# Investigation of the Contact Charging Mechanism between an Organic Salt Doped Polymer Surface and Polymer-Coated Metal Beads

Kock-Yee Law,* Ihor W. Tarnawskyj, Dominic Salamida, and Tom Debies

*Xerox Corporation, Wilson Center for Research and Technology, 800 Phillips Road, 0114-39D, Webster, New York 14580*

*Received March 23, 1995. Revised Manuscript Received June 22, 1995*[⊗]

The mechanism of contact charging between an organic salt modified polymer surface and a dissimilar polymer surface has been studied in the form of a xerographic developer, which consists of toner particles and polymer-coated metal beads. The model toner was prepared by solution coating 0.15 wt % of a negative charge additive, cesium 3,5-di-*tert*-butylsalicylate, on the surface of 9 $\mu$m (diameter) sytrene–butadiene toner particles. The tribocharge was generated at a relative humidity (RH) of ~20%, by tumbling the model toner with polymer-coated beads (~130 $\mu$m in diameter). It was determined by the standard blow-off procedure inside a Faraday cage. The surfaces of the toner and the polymer-coated metal beads, before and after the blow-off experiments, were analyzed by time-of-flight secondary ion mass spectrometry (TOF SIMS) and X-ray photoelectron spectroscopy (XPS). Results show that the cation of the charge additive, $Cs^+$, transfer preferentially from the surface of the toner to the surface of the polymer-coated metal beads. The transferred $Cs^+$ distributes uniformly on the bead surface according to TOF SIMS imaging. The relative $Cs^+$ density on the surface of the beads recovered from experiments where the toner charge varies systematically, either by the length of the contacting time or by the electron affinity of the polymeric surface coating, was determined by both TOF SIMS and XPS techniques. Linear relationships with good correlation coefficients are consistently obtained between the negative toner charge and the relative $Cs^+$ density. The results indicate that the transfer of $Cs^+$ from the toner to the polymer-coated metal beads correlates to not only the sign but also the magnitude of the toner charge. This observation, along with the lack of humidity effect on toner charging, leads us to conclude that the model toner studied in this work is charged predominantly by an ion-transfer mechanism.

## Introduction

When two dissimilar materials are brought into contact or rubbed against each other, charge transfer occurs. This is the essence of contact charging and the phenomenon has been known for centuries. The contact charging between two dissimilar metals is well understood.[1] The direction and the amount of charge that is transferred between the two contacting metals are governed by the contact potential difference and the contact capacitance. In contrast, knowledge of the contacts between metal and insulator or between two different insulators is relatively poor.[1] Our interest in contact charging lies in its relevance to the xerographic process.[2] For instance, after charging and imagewise photodischarging a photoconductor, electrostatic latent images are formed. These electrostatic images are then developed using dry xerographic toner by means of electrostatic forces. The electrostatic charges are usually generated by a charging process which requires contacts between toner particles (an organic polymeric composite material) and polymer-coated metal beads inside a developer housing.[3] Fundamental understanding of the charging process would be beneficial not only for the development of better electrostatic control for xerographic marking but also for the design and synthesis of future improved toner materials.

Studies of contact charging involving organic materials have been documented. Cressman et al.,[4] Gibson,[5–7] Gibson et al.,[8,9] and Bigelow and co-workers[10] reported charge-transfer studies between a metal (nickel beads, ~250 $\mu$m in diameter) and polymer films consisting of substituted phenylazonaphthols, substituted salicylaldehydes, sulfonated polystyrenes, substituted polystyrenes, and substituted poly(olefins). Linear free energy relationships between the charge acquired in the polymer films and the Hammett substituent constant $\sigma$ were obtained in these studies, and an electron-transfer

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* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1995.

