

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Theoretical Considerations

2.1.1 History of Electrophotography

The first electrophotography was invented in 1938 by Chester Carlson who used sulfur as a photoactive material to make an image. In 1959, the Haloid Corporation (present called Xerox) introduced the 914 automatic copier and used selenium metal as the photoconductor. Then, during the 1970s IBM and Kodak introduced copiers based on organic photoactive materials and positive charging toners. During the 1980s Japanese manufacturers (Canon and Minolta) introduced low speed copiers using selenium and cadmium sulfide as the photoreceptors and negative toner. Since 1980s many combinations of single-component and two component developments and positive and negative toners have been used in the industry.¹

2.1.2 The Electrophotographic Process

The electrophotographic process is based on six basic steps in reproducing a document : charging, exposure, development, transfer, fusing, and cleaning. First (the charging step), the photoreceptor is covered with ions through the use of a wire or grid biased to high voltage. Second (the exposure step), an optical system forms an image of the document on the photoreceptor. This step forms a latent electrostatic image on the photoreceptor drum. Third (the development step), a toner of the opposite sign from the latent image is typically brought into contact with this image. Next (the transfer step), the backside of the paper which is brought on to the photoreceptor, is charged with ions opposite in polarity from the toner. This step transfers the image to the paper. Then (the fuser step), the toner is melted onto the

surface of the paper. Finally (the cleaning step), the small amount of toner remaining on the photoreceptor, after being transferred, is removed by an electrostatic brush.¹

2.1.3 Toner components

Dry electrophotographic toners consist mainly of polymer resin and pigment. The additional ingredients contain charge control additives, surface additives, and other additives such as silicone oil.²

2.1.3.1 Resin

The role of the resin in a toner is to bind the pigment to the paper or transparent material to form a permanent image. The selection of the polymer depends on the fusing method, which can be subdivided as follows:

(a) Cold pressure method

The polymer is typically lower molecular weight ethylene-vinyl acetate copolymers, polypropylenes, and polyethylenes.

(b) Continuous radiant source

The molecular weight of the polymers, polyesters and epoxies, ranges from 5,000 to 50,000 and glass transition temperature from 50 to 60 °C.

(c) Flash fusing

The toner is melted into the paper by a very short, high intensity flash of light lasting less than 5 ms. Styrene copolymers, epoxies, and polycarbonates have all been used.

(d) Roll fuser

The paper with the unfused toner passes through a nip formed by a heated roll and a backup roll forced against the heated roll at fairly high pressures. The polymers used are styrene copolymers such as styrene acrylates, methacrylates, and butadienes, which have molecular weights ranging from 30,000 to 100,000 and glass transition temperatures ranging from 50 to 65 °C.

2.1.3.2 Colorants

The common colorant for electrophotographic toners is carbon black which is used in the toner at a 5 to 15% loading. Pigments other than carbon black that are usually used include organic pigments, such as, copper phthalocyanines used for cyans and blues, azo pigments for yellows, and quinacridones or rhodamines for magentas and reds.

2.1.3.3 Charge control additives

Charge control additives, CCA, are added to a toner when the pigment mixed into the polymer does not give an adequate charge level or rate of charging. Two types of charge control additives are used for positive applications. One type is the quaternary ammonium salts which are used in color applications because they are colorless. The other is a nigrosine, which is black, and is therefore unsuitable for color applications. For negative applications, acidified carbon blacks, fumed silica and metal complexes are used.

2.1.3.4 Surface additives

Certain materials, such as fumed silicas, are added to the surface of a toner to improve flow properties and transferring the toner from the photoreceptor to paper. This is done by lowering the adhesion of the toner to the photoreceptor. The silicas also improve the charge stability of the toner and carrier mixture.

2.1.3.5 Other additives

These additives are used in specific application, such as silicone oil, which is used as release agent for the fuser roll.

