

Modeling of the Tribo-Charging Between Toner and Carrier Beads

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Abstract

The tribo-charging characteristics between toner and carrier beads were measured experimentally for various toner concentrations in the flow-agent free toner-carrier systems. We found that Lee's low surface state density model could fit the equilibrium charging data better than Schein's model which assumed high surface state density of carriers and actually was a special case of the Lee's model. However, Lee's model, which was based on the energy equilibrium, could not apply to non-equilibrium transient case. In order to describe the transient behavior of toner charging, a simple kinetic contact model, which assumed random contact probability during toner-carrier tribo-action, was constructed. The calculations of the new model showed excellent agreement with the experimental data of Q/M versus time for the various toner concentrations, and at infinite time, which corresponded to the equilibrium state, the kinetic contact model became identical to Lee's model. As consequence, both equilibrium and transient behavior could be described.

Introduction

Toner is mainly composed of polymer resin and carbon black, together with other ingredients to give it the magnetic and triboelectric functions required for development, transferring, and fixing onto paper during the electrophotographic processes. Yet, in order to achieve the optimized quality of printing, the triboelectric behavior of the toner has to be well understood, empowering us to fully control the tribocharges on each toner particles during development. However, triboelectric phenomena, although discovered thousands of years ago, are still mystic in many aspects especially for the charging between insulating surfaces. In this study, we would like to first experimentally observe the charging behavior of a simple extraparticulate-free toner and carrier system. Then by using the experimental data in comparison with the existing tribo-electrification theories, it is hoped that we can gain understanding toward this complicated phenomenon, and build a quantitative model to describe the charging behind the electrophotographic process.

Tribocharging is a phenomenon that when two materials come in contact or undergo frictional movement, electric charges are generated around the contact area. This

phenomenon was discovered a long time ago, yet up to now, physical meanings behind tribocharging are still obscure. The first well-cited result of the study of the tribocharging is the proposal of the triboelectric series. However, the physical interpretation was not available until 19th century. Helmholtz (1879)¹ proposed that the tribocharging was a result of differential contact potential between the two contact materials. Later on, theories based on dielectric constant and ion transfer were suggested. In 1917, Shaw² first proposed that triboelectrification was due to ionic transfer. Later, Henry³ provided a more complete theory in 1957 that ionic transfer was due to the difference in the binding energy ΔU of the ions at the two contact surfaces. The ion flow continued until the binding energies between the two surfaces were equal, from which the relationship between the surface electric density σ and ΔU can be derived. In his theory, ion transfer was possible between surfaces of the same material. The difference in the ionic density on the surface or local temperature can trigger the flow of the ions, causing the triboelectric effect. The origins of the ions were explained later by Kornfeld (1969)⁴ by a theory based on the electric defects on insulators. In 1977, Ruckdeschel and Hunter⁵ also proposed thermoionic theory to support the ionic transfer theory. However, in 1980, Lowell and Rose-Innes⁶ pointed out that the electric density σ calculated based on the ionic transfer theory is greater than that observed.

The viewpoint of electron transfer by Helmholtz was extended by Harper (1951) who proposed that the so called "contact potential" of metals may be the difference in the Fermi level of the two contacting materials. In 1967, Harper⁷ further pointed out that the triboelectrification between metals is due to the difference of the work function of the contact surfaces via electron tunneling to achieve the thermodynamic equilibrium, or the equalization of the Fermi level. Based on this model, the tribocharges Q can be expressed as

$$Q = C(\phi_{M1} - \phi_{M2})/e$$

where C is the resulted capacitance between the two metals, ϕ_{M1} and ϕ_{M2} are the work functions of the metals. This result was later proved experimentally by Harper⁸ and by Lowell.⁹ The success of the work function theory for metals prompted the research work extending it into the realm

of insulators. In 1969, Davies¹⁰ found that the triboelectric charge on polymer surfaces was related to the work function of the contacting metal. It was also found that the work function theory could be used to explain the experimental results of the earlier workers of Henniker, Fukada¹¹, and Fowler. In 1974, Wahlin¹² and Backstrom also published similar results.

