

Role of Technical Innovation in the Physics of Electrophotography

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Abstract. Over the years, technical innovation in the physics of electrophotography has had mixed results in influencing the technology. Four examples familiar to the author will be discussed and their current and potential future influences on the electrophotographic technology will be described. (1) The introduction of the theory of magnetic brush development had only limited influence on the invention of improved variants. However, it had an enormous influence on the perception that electrophotography was a logical and predictable technology that could be understood with common scientific tools. (2) The introduction and implementation of the ideas of the proximity theory of toner adhesion has allowed the design of the smallest size lowest cost color electrophotographic engine which will be commercially available soon. (3) The demonstration that toner charging is due to Kondo's high density theory surprisingly has failed to help toner material scientists redesign toners; in particular, it has failed to help them design a toner with a narrower charge distribution. Such a narrow-charge distribution toner would allow the average toner charge-to-mass ratio to be reduced, which would be useful in many of the electrophotographic subsystems. Combining a narrow-charge distribution toner with the methods of reducing the toner adhesion based on the proximity theory could lead to a new generation of marking engines based on novel marking technologies. Finally, (4) progress has been made recently in identifying the mechanism by which holes move through photoreceptors. The author conjectures that elucidation of the charge transport mechanism will be beneficial to the design of organic photoreceptors for electrophotographic systems as well as other organic electronic devices. Although today's photoreceptors have adequate mobility, increased process speed will require both higher mobility and a reduction in those factors giving rise to carrier range limitations. For organic electronics higher mobility materials are necessary for practical devices. © 2010 Society for Imaging Science and Technology. [DOI: 10.2352/J.ImagingSci.Technol.2010.54.2.020201]

INTRODUCTION

There exists a tension between empirical methods and technical innovation in every technology but especially in electrophotography in which many variables in many subsystems contribute to the output (the printed or copied page). The question addressed in this article is how technical innovation has advanced the technology of electrophotography by examining specific examples. It will be seen that there are some notable successes and failures. However, even those technical innovations which have not yet been implemented

in electrophotography may provide future directions for the evolution of the technology into novel marking technologies and for advances in organic electronics.

Examples are provided based on the author's knowledge, including (1) the theory of magnetic brush development, (2) the theory of toner adhesion, (3) the theory of toner charging, and (4) the charge transport mechanisms in molecularly doped polymer films which are used in organic photoreceptors. For each example, the technical innovation will be described, its success in influencing the electrophotographic technology will be noted, and its potential to influence the future direction of the technology will be conjectured.

MAGNETIC BRUSH DEVELOPMENT

Magnetic brush development systems are used in virtually all electrophotographic engines that operate above 30 pages/min. It was originally invented at RCA and was used in all electrophotographic copiers and printers after the original Xerox 914 Copier, which was introduced in 1959 and used cascade development.¹ The magnetic brush development system replaced the cascade development system because it allowed higher process speeds and the copying of solid areas. In the late 1960s and early 1970s the design of magnetic brush development systems was almost completely empirical. This was expensive because of the many potential parameters that affected the output, the developed toner mass-per-unit area, such as the toner charge-to-mass ratio, Q/M ; the toner size; the toner charge and size distributions; the toner concentration (ratio of toner to carrier mass); the carrier size, shape, and magnetic properties; the speed ratio between the development roller and the photoreceptor; the gap between the development roller and the photoreceptor; the voltages on the development roller, the voltages on the charged and exposed areas of the photoreceptor, the design of the magnetic fields, etc., (see Figure 1).¹ It was felt by many people that a "theory" of magnetic brush development was not possible because of the many different forces acting on the many different types of toner particles (due to the large variation of diameters and charges). For example, models based on field stripping (the Coulomb force overcomes toner-carrier adhesion) or toner powder clouds (the Coulomb force harvests toner particles that are free of the carrier) were qualitatively discussed as possible explanations for particular data sets.

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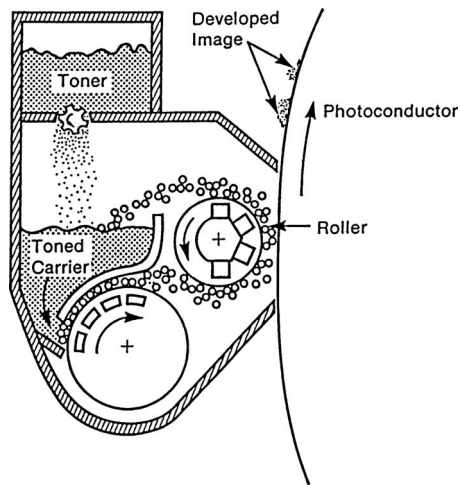


Figure 1. A typical magnetic brush development system. The carrier particles are represented by small circles. The two rollers have internal stationary magnets which use magnetic and friction forces to move the carrier particles into the development zone. This subsystem of electrophotography, in common with most of the others, has many parameters. The theory of magnetic brush development allowed the identification of the first order hardware and material parameters which determined the developed mass per unit area.

Then in 1974 and 1975 two articles were published by Schein^{2,3} in which a technical innovation was introduced; it was demonstrated that the physics of the process was quantifiable and understandable with a simple physical model. In the first article² the toner voltage (the change in electrostatic voltage above the photoreceptor due to the presence of developed toner) was shown to be due to three effects, (1) a constant volume charge density (the charged toner) placed on a dielectric, the photoreceptor; (2) the discharge of the photoreceptor due to toner being developed and subsequently removed during the development process; and (3) size classification of the toner as development time increases, effectively changing the average toner charge-to-mass ratio. In the second article³ it was shown that the output of the magnetic brush development system, the developed toner mass-per-unit area, was due to the competition between two forces, the Coulomb force due to the latent image attracting toner to the photoreceptor and the build up of charge on the carrier beads adjacent to the photoreceptor attracting toner to the charged carrier beads. The build up of charge on the carrier beads was due to the toner being developed onto the photoreceptor earlier in the development zone. This physical model allowed the derivation for the first time of a simple equation relating developed mass-per-unit area to hardware and material parameters and provided a simple intuitive picture of how the development system “worked.”