2.1.4 Two-component development

The two-component developer consists of the toner particles and the carrier beads. The charge is generated on the toner particles by mixing the toner particles with the carrier beads. The mixture is brought in contact with the latent image on the

photoreceptor. The cascade development and the magnetic brush development are typical of the two-component development system.³

2.1.4.1 Cascade development

The cascade development system was invented in 1952 and used on the first electrophotographic copiers. The cascade development system is schematically shown in Figure 2-1. The toner particles (average diameter 10 μm) are mixed with the carrier beads (diameter ~200-500 μm). Charge exchange causes the toner to be electrostatically attracted to the carrier beads. The carrier beads are then literally cascaded down the photoreceptor under the influence of gravity. The interaction of the toner with the latent image clearly depends on the behavior of the cascading carrier beads, such as the bead velocity and the bounce rate. These variables depend on hardware parameters such as the developer flow rate, the angle of the photoreceptor with respect to gravity. The carrier particles are recirculated while the toner is used up as it is developed onto the photoreceptor. Hence, means must be provided to sense the depletion of the toner, the need to add more toner, and the need to mix a new toner with the carrier to produce the proper charge.

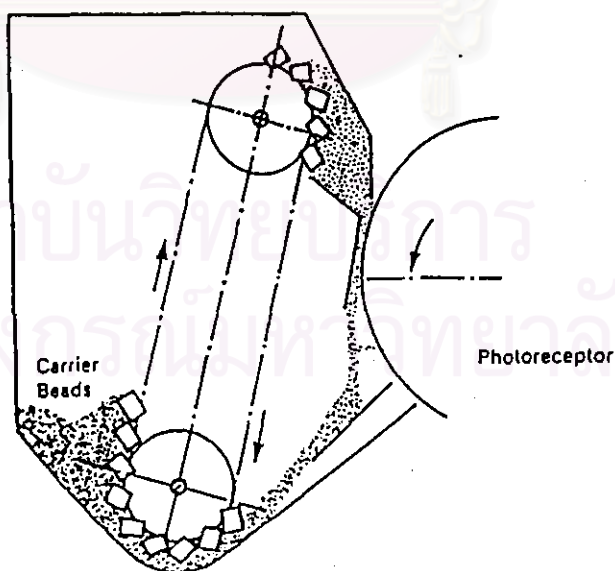


Figure 2-1 Schematic diagram of a cascade development system

2.1.4.2 Magnetic brush development

A magnetic brush development system is shown schematically in Figure 2-2. This system was invented in the late 1950s. The carrier beads are made of magnetically soft material such as iron or ferrite so that they can be moved by the magnetic fields. The carrier beads, with attached toners, are introduced into the vicinity of a roller inside of which are stationary magnets. The friction force, due to the magnetic fields, causes the carrier beads to be carried around the rotating roller. In the gap between the roller and photoreceptor toner moves from the carrier beads to the photoreceptor.

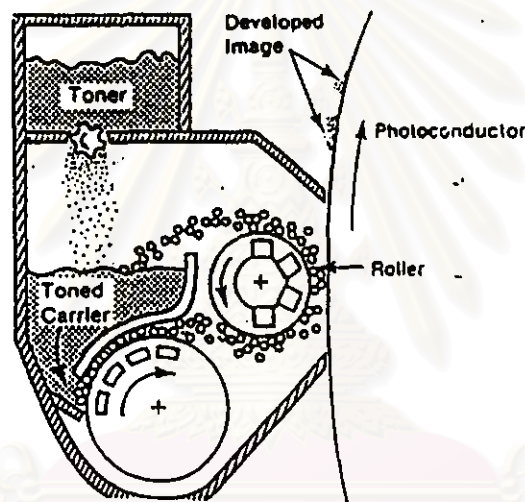


Figure 2-2 Schematic diagram of a magnetic brush development system

2.1.5 Toner charging for two-component development systems

In two-component development systems, two powders, a toner and a carrier are mixed together. The toner particles have diameters of approximately $10\ \mu\text{m}$ which are a mixture of polymers and carbon black pigments. The carrier particles have diameters of approximately $200\ \mu\text{m}$ and are composed of magnetically soft cores coated with a thin polymer coating. Contact between the toner and carrier causes the charges to be exchanged.⁴

The average charge-to-mass ratio (Q/M) determines the amount of toner developed onto solid area and character latent images. The lower the Q/M , the darker

the images on the page. It is believed that a toner of the opposite charge is attracted to the photoconductor, onto non-imaged areas; thus, giving an objectionable gray color to the white paper.

