# Contact charging of organic materials: Ion vs. electron transfer

by A. F. Diaz
J. Guay

**In this paper we describe some of the recent literature on the contact charging (also known as tribocharging and contact electrification) of organic materials. Although it is a very familiar phenomenon, much remains to be understood about the mechanism of charging with organic materials. It has been proposed that the charging is due to the transfer of electrons and/or ions. In some studies, the correlation between the charging and the substituent constants for a substituted series of compounds has been used to support the electron transfer mechanism, and it has been proposed that the correlation reflects systematic changes in the energy levels of the highest and lowest occupied molecular orbitals of the derivatives. In others, the detection of the ions that are transferred during contact and the correspondence between their sign and that of the transferred charge have been used to support the ion transfer mechanism. In this paper, we discuss a selected number of papers that relate the charging behavior to electrochemistry and discuss the results reported in light of the two transfer mechanisms.**

## Introduction

Contact charging pertains to the transfer of charge between two dissimilar materials (solids) when they are brought into contact (with or without friction) and then separated. The current interest in contact charging with organic and ceramic materials lies in its importance in electrophotography [1, 2], and its damaging effects on electronic components [3, 4]. The ability to predict and control the charge transfer is therefore of considerable importance. Despite its long history [5–7], contact charging with organic materials is little understood and has been mostly attributed to electron transfer [8–18] by analogy with metal–metal and metal–semiconductor charging [19, 20].

In the early 1950s, Harper [19] proposed an electron transfer mechanism to explain the contact charging of metals by metals. His results [19] showed that the charge transferred is proportional to the contact potential difference ($V_c$) of the metals, which is defined by $V_c = (\phi_b - \phi_a)/e$, where $\phi_a$ and $\phi_b$ are the work functions

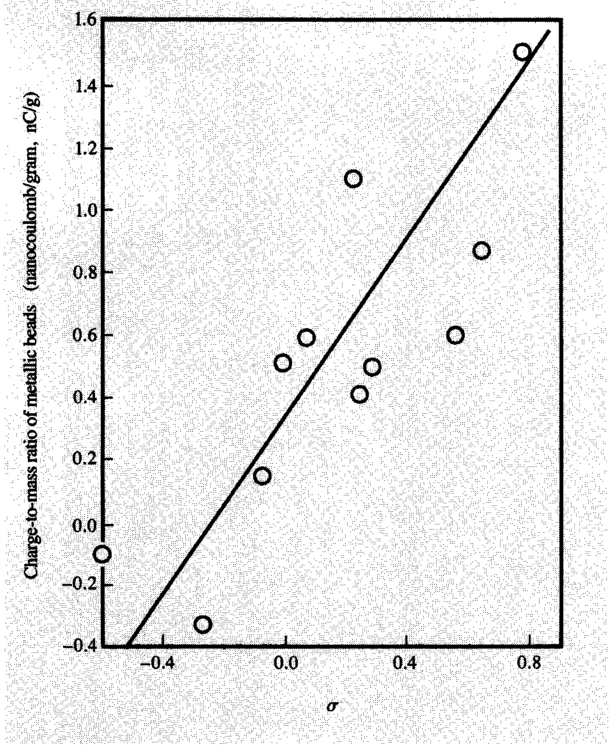

**Figure 1**

Contact charging of a series of p-substituted phenylazo-2-naphthol films as a function of the Hammett substituent constant $\sigma$; the charging was achieved using nickel beads. From [12], reproduced with permission.

of metals a and b, and $e$ is the electron charge. Typically, upon contact between two ideal metals, electrons flow from the metal of lower work function (higher chemical potential) to the metal of higher work function until the Fermi levels of the metals coincide. Some years later, the phenomenon of electron transfer was invoked to explain metal–insulator contact charging because, as in the metal–metal case, the charge on the insulator was found to relate to the contact potential difference [8–10]. However, the charge transfer data contained a considerable amount of scatter, making it difficult to determine the exact relationship between the charge and the work function of the contacting metal. The mechanism of electron transfer with insulators is less clear. The polymeric insulators are described as having empty states that can accept or donate electrons with respect to a metal [10]; the states are characterized by a energy level $E$. By analogy with semiconductors, these energy levels are treated as chemical potentials; they lie close to the Fermi energy of metals, i.e., about 4 to 5 eV below the vacuum level. By analogy with metal–metal charging, electrons are believed to flow between $E_F$ and $E$ until equilibrium is achieved [10].

The relationship between the charge transferred and $V_c$ can be interpreted differently, however, because $V_c$ is also related to the difference in the chemical potential between the two contacting surfaces $\Delta u$. The latter is a thermodynamic parameter that is associated with many types of equilibrium reactions such as electrode reactions (electron transfer), acid/base reactions (proton exchange), and ion exchange. Given this fact, several studies with organic materials have focused on the effect of substituents on charging, and have shown that linear free-energy relationships exist between the charge and, e.g., the Hammett $\sigma$ [12–15]. The existence of these relationships has been taken as evidence for electron transfer.

Much remains to be understood about the mechanism of charging with organic materials. The mechanisms under consideration have many similarities to those of electrochemistry. However, one considerable difference between contact charging and an electrochemical process is that ion or molecule mobility, which is limited in the solid since most of the ions are "frozen" in place, is relatively high in electrochemical processes. It should be mentioned that in many of the recent studies, use is made of organic films and polymeric powders because of the interest in understanding the charge characteristics of the "toner" powders in the electrophotographic printing process; similarly, the charge is often activated by rolling the powder with "carrier" beads.

