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Effect of Counterion on the Tribocharging of Molecular-Salt Charge Control Agents in Xerographic Toners

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A series of model toners were prepared by a solution coating technique. The toner series consisted of equivalent amounts (4 μmol/g) of negative charge control agents (CCAs), 3,5-di-t-butylsalicylic acid (HtBSA) and its metal salts (MtBSA, M = Li, Na, K, Rb, Cs), on the surface of 9 μm unpigmented styrene–butadiene toner. The morphological properties of these CCAs in toner were studied by scanning electron microscopy, time-of-flight secondary ion mass spectrometry, and fluorescence spectroscopy. Results revealed that CCAs exist in a variety of physical states on the toner surface: from monomer for HtBSA to dimer or small aggregates for LitBSA to higher aggregates or small microcrystals for NatBSA, KtBSA, RtBSA, and CstBSA. Charging experiments showed that all the toners studied in this work charge negatively against polymer-coated metal beads and that ion-transfer is the major charging mechanism. A counterion effect on toner charging was observed. Specifically, the toner charge becomes less negative as the CCA changes from LitBSA → NatBSA → KtBSA → RbtBSA → CstBSA. The counterion effect was attributable to either a surface area effect or a thermodynamic effect on the ionization process. The HtBSA toner charged not only less negative but also at a slower rate. The anomalously low tribocharge and slow rate were emphasized in terms of a change in charging mechanism.

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Introduction

In modern xerographic toner, molecular salts ranging from 1 to 5% by weight are often added to the toner as charge control agents (CCAs) to control the charging characteristics of the toner.[1] The toner is usually prepared by melt-mixing the polymer resin with the colorant, the CCA, and other components, followed by extrusion, jetting, and classification. The charging is accomplished by tumbling toner particles with metal or polymer-coated metal beads inside the developer. The tribocharge generated is usually measured by the so-called "blow-off" technique inside a Faraday cage.[2] Recent data by Gutierrez et al.[3] and Anderson and coworkers[4] suggest that the efficacy of the CCA in charging becomes optimal when uniformly distributed in the toner. Guistina et al.[5] further demonstrated that triboactivity originates from CCA molecules locating on the toner surface. While the technological pursuit of molecular CCAs for toner applications has been extensive, relatively little attention has been paid to basic understanding of the charging process. Nevertheless, Mizes and coworkers[6] reported the detention of bromide ion-transfer by secondary ion mass spectrometry between a cetylpyridinium bromide doped polystyrene film and an indium surface. Diaz et al.[7–9] observed the transfer of mobile ions as well as entire molecular salts from toners containing molecular-salt CCAs to the surface of metal beads by x-ray photoelectron spectroscopy (XPS). The central issue required for proposing a charging mechanism is the accountability of the transferred ion to the toner charge for both sign and magnitude.

Using a model toner consisting of CstBSA (a negative CCA, 4 μmol/g) on the surface of 9 μm unpigmented styrene-butadiene toner particles, we were able to establish that ion (Cs^+) transfer is the predominant charging mechanism.[10] Time-of-flight secondary ion mass spectrometry (TOF SIMS) studies show that Cs^+ is transferred from the surface of the toner to the surface of the beads preferentially and that the amount of Cs^+ transferred correlates to the negative tribocharge. Here a systematic investigation on the tribocharging of 3,5-di-t-butylsalicylic acid (HtBSA) and its alkaline metal salts (MtBSA, M = Li, Na, K, Rb, and Cs) in styrene–butadiene toner is reported. Using TOF SIMS and XPS techniques, we show that ion-transfer is a general charging mechanism for all the MtBSA toners prepared in this work. A counterion effect is observed for the tribocharging process and the origin is discussed. The HtBSA toner is shown to charge anomalously. Evidence is provided that the anomaly resulted from the change in charging mechanism.

Experimental

Materials. 3-5-di-t-butylsalicylic acid (HtBSA) was purchased from Yoshitomo, Japan, and was used as received. The alkaline metal salts of HtBSA were prepared by neutralizing HtBSA with equivalent amounts of MOH (M = Li, Na, K, Rb, and Cs) in methanol. LitBSA was purified by a soxhlet extraction process with cyclohexane (Aldrich, Milwaukee, WI , 99%). KtBSA, RbtBSA, and CstBSA were purified analogously, except that anhydrous ether (Fisher, Pittsburg, PA) was used as the extracting solvent. NatBSA was purified by recrystallization from a mixture of ether and cyclohexane. Methanol was spectro grade from Fisher. The unpigmented styrene-buta-diene toner was prepared by a melt-extrusion and jetting process and was classified

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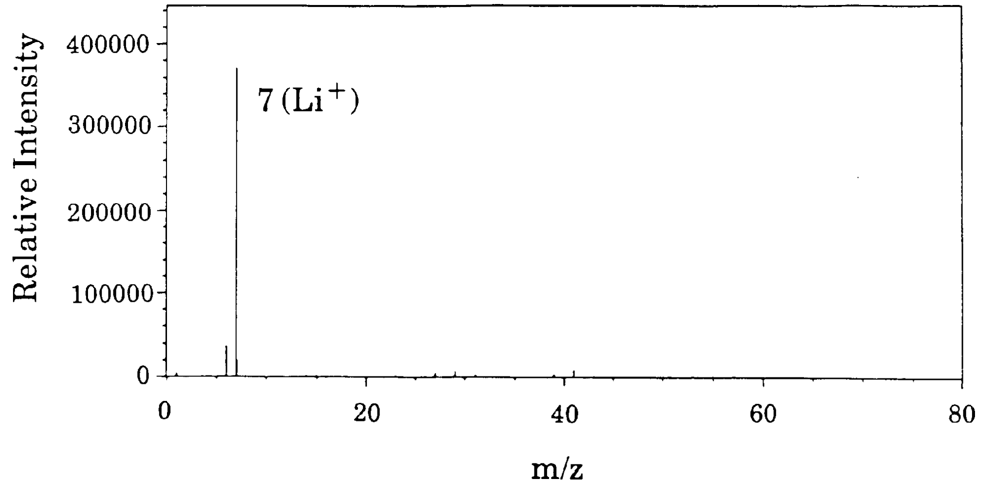


Figure 1. TOF SIMS positive mass spectrum of LitBSA.

to ~9 μm before use. The polymer-coated metal beads were made of steel core (~130 μm) and were[11] powder coated by a mixture of poly(vinylidene fluoride) (tradename Kynar from Pennwalt) and poly(methyl methacrylate) (PMMA) at varying ratios on the bead surface at a total weight loading of 0.7%.

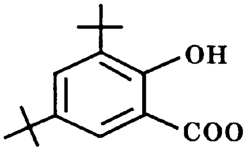
Toner Preparation and Evaluation. The model HtBSA/styrene-butadiene toner was prepared by adding the unpigmented styrene-butadiene toner (9 μm,12.5 g) into a 250 mL round-bottom flask containing 0.0125 g of HtBSA in 100 mL of methanol. After stirring the suspension for half an hour, methanol was removed on an evaporator. The resulting solid was vacuum dried and transferred to a 4-oz bottle and roll-milled with 35 g of 1/4″ steel shot for 30 min at a speed of 90 ft/min, yielding ~12.5 g of a white powder, the model HtBSA/styrene–butadiene toner.