The work function theory based on electron transfer was then employed to study the triboelectrification of toners in the electrophotographic processes. In 1978, Lee¹³ proposed a surface interaction model (the low energy density model) based on electron transfer to explain the tribocharging behavior of toners. It was asserted that when toner came in contact with the carrier beads, electrons flowed from the surface that had the lower work function to the other contact surface, until the Fermi levels of the two surfaces became equalized. Consequently, the electric charges generated from triboactions can be described quantitatively by the following equation:

$$M_t/Q_t = r_c(M_t/M_c)\rho_c/(3ef_cN_c\Delta\phi) + r_t\rho_t/(3ef_tN_t\Delta\phi)$$

where M_t is the toner weight, M_c is the carrier weight, r_t and r_c are the diameters of toner particles and carrier beads respectively, r_t and r_c are the true densities of toner and carrier respectively, N_t and N_c are the energy densities of toner and carrier respectively, f_c and f_t are the effective fractional surface area during contact of toner and carrier respectively, and $\Delta\phi$ is the difference of the electron work function of toner and carrier. The linear relationship between M/Q and M_t/M_c was verified by experiments. Furthermore, in 1988 Nash and Bickmore¹⁴ published their results that showed the relationship between charge and toner concentration to be

$$Q_t/M_t = A_t/(M_t/M_c + b),$$

where A_t and b are constants. This result is consistent with the prediction of Lee's model.

Also in 1988, Bugner and Anderson¹⁵ studied the triboelectrification of the toner made of polystyrene grafted with phosphonium sulfonate salt, and found that the electric charge on the toner was always positive, independent of whether the ionic functional groups are positively or negatively charged. This important result indicated that electron transfer, instead of the ionic mechanism, is the more likely explanation for the tribocharging behavior of toner.

In 1989, Anderson¹⁶ further considered the case of non-uniform distribution of the energy state density on the surfaces. Due to local fluctuation of work function, both toner and carrier could accept and donate electrons during the contact charging. The triboelectric charge thus generated on the toner could be expressed as

$$M_t/Q_t = [(A_c + D_c)/(A_cD_t - A_tD_c) + (M_t/M_c)(A_t + D_t)/(A_cD_t - A_tD_c)]/e$$

where D_t and D_c are respectively the donor energy states of toner and carrier, A_t and A_c are the acceptor energy states of toner and carrier respectively. This result can be reduced to Lee's model for uniform density distribution where the conditions of $4\pi r_t^2N_t = D_t \gg A_t$ and $4\pi r_c^2N_c = D_c \gg A_c$ hold.

In 1992, based on the same work function model of Lee's, Schein¹⁷ considered the condition that the difference in energy states between the two contact surfaces was very large. In this case (the high surface state density limit), the surface that possessed the larger number of energy states served as the "reservoir" during electron transfer, viz. the Fermi level of the surface with high work function increased during electron transfer while the Fermi level of the low work function surface remained unchanged. Schein further considered the effect of electrostatic force due to the electron transfer, and assumed that the electron flow would continue until the electric field between the two contact surfaces equal to the work function difference. With this criterion, the electron transferred can be expressed as

$$M_t/Q_t = r_c(M_t/M_c)\rho_c/(3\varepsilon_0E_e) + r_t\rho_t/(3\varepsilon_0E_e)$$

where E_e is the electric field between toner and carrier. Gutman and Hartmann¹⁸ subsequently obtained the surface density σ_c of the tribo-charges under an external field to be

$$\sigma_c = \varepsilon_0(\phi_t - \phi_c)/(ez - \varepsilon_0E) [1 + (1/N_t + 1/N_c)\varepsilon_0/(e^2z)]$$