## Substituent effects in charging

Cressman et al. [12] and Gibson [13] have studied the solid-state charge transfer between a metal and two well-defined series of substituted aromatic compounds. In the study by Cressman et al. [12], charge was transferred by rolling spherical nickel beads (250-$\mu$m diameter) down an inclined plane coated with a film of various 1-(p-substituted phenylazo)-2-naphthols (X-Ph-azo-Np) derivatives. Within the series, some of the films became charged positively and some negatively. Nevertheless, a linear relationship was obtained between the charge transferred and the Hammett substituent constant $\sigma$, as shown in **Figure 1.** Without going into the theoretical basis of linear free-energy relationships between chemical processes, we note that $\sigma$ is a substituent constant originally defined to reflect in a semiquantitative way the free-energy changes associated with the shift in the acid dissociation equilibrium $K$ for benzoic acid derivatives in aqueous ethanol [21]. For a given substituent, $\sigma$ is related to the logarithm of the ratio of the values of $K$ for the substituted benzoic acid and benzoic acid itself. Currently, use is made of many different values of $\sigma$ in mechanistic organic chemistry to relate both thermodynamic and kinetic processes. However, there are also well-recognized limitations to their application. It should be noted that the substituents affect both the electronic structure and chemical properties (acidity/basicity, redox) of the molecules under consideration, and linear free-energy correlations alone do not permit a distinction between electron transfer and ion transfer processes.

A year after the study by Cressman et al. was reported, Gibson [13] reported a similar study based on the use of a series of substituted salicylaldehyde anils (SAL-X). The charging was again developed by rolling spherical stainless steel beads (250-$\mu$m diameter) down an inclined plane coated with films of the anil derivatives. The films became charged more positively than those used in the previous study, and none became charged negatively. However, in contrast with what had been observed previously, it was the log (charge) which varied linearly with the Hammett $\sigma$ constant (see **Figure 2**). The existence of a charge-$\sigma$ relationship also led Gibson to propose a solid-state electron transfer mechanism for the charging he observed, characterized by the expression

$$\text{Organic} + \text{Metal} \rightarrow \text{Organic}^{+} + \text{Metal}^{-}. \qquad (1)$$

Results were also presented for a substituted polystyrene series which displayed a linear log (charge) versus $\sigma$ relationship; Gibson interpreted this as further evidence that the transfer was due to electron transfer. A plot for substituted polystyrene appeared in Gibson's Figure 2 and is not shown here. Although the comments that follow apply generally to different series of materials, special attention is given to the anil derivatives, for which we have repeated some measurements. The structures of the derivatives are shown in **Figure 3**.

Gibson described the electron transfer mechanism in some detail [13]. He proposed electron transfer from the donating energy levels, those of the highest occupied molecular orbital (HOMO) of the organic compounds, to the Fermi level of the metal ($E_F$) when the organic materials acquire a positive charge—and from $E_F$ to the accepting energy levels, those of the lowest unoccupied molecular levels (LUMO), when the organic materials acquire a negative charge. Gibson also specified that the electron transfer is limited to those cases where $E_{\text{HOMO}}$ is significantly greater than $E_F$ for positively charging organic materials, and where $E_{\text{LUMO}}$ is significantly lower than $E_F$ for negatively charging organic materials. In fact, Gibson described this process as solid-state electrochemistry by analogy with the electron exchange process proposed for contact charging with metals [19]. Thus, for organic compounds which become positively charged, Gibson related the charge to $\sigma$ as follows:

$$\ln(Q/M) \propto E_{\text{HOMO}} - E_F\,;$$

and since $E_{\text{HOMO}} = -m\sigma + b$, it follows that

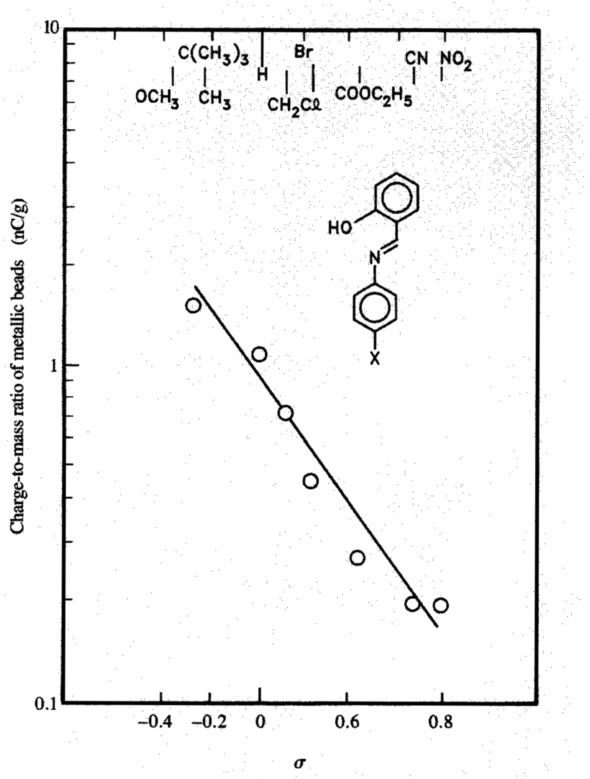

**Figure 2**

Contact charging of a series of substituted salicylaldehyde anil films as a function of the Hammett substituent constant; the charging was achieved by using 250-$\mu$m-diameter steel beads at 0% relative humidity; the films became positively charged in accordance with the relationship $\ln(Q/M) = -1.98\sigma - 0.136$ (correlation coefficient $r = 0.966$). From [13], reproduced with permission.