Model toners containing various MtBSA salts were prepared by coating one of the following: LitBSA, NatBSA, KtBSA, RbtBSA, or CstBSA on the surface of the styrene–butadiene toner analogously with an equivalent amount of LitBSA (0.0128 g), NatBSA (0.0136 g), KtBSA (0.0144 g), RbtBSA (0.0167 g), or CstBSA (0.0191 g).

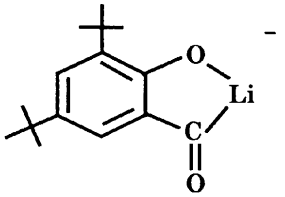
A developer was prepared by placing the toner (1.25 g) and the polymer-coated metal beads (60 g) inside a 2-oz bottle. The content was conditioned at a relative humidity (RH) of 22 ± 4% inside a humidity-controlled glove-box overnight and then sealed. The tribocharge was generated by roll-milling the developer for 1 to 2 h at a speed of 90 ft/min and was evaluated using the standard blow-off procedure.[2]

Surface Analytical Techniques. The surfaces of the toner particles and metal beads were examined by time-of-flight secondary ion mass spectrometry (TOF SIMS) and x-ray photoelectron spectroscopy (XPS). Details of the instruments, sample preparation procedures, and recording conditions were given in an earlier report.[10]

The fluorescence spectra of the model toners were taken on a Perkin-Elmer MPF66 fluorescence spectrophotometer interfaced with a computer Model 7700 from Perkin-Elmer. The spectra were recorded under front-face illumination, and the spectral response was corrected using the quantum counter-method with the RH101 solution supplied by Perkin-Elmer.[12]



m/z 249



m/z 255

Results

Preparation and Characterization of Model Toners. ***Preparation***. Metal 3,5-di-t-butylsalicylates (MtBSA, M = Li, Na, K, Rb, and Cs) were prepared by neutralizing HtBSA with metal hydroxides in methanol. They are white powder solids. Figures 1 and 2 show the positive ion and negative ion mass spectra of LitBSA recorded on our TOF SIMS spectrometer. An intense ion peak at m/z 7, attributable to Li$^+$, is observed in the positive mass spectrum. In the negative TOF SIMS mass spectrum, in addition to tBSA– at m/z 249, a negative complex formed between the tBSA dianion and Li$^+$ at m/z 255 is observed. Other MtBSA salts, e.g., NatBSA, KtBSA, RbtBSA, and CstBSA, show the anion tBSA– at m/z 249 primarily in their negative mass spectra. The spectra for CstBSA are given in an earlier report.[10] The recording conditions for these experiments are then used to analyze the surfaces of the toner particles and the recovered metal beads in this work.

Model toners containing HtBSA and MtBSA salts were prepared by solution coating the CCAs on the surface of unpigmented styrene–butadiene toner particles (9 μm) in methanol. The concentration of the CCAs is 4 μmol/g, enabling fair comparison of their charging properties.

Examinations of the prepared toners by scanning electron microscopy reveal that the size of the toner is ~9 μm and the solution coating process does not seem to have an effect on the morphology of the toner. Note that particles of the CCAs are neither observed on the toner surface nor between toner particles. But intense metal ion peaks from Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ are obtained when the toners are studied by the TOF SIMS technique. Figure 3 shows a typical toner image obtained by TOF SIMS imaging for the LitBSA toner. Within the resolution of the experiment (~0.2 μm), we can conclude that the toner is ~9 μm and Li$^+$ ions are uniformly distributed on the toner surface. The anion tBSA– at 249 is observed in the negative mass spectra of all the model toners. A toner image based on

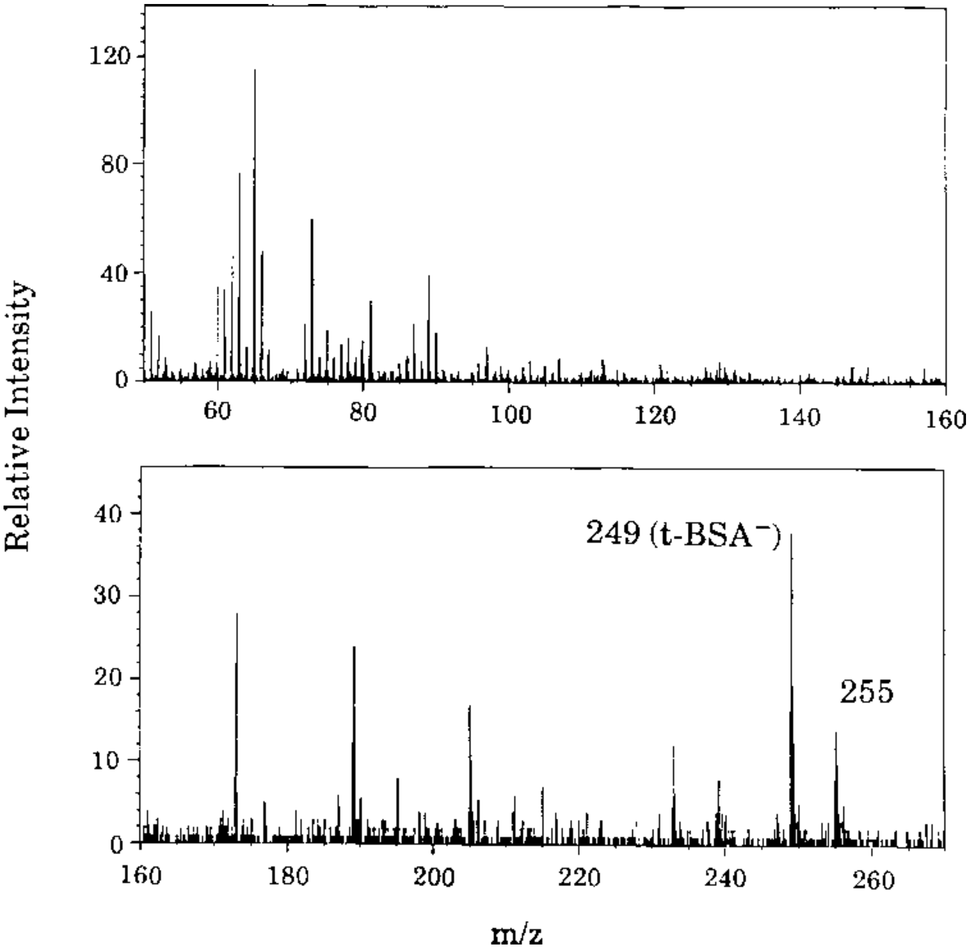


Figure 2. TOF SIMS negative mass spectrum of LitBSA.

