance of the Coulomb force and the force of adhesion between the toner and photoconductor. Therefore, the control of toner adhesion is important for the transfer of toner deposition with high fidelity in the transfer process. The toner adhesion consists of nonelectrostatic and electrostatic components. In order to control the toner adhesion, it is of interest to investigate the effects of various factors on the non-electrostatic and the electrostatic components of toner adhesion. A toner surface treatment by an external additive such as silica, used for improving toner flowability, is one of the important factors that influence the toner adhesion.<sup>1-4</sup> However, the contributions of the non-electrostatic and the electrostatic force of adhesion to the toner adhesion and the effects of the external additive on these force components are not fully understood.

In this article, in order to investigate the dependencies of the non-electrostatic and the electrostatic adhesion on the surface additive coverage, the adhesion between a photoconductor and non-tribocharged toner or tribocharged toner with various toner surface additive coverage is measured by the centrifugal method.<sup>5</sup> We discuss the mechanism for the changes of non-electrostatic and electrostatic adhesion with increasing external additive.

# Experiment

### **Sample Preparation**

Toner samples with various concentrations of the surface additive between 0.1 wt% and 3 wt% by weight were prepared for this study. Toner particles prepared by a pulverization method were irregular in shape. The volume-weighted average diameter of these toner sample was approximately 9  $\mu$ m. The additive was a hydrophobic treated silica with an average primary particle diameter of around 14 nm. The silica had a propensity to charge negatively.

The toner was deposited on the photoconductor in the adhesion measurement. The organic photoconductor film consisted of polycarbonate and a charge transport material formed on an aluminum substrate.

# Measurement of Toner Surface Coverage by Additive

Micrographs of the toner surface of each sample were obtained with a scanning electron microscope (Hitachi S4500). The areas shaded by each additive particle on the toner surface were measured by image analysis of the electron micrographs. The spherical equivalent diameters of each additive particle were calculated from these areas. The toner surface additive coverage was calculated from the measured total area of the additive.

#### **Measurement of Toner Adhesion Force**

The adhesion between toner and the photoconductor was measured by the centrifugal method using a Hitachi Koki CP100 $\alpha$  Ultracentrifuge. Non-tribocharged or tribocharged toner particles were deposited on the photoconductor film with an air stream. The toned photoconductor film, a spacer and a capture substrate were placed in an aluminum holder. The holder was placed in the rotor (Hitachi Koki angle rotor P100AT). The rotational speed of the rotor could be varied from

Original manuscript received March 8, 2000

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**Figure 1.** Relationship between the toner surface additive coverage and the concentration of the additive.

1000 to 100000 rpm. The centrifugal force was normal to the film and the rotational radius of the film was 64.5 mm. If the centrifugal force acting on a toner particle is larger than the force of adhesion between the toner particle and the photoconductor, the toner particle is detached and deposited on the capture substrate. A series of measurements were attained with increasing rotation speed, the surface of the capture substrate was examined with an optical microscope, and the diameters of the toner particles on the capture substrate were evaluated by the image analysis. The force of adhesion between each toner particle and the photoconductor was calculated from the diameter of the toner particle and the rotational speed at which the toner particle was removed. After completing the series of measurements up to the maximum rotational speed, the average adhesion and its distribution could be calculated.

#### **Results and Discussion**

# Surface Coverage by Additive

Figure 1 shows the relationship between the average toner surface coverage and the surface additive concentration. The surface coverage increases with increasing the additive concentration. The additive particles tend to form aggregates on the toner surface. The average diameter of the aggregates was 50 to 60 nm.

# **Non-Electrostatic Adhesion Force**

The adhesion of non-tribocharged toner to a photoconductor was measured for each toner sample. Figure 2 shows the adhesion distributions of non-tribocharged toner. As shown in Fig. 2, the adhesion forces are distributed over a range of  $10^{-10}$  to  $10^{-6}$  N, and the distribution shift to a smaller average force with increasing surface coverage. Moreover, the distributions become narrower with increasing surface coverage. As shown in Fig. 3, the average force of adhesion rapidly decreases with increasing surface coverage and saturates at about 25 % coverage.

Because the adhesion and diameter of each toner particle is measured in this experiment, the average adhesion for each toner diameter can be obtained. Figure 4 shows the size dependence of the toner adhesion. As



**Figure 2.** Adhesion distributions for non-tribocharged toners with various toner surface coverage.



Figure 3. Dependence of the average adhesion on the toner surface coverage for the non-tribocharged toner.

shown in Fig. 4, the adhesion of non-tribocharged toner increases in proportion to the toner diameter and the slope decreases with increasing surface coverage.