This technical innovation, a theory of magnetic brush development, influenced the design of future magnetic brush developed system simply because the first order hardware and materials parameters were identified, allowing for a more straightforward design process. I vividly recall an engineer coming up to me one day saying that he had done a correlation study between developed mass-per-unit area and toner concentration and had found no correlation, to his

surprise, but consistent with the theory. Many people have said to me that the demonstration that a theory worked for magnetic brush development changed electrophotography from an art to a science and gave them confidence to approach the other development systems and other subsystems in a more scientific and systematic manner.

One would have thought that such a theory would have led to innovative approaches to improving the magnetic brush development system. After all, it is clear that if the mass-per-unit area is limited by the build up of charge on the carrier beads adjacent to the photoreceptor, reducing this build up would improve the efficiency of the system. But by 1975, at least two and probably three of the variants had already been discovered. These include (1) the conductive magnetic brush development⁴ in which the carrier charge is shorted to the development roller by making the carrier chain conductive (an Eastman Kodak invention); (2) the Eastman Kodak SPD system,⁵ in which permanent magnetized carrier beads are moved out of the development zone with a rotating magnetic shell inside the development roller; and (3) the use of ac electric fields to move toner down the carrier chain to neutralize the carrier charge. It is possible that only the fourth variant-introduced by Hays⁶ at Xerox in their high speed 9400 series machines, in which magnetic forces in the development zone were significantly reduced to allow the charged carrier to mix with uncharged carrier, was influenced by the theory.

PROXIMITY THEORY OF TONER ADHESION

Toner adhesion is one of the critical parameters in electrophotography that must be taken into account in the design of three of the subsystems, development, transfer, and cleaning. Lower adhesion would obviously be advantageous, allowing for a simpler design of these subsystems. But an understanding of toner adhesion remained elusive for almost 40 years since the first measurements by Goal and Spencer.⁷ Everyone agreed that the simple electrostatic model of adhesion based on the assumption that the toner can be modeled as a spherical dielectric, uniformly charged on the surface, was not valid. In this model the charges on the uniformly surface charged toner particle on a conductive surface are attracted to their image charges. Toner adhesion data always gave adhesion forces at least ten times larger than predicted by this model, as shown by Hays.⁸ This large adhesion was considered a “fact of life,” forcing the electrophotographic subsystems designers to design around this high adhesion. It has been argued by Schein⁹ that innovations in the design of new development systems was basically a process by which this high adhesion was overcome, either by (1) canceling the adhesion of toner to its carrying surface using three-body contact events (magnetic brush development, Ricoh’s non-magnetic monocomponent development), (2) using ac electric fields and low toner charge (Canon’s magnetic monocomponent development system), or (3) using horizontal ac electric fields (Xerox’s carrier-toner iGen3 system). Techniques to overcome high toner adhesion also were

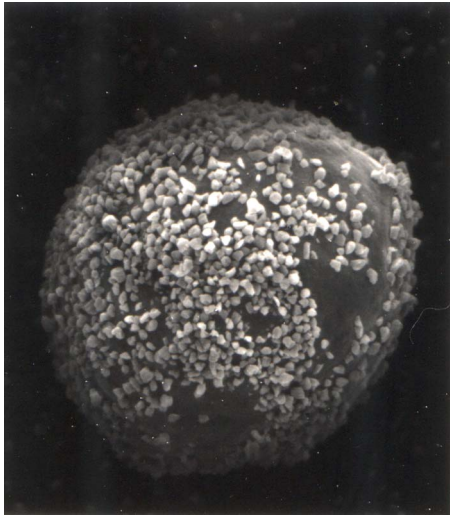


Figure 2. A scanning electron micrograph of $10\text{ }\mu\text{m}$ toner particles on a $300\text{ }\mu\text{m}$ carrier particle used in electrophotography. There is an extra variable present in experiments using toner-carrier mixtures as compared to contact between two insulating sheets, namely the toner concentration which is the ratio of toner mass to carrier mass, i.e., the number of toner particles on a carrier particle can be varied.

needed in the transfer and cleaning subsystems to make them viable.

Over the years, attempts to understand the physical basis of the experimentally observed high toner adhesion were based on two approaches, one that assumed that van der Waals forces dominated and one that assumed that the toner charge was nonuniformly distributed around the surface of the toner particle, as reviewed by Schein.¹⁰ As almost all measurements show that toner adhesion depended on the square of the toner's Q/M , it seems clear that an electrostatic model is needed to explain the data. But the nonuniform charge distribution model had two inconsistencies with data (1) the nonuniform charge density needed to be consistent with adhesion data predicted electric fields in excess of Paschen's breakdown, i.e., they would not be stable in air, and (2) it predicted that Q/M would be independent of the toner concentration in toner-carrier mixtures, inconsistent with data.¹⁰

The technical innovation in toner adhesion was initiated by Wang, the CEO of the Aetas Corporation who wanted to build the smallest size, lowest cost color electrophotographic engine. In order to accomplish this, the four color toner images had to be accumulated on the photoreceptor. This could only be done if the electric fields of the latent image were sufficient to "develop" the toner from a monocomponent development roller to the photoreceptor (without the use of ac electric fields or contact development). This required that toner adhesion to be lowered by at least a factor of ten compared to commercially available toner. In the process of simulating toner adhesion based on image forces with finite element methods, it was found that if the discreteness of toner charge were retained in an electrostatic model, then a new force emerged from the calculations both analytically or by adding up all the image forces between all of the charges. This new force was due almost

entirely to the forces on those charges in closest proximity to the surface on which the toner rested. This was subsequently named the proximity force. This work is summarized by Wang et al.¹¹ and Schein.¹² This force is active at every contact point between the toner and the surface. The number of contact points could be reduced to a minimum (three—a tripod analogy is useful) by coating the toner particle with about a monolayer of nanometer size extraparticulates. Such a toner was made; experimentally shown to have a toner adhesion at least ten times smaller than commercially available toners; shown to have adhesion consistent with three contact points model; and used in the design of the smallest size, lowest cost color electrophotographic printer, which should be commercially available soon. As discussed below, this approach to lowering toner adhesion may in the future influence the evolution of the electrophotographic technology into novel marking technologies and it may affect other technologies outside of the printing field.