Recently, Anderson¹⁹ generalized the models of Schein and Lee by considering the work function changes in toner and carrier and the effect of electrostatic field. At the equilibrium between the two contact surfaces, there should exist a relation between the work functions, electric field, and the change of Fermi levels, i.e.,

$$(\phi_t - \phi_c)e = \Delta\mu_t - \Delta\mu_c + eV$$

where, $\Delta\mu_t$ and $\Delta\mu_c$ are the change of Fermi level in toner and carrier respectively during tribo-contacts, and V is the potential difference between toner and carrier. Therefore the relationship between Q_t and (M_t/M_c) is

$$M_t/Q_t = -z[(\varepsilon_0r_t\rho_t/N_t e^2z) + (M_t/M_c)(\varepsilon_0r_t\rho_t/N_t e^2z) + \varepsilon_0r_t\rho_t + (M_t/M_c)\varepsilon_0r_c\rho_c/[3\varepsilon_0(\phi_t - \phi_c)]]$$

At the high density limit, where $\varepsilon_0/N_t e^2z \ll 1$ and $\varepsilon_0/N_c e^2z \ll 1$, the equation reduced to the form derived by Schein. While at the low density limit, i.e., $\varepsilon_0/N_t e^2z \gg 1$ and $\varepsilon_0/N_c e^2z \gg 1$, the equation reduced to Lee's equation.

All three models by Lee, Schein, and Anderson, however, are theories based on global equilibrium, therefore, they can not predict the transient behavior of toner charging. This study compares the experimental charging data of the extraparticulate free toner with the predictions of the three models, and a dynamic model to describe the transient behavior of toner charging is presented here.

Experimental Procedures

The toner used throughout the whole experiment are the extraparticulate free SX compatible toner kindly supplied by the Trends Tone Company. The average diameter of the toner particles was around 13.0 μm . The true density and apparent density were 1.5 and 0.53 g/cm^3 respectively. The carrier beads (Powder Tech; F141-1030) were acrylate coated ferrite particles with the diameter around 82 μm . The true density and apparent density were 5.5 and 2.6 $\text{g}/$

cm³ respectively. The three types extraparticulates used here were high purity (99.8%) amorphous fumed silica surface treated to yield hydrophobic surface properties: R805; R504 from Degussa and T720 from Cobolt.

To study the tribocharging behavior of toner, the extraparticulate-free SX-compatible toner was blended with carrier beads by a fixed weight fraction before putting in a roller mixer for tribo-charging. The roller mixer turned 200 rpm, and the mixing lasted for a fixed length of time, ranging from 1 minute to 1000 minutes. For the study of the extraparticulate effect on toner charging, a fixed amount of extraparticulate was blended into toner by a V-blender before tribocharged with the carrier. After mixing in the roller mixer, the tribocharged toner was analyzed by Q/M and Q/D meter to measure the tribocharges on toner.

A Q/M meter (Epping GMBH; Q/M meter type 05) was used to measure the average toner charge normalized to toner weight after mixing with carrier beads. The charge distribution was obtained by using the Q/D meter (Epping GMBH) with which toner population versus Q/D, (where D is the diameter of toner particle), was measured by optically detecting the optical density profile versus flight length of the toner laminar flow between two charged parallel plates. A SEM (JEOL; JSM 5200) was used to examine the toner, carrier, and the extraparticulate before and after tribocharging.

Results

Experimental Result of Toner/Carrier Tribocharging

It was found that the Q/M value of the tribocharged toner increased with the mixing time followed by a saturation to a level-off value. As shown in Figure 1(4-1), this behavior is followed for different toner concentration C_t , defined as weight fraction of toner in the toner/carrier mix, from 2.5% to 30%. On the other hand, for a fixed mixing time, the Q/M value decreased with the toner concentration.