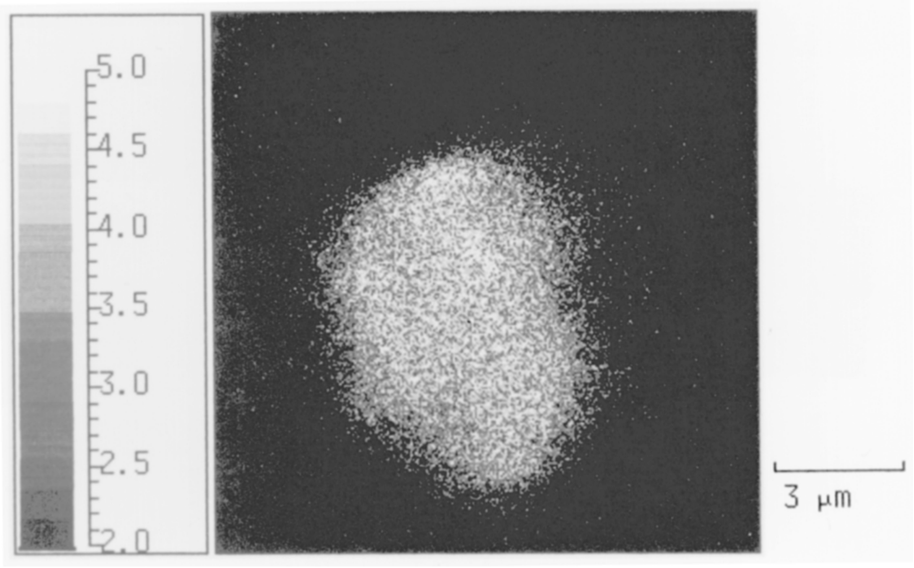


Figure 3. A TOF SIMS image (from Li^+) of the LitBSA styrene–butadiene toner.

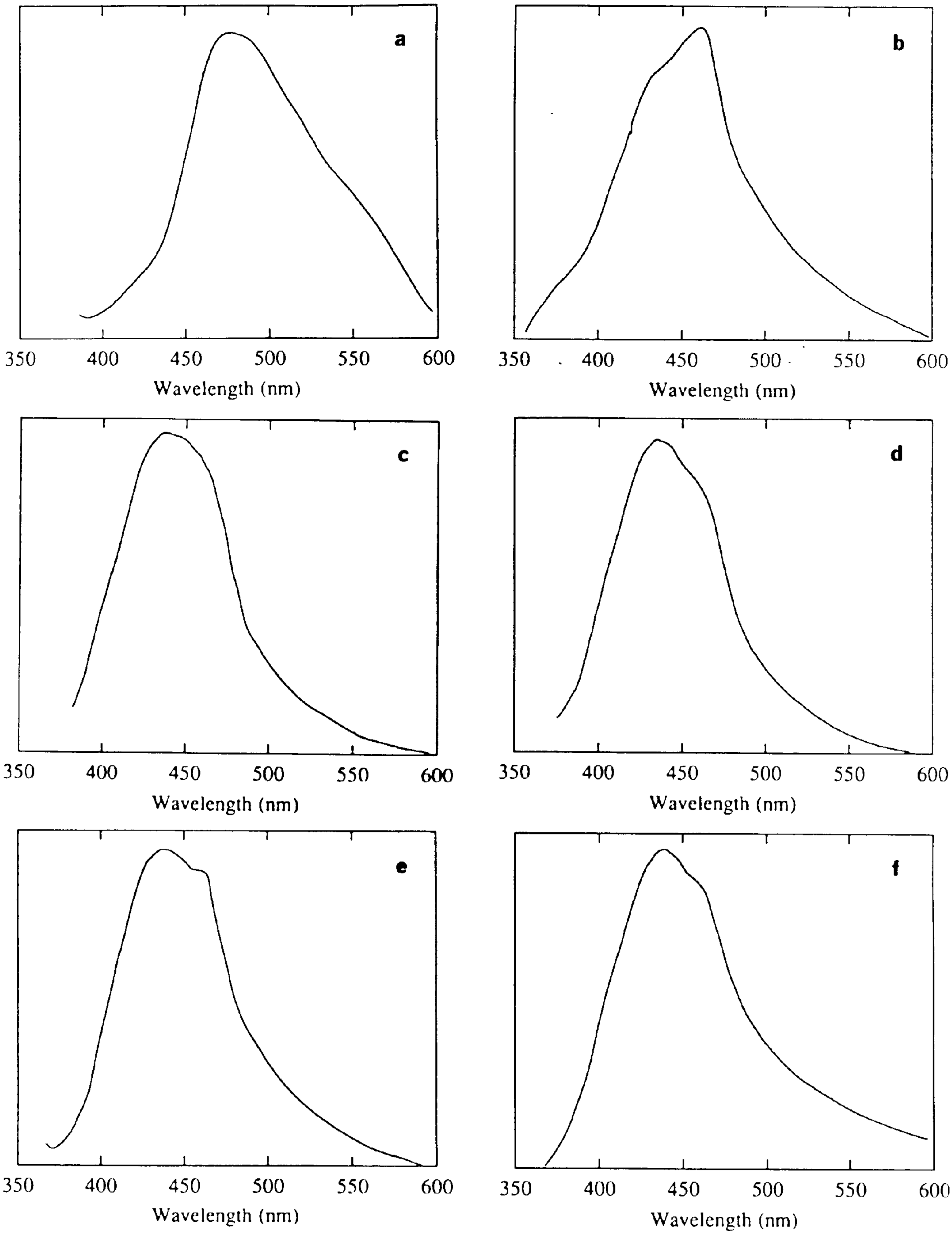


Figure 4. Fluorescence spectra of (a) HtBSA, (b) LitBSA, (c) NatBSA, (d) KtBSA, (e) RbtBSA, and (f) CstBSA on the surfaces of styrene-butadiene toner particles.