The powder geometry of contact charging phenomena has some aspects of static electricity. First, the charging takes place with virtually no electric field being generated over macroscopic distances, which is due to the size of the toner particles. This significantly reduces the possibility of air discharge in affecting the results. Assuming that there are 200 million toner particles in a 10 grams sample of the developer, then a large amount of the particles will come into contact with the contact area. Once these materials come into contact, their charges will be exchanged. The charge exchange between the contacting materials is an important aspect because it occurs between all materials (including metals and insulators, and organic and inorganic material)

The construction of contact charge exchange models require the specification of the following items : the nature of the charge carrier (electrons, ions, or mass transfer), the driving force (difference in work function, concentration gradients), the mechanism (thermionic emission, tunneling), the energy states involved (bulk or surface, extrinsic or intrinsic), and the condition (whether the dynamic or equilibrium condition is being addressed). These parameters are agreed upon only for metal-metal contacts (electrons, difference in work functions, tunneling, bulk intrinsic states, and equilibrium condition).

(a) Metal-Metal Contact Charging

If two metals with different work functions ϕ_i are brought together and electrons are allowed to exchange by tunneling (Figure 2-3), the energy of an electron inside and outside of a metal is shown in (a) and (b), showing that the two metals in close proximity exchange charge until in equilibrium. So that thermodynamic equilibrium is maintained, a contact potential difference V_c is created across the interface and is given by

$$V_c = (\phi_B - \phi_A)/e \quad (2-1)$$

The charge, Q , exchanged by electron tunneling is

$$Q = C_{AB} V_c \quad (2-2)$$

where C_{AB} is the capacitance between the two adjacent bodies. As the two bodies are separated, C_{AB} decreases (and consequently Q decreases) until the charge exchange by tunneling stops.

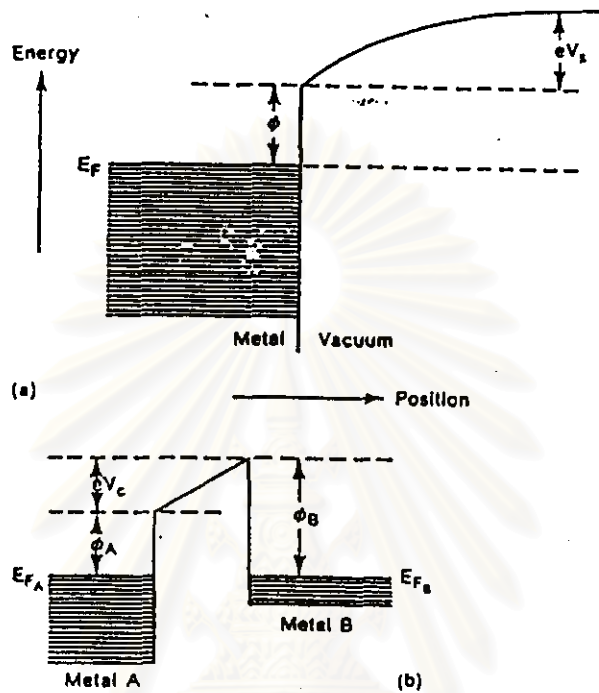


Figure 2-3 The energy of metal-metal transition : (a) the energy of an electron for a metal and (b) two metals exchange charge to equilibrium