KONDO'S HIGH DENSITY THEORY OF TONER CHARGING

What determines a toner's charge? Toner charge, or the more easily measured toner charge-to-mass ratio, Q/M , is of fundamental importance in most of the subsystems in electrophotography. Yet, our control of the toner charge is highly empirical from a materials point of view. Because the toner charge and its distribution has such a strong influence on the behavior of toner particles in the various subsystems, empirical testing of new electrophotographic engines remains a costly, time consuming effort as machine optimization and toner charge distributions are optimized simultaneously and empirically.

The physics/chemistry of toner charging is a subset of the general problem of insulator electrostatic charging. It is one of the oldest areas of solid state physics, yet it is by far one of the least understood areas of solid state physics. The Greeks knew that rubbed amber attracts particles, and Benjamin Franklin's experiments on charging and lightning are well known. It appears to be a surface phenomenon, but all attempts to associate electrostatic charging of insulators with any known material parameters has not yet been successful. The reader is invited to read any of the reviews on the subject (see Chapter 4 in Schein's book¹ and Lowell and Rose-Innes review¹³ and encyclopedia articles¹⁴) to see how rudimentary our understanding is whenever insulators are involved. (Metal-metal contact charging is well understood and determined by the difference in work functions.)

A technical innovation came when it was realized that insulator electrostatic charging experiments using toner particles have two advantages relative to typical experiments that use contacts between insulating sheets: (1) toner particles are made reproducible in their charging behavior because the electrophotographic technology demands it; and (2) there is an extra variable present in experiments using toner-carrier mixtures (see Figure 2), namely, the toner concentration, the ratio of toner mass to carrier mass, i.e., the number of toner particles on a carrier particle, can be varied.

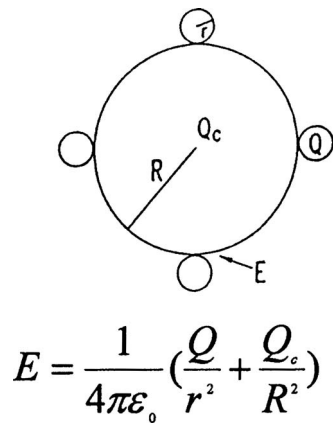


Figure 3. The electric field model (also called the high density surface state model) of toner charging assumes that the toner particles charge up until the electric field E at the surface reaches a material dependent value, called the effective electric field. Q is the toner charge, Q_c is the carrier charge, r is the toner radius, R is the carrier radius, and ϵ_0 is the permittivity of free space.

This extra variable allowed an experimental test that could distinguish between two suggested surface charging models, the low density and the high density theory of charging. The low density theory is similar to the theory of metal-metal electrostatic charging, it is assumed that there are “surface” work functions on the two insulators making contact which determine how many charges move from the surface states of one insulator to the other to equilibrate the work functions. The high density theory assumes that there are so many surface states on the two insulator surfaces that a large voltage drop is created by the movement of charge which, in turn, shuts off the flow of charge (see Figure 3). Lee¹⁵ proposed the equations which describe the low density theory for a toner-carrier mixture. Kondo¹⁶ proposed the equations for the high density theory. Schein and Castle^{17–20} suggested an experiment that would distinguish between the two theories, carried out the experiment (see Figure 4), and showed that only the high density theory is consistent with experiments. The experiment involved comparing the slope-to-intercept ratio in a plot of M/Q versus toner concentration to theory. It is remarkable to note that quantitative agreement was obtained with the predictions of the high density theory with no adjustable parameters, a result that has not been duplicated in any other electrostatic charging experiment, to the author’s knowledge.

Therefore, toner charging appears to be limited by the build up of an electric field between the toner surface and the carrier surface; toner stops charging when this electric field reaches a material-dependent value. Therefore this theory is sometimes called the electric field theory of toner charging. The value of the electric field at which toner charging stops, called the effective electric field, can be obtained from the slope or intercept of the plots mentioned above. It is about $10 \text{ V}/\mu\text{m}$ within a factor of about 4 depending on the materials used. However, no one has been able to associate this electric field with a material property. For example, if one assumes that the electric field is due to the difference in work function between the two materials (which should

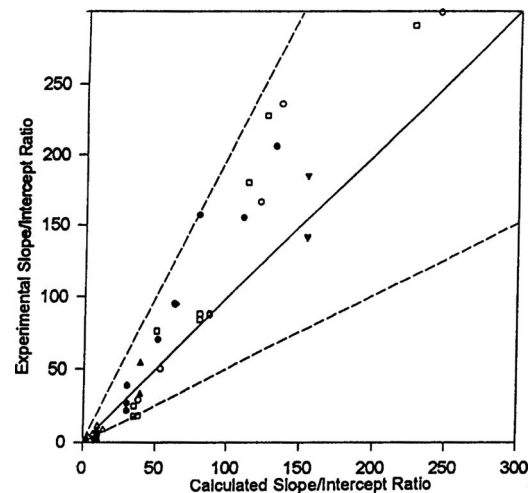


Figure 4. Experimental data (Ref. 20) that distinguishes between the low and high density theory (also called the electric field theory) of toner charging. Plotted are experimental observations taken from the literature of the slope/intercept ratio obtained in measurements of the M/Q (the toner mass-to-charge ratio) vs toner concentration. The predictions of the electric field theory are plotted on the x axis. The straight line is exact agreement with the high density theory and the dotted lines are agreement within a factor of 2. For the data to be consistent with the low density surface state model, the density of surface states on the carrier and toner must be equal within a factor of 2 for all published experiments, which seems unlikely.

be on the order of 1 eV) divided by a tunneling distance (1 nm works for the metal-metal charging experiments), then one predicts electric fields 100 times higher than observed in the charging experiments, $1000 \text{ V}/\mu\text{m}$. In addition, it appears from discussion with chemists that it is not clear how to associate an electric field with material properties. There have been recent experiments by Veregin et al.²¹ in which the surface chemistry of polymers was probed for triboelectric consequences by measuring the residence time of probe molecules using inverse gas chromatography. There also exists new theoretical work on the electrification of granular systems of identical insulators by Kok and Lax.²² However, in these models no association of the effective electric field with material properties emerges. It appears that that the demonstration that the high density theory explains toner charging has had no influence on toner design. But the identification of a material property that determines the toner charge distribution has enormous potential to influence the technology, as discussed below.

