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Effect of Coating Solvent on the Morphology and Charging Properties of Charge-Control-Agent-Modified Silicas in Toners

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Molecular charge control agents (CCAs) of different physical states, ranging from molecular adsorption on the silica surface to particulate mixture with silica particles, were prepared by treating a hydrophobic silica (Aerosil R972 from Degussa), with various CCA coating solutions. The CCAs studied are 3,5-di-t-butylsalicylic acid (t-BSA), potassium bis(3,5-di-t-butylsalicylato)borate (LR120), and potassium tetraphenylborate (KTPB). The physical states of the CCAs in the silica samples are controlled by careful manipulation of the coating solvent (system). The models and assumptions used in the solution coating experiments are discussed and are verified in the case of t-BSA. Studies of the charging properties of the synthesized CCA-modified silicas in styrene-butadiene toner against a series of polymer-coated metal beads show that higher toner charges and shorter admix times are consistently obtained when the CCA is molecularly adsorbed on the silica surface. Since the surface area of the CCA is largest when it is molecularly adsorbed on the silica surface, the high toner charge obtained when these surface modified silicas is incorporated in toner is attributable to a surface area effect. The short admix time can also be attributed to the surface area effect, either due to the rapid charging or to the rapid charge exchange between CCA sites.

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Introduction

Fumed silicas are commonly used as flow aids in dry xerographic toners.[1] They are generally applied on the surface of toner particles by mechanical blending. In addition to the flow enhancing function, they frequently dominate the charging of the toner.[2] One of the identified approaches to regulate and control the charging characteristics of toners that employ silicas is to modify the surface of silica particles with a known charge control agent (CCA).[3] Among the different preparative methods, for example, solution coating, vapor phase reaction, fluidized bed spray method, and the like, that have been used to modify the surface of silicas, the latter process has been shown to be effective and scalable even at a kilogram level.[4] The objectives of this work are (1) to show that CCA molecules may be in different physical states in the silica samples depending on the fabrication conditions and (2) to understand the effect of the different physical states on the charging properties when they are used in toners.

We report here the synthesis of a number of surface-modified silicas by the solution-coating technique. Depending on the interactive force between the CCA and the silica surface, the coating solvent and the final processing conditions, the CCA may be (a) molecularly adsorbed, (b) crystallized on the silica surface, (c) in a very fine particulate mixture homogeneously with the silica particles, or (d) in the form of a combination of (a) to (c). We describe the method and the assumptions used for the synthesis of the three series of CCA-modified silicas in this paper. The starting silica is a hydrophobic fumed silica (Aerosil R972 from Degussa). 3,5-Di-t-butylsalicylic acid (t-BSA), potassium bis(3,5-di-t-butylsalicylato)borate (LR120), and potassium tetraphenylborate (KTPB) were chosen as CCAs. These three CCAs were shown to impart a different degree of negative charging to the styrene-butadiene toner[4] and we are interested in seeing if the trend remains when the physical state of the CCA is changed. The different physical states of the CCAs in the surface-modified silica samples were prepared by the solution-coating technique using the appropriate solvent system. In the case of the t-BSA–R972 system, the synthesized physical states are verified spectroscopically. Studies of the charging properties of the surface modified silicas in styrene-butadiene toner reveal that both charging and admix properties are sensitive to the original physical state of the CCA in the silica sample. The results are rationalized in terms of a surface area effect.

Experimental

Materials. Aerosil R972 is a hydrophobic amorphous fumed silica from Degussa. 3,5-Di-t-butylsalicylic acid (technical) t-BSA, was purchased from Yoshitomi, Japan; potassium bis(3,5-di-t-butysalicylato)borate (tradename LR120) was obtained from Japan Carlit, and potassium tetraphenylborate (KTPB) was synthesized in-house from sodium tetraphenylborate. The coating solvents used in this work, cyclohexane, benzene, methanol, chloroform, and acetone, were either of spectra grade or best reagent grade from Fisher or Aldrich, or an analytical grade from Baker. They were used as received. The toner was made of unpigmented styrene-butadiene (90:10) resin and was prepared by a melt-extrusion and jetting process. It was

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then classified to ~ 9 µm. Metal beads were made of steel cores (~ 130 µm), which were powder-coated by a mixture of poly(vinylidene fluoride) (tradename Kynar from Pennwalt) and poly(methyl methacrylate) (PMMA) at varying ratios on the surface of the steel beads at a weight loading of 0.7%.