Comparison of Experimental Data with the Existing Models

As mentioned in the Introduction, there are three surface charging models based on electron transfer: Lee's model, Schein's model, and Anderson's model. These three models have predictions on the relationship between toner charge M_t/Q_t and the weight ratio M_t/M_c :

Lee's Model:

$$M_t/Q_t = r_c(M_t/M_c)\rho_c/(3ef_cN_c\Delta\phi) + r_t\rho_t/(3ef_tN_t\Delta\phi) \quad (1)$$

Schein's Model:

$$M_t/Q_t = r_c(M_t/M_c)\rho_c/(3\varepsilon_0E_e) + r_t\rho_t/(3\varepsilon_0E_e),$$

where $E_e = (\phi_c - \phi_t) / ez$ (2)

Anderson's Model:

$$M_t/Q_t = -z(\varepsilon_0r_t\rho_t/N_t ez) + (M_t/M_c)(\varepsilon_0r_t\rho_t/N_t ez) + er_t\rho_t + (M_t/M_c)er_c\rho_c/[3\varepsilon_0(\phi_t - \phi_c)] \quad (3)$$

All three models predict a linear relationship between M_t/Q_t and M_t/M_c , the slope and intercept, however, represent different physical meanings for each model. We will utilize the obtained experimental data to compare with the predictions of the three models, and discuss the physical meaning of the empirical quantities obtained from the comparison.

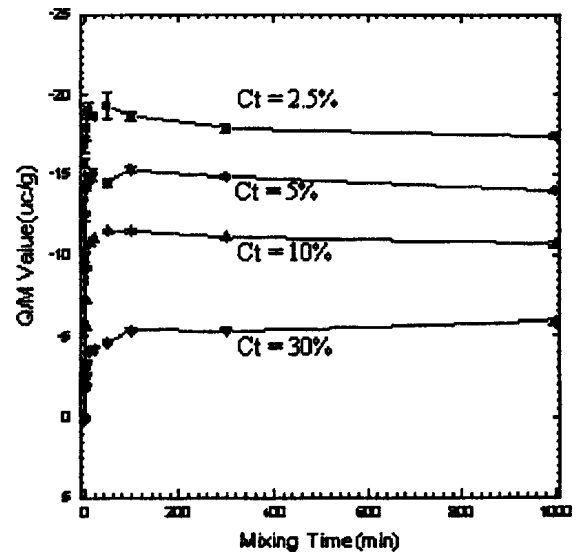


Figure 1. Toner tribocharge Q/M versus mixing time for various toner concentration C_t 's.

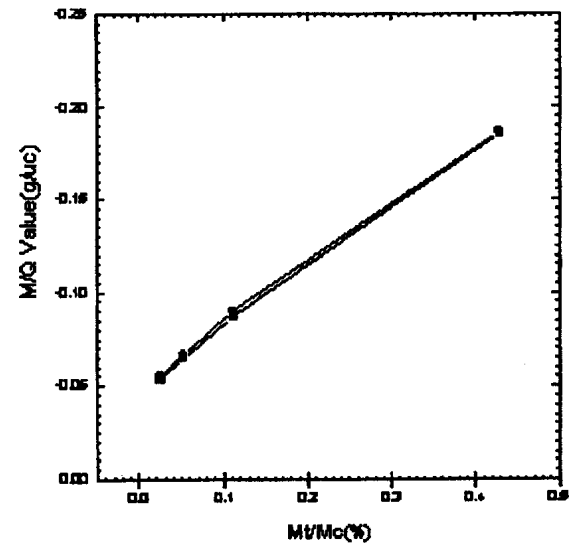


Figure 2. M/Q versus M_t/M_c .

As shown in Figure 2, the experimental data indeed shows a linear relationship between M_t/Q_t and M_t/M_c , consistent with the prediction of the models. We can further use the value of slope and intercept to calculate the various physical quantities in Equations 1, 2, and 3.

First of all, we can use Equation 2 to calculate the electric field E_e and the distance z , the separation above which electrons cease to transfer. However, we found that the electric field E_e calculated from the slope and the intercept are not identical, one being about 30 times greater than the other. Furthermore, the z distance, calculated from $(\phi_c - \phi_t) / E_e e$ using $(\phi_c - \phi_t) \approx 1$ ev, are approximately 3.8 nm and 123.8 nm respectively for calculation from slope and intercept. These value obviously are too large for insulators. For metal-insulator tribocharging, z values had been reported to be around 0.5 nm. Analyzing the experimental data reported by Anderson and Gutman and Hartmann also found the same discrepancy observed in our data, indicating that the high density model probably is not suitable for describing the charging of toner.