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model was inferred in analogy to the metal–metal contact model. Examples that deviated from the linear free energy relationship have been noted for polymers containing phenols, carboxylic acids, and ionic species.[6,7] Diaz and Guay[11,12] recently revisited the phenylazonaphthol and salicylaldehyde systems and suggested that the linear free energy relationship may be compatible with the ion (proton)-transfer mechanism. After all, the acidity of substituted phenylazonaphthols and salicylaldehydes should increase as $\sigma$ increases. The electron-transfer mechanism is further discredited because of the inconsistency between the sign of charging and the energetics of the electron-transfer process. Meanwhile, the involvement of ion transfer in the tribocharging of organic polymeric materials has been suggested for some time. For example, Medley[13] proposed the occurrence of proton and hydroxide anion transfers in acidic and basic resins when these resins were brought in contact. A similar acid–base interaction between two different modified silica surfaces was reported by Horn et al. very recently.[14] Along the theme of ion transfer, Mizes and co-workers[15] reported the detection of bromide ion transfer by secondary ion mass spectrometry between a cetylpyridinium bromide doped polystyrene film and an indium surface. Diaz and collaborators[16–19] reported the transfers of ions from ion-containing polymers to metal beads by X-ray photoelectron spectroscopy. Although ion transfers (from toner to metal beads) have been observed for toners containing molecular salts and the sign acquired by the toner correlates to the transfer of the ion, the conclusion on the ion-transfer charging mechanism is complicated by the simultaneous transfer of the entire molecular salt.[11,15,17] Information on (1) the accountability of the transferred ion to the toner charge and (2) the role of water in the charging process is required for the establishment of the charging mechanism.

In modern xerographic toner, organic salts ranging from 1 to 5 wt % are added in the toner as charge control additives (CCAs).[3] These additives, along with the polymer resin, the pigment, and other components are conventionally melt-mixed, extruded, jetted and classified to a toner of certain size. Recent data indicate that the tribocharging activity in this kind of toner is primarily from CCA molecules that are locating on the toner surface.[20] In this work, we synthesize a model xerographic toner by solution coating a CCA (cesium 3,5-di-*tert*-butylsalicylate, **CstBSA**) onto the surface of 9 $\mu$m (diameter) toner particles made of styrene–butadiene. The charge of the toner was generated by tumbling the toner particles with polymer-coated metal beads and was determined on a blow-off apparatus.[21] The surfaces of the toner particles and the polymer-coated metal beads were examined by time-of-flight secondary ion mass spectroscopy (TOF SIMS) and X-ray photoelectron spectroscopy (XPS). Evidence is provided that Cs$^+$ is transferred upon contact between the toner particles and the polymer-coated metal beads. A charging mechanism is proposed and discussed.

## Experimental Section

**Materials.** **CstBSA** was synthesized by neutralizing 3,5-di-*tert*-butylsalicylic acid (from Yoshitomi, Japan) with an equivalent amount of CsOH (99.9%, 50 wt % solution in water from Aldrich) and was purified by a Soxhlet extraction with ether (Fisher). Methanol was spectrograde from Fisher and was used as received. The toner was made of styrene–butadiene (90:10) and was prepared by a melt-extrusion and jetting process. It was classified to $\sim$9 $\mu$m. The beads ($\sim$130 $\mu$m in diameter) were prepared by powder-coating a mixture of poly(vinylidene fluoride) (tradename Kynar from Pennwalt) and poly(methyl methacrylate) (PMMA) at varying ratio on the surface of steel beads at a total weight loading of 0.7%.[22]

**Preparation and Evaluation of Model Toner.** The styrene–butadiene toner (12.5 g) was added into a 250 mL round-bottom flask containing 0.019 g of **CstBSA** in 100 mL of methanol. After stirring the suspension for half an hour, the solvent was removed on an evaporator. The resulting solid was vacuum dried, transferred to a 4-oz glass bottle and roll-milled with 35 g of $^1/_4$ in. steel shot for 30 min at a speed of 90 ft/min to yield $\sim$12.5 g of a white powder, the model CstBSA/styrene–butadiene toner.

A developer of the model toner was prepared by placing the polymer-coated metal beads (60 g) and the toner (1.25 g) inside a 2-oz glass bottle. It was then conditioned at 20 ± 4% RH inside a humidity-controlled glovebox overnight and sealed. The charge of the toner was generated by tumbling the toner particles and polymer-coated metal beads on a roll-mill for 60 min at a speed of 90 ft/min and was measured using the standard blow-off procedure inside a Faraday cage.[21]

**Analytical Techniques.** Time-of-flight secondary ion mass spectrometry (TOF SIMS) experiments were performed on a TOF SIMS spectrometer, Model TFS from Charles Evans and Associates, Inc. Samples, both beads and toners, were mounted onto silicon wafers using a thin layer of silver paint as an adhesive. The silicon wafers were precleaned with hexane before use. All analyses, in both spectral and imaging modes, were accomplished using a Ga ion gun which was operating at 15 kV in the microprobe mode.