Preparation of Surface Modified R972 Silicas. A charge control additive (0.3 g) was dissolved in ~ 100 mL of an appropriate solvent in a 250-mL round bottom flask. After dissolution, 3.0 g of silica R972 was added and the suspension was stirred for half an hour. Solvent was then removed on an evaporator. The residue obtained was transferred to a crystallization dish and was dried in an oven overnight at ~ 120°C. The solid was then transferred to a 4-oz bottle and roll-milled with 35 g of 1/4 in. steel shot for 30 min at a speed of ~ 90 ft/min, yielding ~ 3 g of a white powder, the surface-modified silica.

Preparation and Evaluation of Experimental Toners. The above surface-modified silica (0.063 g), the styrene-butadiene toner (12.5 g), and 125 g of 1/4 in. steel shot were placed inside a 4-oz bottle. The bottle was roll-milled for 30 min, resulting in an experimental toner. Developers were then prepared using the above experimental toner (1.25 g) and the polymer-coated metal beads (60 g). All developers were conditioned at 20 ± 4% relative humidity (RH) for ~ 16 h before evaluation. The charge of the toner was generated by roll milling the developer for 60 min at a speed of 90 ft/min on a roll mill and was determined on a standard blow-off apparatus.[5] The admix time of the toner was evaluated by adding 1% of the fresh toner into the developer, which had a toner concentration of 2%. The charge distribution of the final developer was recorded on a charge spectrograph apparatus[5] as a function of time, for example, 15 s and 1, 2, 5, and 15 min. The admix time is defined as the roll-milling time required for the fresh toner to become fully equilibrated in charge with the original developer.

Fluorescence Emission. Fluorescence spectra were taken on a Perkin-Elmer MPF-66 fluorescence spectrophotometer, which was interfaced with a professional computer (Model 7700 from Perkin-Elmer). The spectral data were corrected using the quantum counter method with the Rh101 solution supplied by Perkin-Elmer. Details of the instrumentation and procedure have been given elsewhere.[6]

Results and Discussion

Preparation of Surface-Modified R972 Silicas. ***Models and Assumptions.*** All surface-modified silicas studied in this work were prepared by solution coating a CCA (t-BSA, LR120, or KTPB) onto the surface of silica R972 at a CCA to silica ratio of 1 : 10. The physical state of the CCA in the silica sample is expected to be sensitive to the coating solvent, which not only governs the partitioning of the CCA between the solution phase and the silica surface, but also influences the precipitation or crystallization of the CCA when the coating solvent is evaporated. In principle, the amount of CCA molecule that is adsorbed onto the surface will depend on the strength of the molecular interaction between the CCA and the silica surface relative to solvation. In this work, the molecular interaction between the CCA and the silica surface is modeled by thin-layer chromatography (TLC) using reversed phase silica gel plates (Brinkmann Instruments, Inc.). Controlled experiments indicate that the difference in retention time (R_f) between the normal and reversed phase plates is negligible.

TABLE I. Modeling of the Effect of Coating Solvent on the Physical State of CCA Modified Silicas

CCA	Solvent	R_f	Projected physical state
t-BSA	Cyclohexane	0	Molecular adsorption
	Benzene	~ 0.2	*
	Methanol	1.0	Fine physical mixture of particulates
LR120	Chloroform	0	Molecular adsorption
	Methanol	1.0	Fine physical mixture of particulates
	Acetone/heptane†		Physical mixture of particulates

* mixture of molecular adsorption and fine particulate mixture,
† LR120 is precipitated as very fine particles before the silica is added.