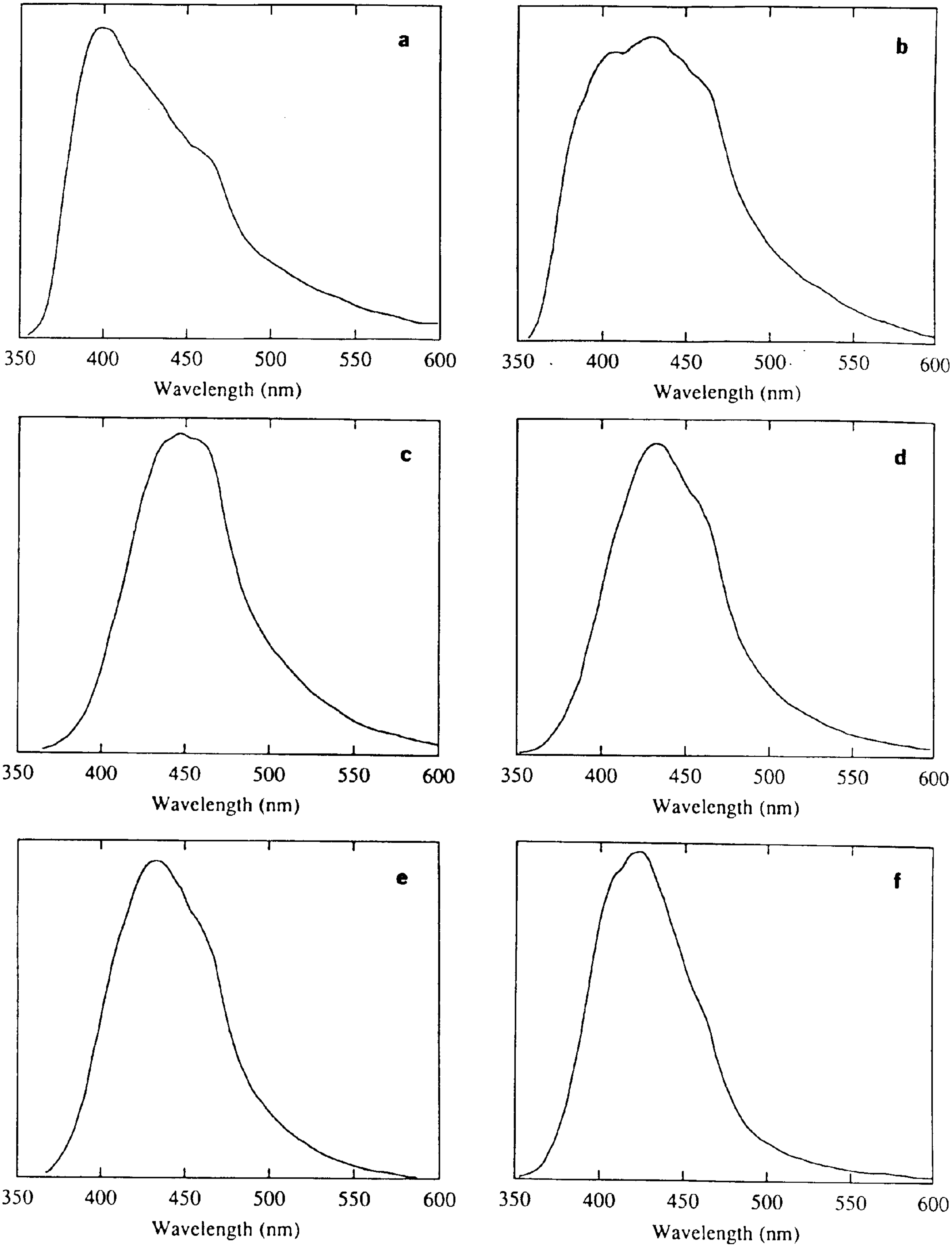


Figure 5. Fluorescence spectra of (a) HtBSA, (b) LitBSA, (c) NatBSA, (d) KtBSA, (e) RbtBSA, and (f) CstBSA solid powders.

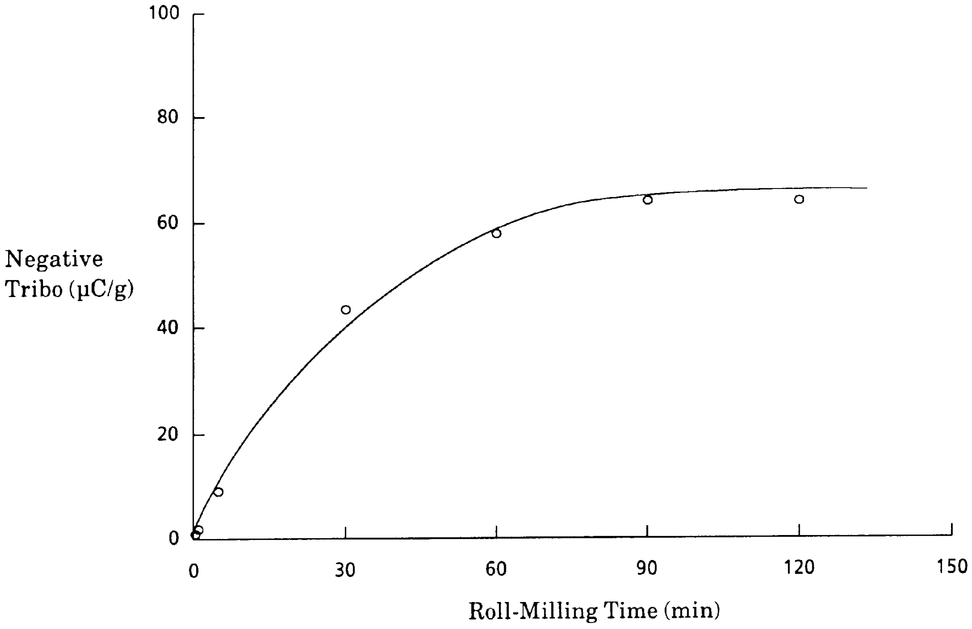


Figure 6. Effect of roll-milling time on the generation of negative tribo from the HtBSA styrene–butadiene toner.

the tBSA– anion is unobtainable however because of the mobility of the toner particle under negative-ion imaging conditions. Nevertheless, we conclude that the CCAs studied in this work are uniformly distributed on the surface of the model toners.

Fluorescence Studies. HtBSA and MtBSA are highly fluorescent materials.[12] In this work, we attempt to study the molecular detail of these CCAs on the toner surface using fluorescence spectroscopy. Figures 4(a) through 4(f) show the fluorescence spectra of HtBSA, LitBSA, NatBSA, KtBSA, RbtBSA, and CstBSA on the toner surfaces, respectively. Figures 5(a) through 5(f) show the fluorescence spectra of the respective solid powders. Because all the fluorescence spectra were taken under similar conditions, the result in Fig. 4(a) suggests that the emission of HtBSA on the toner surface is significantly different from other MtBSA toners. While HtBSA exhibits a fluorescence maximum (λ_F) at ~460 nm, both λ_F and the shape of the emission band are different from the solid powder emission in Fig. 5(a). In fact, the HtBSA fluorescence spectrum on the toner surface is analogous to that of the monomer in hydrocarbon solvent.[12] We hence conclude that HtBSA exists as a monomer on the toner surface. The observed lower fluorescence intensity for the HtBSA toner is consistent with the spectral assignment because the fluorescence quantum yield of HtBSA is known to be lower than that of LitBSA due to the rapid radiationless decay caused by the acidic proton.[12] The total surface area for the 9 μm styrene–butadiene toner can be estimated[13] to be ~9 × 10^{19} Å^2/g. The surface area for the toner turns out to be ~9 times larger than the total area required for HtBSA if we assume that every HtBSA molecule lays flat on the toner surface.* The fact that HtBSA exists as a monomer on the toner surface merely indicates that the interaction between HtBSA and the toner surface is stronger than that of dimerization at the concentration studied.