POTENTIAL FUTURE INFLUENCE OF TECHNICAL INNOVATIONS

One can imagine potential significant influences on the design of electrophotographic subsystems if the electric field theory of toner charging could be used to narrow the toner charge distribution. That would allow the average toner Q/M to be lowered because the charge distribution could be made narrower and the amount of wrong sign toner could be reduced for lower Q/M 's. It is obvious that lower Q/M and therefore lower toner adhesion would be beneficial in the development, transfer, or cleaning of subsystems.

Furthermore, it is interesting to consider the implications of the above technical innovations to novel marking technologies. Novel marking technologies are defined as electrophotographic marking technologies in which one or more of the electrophotographic subsystems have been eliminated. Many have been suggested including contact electrography,^{23,24} TonerJet,^{25–31} traveling electric waves,^{32–36} direct imaging technologies,^{37–39} laser ablation technology,^{40,41} electrostatic powder transfer technology,⁴² laser fusion technology,⁴³ magnetography,^{1,44} and ionography,^{1,44} among others. Very few have been commercialized and none have challenged the electrophotographic technology, yet.

Consider the implications of having a narrow-charge distribution toner combined with lower toner adhesion, two technical innovations discussed above. Let us project reductions and/or control of toner adhesion by another factor of 10 beyond what Aetas has achieved. This reduction/control of toner adhesion could be achieved by several methods. For example, if the physics/materials properties of toner that determine the effective electric field and therefore the width of charge distribution are identified and controlled, it may be possible to reduce the average toner's charge. This would significantly reduce the toner's electrostatic adhesion. Or one could combine Aetas' approach of creating toner with low adhesion with known methods of releasing high adhesion toner, such as the iGen3 approach of using ac electric fields at the surface of a development roller, or Canon's approach of using ac electric fields across the development zone. Another possibility is to combine the Aetas' low adhesion toner with ultrasonics, which has been shown by Crowley et al.⁴⁵ to enhance transfer efficiency by freeing toner of its electrostatic adhesion.

What would a factor of 10 reduction in toner adhesion control allow? Standard desktop color electrophotography will not be made smaller or lower in cost. Aetas has achieved the smallest possible electrophotographic color system architecture; one will always need to accumulate the color images on some surface and Aetas' choice, the photoreceptor, eliminates all extraneous subsystems, such as intermediate belts. The midrange and high-end (Xerox's iGen3, Kodak's Nexpress, and HP's Indigo liquid system) will obviously continue to evolve but not in any step-functional manner.

Instead consider the many suggestions through the years of novel marking technologies. To be specific consider for example TonerJet,^{25–31} schematically shown in Figure 5. This is a toner marking technology in which toner is "jetted" across an interface between a roller and paper in an image-wise method. A voltage is placed on the back of the paper which attracts toner across an air gap. The toner particles go through tiny apertures which can be shut off electrically. Such a technology is sometimes called direct marking. It eliminates the charging, transfer, and exposure subsystems of electrophotography as well as the need for a photoreceptor. It failed to be commercialized because of some obvious technical problems. Wide toner adhesion distributions led to poor release of toner from the roller, slowing down the toner

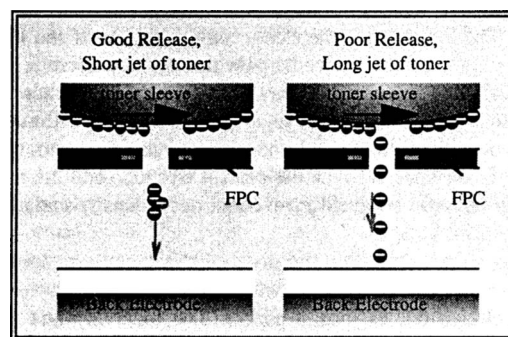


Figure 5. A schematic diagram of the TonerJet technology. The paper sits on the back electrode. The apertures are built on a flexible printed circuit (FPC) board. This diagram shows the effect of wide toner adhesion distributions—poor release and a long time to jet the toner to the paper.

jetting time. Wrong sign toner contaminated the back of the apertures, and the voltages needed to jet the toner were large due to large toner adhesion, in the range of at least several hundred volts, making the electronics prohibitively expensive.

But consider a future in which toner charge can be ten times lower than today and/or overcoming the adhesion of toner particles requires ten times less force, i.e., lower voltages. Perhaps a direct marking technology such as TonerJet would become feasible. It would be small, very inexpensive, and perhaps capable of high speeds. Other novel marking technologies may also be made viable by our assumed ten-fold reduction in toner adhesion.

MECHANISM OF CHARGE TRANSPORT IN MOLECULARLY DOPED POLYMERS

The organic photoreceptor (OPC) used in virtually all electrophotographic engines is made up of a thin charge generation layer and a thick charge transport layer made from a molecularly doped polymer (MDP). The mechanism of charge transport in the MDP has been under discussion for many years. Most articles have used the Gaussian disorder model (GDM) to explain experimental data. The GDM envisions the charge carriers hopping among a Gaussian distribution of states through the MDP, aided by the imposed electric field. The width of the Gaussian distribution states is directly determined by the disorder in the material.