t-BSA was chosen as a model for extensive solubility and TLC studies. Results show that t-BSA is highly soluble in a variety of organic solvents. We thus anticipate that different physical states of t-BSA on the surfaces of silica particles may be prepared by careful manipulation of the coating solvent. The R_f value of t-BSA increases from 0 to ~ 0.2 to 1.0 as the eluting solvent changes from cyclohexane to benzene to methanol. The result is consistent with the eluting power of the solvent.[7] The R_f data suggest that when silica R972 is added to a cyclohexane solution of t-BSA, molecules of t-BSA would be adsorbed on the silica surface due to the strong surface-to-molecule interaction relative to solvation. Surface-modified R972 silica consisting of molecularly adsorbed t-BSA is then prepared by removing the coating solvent. In the other extreme, when the silica is added to a methanol solution of t-BSA, t-BSA is expected to remain in the coating solution. Thus when methanol is removed, t-BSA will either precipitate out of the solution or crystallize on the silica surface, forming a particulate mixture of solid t-BSA and silica particles. The situation with benzene, which has an intermediate R_f value, is expected to be in between the two extreme cases. The R_f data and the projected physical states of t-BSA that can be prepared in the silica samples are summarized in Table I.

A similar solubility and TLC study was also attempted for LR120. Owing to the limited solubility, only chloroform and methanol were selected as coating solvents. The R_f values and the projected physical states for LR120 are included in Table I.

KTPB was shown to produce ill-defined TLC chromatograms. It exhibits high solubility in acetone and is sparingly soluble in chloroform. The use of these two solvents to prepare KTPB modified R972 silicas of different physical states is described below.

Preparation of CCA Modified R972 Silicas and Microscopy Studies. Three types t-BSA surface-modified silicas were prepared using cyclohexane, benzene, and methanol as coating solvents. Examinations of the morphology of these three samples by transmission electron microscopy (TEM) fail to detect any crystals of t-BSA in the silica samples. The microscopy results indicate that t-BSA is homogeneously distributed in the samples. The TEM technique, however, does not differentiate the different physical states of t-BSA in the samples.

Three LR120 surface-modified silicas were prepared. The first and the second samples were coated with chloroform and methanol, respectively. The third sample was coated with a fine dispersion of LR120 prepared by adding *n*-heptane into an acetone solution of LR120. The intention here is to physically prepare a particulate mixture of silica particles and fine LR120 particles. TEM micrographs show that microcrystals of LR120 are distributed uniformly in the acetone and heptane sample (Fig. 1). On the other hand, microcrystals of LR120 are not seen in

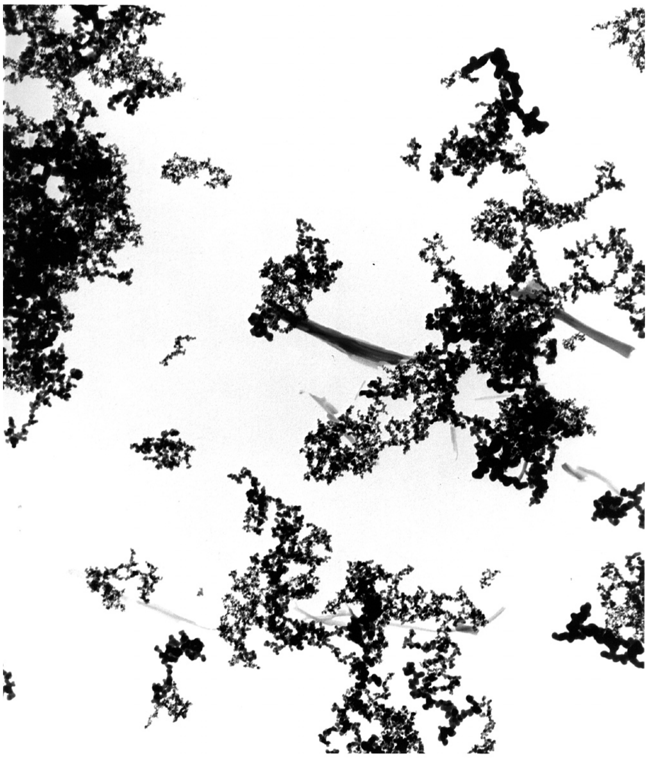

Figure 1. TEM micrograph of a LR120 surface-modified R972 silica sample prepared from a dispersion of LR120 in *n*-heptane and acetone.

the chloroform or methanol coated samples, suggesting that molecules of LR120 may either be molecularly adsorbed or crystallized on the silica surface. They can also exist as fine particulate mixture with silica particles or as a mixture of the above scenarios.