The fluorescence spectrum for the LitBSA toner [Fig. 4(b)] is different from those of the LitBSA solid [Fig. 5(b)] and the monomer in cyclohexane (λ_F 460 nm).[12] We suggest that LitBSA exist either as a dimer or small aggregates on the toner surface.

Comparisons of the emission spectra in Figs. 4(c) through 4(f) with those in Figs. 5(c) through 5(f) reveal remarkable similarity. We conclude that NatBSA, KtBSA, RbtBSA, and CstBSA are probably in the form of higher aggregates or very fine microcrystals on the toner surfaces. If these CCAs are fine microcrystals, their sizes must be smaller than 500 Å, otherwise they would have been detected by scanning electron microscopy.

Charging Studies of Various Model Toners. The charging properties of the model toners were studied by first mixing the toner with the polymer-coated metal beads inside a 2-oz bottle, conditioning the content at ~20% RH for 12 to 20 h, and followed by tumbling the toner particles with the beads on a roll-mill at 90 ft/min. The tribocharge was generated during these toner-bead contacts and was determined by the blow-off technique.[2] Figure 6 shows the build-up of the negative toner charge as a function of the roll-up time for the HtBSA/styrene–butadiene toner. Figure 7 shows the build-up of the negative charges for the LitBSA, NatBSA, KtBSA, RbtBSA, and CstBSA toners as a function of the roll-up time. The polymer-coated metal beads used in these experiments were ~130 μm in size, made of steel, and consisted of a Kynar/PMMA (20/80) surface coating (0.7% by weight). Comparison of the results in Figs. 6 and 7 indicates that the charging rate of the HtBSA toner is about 2 times slower than those of the MtBSA toners. While it takes the HtBSA toner ~60 min to reach the equilibrated tribo level, the MtBSA toners can acquire the equilibrated charges within 30 min.

The charging behaviors of all the model toners were examined by roll-milling them against a series of beads of varying electronegativity. The roll-up times for the HtBSA and MtBSA toners were 2 and 1 h, respectively. The electronegativity of the bead surface was adjusted by variation

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* Molecular modeling suggests that each HtBSA molecule should occupy ~30 Å^2 if it lays flat on the toner surface.

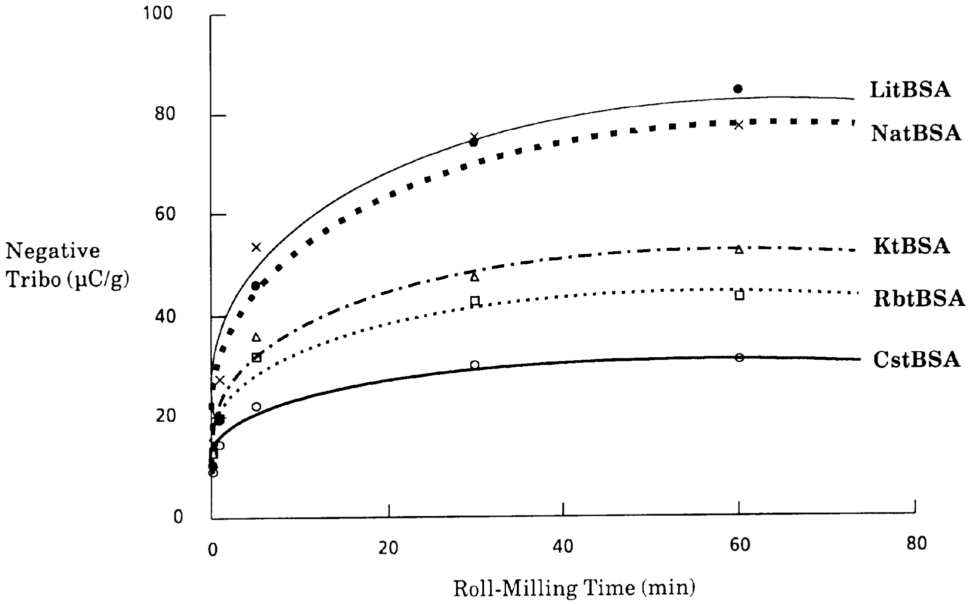

Figure 7. Effect of roll-milling time on the generation of negative tribos from various MtBSA styrene–butadiene (M = Li, Na, K, Rb, Cs) toners.

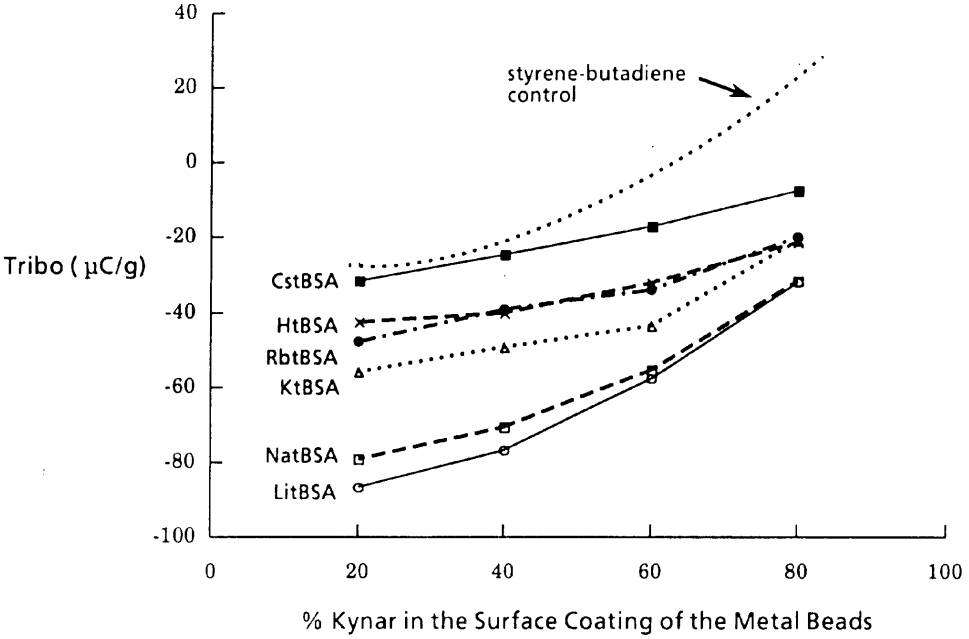

Figure 8. A tribo plot for various model toners.

of the Kynar/PMMA ratio in the surface coating, and the higher the Kynar content, the higher the electronegativity. Tribo data are plotted in Fig. 8. The results show that all the toners charge negatively against the beads used and that the negative charge increases monotonically as the Kynar/PMMA ratio decreases. A controlled experiment studying the tribo behavior of the styrene–butadiene toner was performed under identical conditions (Fig. 8). The styrene-butadiene toner was shown to charge positively at high Kynar/PMMA ratios (60/40 and 80/40) and charge negatively when the Kynar/PM MA ratios were 20/80 and 40/60. The difference in charging behavior between the HtBSA and MtBSA toners and that of the control suggests that the added CCAs in the model toners drive the toner to charge negatively and that the CCAs dominate the charging behavior of the toners.