X-ray photoelectron spectroscopy (XPS) studies were performed on a Kratos XSAM 800 electron spectrometer. The sample holder for the polymer-coated beads consisted of a piece of $1 \times 1$ cm$^2$ $\langle 100 \rangle$ silicon onto which Scotch brand double-sided tape was fixed. The beads were then poured onto the holder and were pressed repeatedly until the Scotch tape was completely covered with the beads. The coverage was verified by a stereomicroscope. The sample were illuminated with Mg K$\alpha$ X-rays at a power of 300 W (15 kV, 20 mA) under a background pressure between $2 \times 10^{-9}$ and $3 \times 10^{-8}$ Torr. Spectra were acquired at a low-energy resolution to achieve maximum sensitivity.

## Results

**Characterization of the Model CstBSA/Styrene–Butadiene Toner.** Figures 1 and 2 show the positive ion and negative ion mass spectra of **CstBSA** taken on our TOF SIMS spectrometer. Intense Cs$^+$ at *m/z* 133 and tBSA$^-$ at *m/z* 249 are observed in the respective

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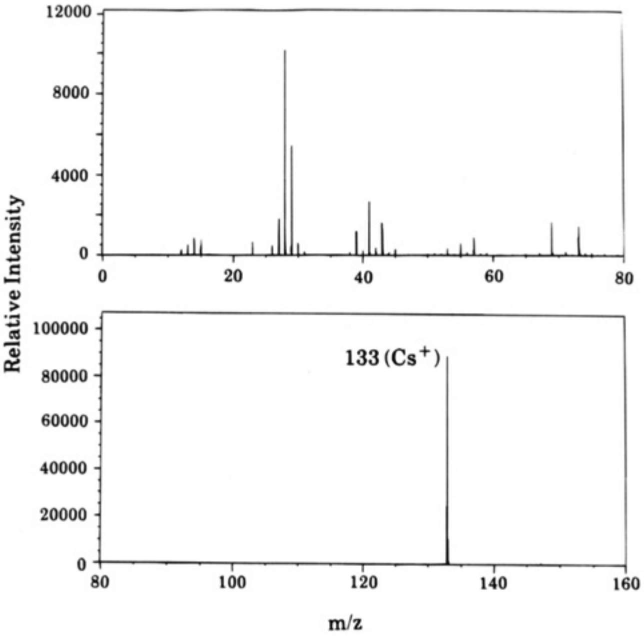