The technical innovation that has occurred in the last two years is embodied in a series of papers which have compared the GDM and other transport theories to the whole body of experimental data, instead of focusing on one material at a time. When this was done, it was found that (1) the GDM does not adequately describe charge transport data in MDP because the disorder energy, which can be obtained from the temperature dependence of the mobility, does not change as predicted by the theory when the disorder is changed;⁴⁶ (2) the transient current shape is not understandable in terms of any known transport theory;⁴⁷ and (3) the activation energy scale, which has been derived from the disorder energies, is approximately 0.3–0.8 eV, which is larger than predicted for the disorder or the polaron binding

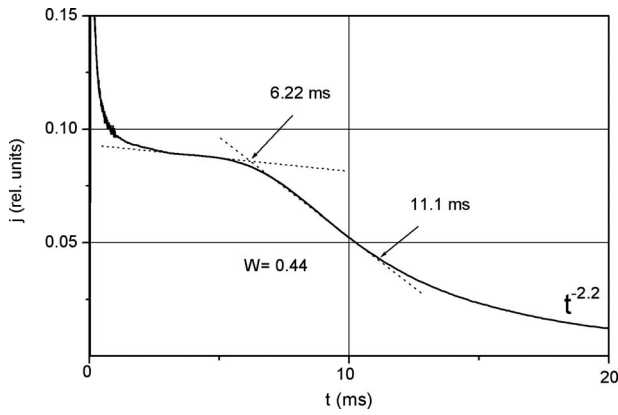


Figure 6. Current transient from holes which transit a MDP, 30%DEH (*p*-diethylaminobenzaldehyde diphenylhydrazone) in PC (bisphenol A polycarbonate) presented in linear current-linear time representation. The sample thickness was 18 μm and the electric field was 33 V/ μm .

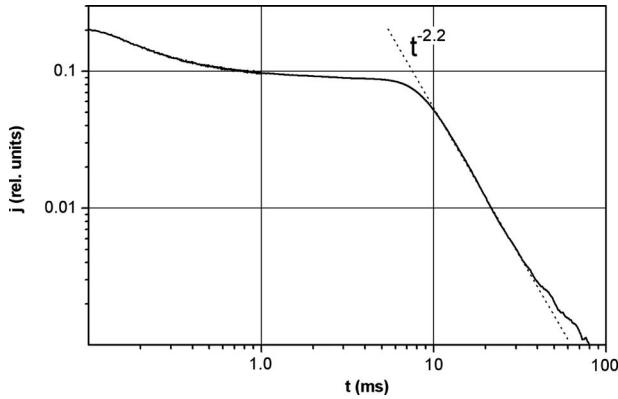


Figure 7. The current transient of Fig. 6 replotted on log-log axes.

energies.⁴⁸ It appears that something critical is missing from our understanding of charge transport in MDP and perhaps in all organic materials.

The reasoning that led to the conclusion (1) that GDM does not adequately describe charge transport data in MDP is discussed in a review article by Schein and Tyutnev,⁴⁶ and at NIP24.⁴⁹ the GDM has difficulties explaining the electric field dependence of the mobility and experimental effects of changing disorder on the activation energy. In addition, the slope of the current because before the transit time is observed to be more shallow than predicted and the field independence of the slope is not predicted. Field independent slopes appear to be a general phenomenon of molecularly doped polymers.⁴⁷ To illustrate the discussion concerning conclusion (2) consider the two figures, Figures 6 and 7, in which the shape of the transient conductivity pulse in standard linear current-linear time axes and in log-log axes are shown. The plot on linear-linear axes gives familiar results: an initial spike followed by a relatively flat current before the transit time, a mobility that follows the Poole-Frenkel law, being exponential in the square root of the electric field, and a current after the transit time that falls much more slowly than can be accounted for using Gaussian statistics. The same data plotted using log-log axes reveals the behavior

Table I. Complete list of activation energies Δ of all MDP's which have been characterized as a function of dopant concentration in which the activation energy is independent of the dopant concentration. σ is the disorder energy.

	Dipole moment of dopant (D)		σ (eV)	Δ (eV)
Hole transport				
1	DTNA:PS	5.78	0.15	0.79
2	2DEASP:PS	4.34	$0.11 \pm 3\%$	0.61
3	DEASP:PC	4.34	0.11	0.61
4	DEH:PS	3.16	$0.13 \pm 4\%$	0.60
5	DEH:PC	3.16	0.13	0.60
6	DEH-A:PC	2.67	0.13	0.60
7	DEH-B:PC	2.57	0.13	0.60
8	DEH-C:PC	2.48	0.13	0.60
9	TPM-E:PS	2.1	0.110	0.47
10	TPA-4:PS	2.1	0.115	0.49
11	TPA-3:PS	2.1	0.11	0.45
12	TPA-2:PS	2.0	0.110	0.45
13	TPM-D:PS	1.81	0.110	0.47
14	TPM-C:PS	1.7	0.110	0.47
15	TPM-B:PS	1.51	0.108	0.45
16	PDA:MBDQ	≈ 1.4		0.32
17	TPM:PS	1.33	$0.122 \pm .013$	0.43
18	TPM:PC	1.33	0.126 ± 0.1	0.66
19	TPA:PC	0.8	≈ 0.095	0.30
20	TASB:PS	0.54	0.103	0.46
21	DOA:PMPs	≈ 0.5	0.086	0.29
Electron transport				
22	DPQ:PS	0.4	0.118	0.52
23	MBDQ:PCZ	0.5		0.49
24	PTS:PC	2.2	0.134	0.57
25	DCAQ:PC	3.3	0.132	0.63
26	DCAQ:PS	3.3	0.132	0.63

over long times and low currents. Before the transit time the decrease of the current can be characterized by two power laws, $t^{-0.3}$, which is the time dependence of the spike, and approximately t^0 , which is the time (in)dependence of the plateau. After the transit time the current decreases algebraically as $t^{-2.2}$ to a current value of about 10^{-2} of the value at the transit time. The slope after the transit time ($t^{-2.2}$) is also independent of electric field. Available theoretical models are not consistent with these data.

The nearly constant current before the transit time suggests that the carriers are hopping with an approximately constant mobility by some intrinsic hopping mechanism or that they are in dynamic equilibrium with an intrinsic shallow trap. The small decrease in slope could indicate that a small amount of deep trapping exists with a very long release time (with respect to the transit time). This is consistent

Table II. Complete list of activation energies Δ of all MDP's which have been characterized as a function of dopant concentration in which the activation energy is dependent on the dopant concentration; σ is the disorder energy.