In fact, we can calculate the z value direct from the Q/M data by approximating the local contact between toner and carrier to behave similarly to a capacitor, where the potential w is the work function difference $\Delta\phi$ given as

$$w = \Delta\phi = Q^2/(2C) = Q^2/[2A\epsilon_0/d] = Q^2z/(2A\epsilon_0)$$

The charge Q can be calculated from the Q/M data to be around 3.3 esu charge per transfer²⁰. Let $\Delta\phi = 1\text{ev}$, and $A = \pi z^2$, the z is calculated to be 0.54 nm, in good agreement with that reported for metal-insulator contact charging.

The surface state density N_t and N_c on toner and carrier surface respectively was calculated using the slope and intercept in Figure 3 by Equation 1. The ratio of N_c/N_t , calculated to be around 33, seems to be an acceptable result. In fact, the ratio of N_c/N_t was found to be very close to the surface areal ratio between carrier and toner.

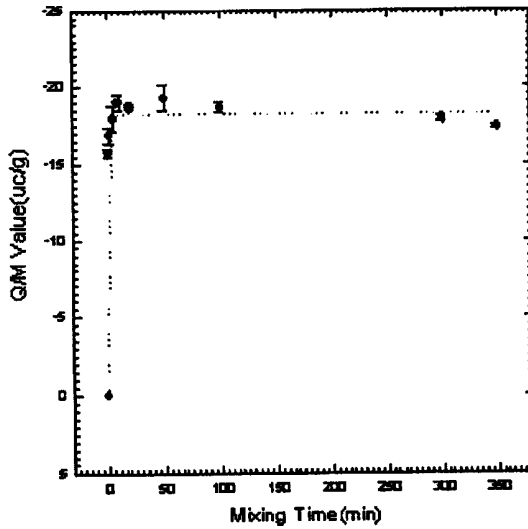


Figure 3. Comparison of calculation of the dynamic model (dash line) with experimental Q/M data for $C_t = 2.5\%$.

It is therefore concluded that the Lee's model is more appropriate for the toner-carrier system studied in this research. Also, at the limit of low density of $\epsilon_0/N_t e^2 z \gg 1$ and $\epsilon_0/N_c e^2 z \gg 1$, Equation 3 (Anderson) reduced to Equation 1.

The Dynamic Model of Tribocharging Between Toner and Carrier Beads

Although the previous models can satisfactorily describe the charge equilibrium behavior of toner, they cannot describe the transient behavior. As shown in Figure 1, it may take as long as 5 minutes ($C_t = 2.5\%$) to achieve the charge equilibrium to be described by the work function model. Therefore, as an extension of the previous equilibrium models, we assume the work function concept for local equilibrium to construct a dynamic model which may describe the transient behavior of toner.

The dynamic model is built upon the following assumptions: 1) charge transfer takes place only when a toner particle is contacting a carrier bead; 2) the tribocharging is limited to the surface and the surface properties is uniform for toner particles and carrier beads. 3) local charge equilibrium is achieved by local charge transfer during a single contact, and the local spots that have undergone charge

transfer are not able to undergo another charge transfer; and finally 4) the probability of contact between a toner particle and a carrier bead is independent of time.

We consider an "average toner particle" tribo-charging with an "average carrier bead" and divide the tribo-charging process into many infinitesimal equal time segments. We also define P_i to be the probably that the toner particle acquires charge transfer during contact with the carrier bead in the i -th time segment; $\Psi(C_i)$ to be probably of contact between the toner particle and the carrier bead during an infinitesimal time segment, A to be the total surface area of the toner particle; B to be the total surface area of a carrier bead; a and b to be the effective local contact area respectively on toner and carrier during tribo-contact, q to be the amount of charge transfer during one contact, r_t and r_c to be radius of the toner and carrier respectively, ρ_t and ρ_c to be the density of the toner and carrier respectively, and finally n to be the number ratio between toner and carrier in the toner/carrier mix.