**Figure 1.** TOF SIMS positive mass spectrum of **CstBSA**.

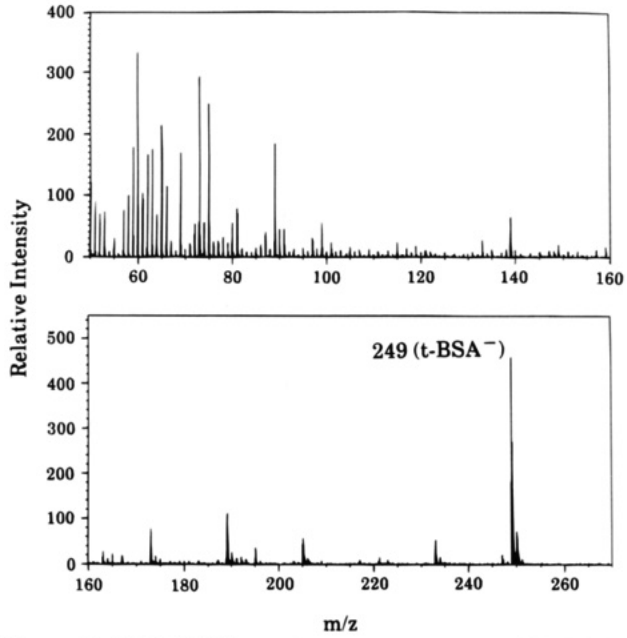

**Figure 2.** TOF SIMS negative mass spectrum of **CstBSA**.

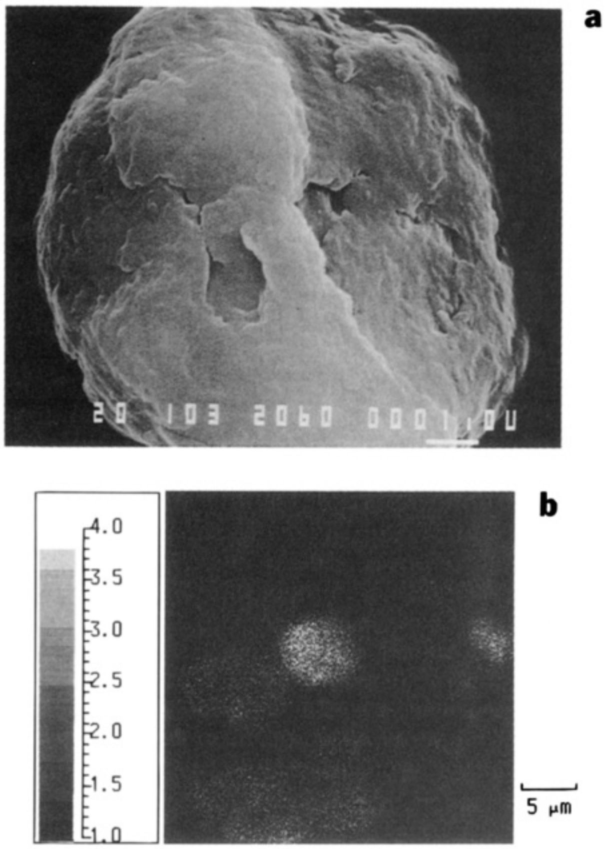

**Figure 3.** (a) SEM micrograph and (b) TOF SIMS image (from the $Cs^+$ ion) of the CstBSA/styrene−butadiene toner.

spectra. These data and the recording conditions are then used as references for the surface analyses of the toner particles and the polymer-coated metal beads.

The model CstBSA/styrene−butadiene toner was prepared by solution coating **CstBSA** onto the surface of 9 $\mu$m (diameter) styrene−butadiene toner particles in methanol. The concentration of **CstBSA** in the toner was ~0.15% by wt. Figure 3a shows a scanning electron micrograph (SEM) of the CstBSA/styrene−butadiene toner. The morphology of the toner is similar to that of the control, indicating that toner particles retain their integrity after the solution coating process. It is important to note that particles of **CstBSA** are observed neither in the toner sample nor on the toner surface. We have also examined the toner surface by the energy-dispersive X-ray analysis (EDXA) technique in the same electron microscope and failed to observe any Cs signal from the sample. The absence of the Cs signal is attributable to the low concentration of **CstBSA** in the toner, which is below the minimum detection limit of the EDXA technique. On the other hand, strong $Cs^+$ and $tBSA^-$ signals are observed in the positive ion and negative ion mass spectra, respectively, when the toner is examined by the much more sensitive TOF SIMS technique. Figure 3b shows a $Cs^+$ TOF SIMS image of the toner. Within the spatial resolution of the technique (0.2 $\mu$m), we can conclude that the toner is ~9 $\mu$m and $Cs^+$ ions are uniformly distributed on the toner surface. A similar toner image based on the $tBSA^-$ anion has been elusive. Although toner images were visible during experimentation, imaging them has been difficult owing to the buildup of electrostatic charges. Nevertheless, we conclude from the TOF SIMS results that **CstBSA** is uniformly distributed on the surface of the model toner.

**Tribocharging.** The tribocharging of the model toner was studied by first mixing the toner with polymer-coated metal beads inside a 2-oz glass bottle, followed by conditioning it at ~20% RH for 16 h. The toner was then charged by tumbling the toner particles with polymer-coated metal beads inside the 2-oz bottle on a roll-mill at a speed of 90 ft/min. The charge generated was determined by the standard blow-off technique.[21] Figure 4 shows the buildup of the negative toner charge as a function of the roll-milling time. The beads used in this experiment consisted of a Kynar/PMMA (20/80) surface coating (0.7 wt %). The results show that the toner acquires a negative charge rapidly upon contact with the beads. The charging process becomes saturated when the toner is rolled for ≥30 min. It is important to note that we have analyzed the bead