Two surface-modified silica samples were prepared from KTPB. The first sample was prepared using acetone as a coating solvent. The second sample was coated from a mixture of chloroform and acetone (1:1). In this solvent mixture, acetone is a good solvent as well as being a more volatile component. During the solution coating process, the coating solution becomes chloroform rich as acetone is evaporated (first) during the solvent removal step. By doing that, KTPB may be forced to crystallize or adsorb on the silica surface. The surface-modified silica generated in this fashion is expected to be different from that coated from pure acetone. Indeed, the appearances of the two surface-modified silicas are different. While the acetone-coated sample is "pure" white, the sample that is coated from the chloroform and acetone mixture has a light tan appearance. TEM analyses of these two samples fail to detect any discernible difference; microcrystals of KTPB are not seen in either sample. The only useful information from TEM is that KTPB is distributed uniformly within the sample. Information on the precise physical states is not accessible thus far.

Verification of the Physical States. One of the easiest ways to find out whether or not the CCA is adsorbing onto the silica surface from the coating solution is to physically separate these two components by filtration. Indeed, experiments were performed with t-BSA in cyclohexane and methanol. The amount of t-BSA that remains in the coating solution after filtration is determined by absorption spectroscopy. Results indicate that about 80% of the t-BSA molecules remain un-adsorbed in *both* solvents within experimental error (~ 0.5%). The result is surprising because the surface areas available for t-BSA adsorption for 3 g of R972 silica is ~ 360 m^2, which is plentiful for 0.3 g t-BSA.[8] We attribute the results to the high solubility of t-BSA in the coating solvents. The results suggest that while the R_f value may be useful in modeling the molecular interaction, it is not useful in estimating the partition coefficient between the two phases.

Previous investigation in our laboratory showed that t-BSA is a strong fluorophore.[6,9] Here we attempt to use fluorescence spectroscopy to gain information on the physical states of t-BSA in various samples. Figure 2(a) shows the fluorescence emission spectrum of t-BSA in dilute ethanol and Fig. 2(b) shows the emission spectrum of solid t-BSA. A control sample consisting of 1:10 t-BSA to R972 silica prepared by the fluidized bed spray method is shown in Fig. 2(c). The three t-BSA/R972 silica samples, coated with cyclohexane, benzene, and methanol are shown in Figs. 2(d), 2(e), and 2(f), respectively. While the monomeric emission of t-BSA is relatively narrow with λ_F at 430 nm [Fig. 2(a)], the emission from the solid state is broad [Fig. 2(b)]. The similarity between the spectra in Figs. 2(b) and 2(c) suggests that t-BSA exists as fine particulates, mixing homogeneously with the silica particles in the fluidized bed sample. The benzene and methanol coated samples also give very similar fluorescence spectra as compared to the spectrum in Fig. 2(b), indicating that t-BSA also exists as fine particulates in these two silica samples. The spectrum in Fig. 2(d) appears to be midway between those in Figs. 2(a) and 2(b). We suggest that t-BSA forms aggregates on the silica surface when it is coated with cyclohexane. The different physical states of t-BSA prepared from different solvents are verified reasonably well (Table I).

Unfortunately, similar studies for LR120 and KTPB could not be performed. While LR120 is a reasonable fluorophore in solution,[6] the similarity between the solution and the solid state emission spectra makes distinction of the different physical state not possible. In the case of KTPB, it is simply not emissive. Nevertheless, we feel that the information gained in the t-BSA study would enable a reasonable rationalization of the physical states of the LR120 and KTPB modified silica samples.