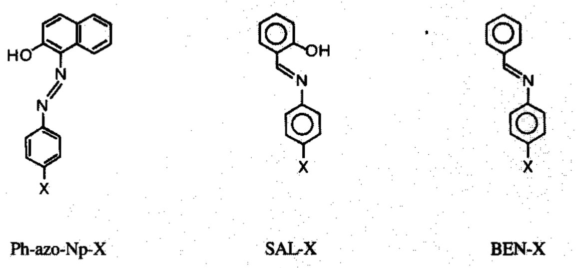

**Figure 3**

Anil derivatives used in [12] and [13].

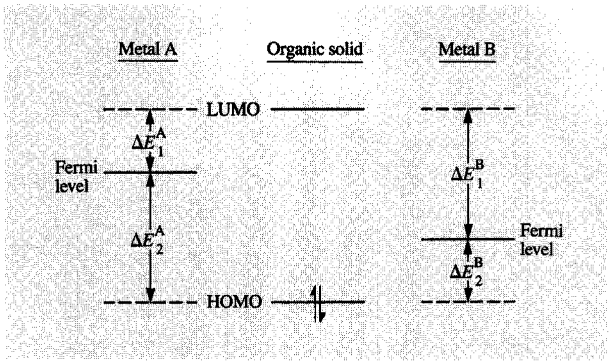

**Figure 4**

Gibson's model for contact charging of an organic material, based on the location of the molecular orbital energy levels. For metal A: when $\Delta E_2^A$ is greater than $\Delta E_1^A$, the organic solid becomes negatively charged, and $\ln(Q/M)$ is proportional to $\Delta E_1^A$. For metal B: when $\Delta E_2^B$ is less than $\Delta E_1^B$, the organic solid becomes positively charged, and $\ln(Q/M)$ is proportional to $\Delta E_2^B$. From [14], reproduced with permission.

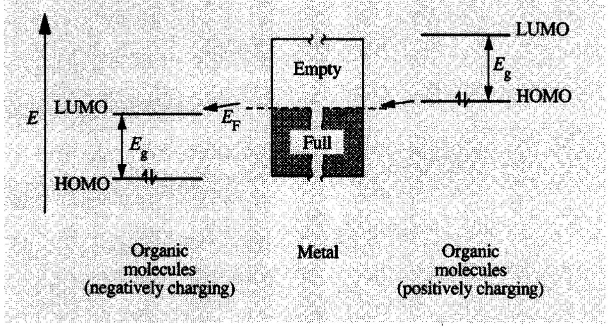

**Figure 5**

Energy schematic for charge transfer between a metal and negatively and positively charging organic materials.

$$\ln(Q/M) \propto -m\sigma - E_F + b.$$

- By analogy, then, for compounds that charge negatively, $\ln(Q/M) \propto E_F - E_{LUMO}$;

  and since $E_{LUMO} = -m'\sigma + b'$, it follows that

  $\ln(Q/M) \propto m'\sigma + E_F - b'$.

Gibson [14] suggested that the linear relationship between the charge (solid state) and $\sigma$ (solution) was consistent with the observation that in both the gas and solution phases the molecular orbital energy levels usually vary linearly with $\sigma$. In going from the isolated molecules in the gas phase to an organic solid, these energy levels are modified only by the polarization energy, and are thus shifted linearly [14]. By analogy with solution electrochemistry, he suggested that the equilibration of the charge between the two surfaces is governed by the difference between $E_F$ and $E_{HOMO}$ or $E_{LUMO}$. He later proposed a second model, in which $E_F$ lies between the $E_{HOMO}$ and $E_{LUMO}$ levels [14] and the extent of charge transfer is exponentially governed by the energy difference between $E_F$ and the HOMO or LUMO energy levels of the organic materials. The smaller energy gap determines the direction of the charge exchange (**Figure 4**) [14]. Thus, Gibson proposed that the logarithm of the charge is directly proportional to the difference between $E_F$ and the appropriate molecular orbital energy level (see caption for Figure 4).

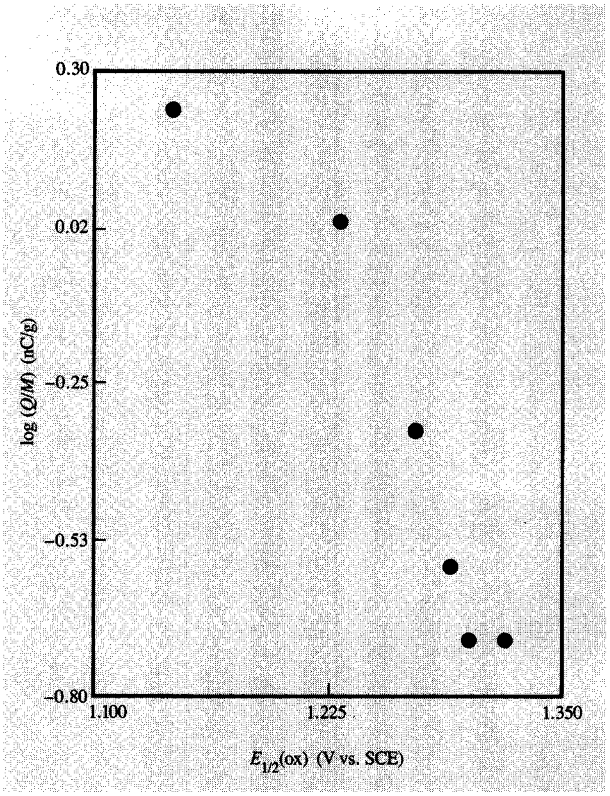

**Figure 6**

$\text{Log}(Q/M)$ vs. $E_{1/2}$(ox) for some p-substituted salicylaldhyde anil derivatives. These materials acquired a positive charge upon contact with steel beads. (Data from [13] and [23]).