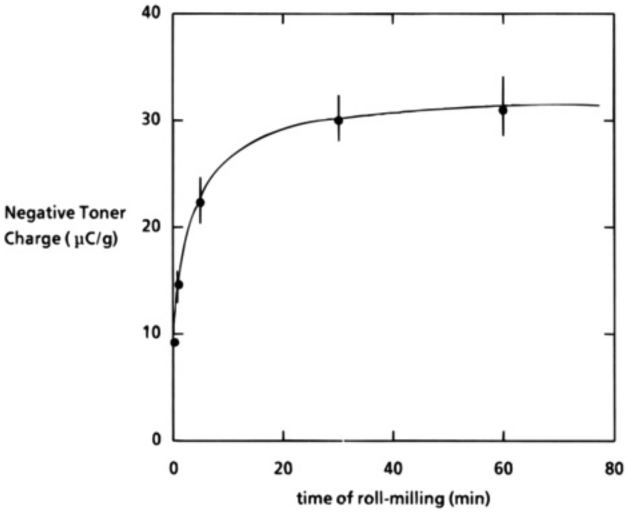

**Figure 4.** Plot of the generation of the negative toner charge as a function of roll-milling time.

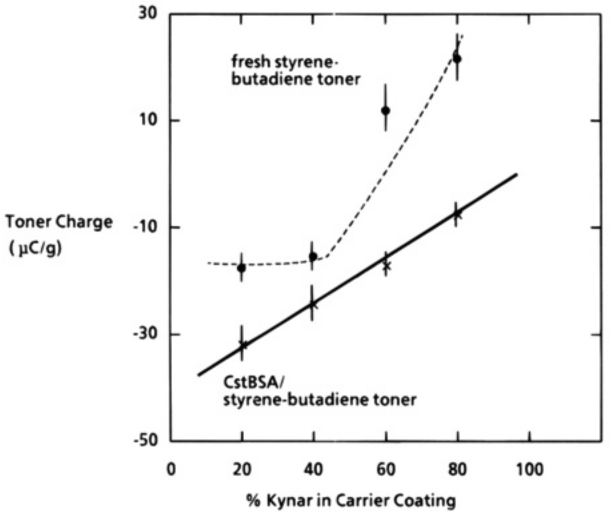

**Figure 5.** Plot of the charging of the CstBSA/styrene–butadiene toner against various Kynar/PMMA coated metal beads.

surface by X-ray photoelectron spectroscopy and found that the metal surface is essentially covered by the polymer coating. *In other words, the study in this work deals with contact charging between two dissimilar organic surfaces, not between an organic surface and a metal surface.*

The charging behavior of the model toner was examined by roll-milling the toner (60 min) against a series of polymer-coated beads with varying electron affinity. The electron affinity of the beads is varied by the ratio of the Kynar/PMMA surface coating, the higher the Kynar content the higher the electron affinity. It is expected that a surface with high electron affinity will drive the toner less negative (or positive) and vice versa.[3,22] Even though the Kynar/PMMA pair is designed for contact charging based on the electron-transfer model, there is recent evidence that the same driving force applies to the ion-transfer model.[11] The equilibrated charges acquired by the toner are plotted against the Kynar/PMMA ratio in the surface coating (Figure 5). The toner charges negatively against all beads, the negative charges increase monotonically as the Kynar/PMMA ratio decreases.

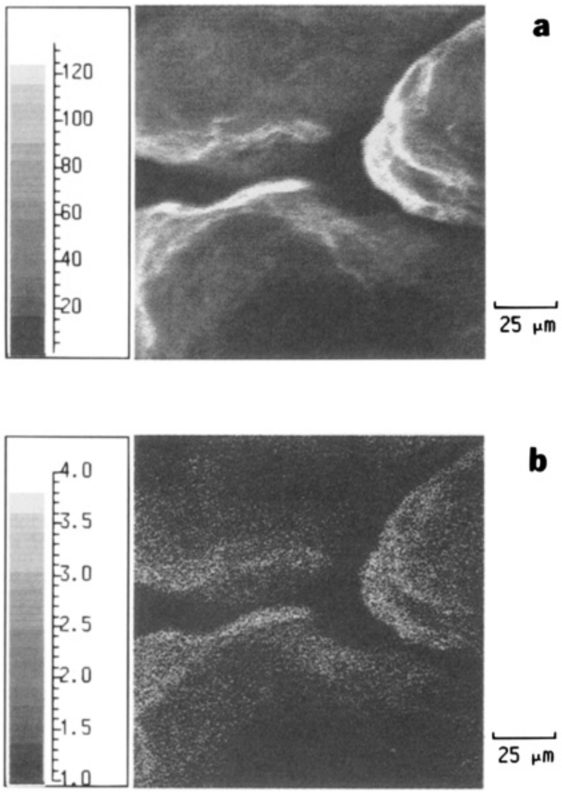

**Figure 6.** TOF SIMS images of polymer-coated metal beads recovered from the blow-off experiment: (a) from all cations; (b) from the Cs$^+$ ion.