Charging Studies in Model Styrene-Butadiene Toner. ***1.t-BSA.*** The charging properties of the three t-BSA/R972 samples prepared by the solution coating technique were studied by first blending them with 9-μm unpigmented styrene-butadiene toner and then measuring the toner charges generated against a series of metal beads that were powder-coated by a mixture of Kynar/PMMA of varying ratios at a weight loading of 0.7%. All the developers were conditioned inside a glove box at 20 ± 4% RH overnight prior to roll-milling and tribo (toner charge) measurements. Controlled time-track experiments suggest that the charging of the toner is basically saturated in 60 min. The tribo data are plotted in Fig. 3. The data for the two control toners are included (dotted lines) for comparison. These controls are (1) the pure styrene-butadiene toner and (2) the styrene butadiene toner containing silica R972.[10] The data suggest that the added t-BSA in the silica samples influences the charging behavior of the resulting toners. Note that the cyclohexane coated sample (❍) charges more negatively than the benzene coated sample (☐), which charges more negatively than the methanol sample (Δ). The charging of the methanol sample is comparable to that of fluidized bed

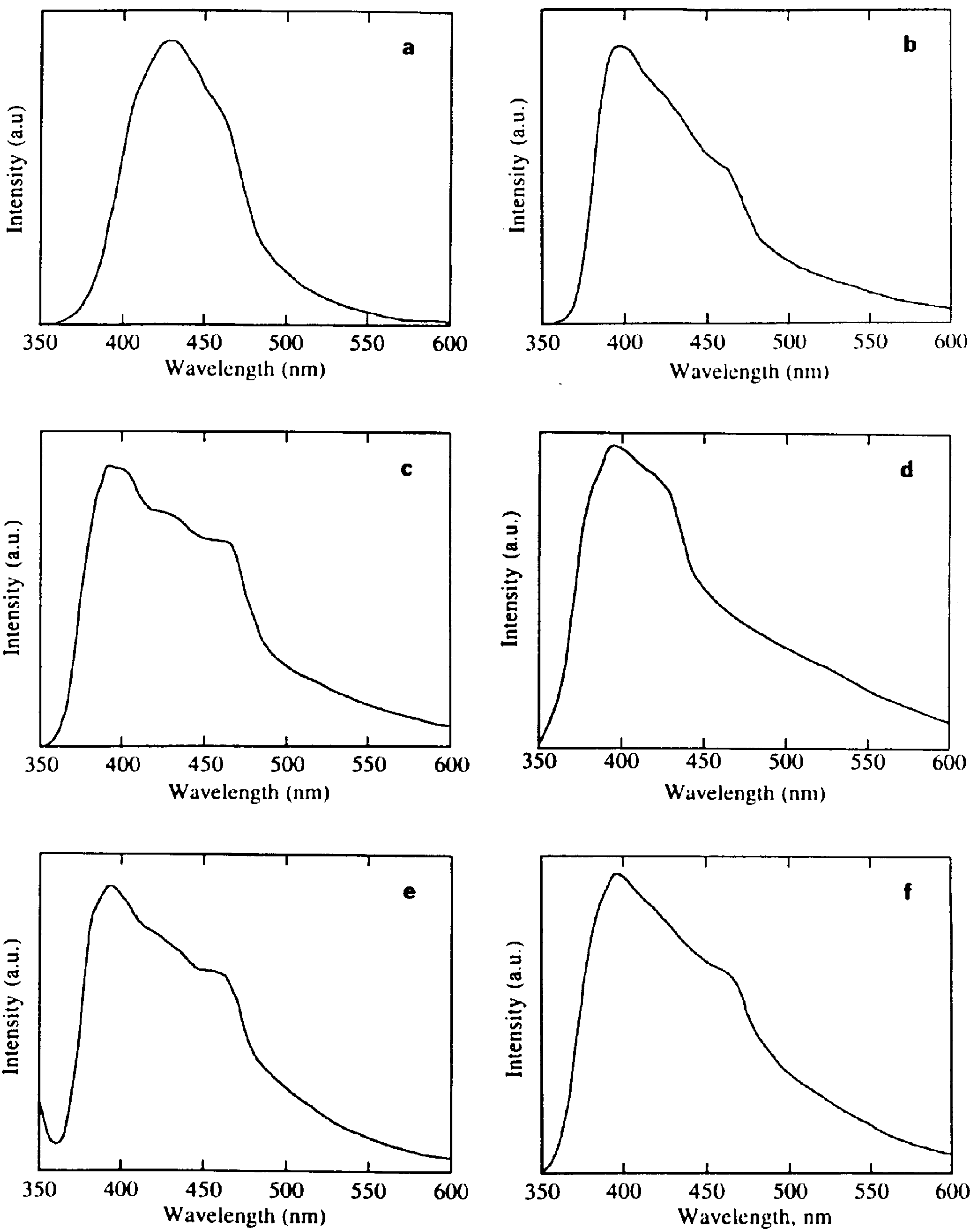