There are, however, some concerns with the above two electron transfer mechanisms. First, inspection of Gibson's energy diagram (Figure 4) reveals that the charge transfer within the derivative series should increase as $\Delta E$

decreases, and should not be directly related to it (see caption). Second, Gibson's early model did not explain the change in the sign of the charge observed with the X-Ph-azo-Np derivatives [12]. To comply with this mechanism, $E_{\mathrm{HOMO}}$ should be higher than $E_{\mathrm{F}}$ for the compounds that charge positively, and $E_{\mathrm{LUMO}}$ should be lower than $E_{\mathrm{F}}$ for compounds that charge negatively. We show this schematically in **Figure 5**. Thus, the change in the sign of the charge requires that the energy of the molecular orbitals of these compounds shift by about the width of the energy gap $E_g$, which is ~2.4 eV for typical aromatic compounds. Not only is this unrealistic, but the range in the oxidation potentials within the series suggests a maximum shift of less than 0.8 eV.

Third, if charging is the result of a well-behaved electron transfer process, the logarithm of the charge should scale with the oxidation or reduction potentials of the compounds. As can be seen in **Figure 6**, this does not apply to the salicylaldehyde derivatives [13, 22]. In addition, the data for those which charge with the same sign should lie on a common line. Yet with the aniline and aromatic anil derivatives, we have found that each series generates a separate line, for which the aniline (AN-X) derivatives charge less (except for AN-$NH_2$), even though they are more easily oxidized, corresponding to a lower value of the solution half-wave oxidation potential $E_{1/2}$(ox) [23]. This is seen in **Figure 7**. In addition, p-nitroaniline (not shown in the figure) unexpectedly acquires a charge of the opposite sign. This can be seen in **Table 1**. The slopes of the lines are similar, −3.6 for AN-X and −3.4 for SAL-X and BEN-X, reflecting similar sensitivities to the electronic effects of the substituents. On the other hand, support for proton transfer is provided by the linear relationship between $\log(Q/N)$, with $Q/N$ expressed in μC/mol, and log (basicity constants) observed with the aniline derivatives [23]. The source of protons is most likely associated with the dissociation of surface water molecules. Therefore, the existence of linear free-energy correlations alone does not permit a distinction between electron transfer and ion transfer processes, since the same qualitative trends are produced by both. With regard to the sensitivity of the logarithm of the charge to the substituent $\sigma$, i.e., $\rho$, the plot in Figure 2 has a $\rho$ value of $\sim -1.1$. It should be noted that this value is close to those (1–2) observed for processes involving ions in solution, and not to those (7–22) normally observed for processes involving ions in the gas phase[1] [24].

Finally, in the case of the X-Ph-azo-Np, SAL-X, and aniline derivatives, we have observed that charging is accompanied by an extensive amount of material transfer $N_R$ (in μmol derivative per gram of the beads used). The data are summarized in Table 1. As shown in **Figure 8**, the amount of charge and material transfer responded linearly

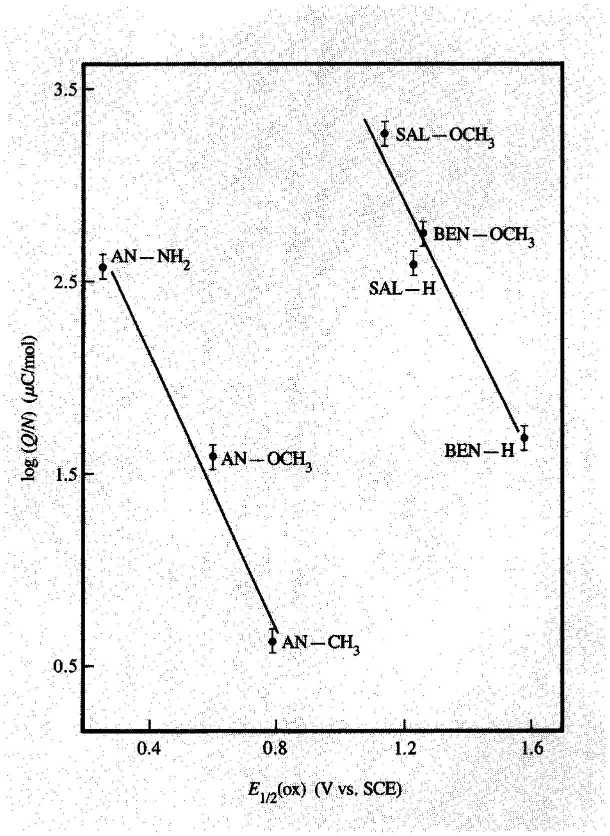

**Figure 7**

Log($Q/N$) vs. $E_{1/2}$(ox) for the substituted aniline, benzaldehyde anil, and salicylaldehyde anil derivatives. From [23], reproduced with permission.

**Table 1** Charging and material transfer data for various anils and anilines (from [23], reproduced with permission).

| *p-X* | *$E_{1/2}$(ox)* (V vs. SCE) | *Iron beads* | | *Organic powders* | |
|---|---|---|---|---|---|
| | | *Q/M* (nC/g) | $N_R^*$ (μmol/g) | *Q/M* (μC/g) | *Q/N* (μC/mol) |
| *p-X-salicylaldehyde anils* | | | | | |
| H | 1.23 | −55 | 1.7 | 2.2 | 433 |
| $CH_3O$ | 1.15 | −210 | 2.3 | 8.4 | 1900 |
| *p-X-benzaldehyde anils* | | | | | |
| H | 1.58 | −6.7 | 0.9 | 0.27 | 49 |
| $CH_3O$ | 1.26 | −63 | 1.4 | 2.51 | 530 |
| *p-X-anilines* | | | | | |
| $NO_2$ | 1.34 | +20 | 0.8 | −0.8 | −110 |
| $CH_3$ | 0.79 | −1.0 | 0.4 | 0.04 | 4.3 |
| $CH_3O$ | 0.60 | −7.8 | 1.1 | 0.31 | 38 |
| $NH_2$ | 0.26 | −87 | 2.0 | 3.47 | 375 |

*$N_R$ is the amount of derivative found on the beads in μmol derivative per gram of beads.