A controlled experiment on the starting styrene–butadiene toner (Figure 5 dashed line) shows that it charges positively at high Kynar/PMMA ratios. The positive charge decreases and eventually becomes negative when the toner is rolled against beads with Kynar/PMMA ratios <40/60. Further decrease in the Kynar/PMMA ratio has very little effect on the charging. The difference in charging behaviors between the CstBSA/styrene–butadiene model toner and the control suggests that the added **CstBSA** on the toner surface dominates the charging of the model toner. The observation is consistent with the fact that **CstBSA** is on the toner surface and that contact charging of toner is a surface phenomenon.[1,20]

**TOF SIMS Studies.** After each blow-off experiment, the polymer-coated metal beads were recovered for surface analyses. For beads that were contacted with the CstBSA/styrene-butadiene toner, we detected a strong signal at $m/z$ 133, attributable to the Cs$^+$ ion. Figure 6a shows a total positive ion TOF SIMS image of a recovered bead sample (20/80 Kynar/PMMA surface coating). The TOF SIMS image of the same sample imaged from the Cs$^+$ ion is given in Figure 6b. An identical Cs$^+$ ion image is obtained, indicating that the Cs$^+$ ion is uniformly distributed on the surface of the beads after contact charging. The corresponding anion, tBSA$^-$ at $m/z$ 249, is absent in the negative mass spectrum (Figure 7). This observation along with the absence of Cs$^+$ in the beads recovered from the styrene–butadiene controlled experiment leads to the conclusions that (1) Cs$^+$ is transferred from the surface of the model toner to the surface of the polymer-coated beads preferentially; (2) transfer of **CstBSA** does not occur during the toner-bead contacts, or at least it is not a significant process under the experimental condition.

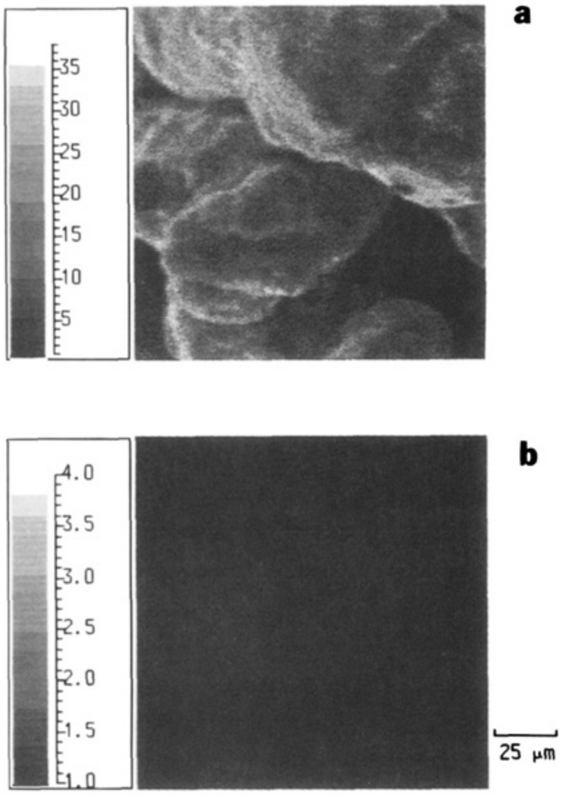

**Figure 7.** TOF SIMS images of beads recovered from the blow-off experiment: (a) from all anions; (b) from the tBSA$^-$ ion.