Surface Analses of the Recovered Polmer-Coated Metal Beads. After each blow-off experiment, the beads were recovered for surface analyses by both TOF SIMS and XPS techniques. With the exception of the beads recovered from the HtBSA/styrene-butadiene experiment, which was not analyzable, intense ion peaks corresponding to the cations were observed in the positive TOF SIMS mass spectra for beads recovered from the LitBSA, NatBSA, KtBSA, RbtBSA, and CstBSA experiments. The intensities of these cations in the positive mass spectra

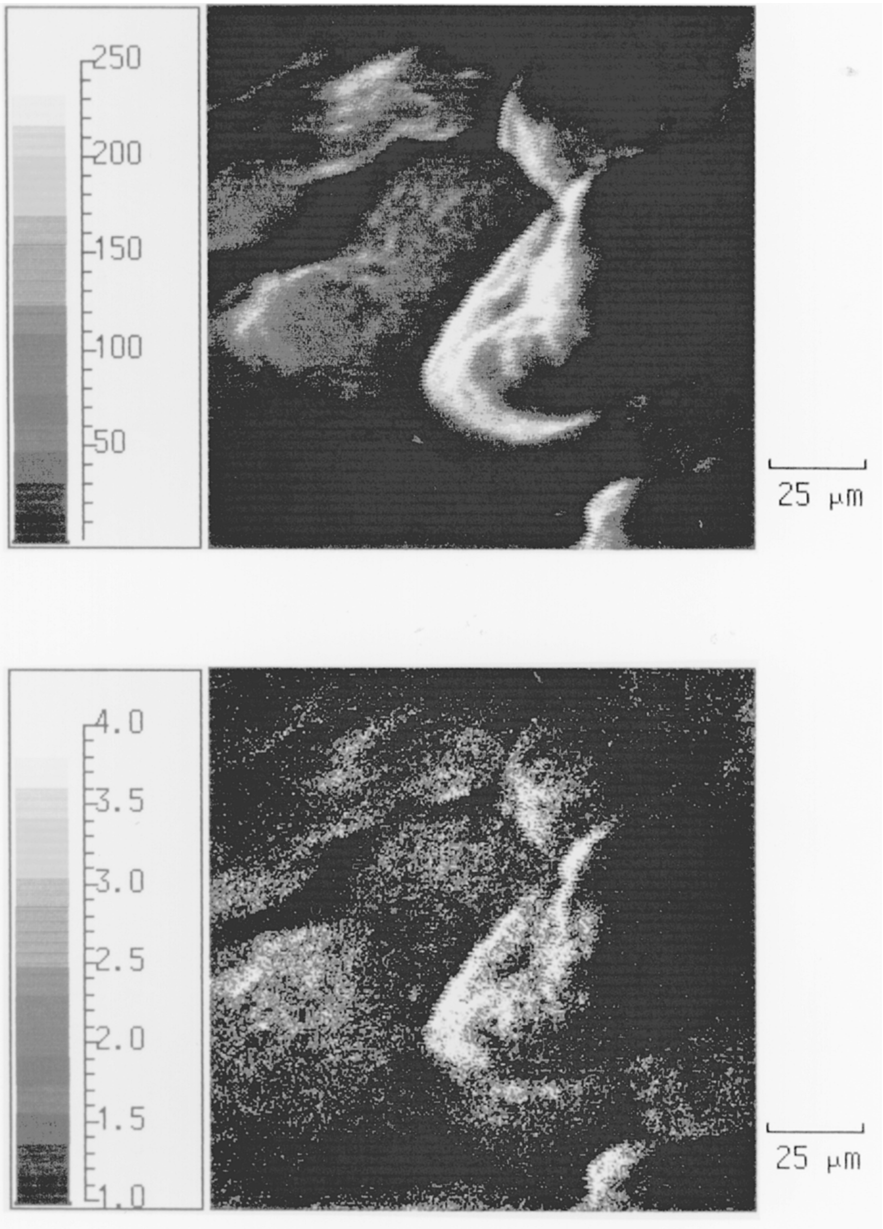

Figure 9. TOF SIMS images of polymer-coated metal beads recovered from the LitBSA toner experiment (a) from all cations; (b) from Li·.

were significantly higher than the starting beads or the background, suggesting that the cations transferred from the surface of the toner to the surface of the beads during toner–bead contact. A similar conclusion can also be reached for the NatBSA, KtBSA, RbtBSA, and CstBSA experiments according to XPS analyses. The ion-transfer process is found to be preferential, because the tBSA– anion at m/z 249 is absent in the negative TOF SIMS mass spectra of all the recovered bead samples.

Figure 9(a) shows the TOF SIMS total positive-ion image for the beads recovered from the LitBSA toner experiment. The same bead sample imaged from Li^+ is given in Fig. 9(b). Identical bead images were obtained, suggesting that Li^+ distributes uniformly on the bead surface. Similar ion images were also obtained from the beads recovered from the NatBSA, KtBSA, RbtBSA, and CstBSA toner experiments. The ion images for the CstBSA experiment are in an earlier report.[10]

Discussion

Toner Charging Mechanism. Comparison of the charging behavior of the HtBSA and MtBSA (M = Li, Na, K, Rb, and Cs) toners with that of the styrene–butadiene control clearly shows that the added CCAs on the toner surface dominate the charging of the toner. With the exception of the HtBSA toner, which is not analyzable by the surface techniques used in this work, we consistently demonstrate that a transfer of the cation occurs, e.g., Li^+, Na^+, K^+, Rb^+, and Cs^+, from the surface of the toner to the surface of the polymer-coated metal beads during toner–bead contacts (or toner charging). The transfers of Na^+, K^+, Rb^+, and Cs^+ are also detected by the XPS technique. The transfer of the cation occurs preferentially. For example, we have not been able to detect the anion tBSA– at m/z 249 in any of the recovered bead samples. Our results, thus, suggest that transfer of molecular salts (MtBSAs) is not a significant

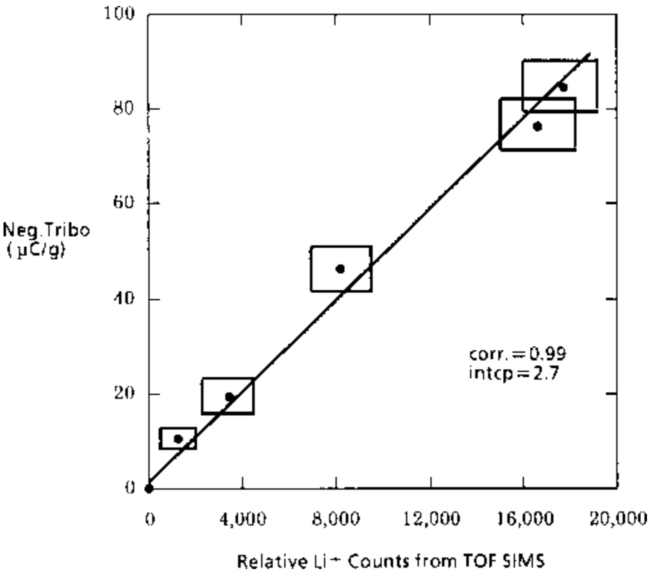

Figure 10. Plot of the negative tribo of the LitBSA toner versus the relative Li⁺ counts on the surface of the recovered beads (by TOF SIMS).