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[1] J. L. Brauman, Stanford University, CA, private communication.

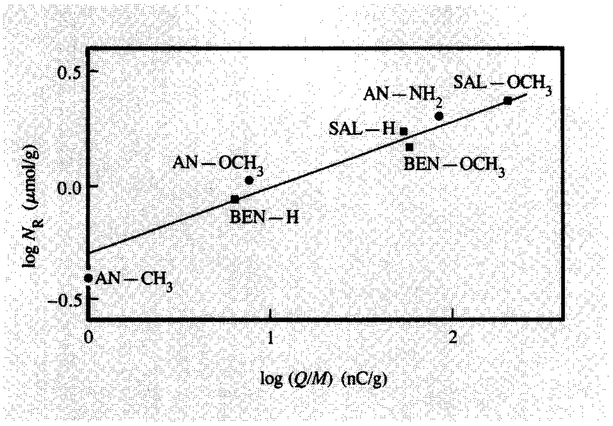

**Figure 8**

Log($N_R$) vs. log(Q/M) for various substituted derivatives. From [23], reproduced with permission.

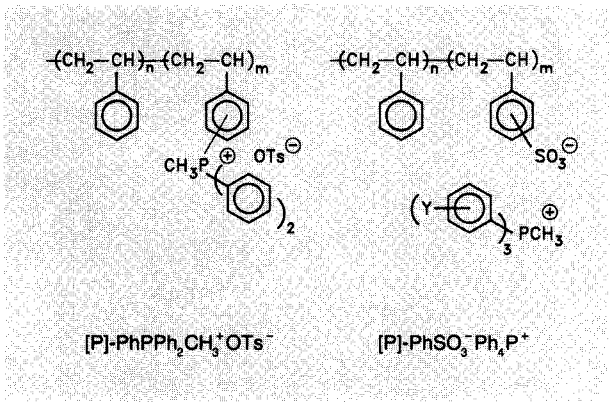

**Figure 9**

Ionomers with arylphosphonate and arylsulfonate ions.

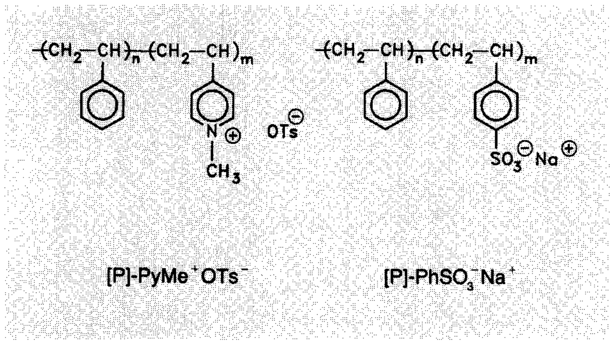

**Figure 10**

Ionomers with N-methylpyridinium and sodium arylsulfonate ions.

to the structural changes. This material transfer contaminates the surface of the beads [23] and thus renders the conclusions regarding charge transfer to and from these materials in question [12, 13].

## Charging with polymers containing ions

Contact charging of polymers is known to be strongly influenced by the presence of added salts or protic acids [17, 25–35]. These additives affect both the sign and the magnitude of the charge transferred. When ionomers (a class of polymers containing a low concentration of ions in which one of the ions of the ion pair is covalently bonded to the polymer chain) are used as the source of ions, a larger influence on the magnitude of the contact charge is observed. Because polymer blends containing ionomers will charge 5–12 times higher than with the corresponding molecular salts [27–30, 32], there has been recent interest in the charging characteristics of such materials.

Anderson and Bugner [17] have blended a series of triarylmethylphosphonium arylsulfonates, $(Y\text{-}Ph)_3PCH_3^+$ 4-X-$PhSO_3^-$ (where Y and X are para substituents) into polystyrene and formed them into powders. The powders were charged using "carrier" beads. The powders became charged positively, and their charge responded to the substituents in the anion; a higher level of charging resulted for the ions having the electron-rich substituents. The anions with the electron-withdrawing substituents all acquired the same charge. On the other hand, the charge did not vary with the substituents on the cation. Although the results did not provide convincing charge-$\sigma$ correlations, an electron transfer process for charging was proposed.

Electron transfer was again proposed for the charging mechanism for the ionomers containing methyltriarylphosphonium arylsulfonate salts. In one of the ionomers used, the phosphonium cation was attached covalently to the ionomer chain, [P], which we designate here by [P]-$PhPPh_2CH_3^+OTs^-$ (toluenesulfonate), while in the other, the arylsulfonate anion was attached, [P]-$PhSO_3^-$ $Ph_4P^+$ [27, 31, 32]. The ionomers are shown in **Figure 9**. They were blended with a polymer and the blends were formed into powders. The powders acquired a positive charge upon contact with a metal, regardless of which ionomer was used, i.e., whether it had an "anchored" cation (mobile anion) or an "anchored" anion (mobile cation). The charge levels shifted with the introduction of p-substituents into either the arylphosphonium or the arylsulfonate ions. In both cases, a higher charge was observed with the electron-rich substituents, and a correlation was observed between the charge and the theoretically calculated HOMO energy levels and Hammett $\sigma$ values. A concern with invoking electron transfer with regard to these ions is the lack of sufficient energy at ambient conditions to ionize them