(b) Metal-Insulator Contact Charging

Surface states on insulators can be intrinsic or extrinsic. Figure 2-4 shows the surface state theory of contact electrification : (a) the insulator is uncharged and the surface states are filled below the neutral level ϕ_I and empty above, (b) when the insulator is brought into contact with a metal, insulator surface states below the metal Fermi level E_F will fill and those above will remain empty and (c) the opposite limit of high surface state density, the surface states need only be filled to a level slightly above ϕ_I , which raises the energy of all the insulator states. For either case, one might expect that on contact with a metal, empty states below the metal Fermi level E_F will be filled and full states above it will be emptied. If there are $n(E)dE$ insulator states per unit area whose energy falls in the range between E and $E+dE$, the number of electrons per unit area σ/e which pass from the metal to the insulator surface is

$$\frac{\sigma_s}{e} = \int_{\phi_i}^{\phi_M} n(E) dE \quad (2-3)$$

where ϕ_I is the insulator work function, the boundary between filled and unfilled surface states on the insulator. This is valid if the density of insulator surface states is low enough so that the transfer of charge does not alter the energy of the states, which is usually a reasonable assumption. This assumption is based upon the non-equilibrium of the bulk and thermodynamic equilibrium among the surface states.

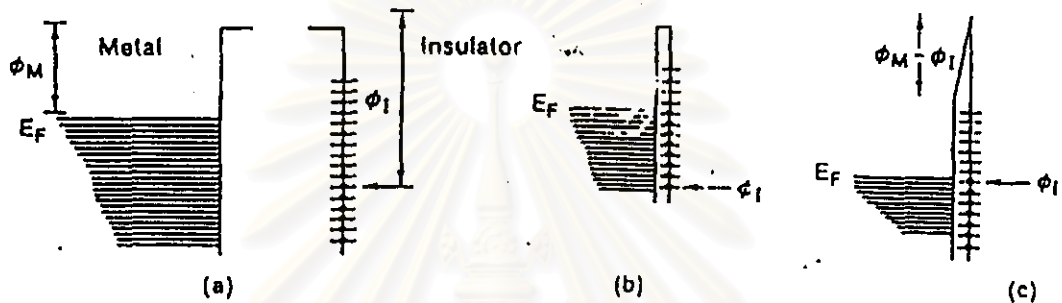


Figure 2-4 Surface states of metal-insulator contact charging : (a) the uncharged insulator, (b) the insulator contact with a metal, and (c) the increasing energy of the insulator states

(c) Ion Transfer Theories

The first mechanism of ion transfer depends upon the different affinities of the two surfaces for the charged particles that is shown in Figure 2-5. When this mechanism is applied to electrons, this mechanism is the difference in work functions. For ions, the difference in energy is $U_1 - U_2$. The charge per unit area, σ_s , that must be transferred over a distance, z , to equal this energy difference is

$$\sigma_s z / K\epsilon_0 = U_1 - U_2 \quad (2-4)$$

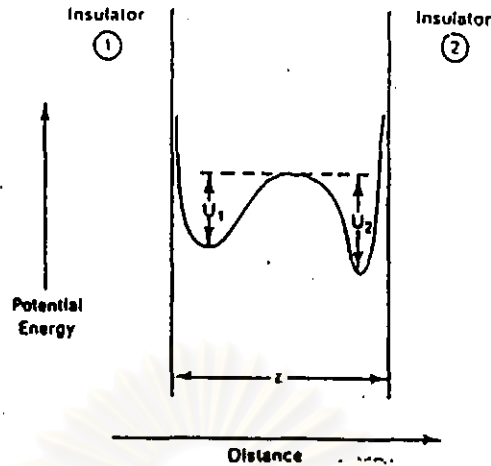


Figure 2-5 Dependence of the potential energy of an ion on its position between two plane parallel insulator surfaces

The second mechanism depends on the abundance of a particular ion on one surface. When one ion per 10 \AA^2 exists on one surface, it corresponds to $10^{15} (n_i)$ ions per cm^2 available for charging. Even if the charge were as small as 0.2 eV , the number of ions that would transfer would be $3.3 \times 10^{11} \text{ cm}^2$, which is well within the usually observed exchanged charge densities.