Figure 2. Fluorescence emission spectra of t-BSA (a) in dilute ethanol; (b) solid powder, (c) 1:10 in R972 silica prepared by the fluidized bed spray method; (d) 1:10 in R972 silica coated from cyclohexane; (e) 1:10 in R972 silica coated from benzene; and (f) 1:10 in R972 silica coated from methanol.

TABLE II. Tribo and Admix Properties of Surface-Modified R972 Silicas (CCA:R972 = 1:10, RH = 20%)

CCA	Method of CCA deposition	Projected physical state	Tribo*	Admix time
t-BSA	Cyclohexane	Molecular adsorption	– 82.9 μC/g	2 min
	Benzene	†	– 75.7 μC/g	2 min
	Methanol	Fine particulate mixture	– 64.3 μC/g	15 min
	Fluidized bed	Fine particulate mixture	– 64.8 μC/g	5–15 min
LR120	Chloroform	Molecular adsorption	– 51.7 μC/g	30 sec
	Methanol	Fine particulate mixture	– 56.3 μC/g	1 min
	Heptane and acetone	Particulate mixture	– 42.3 μC/g	‡
	Fluidized bed	Fine particulate mixture	– 41.0 μC/g	5 min
KTPB	Chloroform and acetone	Molecular adsorption?	– 94.9 μC/g	2 min
	Acetone	Fine particulate mixture	– 30.9 μC/g	15 min
	Fluidized bed	Inhomogeneous mixture	– 27.3 μC/g	15 min

* Against polymer-coated metal beads with a Kynar/PMMA (20:80) surface coating

† Mixture of molecular adsorption and fine particulate mixture

‡ Due to the charge through problem, the admix time of this sample could not be determined accurately.