It is evident that the probability for charge transfer between the toner particle and carrier bead at the i -th time segment, P_i , should be equal to the product of Ψ multiplied by the fractions of effective surface area capable of charge transfer on toner and carrier. Since at the first time segment no surfaces have undergone charge transfer, the effective area fraction on both toner and carrier being 1, therefore, P_1 can be readily expressed as

$$P_1 = 1 \times 1 \times \Psi.$$

At the second time segment, the area fractions have to be reduced by the amount that have undergone charge transfer, so we have $P_2 = (1 - P_1 a/A)(1 - P_1 n b/B)\Psi$. Substitute P_1 into P_2 , we have $P_2 = [1 - a\Psi/A - nb\Psi/B + nab\Psi^2/(AB)]\Psi \approx (1 - a\Psi/A - nb\Psi/B)\Psi$, since $nab\Psi^2/(AB) \ll a\Psi/A$ or $nb\Psi/B$. For the sake of convenience, let c to be $[1 - a\Psi/A - nb\Psi/B]$, therefore, we have

$$P_2 = c\Psi$$

Similarly, P_3 can be written as

$$\begin{aligned} P_3 &= (1 - P_1 a/A - P_2 a/A)(1 - P_1 n b/B - P_2 n b/B)\Psi \\ &= (1 - a\Psi/A - ac\Psi/A)(1 - nb\Psi/B - nbc\Psi/B)\Psi \\ &\approx [c - ca\Psi/A + cnab\Psi^2/(AB) - cnb\Psi/B + cnab\Psi/(AB) + c2nabc\Psi/(AB)]\Psi \\ &\approx c\Psi[1 - a\Psi/A - nb\Psi/B + nab\Psi/(AB) + cnab\Psi/(AB)] \\ &\approx c\Psi(1 - a\Psi/A - nb\Psi/B) = c^2\Psi \end{aligned}$$

and

$$P_4 = (1 - P_1 a/A - P_2 a/A - P_3 a/A)(1 - P_1 n b/B - P_2 n b/B - P_3 n b/B)\Psi \approx c^3\Psi$$

and we should have a general form for P_i to be

$$P_i \approx c^{(i-1)}\Psi$$

Therefore, the total charges accumulated on a toner particle, q^t , should be $q\sum P_i = q\Psi(1-c^i)/(1-c)$, and the total tribocharges of the toner, Q_t , should be q^t multiplied by the total number of toner particles, i.e., $Q_t = q\Psi(1-c^i)/(1-c) \times M_t/(4\pi\rho_t r_t^3/3)$. Consequently, we obtain

$$Q_t / M_t = q\Psi(1-c)/(a/A + nb/B)(4\pi\rho_t r_t^3/3). \quad (4)$$

The contact probability Ψ can be estimated by the product of swept volume during the time segment Δt by a traveling toner particle with velocity v and the number of carrier beads per unit volume,

$$\Psi = \pi(r_t + r_c)^2 v \Delta t \times 3 M_c / (4\pi r_c^3 \rho_c) / (M_t / \rho_t + M_c / \rho_c)$$

Since the probability is uniform in time, we select a time segment corresponding to $\Psi = 1$. That is,

$$\Delta t = 4r_c [1 + (\rho_t / \rho_c)(M_t / M_c)] / 3v \approx 4r_c / (3v).$$

With this choice of time segment, Equation 4 can be rewritten as

$$\begin{aligned} Q_t(t) / M_t &= q[1 - e^{-(t/\Delta t)}] / (a/A + nb/B)(4\pi\rho_t r_t^3/3) \\ &= [1 - e^{-\zeta t}] [r_t \rho_t / (3q/a) + r_c \rho_c (M_t / M_c) / (3q/b)] \end{aligned} \quad (5)$$

where $\zeta = 3v / (4r_c)$. At equilibrium, t approaches infinity, and Equation 5 can be expressed

$$M_t / Q_t(t) = r_t \rho_t / (3q/a) + r_c \rho_c (M_t / M_c) / (3q/b) \quad (6)$$

If we use the definitions of $q/a N_c e \Delta \phi$ and $q/b N_c e \Delta \phi$, Equation 6 reduced to a form identical to the Lee's equation (Equation 1).