The third mechanism is based on a kinetic effect. The amount of charge transferred would depend on the number of surface ions compensating the “intrinsic” electric field and the details of the shearing motion. Any of the above three mechanisms could be operative if water layers exist between the two surfaces.

(d) Insulator-Insulator Contact Charging

This approach attempts to place the insulators in such an order so that the materials in the higher levels of the series will have a positive charge when they come in to contact with materials in the lower levels. This type of series is known as a “triboelectric series”, which will exist if one particular mechanism of charge exchange is operative.

The charge exchanged between particles in a powder is measured using a unique method such as the blow off method and the E-SPART analyzer as described below:

(i) Blow off method

Both powders are placed in a Faraday cage (Figure 2-6) with screens on both ends. The screens have mesh sizes ranging between the diameter of the toner and the carrier. An air jet forces the toner out of the cage. Measuring the change in charge and mass gives the average charge to mass ratio (q/m) of the toner.⁴

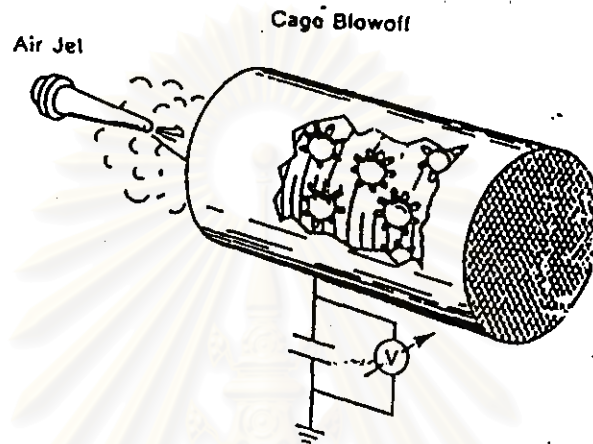


Figure 2-6 An apparatus used in the Blow off measurement

(ii) E-SPART analyzer

The instrument used for a real time simultaneous measurement of aerodynamic size and electrostatic charge distribution of particles on a single particle basis is the Electrical Single Particle Aerodynamic Relaxation Time (E-SPART) Analyzer as shown in Figure 2-7.⁵

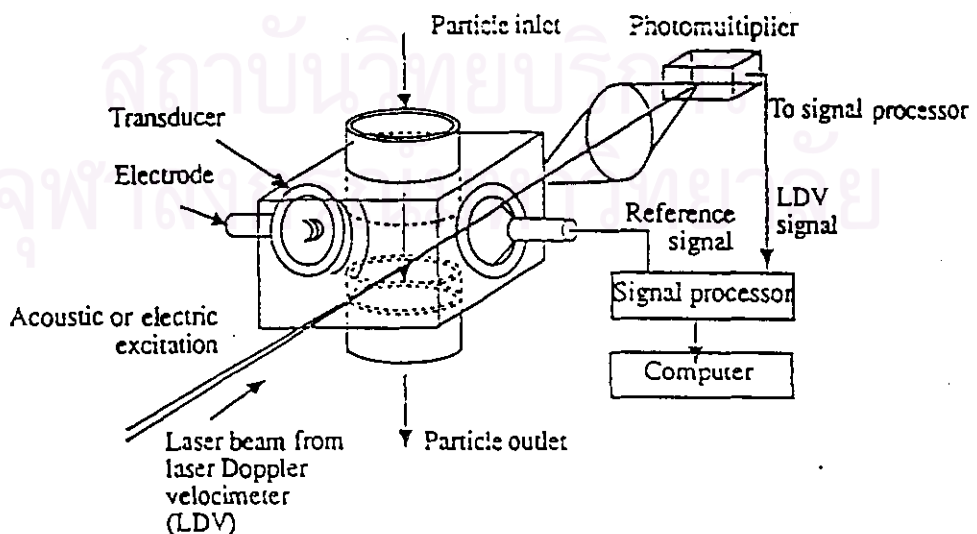


Figure 2-7 Schematic diagram of the E-SPART analyzer

The E-SPART analyzer simultaneously measures the size ranging from sub-micron to 100 μm and particle charge distribution ranging from zero to saturated levels.