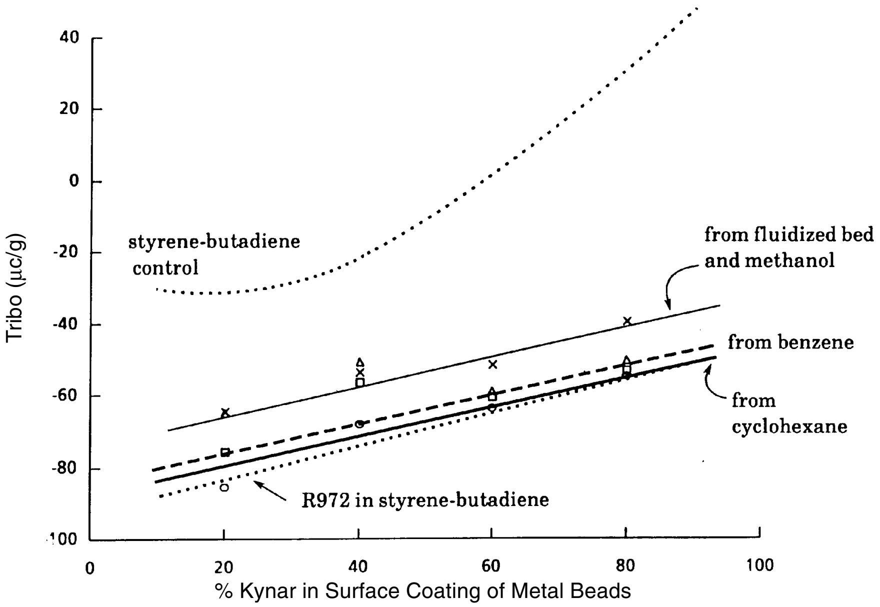

Figure 3. A tribo plot of various t-BSA-modified R972 silicas in styrene-butadiene toner.

sample.[4] The results suggest that t-BSA is in the powder form in the surface-modified silica sample.

The admix times of all the toners were evaluated on a charge spectrograph apparatus. The results, along with the tribo data and the physical state of t-BSA, are tabulated in Table II. The data show that the admix time is also very sensitive to the coating solvent used in the solution coating step, with cyclohexane generating the shortest admix time and methanol producing the longest admix time.

2. LR120. The charging properties of various LR120-modified R972 silicas were studied analogously. The data are plotted in Fig. 4. The tribo data from the heptane and acetone-coated sample is found to be identical to those obtained from the equivalent sample fabricated by the fluidized bed spray technique.[4] Because LR120 is shown to form a particulate mixture with silica particles in the heptane and acetone sample (Fig. 1), the tribo results simply reaffirm the conclusion from the t-BSA experiments that surface modification of silica by the fluidized bed spray method primarily produces a fine particulate mixture of the solid CCA and the silica particles.

The tribo data of the chloroform- and methanol-coated samples are very similar, suggesting that the physical state of LR120 is very similar also. The admix times for these two samples are 0.5–1 min, significantly shorter than that of the fluidized bed sample. The data indicate that the physical state of LR120 in these two solution-coated samples is different from that resulting from the fluidized bed spray process. We suggest that LR120 molecules are either molecularly adsorbed or crystallized, or form aggregates on the silica surface. They can also exist as a mixture of the above possibilities. At present we cannot distinguish them individually.

3. KTPB. The tribo data for the KTPB surface-modified silica samples are plotted in Fig. 5 and also given in Table II, along with the admix times. The results suggest that although microcrystals of KTPB are not observable for the acetone-coated sample, both tribo and admix data indicate that KTPB may be distributed imhomogeneously as in the case of the fluidized bed sample. On the other hand, when KTPB molecules are *forced* onto the silica surface by a nonpolar solvent, such as in the chloroform and acetone mixture, a remarkably different result is obtained. The CCA dominates the charging of the toner, leading to very negative tribo values and a tremendous decrease in admix time.

Interpretative Discussion. A correlation exists when comparing the physical states of the CCA in the silica sample and the charging results in Table II. For example, we consistently observe a higher tribo value and a shorter