To explain these results, the van der Waals force is considered source of the non-electrostatic adhesion force. The van der Waals force,  $F_v$ , between a spherical particle and a plane<sup>6</sup> is:

$$F_{\nu} = \frac{HD}{12Z^2} \tag{1}$$



**Figure 4.** Size dependence of the adhesion for the non-tribocharged toners with various toner surface coverage.

where *H* is the Hamaker constant, *D* is the diameter of particle, and *Z* is an atomic dimension. The van der Waals force is proportional to particle diameter, and the data shown in Fig. 4 is consistent with the size dependence of the van der Waals force. For  $H = 7 \times 10^{-20} J$ ,  $D = 9 \mu m$  and Z = 0.4 nm, the van der Waals force calculated from Eq. 1 is 330 nN. The average adhesion of 9  $\mu m$  toner particles without the additive is 100 nN, which is of the same order of but smaller than the calculated value. The reason for this is that the radius of curvature of an irregularly shaped real toner surface is smaller than the equivalent spherical radius of the toner particle.

The effects of the additives on the average van der Waals force are discussed using the contact model illustrated in Fig. 5. The contact between a photoconductor and a toner particle with the additive can be characterized by two cases: (1) the toner surface directly contacts the photoconductor as illustrated in Fig. 5(a), (2) additives on the toner surface contact the photoconductor as illustrated in Fig. 5(b). The diameter of a toner particle is much larger than the diameter of an additive particle. Because the van der Waals force is proportional to particle diameter, the force between a toner surface and photoconductor is larger than the force between an additive and photoconductor. In the case of a lower surface coverage, the average van der Waals force must be large because there are many toner particles like that shown in Fig. 5(a). On the other hand, when the number of toner particles like that shown in Fig. 5(a) decrease with increasing surface coverage, the average van der Waals force tends to decrease. In the case of higher surface coverage, there is almost no toner particle like that shown in Fig. 5(a). In this limit, the average van der Waals force is small, and does not depend on the surface coverage.

In considering the width of the adhesion distribution, the van der Waals force of the toner without an additive depends on the radius of curvature of the toner surface. The radius of curvature of the toner surface depends on the toner diameter and particle shape. The van der Waals force distribution of irregularly shaped toner without the additive must be broad because the distribution of the toner diameter and particle shape is broad. On the other hand, the van der Waals force of toner covered with the additive is dominated by van der Waals force between the additive and photoconductor. Hence, the van der Waals force distribution of toner covered with the additive must be narrow because the effect of the toner diameter and the toner shape on van der Waals force is small.



**Figure 5.** Contact models between a toner particle with additives and a photoconductor: (a) toner surface contacts photoconductor, (b) additives contact photoconductor.



Figure 6. Dependence of the average adhesion on the square of toner charge to mass ratio,  $(Q/M)^2\!.$ 

#### **Electrostatic Adhesion Force**

The adhesion between charged toner and a photoconductor has been measured for each toner sample. The toner is charged by mixing with polymer coated carrier beads. The toner charge-to-mass ratio, Q/M, is measured by the blow-off method<sup>7</sup> and controlled by the toner concentration. The toner is charged negatively in this study.

Figure 6 shows the dependence of the average adhesion on  $(Q/M)^2$  for each toner sample. As shown in Fig. 6, the average adhesion is proportional to  $(Q/M)^2$ , and the slope  $\gamma$  decreases with increasing surface coverage. The average adhesion of charged toner, say *F*, can be expressed as:

$$F = F_{ne} + \gamma (Q / M)^2 \tag{2}$$

where  $F_{ne}$  is the average non-electrostatic adhesion force. The average electrostatic adhesion force can be obtained from the slope  $\gamma$  and Q/M in Eq. 2.

Figure 7 shows the dependence of the slope  $\gamma$  on the surface coverage. The slope  $\gamma$  decreases with increasing surface coverage. Figure 8 shows the dependence of the average electrostatic adhesion force on the surface coverage for Q/M = -20  $\mu$ C/g. As shown in Fig. 8, the log of the electrostatic adhesion decreases in proportion to the surface coverage. Therefore, at the same Q/M, the electrostatic adhesion decreases exponentially with increasing surface coverage.

To explain these results, the electrostatic image force,  $F_i$ , of a uniformly charged spherical particle, is estimated.  $F_i$  can be expressed<sup>8</sup> as:

$$F_i = \alpha \frac{\varepsilon' - 1}{\varepsilon' + 1} \frac{q^2}{4\pi\varepsilon_0 D^2}$$
(3)

where  $\alpha$  is the polarization correction factor,  $\varepsilon'$  is the relative dielectric constant of the photoconductor,  $\varepsilon_0$  is the dielectric constant of free space, q is the total charge on the toner particle, and D is the particle diameter.



Figure 7. Slope between the average adhesion and  $(Q/M)^2$ ,  $\gamma$ , plotted against the toner surface coverage.