The particles are sampled in a laminar flow field through the Laser Dopple Velocimeter (LDV) sensing volume. As each particle passes through the sensing volume it experiences the acoustic excitation and the superimposed DC electric field in a direction perpendicular to the direction of the laminar air flow.

2.2 Literature review

The triboelectric properties of two-component developers are the important parameters that control the developed mass. A measurable parameter is the time dependence of the toner charge-to-mass ratio, q/m , which depends on the concentration of the toner in the developer, the sizes of toner and carrier, the material composition, and the material parameters relevant to contact electrification. A physical model assumes field dependent contact electrification as the basic contact charge exchange mechanism and treats the time dependence of q/m arising from developer agitation, and from charging and mass transfer mechanisms between toner and carrier.⁶

Nash and Bickmore⁷ presented a model for the toner impaction and triboelectric aging processes. The developer aging varies inversely with the total developer mass. The mode of toner impaction and triboelectric aging are unaltered by the changes in toner size, while the reduction in carrier size does indeed reduce the rate of triboelectric aging and the rate of toner impaction.

Kutsuwada and Nakamura⁸ applied Millikan's method for the measurement of the radius and the electric charge on a single particle. On the other hand, the Blow-off Tribocharging method cannot determine the magnitude and the sign of an electric charge on one particle of toner. The charge efficiency and the radius on a single particle of toner in the air can be determined by this apparatus. The efficiency of electric charge of toners is nearly proportional to the third power of the radius of the toner particles, especially to the type of spherical toner. In different types of tribocharging, the quantity of electric charge of the toners is different for each

charging mechanism, but there is a similar tendency for the radius of the toner particles to be dependent on the electric charge.

Hays⁹ elucidated the electrical properties of the insulative developer. Measurements were obtained on an electrode cell of developer under magnetic-field-free conditions. The measurements were based upon the toner charge transport. Toner charge transport within the developer and toner deposition on an electrode depend on developer agitation supplied by moving the upper electrode. The role of agitation in Hays' development model was accounted for including a term in the toner and triboelectric current densities, which is the relative velocity between the moving electrode and developer.

When an insulating over layer is used, the toner density deposited on the conducting electrode was more than the toner density that was not used. The developed toner density is limited by an electric field which collapses near the developer-electrode interface. For magnetic brush development, the developed toner density should be proportional to the ratio of the brush-to-roller speed. This is possible if an equilibrium is established within the distance that an element of developer interacts with the photoreceptor and that the electric field due to the toner deposition on the photoreceptor is much less than the electric field driving development.

Hays¹⁰ described a mechanism for background toner deposition in magnetic brush development with two-component xerographic developers. The mechanism is based on an electric-field-dependent contact charge modification of toner nudged between carrier beads and the image receiver. The toner charge can be reduced and even cause opposite charges to occur during background development. The toner charge modification mechanism was incorporated in the background model, and successfully describes the generation and deposition of wrong-sign toner in electrode cell measurements.

Kimura et al.¹¹ described a new charge spectrography for toner particles due to the drawbacks of using conventional charge spectrography. These drawbacks are that the measurement conditions differ from those of the actual development and the apparatus takes too much time to measure the amount of toner which is quickly collected from the reflection density.

Takahashi et al.¹² studied the triboelectric charge polarity and charge distribution on toner particles by using the micro-probe charge detection method, which makes use of the laser scattering video recording system. This method has been measured for the simultaneous measurement of both toner size and its triboelectric charge of one toner particle.