	Dipole moment of dopant (D)		σ (eV)	Δ (eV)
Hole Transport				
1	TAA-A:PS	2.1	0.105–0.115	0.43–0.52
2	DPH:PCZ	≈ 2		0.45–0.52
3	TPD:PC	1.52		0.33–0.55
4	TPD:PS	1.52		0.22–0.40
5	ETPD:PC	1.5		1.32–0.45
6	ETPD:PS	1.5		0.18–0.33
7	PDA:PC-Z	≈ 1.4		0.35–0.60
8	TAPC:PC	1.0	0.090–0.136	0.31–0.70
9	TAPC:PS	1.0	0.067–0.080	
(σ measured at $E=30$ V/ μm)				
10	ENA-B:PS	0.86	0.077–0.097	0.23–0.37
11	ENA-C:PS	0.86	0.080–0.096	0.25–0.36
12	TTA:PC	0.8	0.11–0.14	0.40–0.60
13	TTA:PS	0.8	0.075–0.116	0.17–0.42
14	TTA:PS-2	0.8	0.079–0.108	0.21–0.38
15	TTA:PS-3	0.8	0.106–0.137	0.37–0.62
16	ENA-A:PS	0.66	0.079–0.104	0.24–0.42
17	ENA-D:PS	0.38	0.078–0.100	0.24–0.39

with the known temperature dependence of this current: it decreases more steeply as the temperature is lowered. But the origin of the initial spike and its time dependence, $t^{-0.3}$, are not understood.

The behavior after the transit time is puzzling. Attempts to explain this behavior with all known theories have failed to account for it. It is much wider than Gaussian transport would predict, and it is not consistent with the width being determined by the generation region, Rudenko and Arkhipov's field diffusion, Coulomb repulsion, or an intrinsic shallow-trap controlled mobility.⁴⁷ The data are also inconsistent with the Scher–Montrol theory that assumes waiting time distribution functions which are longer than the transit time and its predicted electric field dependence.⁴⁷

Point (3) deals with the confusion caused by the disagreement on the role of disorder, which has led to disagreement on how to analyze the experimental mobility data. Plotting the mobility versus T^{-1} or T^{-2} where T is temperature gives activation energies or disorder energies, respectively, which cannot be compared. Methods of obtaining the activation energy Δ from the disorder energy σ have been suggested and implemented.⁴⁸ The results are shown in Tables I and II. (The abbreviations for the charge transport dopants listed in Tables I and II are given in Table III). The activation energies in bold are directly measured; those in normal print are calculated from the disorder energies. The results are that the activation energies are between 0.3 and

Table III. Definition of Initials used in this article ("=" sign indicates different abbreviations of the chemical name are used for the same material).

DCAQ–2- <i>t</i> -butyl-9,10-N,N'-dicyanoanthraquinonediiimine
DEASP–1-phenyl-3-((diethylamino)styryl)-5-(<i>p</i> -(diethylamino)phenyl)pyrazoline
DEH– <i>p</i> -diethylaminobenzaldehyde diphenylhydrazone
DEH-A–9-ethylcarbazole-3-carbaldehyde diphenylhydrazone
DEH-B–9-ethylcarbazole-3-carbaldehyde methylphenylhydrazone
DEH-C–1-pyrenecarbaldehyde diphenylhydrazone
DTNA–di- <i>p</i> -tolyl- <i>p</i> -nitrophenylamine
DOA–plasticizer dioctyl adipate
DPH– <i>p</i> -diphenyl-aminobenzaldehyde diphenylhydrazone
DPQ–3,3'-dimethyl-5,5'-di- <i>t</i> -butyldiphenylquinone
ENA-A–N,N-bis(2-methyl-2-phenylvinyl)-N,N'-diphenylbenzidine
ENA-B–N-(2,2-diphenylvinyl)-4,4'-dimethyldiphenylamine
ENA-C–N,N-bis(2,2-diphenylvinyl)-N,N' diphenylbenzidine
ENA-D–N-(2,2-diphenylvinyl)diphenylamine
ETPD–N,N'-bis(4-methylphenyl)-N,N'-bis(4-ethylphenyl)-(3,3'-dimethylbiphenyl)-4,4'-diamine
MBDQ–3,5-dimethyl-3',5'-di- <i>t</i> -butyl-4,4'-diphenylquinone
PC–bisphenol A polycarbonate
PCZ–poly(4,4'-cyclohexyldenediphenyl)carbonate
PDA–N,N,N',N'-tetrakis(<i>m</i> -methylphenyl)-1,3-diamino-benzene
PS–polystyrene
PS-2–poly(4- <i>t</i> -butylstyrene)
PS-3–poly(4-chlorostyrene)
PTS–1,1-dioxo-2-(4-methylphenyl)-6-phenyl-4-(dicyanomethylidene)thiopyran
TAA-A–ethyl ester of 4-[bis(4-methylphenyl)amino]benzenepropanoic acid
TAPC–1,1-bis(di-4-tolylaminophenyl)cyclohexane
TASB–bis(ditolylaminostyryl)benzene
TPA–Triphenylamine
TPM = TPM-A = MPMP-bis(4-N,N-diethylamino-2-methylphenyl)-4-methylphenylmethane
TPM-B-bis(4-N,N-diethylamino-2-methylphenyl)(4-propylphenyl) methane
TPM-C-bis(4-N,N-diethylamino-2-methylphenyl)(4-phenylphenyl) methane
TPM-D-bis(4-N,N-diethylamino-2-methylphenyl)(4-phenyl) methane
TPM-E-bis(4-N,N-diethylamino-2-methylphenyl)(4-methoxyphenyl) methane
TTA = TPA-1 = TAA-1-tri- <i>p</i> -tolylamine
TPA-2 = TAA-2-tri- <i>p</i> -anisylamine
TPA-3 = TAA-3-methyl 3-(<i>p</i> -(di- <i>p</i> -tolylamino)phenyl)propionate
TPA-4 = TAA-4-4-bromo-4'-4''-dimethyltriphenylamine
TPD–N,N'-diphenyl-N,N-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4' diamine

0.8 eV. Calculated polaron binding energies are smaller,⁵⁰ 0.3 ± 0.1 eV compared to the experimental observations (the polaron binding energy should be twice the observed activation energy or 0.6–1.6 eV), suggesting that polarons do not govern charge transport in molecularly doped polymers. The large values of the observed activation energies suggest that

some higher energy process determines the charge transport mechanism in MDP.