**Table 2** Contact charging and XPS results (from [38], reproduced with permission).

| *8–12-μm-diameter powder* | | | *140-μm-diameter beads Concentration*[*] (at. %) | | | | |
|---|---|---|---|---|---|---|---|
| *Ions in powder* | *Salt conc.* (μmol/g) | *Q/M* (μC/g) | *C* | *O* | *S* | *N* | *Na* |
| *Bare beads (conductive)* | | | | | | | |
| No. ions | 0 | −11 | 49.6 | 39.8 | 0.9 | nd[†] | |
| [P]-PyMe$^+$OTs$^-$ | 36.4 | 72 | 69.5 | 29.3 | 1.16 | nd | |
| 4-Et-PyMe$^+$OTs$^-$ | 51.0 | −1.0 | 58.0 | 39.3 | 1.92 | 0.74 | |
| [P]-PhSO$_3^-$Na$^+$ | 21.9 | −16 | 48.4 | 39.6 | 0.8 | | 0.03 |
| *Coated beads (insulating)* | | | | | | | |
| No. ions | 0 | 0.7 | 47.7 | 7.70 | nd | 1.85 | nd |
| [P]PyMe$^+$OTs$^-$ | 52.0 | 72 | 58.3 | 7.68 | 0.19 | 1.04 | |
| 4-Et-PyMe$^+$OTs$^-$ | 51.0 | 5.4 | 50.5 | 8.00 | 0.68 | 2.3 | |
| [P]-PhSO$_3^-$ Na$^+$ | 21.9 | −14 | 49.6 | 7.56 | nd | | 0.07 |

[*] XPS analysis after rolling and removal of powder.
[†] Not detected, less than 0.02.

**Table 3** Possible location of ions.

| | *Surface 1* | *Surface 2* |
|---|---|---|
| *Ionomer with "anchored" PyMe$^+$ cation* | | |
| Before contact: | [P]-PyMe$^+$, OTs$^-$ | |
| After contact: | [P]-PyMe$^+$, OTs$^-$ | OTs$^-$ |
| *Ionomer with "anchored" PhSO$_3^-$ anion* | | |
| Before contact: | [P]-PhSO$_3^-$ , Na$^+$ | |
| After contact: | [P]-PhSO$_3^-$ , Na$^+$ | Na$^+$ |
| *Molecular salt with two mobile ions* | | |
| Before contact: | PyMe$^+$, OTs$^-$ | |
| After contact: | PyMe$^+$, OTs$^-$ | PyMe$^+$, OTs$^-$ |

[36, 37]. Even under electrochemical conditions the arylsulfonate ions are not easily oxidized. In fact, water oxidizes at lower potentials than the arylsulfonate anions; thus, surface moisture would more likely be involved in an electron transfer process if it occurred.

A case for ion transfer has been made recently by two groups. In our own laboratory, blends of a styrene-butyl methacrylate copolymer and the poly(styrene-co-N-methyl-4-vinylpyridinium toluenesulfonate) ionomer ([P]-PyMe$^+$OTs$^-$) were formed into powders and were charge-activated by rolling with ferrite beads [28–30]. The ionomer structure is shown in **Figure 10**. The ionomer-blended powders developed a positive charge that increased with ionomer content; correspondingly, the beads acquired a complementary negative charge. Furthermore, the OTs$^-$ anions were observed by XPS on the surface of the beads after contact and removal of the powders (see **Table 2**); cations were not observed. This provided a good correspondence between the ion type and the sign of the charge on the beads. The charging behavior was explained by ion transfer, specifically the transfer of OTs$^-$. Thus, it was concluded that the polymer blend acquires the positive charge of the cation ("anchored"), and the second surface the negative charge of the anion (mobile). This is illustrated in **Table 3**, which depicts the surfaces on which the ions can reside. The scheme depicted does not take into account stoichiometry and material balance: It is qualitative and applies only to those cases in which ions are added to the polymer. It does not address the relative transfer "aptitudes" between the mobile ions with similar structures, but does apply generally to large ions which, although not "anchored," have little or no mobility. It does not take into account the effects of ionic impurities and moisture.

When the anion of the ion pair is bonded to the ionomer, as in the case of partially sulfonated polystyrene sodium salt, [P]-PhSO$_3^-$Na$^+$, the polymer blends charge negatively; the Na$^+$ cation (but no PhSO$_3^-$) [38] was found on the beads after contact and separation. Finally, with [P]-PyMe$^+$OTs$^-$ and [P]-PhSO$_3^-$Na$^+$, the same results were observed with both polymer-coated beads and bare ferrite beads, independent of the conductivity. Thus, the conductivity of the second surface does not appear to be important with regard to charging when mobile ions are present in the polymer.

Ion transfer was also observed in charging experiments involving N-cetylpyridinium bromide (**Figure 11**) blended with polystyrene and indium [33]. The polymer acquired a

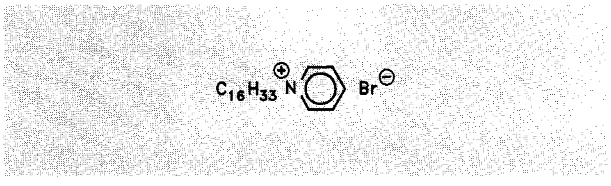

**Figure 11**

Structure of N-cetylpyridinium bromide.