Anderson¹³ presented a model of charging for the two-component electrophotographic developer which is based on electron donors and acceptor states on the surfaces of the carrier and the toner. If the donor and acceptor states reach an equilibrium during mixing the developer, then Fermi-Dirac statistic can be used to calculate the number of charged donor and acceptor sites. The model correctly predicts the relationship between toner charge-to-mass ratio and toner concentration, toner particle size, and carrier particle size.

Schein et al.¹⁴ studied the electrostatic charging characteristics of two insulating powders, the toner particle and the carrier particle using a charge spectrometer which allows complete characterization of the charge and radius distribution function. Powder mixtures with Q/M values less than $15 \mu\text{C/g}$ can be analyzed more accurately with the current design, by collecting fewer toner particles for higher charged mixtures. The toner charge depends on the toner diameter (d). The tendency towards diameter (d) as the toner concentration (C_t) increases is consistent in which the total toner area is contacted only when relatively few toners are mixed with the carrier. As C_t increases, the area charged is limited by contact events before the whole area is charged. Schein et al. tested the dependence of the toner charge on C_t and found that Q/M decreased as C_t increased.

Noshiro et al.¹⁵ presented the tribocharging behavior of two kinds of toners which had the same composition but different shapes. Ferrite carrier were mixed with the toner. The tribocharge of the different toners, (spherical shaped toner and irregularly shaped toner) was measured by the blow-off method. The $(Q/M)_{\text{max}}$ of the irregular toner was found to be larger than that of the spherical toner at the same agitation condition. But the time constant for the charging of the irregular toner was smaller than that of the spherical toner. The time constant increased and the toner charge decreased with an increase in toner concentration of the developer. The shape factor of the toner particles was evaluated quantitatively by an image analyzer.

Kamiyama et al.¹⁶ described the spherical particles of the toner which had a smooth and efficient agitation on the magnetic brush. This caused the toner particles to form a very uniform triboelectric charge. The polymerization method was used to reduce the number of manufacturing processes involved in making small particle toners. The image quality with this toner was also enhanced in the reproduction of fine lines and small dots.

Poomtien et al.¹⁷ studied charging behavior of three types of CCA on various concentrations. The presence of CCA helps increase the effectivity of the charging sites on the toner, so that proper increase in CCA amounts increases the q/m values. The charging properties of the toners were measured by an E-SPART analyzer and a blow off measurement unit. The charging properties influenced the quality of the printed images. The toners without CCA had the lowest print density. The higher the CCA amount, the higher the print density. But, the background density of the toners without CCA were higher than the toners with CCA.

Netpradit et al.¹⁸ investigated the dependence of the toner charge-to-mass ratio (q/m) in the two-component developer on the toner concentration (T/C), the carrier size, and the toner size in order to acquire the relationship of the print qualities, in terms of print density, with the background density. The q/m values measured by blow-off measurement showed that the toner q/m values decreased with increasing T/C. The toner charge properties which depend on the toner resin and the carrier coating polymer are controlled by the toner size and the carrier size. Smaller toner size increased the print quality, but decreased the latitude of T/C. But smaller carrier size gave a wider latitude of T/C with an optimum range of q/m . A low T/C resulted in higher toner charge, which also produced a lower print density. On the other hand, a high T/C induced a very low toner charge and the background density was very high.

Aoike et al.¹⁹ proposed a model for the toner tribo-charging to help explain the dependence of the toner charge on the mass ratio (q/m) of the two-component developer on the toner concentration, which is affected by the toner and the carrier properties. The carrier charge to mass ratio, Q_C/M_C , to the metal plate will have different work functions, which depend on the amount of toner concentration.