Calculation from Dynamic Model Compared with the Experimental Data

The derivation of the transient behavior of Q/M for toner charging using the dynamic model is in excellent agreement with the experimental data. The constant a and b were first measured by using the equilibrium Q/M data and then the time dependent curve of Equation 6 was calculated with a single fitting parameter ζ . Figure 3 shows excellent agreement with the experimental data for $C_t = 2.5\%$. The same agreement was also observed for all other data of different C_t 's.

The dimensions of the local contact calculated from the data using Equation 6 are quite reasonable. The local contact area a on a toner particle was found to be around $0.09 \mu\text{m} \times 0.09 \mu\text{m}$, and the corresponding contact area b on carrier bead was approximately $0.05 \mu\text{m} \times 0.05 \mu\text{m}$. Using spherical topography for the particles, the radial thickness of the contact area is approximately 17 nm for toner and 0.8 nm for the carrier.

Conclusions

It therefore can be concluded that:

1. The high density model cannot describe the tribocharging behavior of toner. On the other hand, the low density and the Anderson model can better explain the equilibrium charging process of tribo-action between toner and carrier.

2. A dynamic charging model was developed to describe the transient behavior of toner charging. The model was constructed based on assumptions of instantaneous local equilibrium by electron transfer across a work function difference between toner and carrier. Excellent agreement was found between the prediction of this model and the broad experimental data. The scales of the local contact on toner and carrier were found to be of atomic scale.

References

1. H. Helmholtz, *Ann. phys. Lpz.*, **7** : 337 (1879)
2. P. E. Shaw, *Proc. R. Soc.* **94** : **16** (1917)
3. P. S. H. Henry, *Br. J. Appl. Phys.* **4**, **6**, (1957)
4. M. I. Kornfeld, *J. Phys. D.* **2**, **1533**, (1976), *Soviet Phys. Solid St.* **11** : **1306** (1976)
5. F. R. Ruckdeshel, L. P. Hunter, *J. Appl. Phys.* **48** : 4898
6. J. Lowell, A. C. Rose-Innes, *Adv. Phys.* **29** : 947 (1980)
7. W. R. Harper, *Nature*, **167**, 1951.
8. W. R. Harper, *Contact and Frictional Electrification*, Oxford University Press, Oxford (1967).
9. J. Lowell, *J. Phys. D* **8**, 53, 1975.
10. D. K. Davies, *Brit. J. Appl. Phys.* 1969 SER2 Vol. **2**, 1533-1537.
11. E. Fukada, J. F. Fowler, *Nature* **181** : 693 (1958).
12. A. Wahlin, G. Backstrom, *J. Appl. Phys.* **45** (5) (1974).
13. L.-H. Lee, *Photogr. Sci. Eng.* **22** : 228 (1978).
14. J. T. Bickmore, R. J. Nash, *IS&T Proceedings of the 8th International Congress on Advances in Non-Impact Printing Technologies*, p113-126 (1992).
15. D. E. Bugner, J. H. Anderson, ACS National Meeting: *Polymer Reprints* **29** : 463, 1988.
16. J. H. Anderson, *J. Imaging Sci.* **33**(6) : 2000 (1989) .
17. L. B. Schein, *IS&T Proceedings of the 8th International Congress on Advances in Non-Impact Printing Technologies*, p35-38 (1992), *J. Imaging Sci. Tech.* **37** : 1 (1993).
18. E. J. Gutman and G. C. Hartmann, *J. Imaging Sci. Tech.* **36**: 335 (1992).
19. J. H. Anderson, *J. Imaging Sci. Tech.* **38**(4) : 378 (1994).
20. C.Y. Chou, Master thesis, National Tsing Hua University, Department of Materials Science and Engineering, 1995.