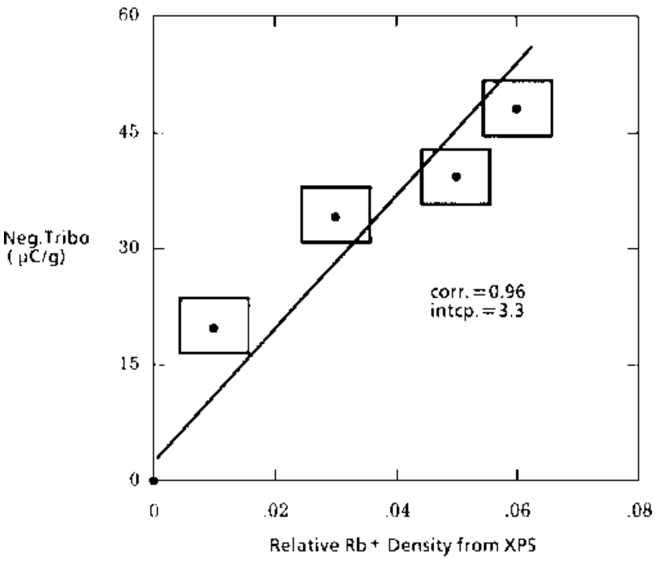

Figure 11. Plot of the negative tribo of the RbtBSA toner versus the relative Rb⁺ density on the surface of the recovered beads (by XPS).

process during toner charging. Our finding is different from the results obtained by Diaz and coworkers who reported on ion as well as salt transfer for toners containing molecular salts.[7–9] We attribute our results to the large mobility difference between the cations and the bulky tBSA– anion.

All the model toner charged negatively as a result of the toner–bead contacts. The sign of the toner charge corresponded to the transfer of the cation. In this work, the charge versus ion issue was studied by a correlation between the tribo acquired by the toner and the ion density on the surface of the bead. Figure 10 shows a plot of the toner tribo generated in the time-track experiment for the LitBSA toner (Fig. 7) as a function of the relative Li^+ density on the surface of the recovered bead as estimated by the TOF SIMS technique. A linear relationship with excellent correlation coefficient (0.99) was obtained. The intercept was very small, suggesting that the transferred Li^+ accounts for most of the toner charge. While analogous in-depth analysis for the beads recovered from the NatBSA and KtBSA experiments were masked by the relatively high background of Na and K in the ambient, we performed similar analyses, by both TOF SIMS and XPS, for the beads recovered from the CstBSA experiments and similar results were obtained.[10] To show the generality of the observation, Fig. 11 shows the plot of the negative tribo of the RbtBSA experiment (in Fig. 8) as a function of the relative Rb^+ density on the recovered beads (estimated by XPS). Another good correlation was obtained. The preferential cation transfer and the numerous tribo to ion density correlations has lead us to conclude that ion-transfer is the charging mechanism for the model toners studied in this work.

Counterion Effect. The results in Figs. 6 through 8 show a counterion effect occurs on toner charging. The effect is illustrated in Fig. 12 using the tribo values obtained from the beads with a 20/80 Kynar/PMMA surface coating. The negative tribo increases as the cation in the CCA changes from Cs^+ to Rb^+ to K^+ to Na^+ to Li^+. The HtBSA toner is an exception and will be discussed in the next section. Because the mobility of the cation also increases in the same direction, it is very tempting to interpret the counterion effect based on ionic mobility. However, if ionic mobility is a contributing factor to toner charging, it should have an effect on the charging rate too. As seen in the time-track plots in Fig. 7, there does not seem to be any counterion effect on the charging rate.

TABLE I. Solubility of MtBSAs in Heptane and Aggregated States of MtBSAs in Styrene–Butadiene Toner

MtBSA	Saturated solubility in heptane	State of aggregation
HtBSA	$>6.9 \times 10^{-3}$ M	Monomer
LitBSA	$<5 \times 10^{-6}$ M	Dimer or small aggregates
NatBSA	$<1.5 \times 10^{-6}$ M	Higher aggregates or microcrystals
KtBSA	$<10^{-6}$ M	Higher aggregates or microcrystals
RbtBSA	$<10^{-6}$ M	Higher aggregates or microcrystals
CstBSA	$<5 \times 10^{-7}$ M	Higher aggregates or microcrystals

To comprehend the counterion effect, we studied the solubility of all the CCAs used in this work in a hydrocarbon solvent (heptane). The data are tabulated in Table I, along with the aggregated state of the same material on the toner surface as studied by fluorescence spectroscopy. The solubility of the CCAs decreased from HtBSA → LitBSA → NatBSA → KtBSA → RbtBSA → CstBSA. At the same time the tendency for the CCA to form high aggregates or microcrystals increased. Because toner charging by molecular CCA is a surface phenomenon,[3–5] its efficacy should increase as its effective surface area on the toner surface increases. According to the aggregated state revealed by fluorescence, the relative surface area for MtBSA on the toner surface decreased from LitBSA → NatBSA → KtBSA → RbtBSA → CstBSA. The decrease in tribo, which is in the same direction, suggests that the counterion effect in Fig. 12 may simply be a matter of variations in the effective surface area of the CCA.

Alternatively, the counterion effect may be rationalized based on the thermodynamics of the ion-separation process. For instance, the crystallization energy of the MtBSA CCAs can be expressed as