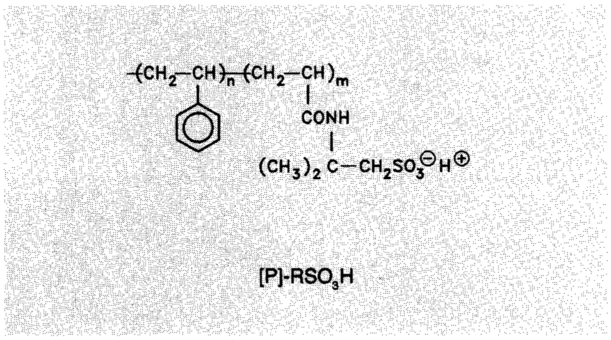

**Figure 12**

Structure of $[P]-RSO_3H$, a protic ionomer.

positive charge, and the indium acquired a negative charge. Both types of ions were detected by SIMS on the negatively charged indium surface after contact and removal of the powder. However, the $Br^-$ concentration exceeded considerably that of the cation. The charging was explained by ion transfer in which the sign reflected the higher mobility of the $Br^-$ ion. The results reported in the patent by Watanabe and Nagase [34] are also consistent with an ion transfer mechanism. The authors showed that a copolymer of styrene and alkyl methacrylates containing an attached aliphatic sulfonic acid group (through methacrylamide linkages) ($[P]-RSO_3H$) functions as a charge enhancer, and that it develops a negative charge. The structure of the copolymer is shown in **Figure 12.** Although not demonstrated, it is reasonable to infer that the mobile proton is transferred out of the sample, leaving behind the arylsulfonate anion, which is the basis of the negative charge. The proton is mobile in the material, whether it resides on the sulfonate or the amide group. Unfortunately, the question of what mechanism might apply was not addressed.

Clearly, ion transfer occurs between the surfaces during contact. Although the results with [P]-PyMeOTs and $[P]-PhSO_3^-\ Na^+$ ionomers and with N-cetylpyridinium bromide do not disprove the electron transfer model, there is also no need to invoke it. The occurrence of concurrent electron transfer and $OTs^-$, $Na^+$, or $Br^-$ transfer processes for charging would be highly coincidental. It would not account for the correspondence between the sign of the transferred charge and the transferred ion.

Returning to Anderson's result with the $[P]-PhSO_3^-Ph_4P^+$ ionomer [27], the sign of the charge transferred is not the same as the sign of the mobile $Ph_4P^+$ ion. Instead, a negative charge is transferred. This is contrary to the expectation for an ion transfer mechanism; it is inferred from the latter that the powder with the attached arylsulfonate anion should acquire a negative charge, since only the mobile cation can transfer to the beads. However, the samples examined were found to contain $Na^+$ and $I^-$ (10% and 20% based on the P content, respectively [27]); these impurities may have dominated the charge. The $Na^+$ and $I^-$ ions are mobile, and the presence of $I^-$ in excess of $Na^+$ probably leads to $I^-$ transfer in excess of $Na^+$ transfer, leaving behind a net positive charge. In addition, the $Ph_3PMe^+$ ion is large and has a very low mobility, even if not "anchored" to the polymer. It is certainly less mobile than the $Na^+$ and $I^-$ ions. This is borne out by the molecular analog, $Ph_3PMe^+OTs^-$, which transfers a negative charge[2] [17], and observations in our laboratory of $OTs^-$ on the surface of recovered beads.[2] The presence of the ionic impurities (mobile) counteracts the effect of immobilizing one of the ions in the ion pair.

With molecular salts for which both ionic constituents can be mobile [28–30], the situation is more complicated. As can be seen in Table 2, the charge levels are often lower because both constituents transfer [28, 30, 32]. Since the relative transfer capabilities of the ions cannot be anticipated, the sign of the resulting charge is somewhat unpredictable. The situation is also unclear in the case of betaines, in which both ionic constituents are united [35]. In a patent by Barbetta et al. [35], zwitterions, referred to as "inner salts," were attached to a polymer; the attached ions were quaternary ammonium cations and sulfonate anions. It was found that these "inner salts" do little to modify the charge of the polymer but do enhance the rate of charging.

Finally, the importance of surface moisture on charging cannot be overemphasized. Any water molecules which are associated with the ionic centers can dissociate to produce $H^+$ and $OH^-$ ions, and this quickly complicates the charging process. Thus, the transferred ions ($OTs^-$, $Na^+$, $Br^-$) may be accompanied by the transfer of protons and hydroxide ions from the dissociation of surface moisture [39, 40]. Unlike metal–metal charging, for which electron transfer is well modeled [19], in polymer–polymer and polymer–metal charging, charging results from the

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[2] D. Wollmann and A. Diaz, IBM Almaden Research Center, 1990, unpublished results.

transfer of (mobile) ions, if present. It is important to note that the models developed for the equilibration of charge between two dissimilar surfaces [16, 18, 19, 41, 42] apply equally well to ion transfer (with modification of terms), even though they were developed for electron transfer.

## Contact charging in electrophotography

As mentioned briefly above, the phenomenon of contact charging is important in the functioning of dry electrophotographic developers used in printers and copiers. The developers usually consist of a mixture of "toner" particles and "carrier" beads. The "toner" particles are polymeric composites containing either carbon black or color dyes and a charge control agent. The "carrier" beads are metallic. In an electrophotographic processor, charged toner particles move from a supply bin through the processor to designated areas on a sheet of paper. The steps in the process rely heavily on the charge on the toner. The charge is activated by agitation of the mixture in the storage bin and is characterized by the charge/mass ratio. "Charge control agents" are normally added to the toner composition to control the magnitude and the sign of the charge on the toner. Currently, a wide variety of commercially available pigments are used as charge control agents. Examples of some of these and their charging ranges have been provided by Macholdt and Sieber [43], and are listed here in **Table 4** in the approximate order of their capacity to acquire positive and negative charge.