Figure 8. Dependence of the average electrostatic adhesion on the surface coverage for Q/M =  $-20~\mu C/g.$ 

For  $\alpha = 1.3$ ,  $\varepsilon' = 3.3$ ,  $D = 9 \mu m$  and q = -9.7 fC (Q/M =  $-20 \mu C/g$ ),  $F_i$  is calculated to be approximately 7 nN. On the other hand, the measured electrostatic adhesion for Q/M =  $-20 \mu C/g$  ranges from 17 to 388 nN. Accordingly, the electrostatic image force of an uniformly charged particle does not explain the magnitude of the measured electrostatic adhesion and the change of the electrostatic adhesion force by the surface additive.

The charge patch model,<sup>9,10</sup> which is the electrostatic adhesion model for a particle with a non-uniform charge distribution, is discussed next. In this model, the electrostatic adhesion,  $F_e$ , between a toner and photoconductor can be expressed<sup>10</sup> as:

$$F_e = \frac{\varepsilon' - 1}{\varepsilon' + 1} \frac{q^2 f}{2\varepsilon_0 A_t} \tag{4}$$





Figure 9. Ratio of the total charged area on the toner surface to the surface area of the toner,  $A_t/S$ , plotted against the toner surface coverage.

where  $A_i$  is the total charged area on the toner particle, f is the ratio of the charged area in contact with the photoconductor to the total charged area on the toner particle. From Eq. 4, if the total charge of toner particles is the same, the electrostatic adhesion force depends on  $A_i$ . We assume that f is a constant. Thus, it is proposed that the change of electrostatic adhesion by the additive can be explained by the change of  $A_{i}$ . The measured values of electrostatic adhesion decrease with increasing surface coverage. It is assumed that  $A_t$  increases with increasing surface coverage because the electrostatic adhesion force is inversely proportional to  $A_i$ . The values of  $A_i$  can be estimated from the measured values of the electrostatic adhesion. The ratio of  $A_t$  to S(the surface area of the spherical particle with the toner particle diameter) is calculated. For  $\varepsilon' = 3.3$ ,  $D = 9 \mu m$ , q = -9.7 fC and f = 0.2 (see Ref. 10), the dependence of the calculated value of  $A_{\ell}/S$  on the surface coverage are shown in Fig. 9. For a toner particle without the additive,  $A_t$  will be small because the surface charges concentrate at the high chargeability region such as exposed CCA (charge control agent) region. When toner particles with the additive are mixed with carrier beads, both the toner surface and the additive will be charged. Therefore,  $A_t$  of the toner particle will increase with increasing surface coverage because the total area of the charged additive on the toner particle increases at the same time. To confirm this, it will be necessary to measure the surface charge distribution on individual toner particles.

# Comparison of Non-Electrostatic and Electrostatic Adhesion Forces

Figure 10 shows the dependencies of the measured average adhesion on the surface coverage for non-

Figure 10. Dependence of the average adhesion on the toner surface coverage for the non-tribocharged and tribocharged toner ( $Q/M = -20 \ \mu C/g$ ).

tribocharged and tribocharged toner (Q/M =  $-20~\mu C/g$ ). The adhesion of the tribocharged toner is about 3 to 10 times larger than the adhesion of the non-tribocharged toner. Therefore, the contribution of the electrostatic adhesion is larger than that of the non-electrostatic adhesion, and depends on the amount of toner charge.

# Conclusions

The dependencies of the non-electrostatic and the electrostatic adhesion of toner on the toner surface coverage by an external additive were measured with the centrifugal method. The non-electrostatic adhesion rapidly decreases with increasing surface coverage, and saturates at a certain coverage. The electrostatic adhesion decreases exponentially with increasing surface coverage. The change of the non-electrostatic adhesion can be explained as the change of van der Waals force of the toner. The change in the electrostatic adhesion is caused by a change in the charge distribution on the toner surface by the external additive.

#### References

- 1. H. Akagi, Proc. SPIE 1670, 138 (1992).
- 2. M. Ott and H. Mizes, Colloids and Surfaces A 87, 245 (1994).
- 3. K. Terao and K. Shigehiro, J. Soc. Electrophotogr. Japan 34, 83 (1995).
- B. Gady, D. J. Quesnel, D. S. Rimai, S. Leone and P. Alexandrovich, IS&T's NIP14: Int. Conf. on Digital Printing Tech. IS&T, Springfield, Va,1998, p. 363.
- M. Takeuchi and A. Onose, M. Anzai, R. Kojima and K. Kawai, *IS&T's Tth Int. Congress on Advances Non-Impact Printing Tech.*, IS&T, Spring-field, Va,1991, p. 200.
- 6. H. C. Hamaker, *Physica* 4, 1058 (1937).
- E. Lehmann and G. R. Mott, *Xerography and Related Process*, J. H. Dessauer and H. E. Clark, Eds. Focal Press, New York, 1965, p. 289.
- 8. T. B. Jones, Electromechanics of Particles, Cambridge University Press, New York, 1995, p. 197.
- 9. M. H. Lee and J. Ayala, J. Imaging Tech. 11, 279 (1985).
- 10. D. A. Hays, J. Adhesion 51, 41 (1995).