Given the uniformity of behavior of the mobility in all of these MDP's (with respect to electric field, temperature, current shape, and sample thickness), we do not find it reasonable that there are two types of mobility characteristics in MPD's which are represented by Tables I and II: those that have an activation energy that is independent of dopant concentration (Table I) and those that have an activation energy that depends on dopant concentration (Table II). It is suggested that the intrinsic mobilities in MDP's are activated, with an activation energy that is independent of dopant concentration, and has a prefactor that is exponential in ρ , the calculated distance between hopping sites, as expected for a hopping theory. The experimental observations of other behaviors, activation energies that depend on ρ (see Table II) and prefactors independent of ρ (Refs. 46 and 48), are attributed to either interactions among the dopant molecules or the failure of the lattice gas model to properly calculate ρ at high dopant concentrations.

It appears that something critical is missing from our understanding of charge transport in MDP and perhaps in all organic materials. While progress is being made in the elucidation of the charge transport mechanism in molecularly doped polymer, much work remains. Our current focus is understanding the origin of the initial spike using a new experimental technique called Time-of-Flight 1A (TOF1A), in which the hole generation region is varied from the surface to the entire bulk using electron beam excitation. We conjecture that identifying the charge transport mechanism will be beneficial to the design of organic photoreceptors for electrophotographic systems as well as other organic electronic devices. Although today's photoreceptors have adequate mobility, increased process speed will require both higher mobility and a reduction in those factors giving rise to carrier range limitations. For organic electronics higher mobility materials are necessary for practical devices.

REFERENCES

- L. B. Schein, *Electrophotography and Development Physics* (Laplacian Press, Morgan Hill, CA, 1996).
- L. B. Schein, "The electric field in magnetic brush developer", *Electrophotography: Second International Conference on Electrophotography* (SPSE, Washington, D.C., 1974) p. 65.
- L. B. Schein, "Microscopic theory of magnetic brush development", *Photograph. Sci. Eng.* **19**, 255 (1975).
- W. S. Jewett, *IEEE-IAS Annual Meeting Conference Record* (IEEE, Piscataway, NJ, 1977) pp. 557-568; G. P. Kasper, US Patent 4,076,857 (1978).
- E. Miskinis, "Designing materials for the Kodak coloredge copier program", *Proc. IS&T's NIP6* (IS&T, Springfield, VA, 1990) p. 101; E. Miskinis, US Patent 4,546,060 (1985).
- D. A. Hays, US Patent 4,368,970 (1983); US Patent 4,370,056 (1983).
- N. S. Goel and P. R. Spencer, *Adhesion Science and Technology* (Plenum Press, New York, 1975), pp. 763-829.
- D. A. Hays, "Toner adhesion", *J. Adhesion*, **51**, 41 (1995).
- L. B. Schein, "50 years of toner adhesion control in electrophotography", *J. Imaging Soc. Japan* **47**, 13 (2008).
- L. B. Schein, "Comparison of toner adhesion theories", *J. Imaging Sci. Technol.* **53**, 010506 (2009).
- B. Wang, E. Shih, T. Mu, D. Tsai, and L. B. Schein, "A direct-current jump non-magnetic monocomponent electrophotographic development system", *J. Imaging Sci. Technol.* **50**, 368 (2006).
- L. B. Schein, "Electrostatic proximity force, toner adhesion, and a new electrophotographic development system", *J. Electrostat.* **65**, 613 (2007).
- J. Lowell and A. C. Rose-Innes, "Contact electrification", *Adv. Phys.* **29**, 947 (1980).
- L. B. Schein and G. S. P. Castle, "Triboelectricity", in *Wiley Encyclopedia of Electrical and Electronics Engineering* (John Wiley and Sons, New York, 1999), Vol. **22**.
- L.-H. Lee, "A surface interaction model for triboelectrification of toner-carrier pair", *Photograph. Sci. Eng.* **22**, 228 (1978).
- A. Kondo, "Triboelectrification mechanism of powder developers", *TAPPI Reprographics Conference* (TAPPI, 1980) p. 153.
- L. B. Schein, M. LaHa, and D. Novotny, "Theory of insulator charging", *Phys. Lett. A* **167**, 79 (1992); L. B. Schein, "Theory of toner charging", *J. Imaging Sci. Technol.* **37**, 1 (1993).
- L. B. Schein, "Recent advances in our understanding of toner charging", *J. Electrostat.* **46**, 29 (1999).
- L. B. Schein, "Electric field theory of toner charging", *J. Imaging Sci. Technol.* **44**, 475 (2000).
- G. S. P. Castle and L. B. Schein, "General model of sphere-sphere insulator contact electrification", *J. Electrostat.* **36**, 165 (1995).
- R. P. N. Veregin, M. N. V. McDougall, M. S. Hawkins, C. Vong, V. Skorokhod, and H. P. Schreiber, "A bidirectional acid-base charging model for triboelectrification: Part I. Theory", *J. Imaging Sci. Technol.* **50**, 282 (2006); *ibid.* "A bidirectional acid-base charging model for triboelectrification: Part II. Experimental verification by inverse gas chromatography and charging of metal oxides", **50**, 288 (2006); "Understanding the influence of surface acid and base properties and water on work functions and triboelectric charging using inverse gas chromatography", *Proc. IS&T's NIP22* (IS&T, Springfield, VA, 2006) p. 131; "A bidirectional acid-base charging model for triboelectrification: Experimental verification by inverse gas chromatography and xerographic charging of toner and carrier", *Proc. IS&T's NIP24* (IS&T, Springfield, VA, 2008) p. 30.
- J. F. Kok and D. J. Lacks, "Electrification of granular systems of identical insulators", *Phys. Rev. E* **79**, 051304 (2009).
- G. Bartscher, S. O. Cormier, R. Lyness, and L. B. Schein, "Comparison of the electric fields of electrophotography and contact electrography", *J. Electrostat.* **53**, 295 (2001).
- G. Bartscher, F. Morgenweck, K.-U. Preissig, D. Rohde, S. O. Cormier, D. Kostyk, R. Lyness, G. Hauptmann, and L. B. Schein, "Single pixel development in a new electrographic printing system", *J. Imaging Sci. Technol.* **45**, 523 (2001).
- O. Larson, "Findings from 15 years of TonerJet research", *Proc. IS&T's NIP17* (IS&T, Springfield, VA, 2001) p. 657; see also Ref. 27.
- H.-P. Starchk-Johnson and A. Berg-Palmqvist, "Uniformity in solid areas with TonerJet printing technology", *Proc. IS&T's NIP15* (IS&T, Springfield, Virginia, 1999) p. 289.
- A. Sandberg, "TonerJet tandem color has reached prototype stage", *Proc. IS&T's NIP14* (IS&T, Springfield, VA, 1998) p. 180.
- N. Kutsuwada and T. Shohdohji, "An evaluation of image formation of TonerJet method for non-impact printing", *Proc. IS&T's NIP9* (IS&T, Springfield, VA, 1993) p. 513.
- J. Johnson, "Dynamic simulation of toner particles motion in a TonerJet printer", *Proc. IS&T's NIP11* (IS&T, Springfield, VA, 1995) p. 511.
- J. Johnson, "TonerJet color printing", *Proc. IS&T's NIP12* (IS&T, Springfield, VA, 1996) p. 267.
- G. Desie, J. Leonard, H. Vanden Syngaert, M. De Kegelaer, L. Deparez, and L. Joly, "Industrial digital printing using EleJet technology", *Proc. IS&T's NIP15* (IS&T, Springfield, VA, 1999) p. 315 for a history of early TonerJet concepts.
- R. Kober, "Simulation of traveling wave transport", *Proc. IS&T's NIP18* (IS&T, Springfield, VA, 2002) p. 453; "Traveling wave transport of conductive toner particles", *Proc. IS&T's NIP16* (IS&T, Springfield, VA, 2000) p. 736.
- J. R. Melcher, E. P. Warren, and R. H. Kotwal, *Part. Sci. Technol.* **7**, 1 (1989); *IEEE Trans. Ind. Appl.* **25**, 949 (1989).
- F. Schmidlin, "The role of traveling wave toner transport in powder printing", *Proc. IS&T's NIP11* (IS&T, Springfield, VA, 1995) p. 515; "Advances in traveling wave toner transport", *Proc. IS&T's NIP15* (IS&T, Springfield, VA, 1999) p. 302; *J. Electrostat.* **34**, 225 (1995).
- P. Salmon, US Patent, 5,400,062 (1995).
- H. Kawamoto, K. Seki, and N. Kuromiya, "Mechanism of traveling-wave transport of particles", *J. Phys. D* **39**, 1249 (2006).
- M. Slot and R. van der Meer, "Smart printhead electronics controls print quality in Océ's direct imaging process", *Proc. IS&T's NIP17* (IS&T, Springfield, VA, 2001), p. 690.
- R. J. van der Meer, *Elektronika* **3**, 87 (2001).