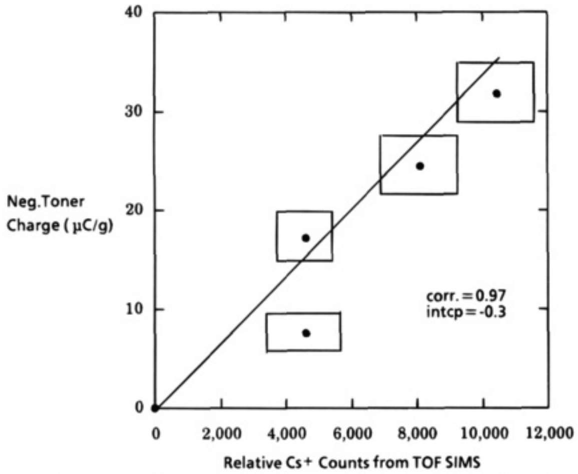

**Figure 8.** Plot of the negative toner charge versus the relative Cs$^+$ count on the surface of the recovered beads by TOF SIMS.

The four-bead samples in the toner charging experiment in Figure 5 were subjected to further analyses. We measured the relative Cs$^+$ density on the surface by integrating the Cs$^+$ signal collected within a given area over 3 min. The relative Cs$^+$ counts are then plotted as a function of the negative charge of the toner (Figure 8). A linear relationship with reasonable correlation (0.97) is obtained. The linear correlation suggests that the transferred Cs$^+$ correlates to not only the sign but also the magnitude of the toner charges. The intercept is close to zero, implying that the transfer of Cs$^+$ is primarily responsible for the tribocharging of the toner.

**XPS Studies.** The beads recovered in the experiments in Figures 4 and 5 were also studied by XPS. Strong Cs 3d signals were observed, whereas Cs signals were absent in the spectrum of the control beads. Due to the presence of the Kynar/PMMA surface coating, other signals such as $C_{1S}$, $O_{1S}$, and $F_{1S}$ were also detected. It is important to note that the main element from the core of the bead, Fe, is absent. Its absence suggests that the surface polymer coating covers the core very well. The atomic concentration of any element X on the surface, $C_x$, can be estimated by the following simplified expression:

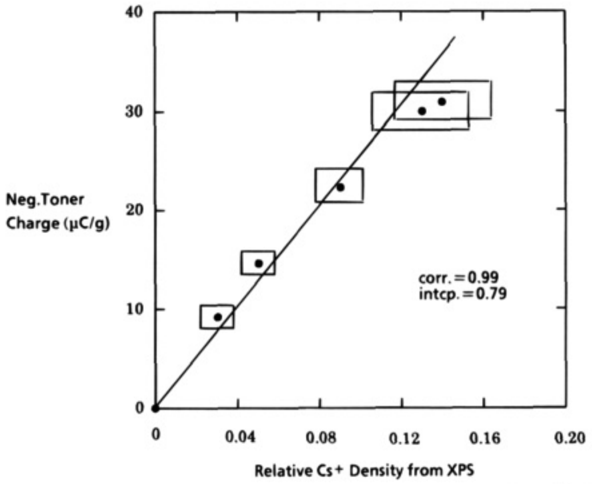

**Figure 9.** Plot of the negative toner charge versus the relative Cs$^+$ density on the surface of the recovered beads by XPS.

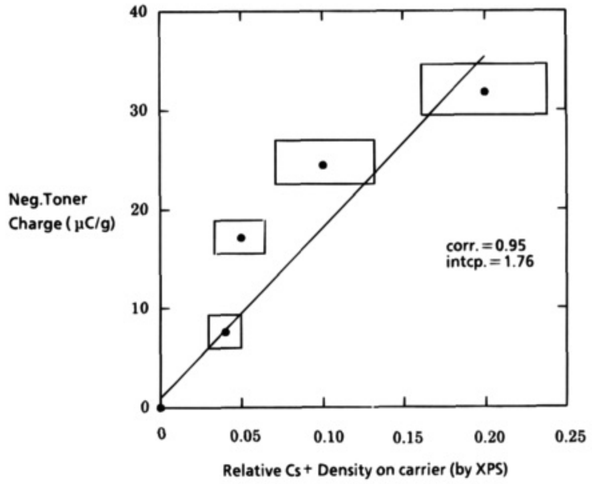

**Figure 10.** Plot of the negative toner charge versus the relative Cs$^+$ density on the surface of the recovered beads by XPS.

$$C_X = \frac{I_X/S_X}{\sum I_X/S_X}$$

where $C_X$ is the atom concentration of element X, $I_X$ is the peak area for the spectral line of X, and $S_X$ is the sensitivity factor for X.