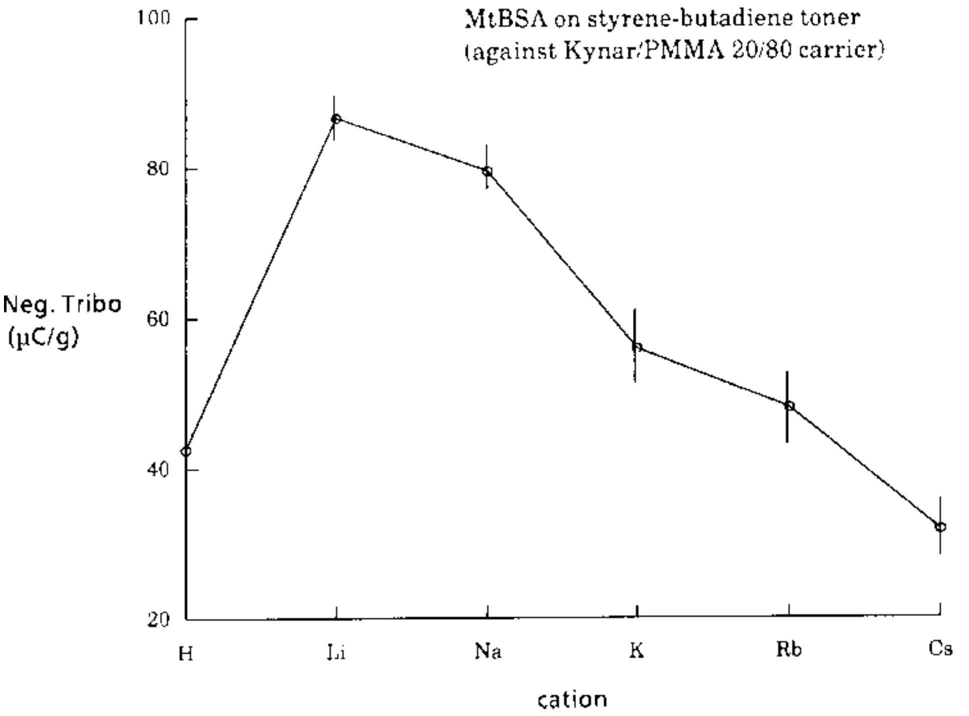

Figure 12. A plot of the tribocharges of all model toners against the cations in the CCAs.

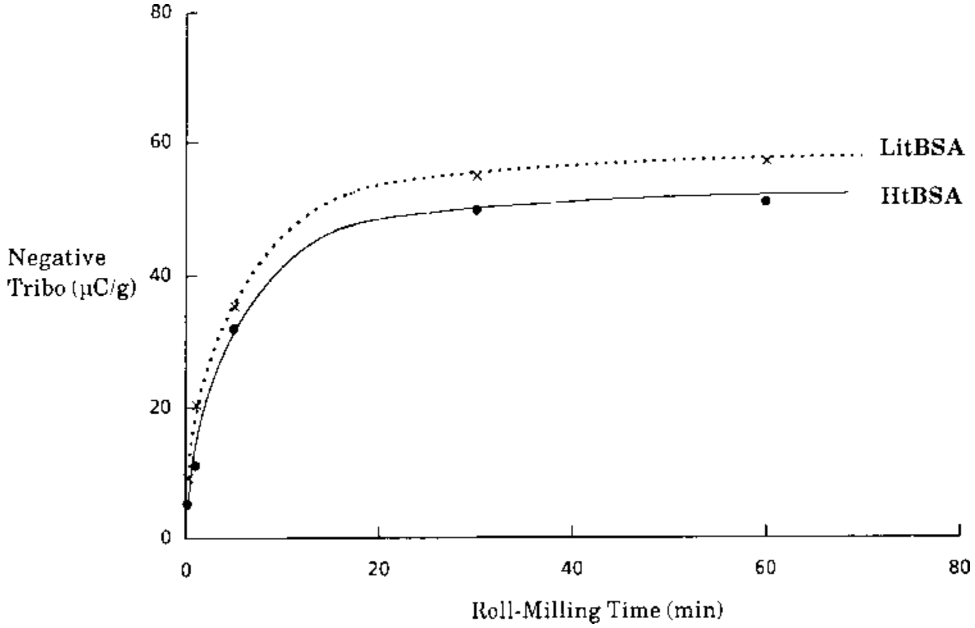

Figure 13. Effect of roll-milling time on the tribo generations of the HtBSA and LitBSA toners at 80% RH [against polymer-coated metal beads with a Kynar/PMMA (20/80) surface coating].

$$\text{crystallization energy} = \Delta H_{\text{electrostatic}} + \Delta H_{\text{Van der Waals}}.$$

The Van der Waals interaction is expected to be dominated by interactions between the tBSA groups and should be very similar among all the MtBSA salts. The decrease in solubility as the size of the cation increases (Table I) suggests that the electrostatic interaction between the cation and the anion increases in the following order: LitBSA → NatBSA → KtBSA → RbtBSA → CstBSA. Because the ion-transfer mechanism requires the separation of the cation from the anion during contact charging, the efficacy of the charging process should decrease when the electrostatic interaction is strong. Consequently, the observed counterion effect may be attributable to the thermodynamics of the ion-separation process. At present, we do not have enough information to differentiate the above two possibilities.

Ionic versus Covalent Charging. According to Table I, HtBSA should have the largest surface area on the toner surface. Incidentally, it also has the most mobile cation, the proton. Therefore, if the counterion effect is operating, the HtBSA toner should have the highest negative tribo among all the toners studied. Experimentally, the equilibrated tribo for the HtBSA toner was lower than that of the LitBSA toner and only comparable to the KtBSA toner whose mobile ion is significantly larger than a proton or a hydrated proton. In addition to the anomalously low toner charge, the charging rate was 2 times slower than other MtBSA toners (Figs. 6 and 7). We attribute the unexpected charging results for the HtBSA toner to the change in the charging mechanism. While the ion-transfer mechanism is expected to operate according to the tribo plot in Fig. 8, the charging in the HtBSA toner involves the dissociation of a proton from the carboxylic acid group. We suspect that the breaking of the covalent, polar O–H bond, which is different from ionic dissociation, is responsible for the low charging rate and the anomalously low tribocharge. To support the hypothesis, we studied the charging of the HtBSA and LitBSA toners at 80% relative humidity. A plot for the generations of the negative tribos as a function of the roll-milling time is provided in Fig. 13. Both toners were shown to charge less efficiently at 80% relative humidity, and this is attributed to the humidity effect on electrostatic charging. The most significant observation in Fig. 13 is the 2 times rate increase for the HtBSA toner at 80% RH relative to that at 20% RH, contrasting to the insensitivity of the charging rate observed for the LitBSA toner. We propose that water molecules enhance the rate of toner charging in the HtBSA toner because they are known to be capable of assisting the ionization of carboxylic acid groups.† The involvement of water in toner charging under similar conditions has been reported by Pence and coworkers lately.[14]

Conclusions

This work demonstrates that ion-transfer is the major charging mechanism in styrene–butadiene xerographic toners containing 3,5-di-t-butylsalicylic acid or metal 3,5-di-t-butylsalicylates (M = Li, Na, K, Rb, and Cs) as charge control additives on the toner surface. A counterion effect on toner charging is observed, the toner charges less negative as the CCA changes from LitBSA → NatBSA → KtBSA → RbtBSA → CstBSA. Evidence is provided that the counterion effect is either a surface area effect or a thermodynamic effect on the ionization process. The HtBSA toner is found to charge not only less negative but also at a slower rate. Charging results at 80% relative humidity suggest that the anomalously low tribo and slow rate may be due to the change in charging mechanism from dissociation of the ionic bond in MtBSA to dissociation of a proton from the carboxylic acid group in HtBSA.

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† At high humidity, water molecules become abundant on the surface of the metal beads. These water molecules probably facilitate the following ionization reaction: $HtBSA + H_2O \rightarrow tBSA^- + H_3O^+$.