- ³⁹J. M. P. Geraedts and S. K. J. Lenczowski, *Proc. IS&T's NIP13* (IS&T, Springfield, VA, 1997) pp. 728–731.
- ⁴⁰I-Yin S. Lee, W. A. Tolbert, and D. D. Dlott, “Dynamics of laser ablation transfer imaging investigated by ultrafast microscopy”, *J. Imaging Sci. Technol.* **36**, 180 (1992).
- ⁴¹A. Arimoto, T. Sugita, T. Mitsuya, and Y. Takuma, “A new printing method with transfer of toners by flash light”, *Proc. IS&T's NIP11* (IS&T, Springfield, VA, 1995) p. 519.
- ⁴²K. Ito, M. Watanabe, Y. Watanabe, Y. Suwabe, and K. Terao, “Electrostatic powder transfer technology (EPT)—A simple powder imaging process”, *Proc. IS&T's NIP7* (IS&T, Springfield, VA, 1991) p. 519.
- ⁴³W. Mey and D. R. Kamp, “Laser toner fusion: An imaging process for graphic arts applications”, *Proc. IS&T's NIP15* (IS&T, Springfield, VA, 1999) p. 297.
- ⁴⁴R. M. Schaffert, *Electrophotography* (Focal Press, London, 1975).
- ⁴⁵J. Crowley, C. Snelling, C. Radulski, and K. Pietrowski, “Acoustically assisted xerographic toner transfer”, *Proc. IS&T's NIP8* (IS&T, Springfield, VA, 1992) p. 91.
- ⁴⁶L. B. Schein and A. Tyutnev, “The contribution of energetic disorder to charge transport in molecularly doped polymers”, *J. Phys. Chem. C* **112**, 7295 (2008).
- ⁴⁷L. B. Schein, V. Saenko, E. D. Pozhidaev, A. Tyutnev, and D. S. Weiss, “Transient conductivity measurements in a molecularly doped polymer over wide dynamic ranges”, *J. Phys. Chem. C* **113**, 1067 (2009).
- ⁴⁸L. B. Schein and D. S. Weiss, “Andrey Tyutnev: The charge carrier mobility's hopping activation energy and pre-factor dependence on dopant concentration in molecularly doped polymers”, *Chem. Phys.* **365**, 101 (2009).
- ⁴⁹L. B. Schein, “The source of the charge transport activation energy in molecularly doped polymers”, *Proc. IS&T's NIP8* (IS&T, Springfield, VA, 1992), p. 173.
- ⁵⁰J.-L. Bredas, V. Coropceanu, and S. Salman (private communications).