The plots of the relative Cs$^+$ density on the surface of the beads, which is estimated as $C_X$ by the XPS technique, versus the negative charge on the toner for the experiments in Figures 4 and 5 are given in Figures 9 and 10, respectively. Linear relationships are obtained in both experiments. Again, these correlations suggest that the transfer of Cs$^+$ is responsible not only for the sign but also for the amount of charges on the toner. It is interesting to note that the correlation in Figure 9 is superior to that in Figure 10. The better correlation in Figure 9 may be attributable to the use of one kind of bead in the time-track experiment, where variations in the morphology of the beads and elemental content are minimal.

## Discussion

The difference in charging behavior between the CstBSA/styrene–butadiene toner and the control toner indicates that the added **CstBSA**, which is on the surface of the toner, dominates the charging of the model toner. Using the TOF SIMS technique, we demonstrate that $Cs^+$ transfers from the surface of the toner to the surface of the polymer-coated beads during contact charging. The $tBSA^-$ anion, an observable ion in the negative mass spectrum, was not detected. The results are different from those of Diaz and co-workers, who reported the transfers of ion as well as the entire molecular salt during contact charging between toner surfaces and metal beads.[11,17] We, however, show that the transfer of $Cs^+$ is preferential. We attribute the different results to the large difference in the mobility between the cation ($Cs^+$) and the anion ($tBSA^-$) in this work. TOF SIMS imaging further shows that the transferred $Cs^+$ ions distribute uniformly on the surface of the beads. The toner charges negatively as a result, correlating to the sign of ion transfer. The significance of this work lies in our ability to correlate not only the sign but also the magnitude of the ion-transfer process. We have analyzed the relative $Cs^+$ density on the surfaces of two series of beads from which the toner charges are varied systematically, either by the contacting time or by the electron affinity of the contacting surface. We show repeatedly that there exists good linear correlation between the negative toner charge and the relative density of $Cs^+$ on the surface of the beads. In addition, we have also performed our charging experiments at 80% relative humidity and found that both the negative toner charge and the amount of $Cs^+$ that is transferred are unaffected by the humidity charges.[23] The lack of a humidity effect suggests that water does not play a significant role in the charging process. We therefore conclude that the CstBSA/styrene–butadiene toner studied in this work is charged predominantly by an ion-transfer mechanism.

The operation of the ion-transfer charging mechanism is intuitively derived from the large mobility difference between the two ions in the organic salt. In principle, one can improve the efficacy of the charging process by increasing the mobility of the mobile ion. Indeed, we have systematically studied the counterion effect on the tribocharging process and found that the efficacy improves from $Cs^+ \rightarrow Rb^+ \rightarrow K^+ \rightarrow Na^+ \rightarrow Li^+$ for a series of metal di-*tert*-butylsalicylates.[24] The tribocharge acquired by the LitBSA/styrene–butadiene toner is about twice that of the CstBSA/styrene–butadiene toner under identical conditions.

In conventional toners, organic salts are frequently used in 1–5 wt % in the toner as charge control additives to dominate the charging of the toner. We, as well as Anderson et al.,[20] now show that these charge control additives operate on the surface of the toner. This demonstration is by no means surprising. After all, contact charging is a surface phenomenon. The fact that we are able to use 0.15 wt % of **CstBSA** to dominate the charging of the toner suggests that direct incorporation of the charge control additive on the surface would improve not only its effectiveness in charging but also the final material cost of the toner.

## Conclusion

Using a model CstBSA/styrene–butadiene toner, this work demonstrates that $Cs^+$ ions are preferentially transferred from the surface of the toner to another polymer surface (in the form of polymer-coated metal beads) during (toner) contact charging. The transfer of $Cs^+$ correlates to not only the sign but also the magnitude of the tribocharge acquired by the toner. This observation, along with the lack of a humidity effect on the charging process, leads to the conclusion that the model toner is predominantly charged by an ion-transfer mechanism.

**Acknowledgment.** The authors thank Mr. W. Niedzialkowski for the SEM micrograph described in this work and Drs. H. Mizes, E. Conwell, P. Julien, R. Lewis, and T. W. Smith for helpful discussions.

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[23] We observed that the charging of the CstBSA/styrene–butadiene toner is insensitive to the relative humidity: Law, K. Y.; Tarnawskyl, I. W., to be published.

[24] Law, K. Y.; Tarnawskyj, I. W.; Salamida, D.; Debies, T., manuscript in preparation.