Lee et al.²⁰ studied the influence of charge control agent (CCA) in toner surface to toner tribocharge. The variation of CCA materials on toner surface and toner concentration had been examined by the blow off method. The toner q/m slightly increased as CCA content decreased. The toner q/m value was smaller for the metal including CCA than the CCA, which did not include any metal. The toner tribocharge characteristics are strongly influenced by the carrier surface properties even if the toner surface properties are changed by CCA.

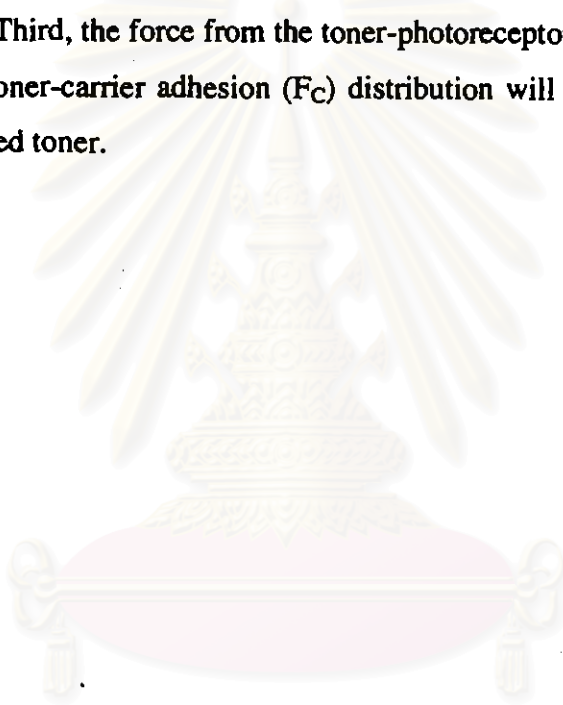
Anderson and Bugner²¹ observed the electronic model of triboelectrification, which was applied to the two-component developer. A charge-control agent is added to the toner to control the magnitude and polarity of the electrostatic charge. As the donor energy of the charge agent decreases, the charge-to-mass of toner particles generated by contact with a reference carrier also decreases. The acceptor energy of the charge agent over a similar range has a small effect on the charging behavior.

Fujita et al.²² described tribocharging characteristics of the toner using the blow off measurement which was carried out in the nitrogen (N_2) and argon (Ar) atmosphere. The toner charge level Q/M for the spherical toner was higher than that for the irregular toner. The toner charge level Q/M in Ar was lower than in N_2 for the whole rubbing media. Under all circumstances, the toner charge Q/M decreased with a decrease in gas pressure.

Schein²³ introduced the toner charge-to-mass ratio dependence on the toner concentration and charge control agent concentration in a toner-carrier mixture. The surface state theory observes the inverse dependence of the toner charge-to-mass, Q/M , on toner concentration, C_t , in toner-carrier mixtures. According to this theory, a charge is exchanged between the surface states of the two materials, driven by the surface work function difference between the materials.

Law et al.²⁴ researched on the effects of surface area and surface modification of amorphous fumed silicas on the tribocharging and admix properties of styrene-butadiene toner. The effect of the relative humidity, RH, on toner charging indicated that the tribocharge decreased as the RH increased. Hydrophobic silicas were more resistant to RH changes. A reduction in admix time was observed at high RH for toners consisting of hydrophobic silicas. The tribocharge in this condition was decreased.

Schein and Beardsley²⁵ studied the background development in the insulative magnetic brush development system. The background of the photoconductor (PC) has an opposite charge when compared to the toner. The charge of the PC will increase as the reverse bias and toner concentration increases. Schein and Beardsley suggested that the reverse bias mechanism would cause a positively charged toner on the PC. There are three reasons for the toner to be oppositely charged. First, a space between the carrier beads, which are adjacent to the PC, will cause the toner to be oppositely charged. Second, the reverse bias mechanism will cause the opposite charge of the toner to double. Third, the force from the toner-photoreceptor adhesion (F_p) minus the force from the toner-carrier adhesion (F_c) distribution will alter the presence of the oppositely charged toner.



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