In **Table 5** we have compiled the data on charging and oxidation potentials for some of the pigments listed in Table 4. As can be seen, there is no correlation between the magnitude of the acquired charge and the oxidation potential. We have also prepared a series of powder blends with ferrocene, nigrosine, and three aromatic hydrocarbons, perylene, pyrene, and triphenylene, and have measured their acquired charge. The results are listed in **Table 6**, along with values of the solid-state ionization potential (*IP*) and solution half-wave oxidation potentials [$E_{1/2}$(ox)] of the compounds. Again, no correlation is seen between the acquired charge and the oxidation potential, and additionally, between the acquired charge and the solid-state ionization potential. Given these results, it is difficult to infer that electron transfer is important in the charging of such charge control agents.

In accordance with the above discussion, it appears that charging also results from ion transfer when these pigments are in use. Many of them are salts. The charging categories depicted in Table 4 are easily understood when the chemical structure of the pigments is considered.

Most of the pigments which can be used to induce a positive charge consist of a large organic cation and a smaller inorganic anion. Because of the lower mobility of the large cation, it is inferred that when a pigment with such a combination of ions is added to a polymer, the polymer will acquire a positive contact charge.

Most of the pigments which can be used to induce a negative charge consist of a large anion and protons (cations). Because of the lower mobility of the large anion, it is inferred that when such a pigment is added to a polymer, it will acquire a negative contact charge. Pigments such as phthalocyanines and perylenes are neutral species and are expected to have very little effect on the charge induced.

**Table 4** Commercially available pigments used as charge control agents. From [43], reproduced with permission.

| | |
|---|---|
| *Pigments that acquire a positive charge* | |
| Nigrosines | (most positive) |
| Tri(aminophenyl)methanes | |
| Cationic dyes | |
| Dioxazines | |
| *Pigments that acquire a minimal charge* | |
| Copper phthalocyanines | |
| Perylenes | |
| *Pigments that acquire a negative charge* | |
| Quinacridones | |
| Azo pigments | |
| Metal salt azo pigments | |
| Azochromium complexes | (most negative) |

**Table 5** Acquired charge and oxidation potentials for some of the pigments of Table 4.

| *Additive* | *Q/M* ($\mu$C/g) | $E_{ox}$ (V vs. SCE) |
|---|---|---|
| Nigrosine | 45 to 55 | 1.3 |
| Cationic dyes | 5 to 25 | 0.7 to 1.5 [14, 44] |
| Copper phthalocyanines | −10 to 5 | 0.8 to 0.9 [44] |
| Perylene | −10 to 5 | 0.85 to 1.06 [44, 45] |

**Table 6** Acquired charge for various powder blends and the oxidation potential of the additives.

| *Additive* | *Q/M* ($\mu$C/g) | $E_{1/2}(ox)$ (V vs. SCE) | *IP [46]* |
|---|---|---|---|
| Perylene | +2 | 0.85 to 1.06 [44, 45] | 5.2 |
| Triphenylene | +6 | 1.7 [45] | 6.2 |
| Pyrene | +9 | 1.36 [45] | 5.8 |
| Ferrocene | +9 | 0.4 | — |
| Nigrosine | +45 | 1.3 | — |

## Summary

We have reviewed the results from different laboratories which bear on the question of the mechanisms of charging of organic materials containing ions.

A case for electron transfer is made on the basis of correlations between charge and substituents for a derivative series, and a correlation is proposed to reflect the variation in the HOMO and LUMO energy levels of the members of the series. In some studies, correlations between the charge and the HOMO or LUMO energy levels of the compounds have been used to support an electron transfer mechanism. We point out that such correlations are not sufficient evidence for the applicability of such a mechanism because the substituents produce linear responses in many other properties, for example, in the acidity and basicity of the compounds. In particular, the materials used in studies of the mechanism of charging also produce a substantial amount of material transfer, which contaminates the surface of the beads used in such studies. This material transfer makes the interpretation of the results obtained much more difficult. The further concern with electron transfer is whether enough energy is available at ambient conditions and in the absence of an electric field to disengage an electron from a stable compound or ion.

A case for ion transfer is made for materials containing ionomers on the basis of observed correlations between the sign of the charge transferred and the sign of the mobile ion, and the observed presence of the mobile ion species on the surface of the beads used to achieve the charge transfer. Similar results have been observed for molecular salts. Thus, ion transfer is proposed as the mechanism for contact charging if salts with mobile ions are present in the polymer.

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**Arthur F. Diaz** *IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120 (ADIAZ at ALMADEN, adiaz@almaden.ibm.com).* Dr. Diaz received a Ph.D. in chemistry from UCLA in 1965. He remained there as a Postdoctoral Fellow for two years and taught in the graduate program in chemistry at Long Beach State University for one year before joining the faculty in the chemistry department at the University of California at San Diego. He joined the IBM Almaden Research Center at San Jose in 1975 and currently manages their Basic Studies and Materials for Printing group. His research activities since joining IBM have been in the areas of electrochemistry and interfaces. His early work on the electrochemistry of conducting pyrrole, thiophene, and aniline polymers has attracted the attention of many universities and industrial laboratories. Dr. Diaz was the first to provide an electrochemical means for the preparation of conducting polymer films and to demonstrate their electrochemical and electrochromic properties.

**Jean Guay** *Lexmark International, 6555 Monarch Road, P.O. Box 9042, Boulder, Colorado 80301.* Dr. Guay received B.S. and M.S. degrees from Laval University in 1985 and 1987, respectively, and a Ph.D. degree in chemistry in 1990 from l'Institut National de la Recherche Scientifique en Energie, Quebec. He then spent two years as a Postdoctoral Fellow at the IBM Almaden Research Center at San Jose, working on triboelectrification and the electrochemistry of polymers. In 1992, he joined Lexmark International, where he continues to work on printing-related materials.