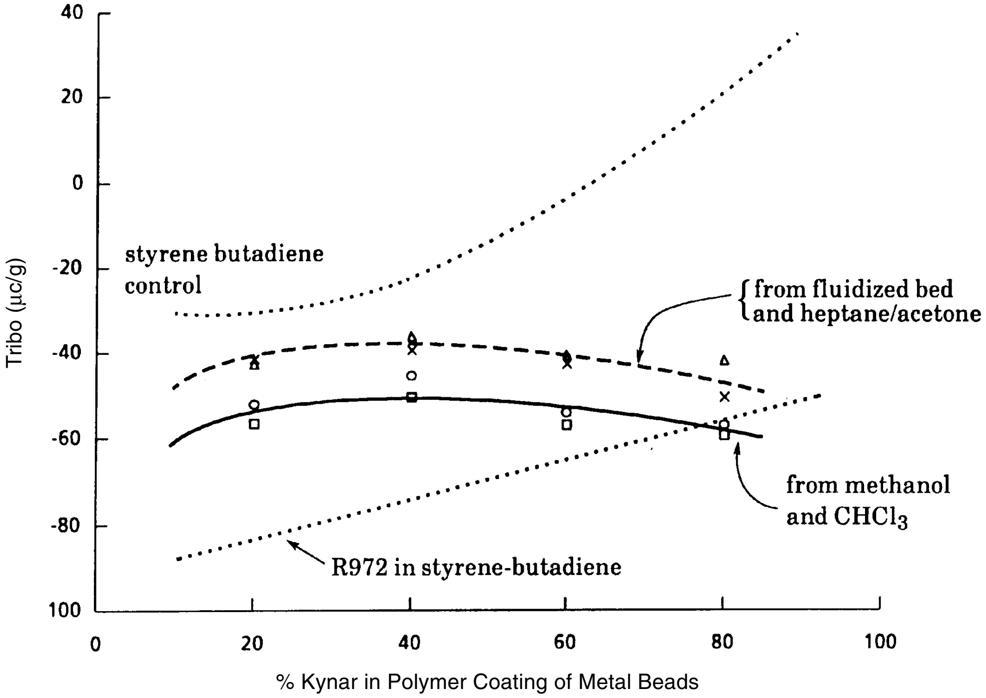

Figure 4. A tribo plot of various LR120-modified R972 silicas in styrene-butadiene toner.

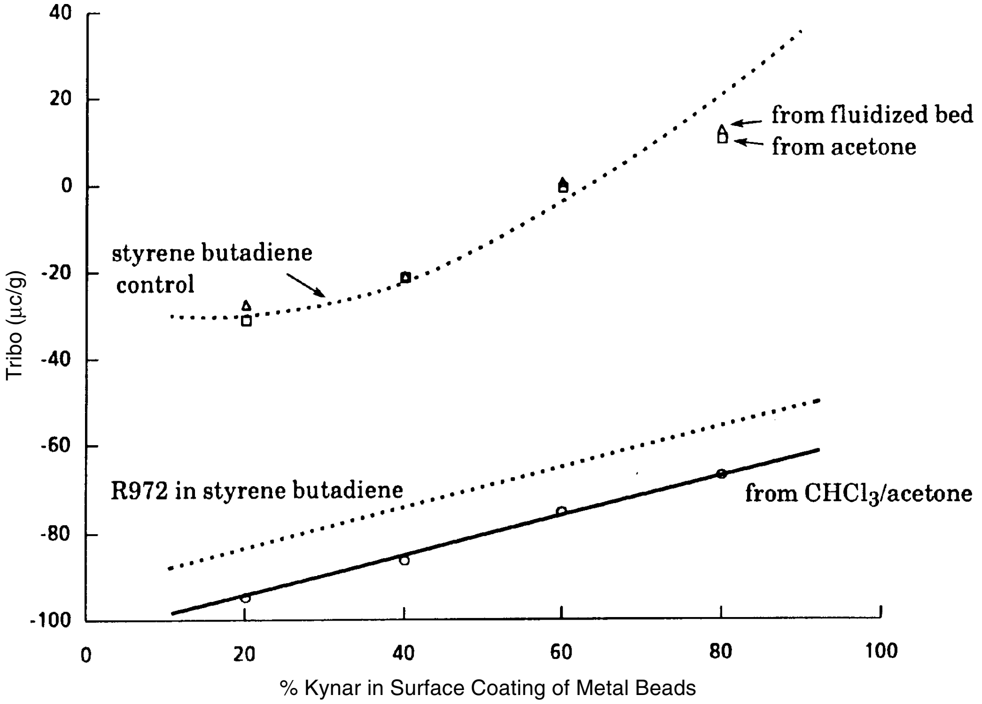

Figure 5. A tribo plot of various KTPB-modified R972 silicas in styrene-butadiene toner.

admix time when the CCA is "molecularly" adsorbed on the silica surface. The attainment of higher tribo for the molecularly adsorbed samples can be rationalized in terms of a surface area effect. Because the CCA to silica ratio is held the same in all experiments, the surface areas that are covered by the CCA will be largest if the CCA is spread molecularly. This, in turn, translates into the largest active area for the CCA in toner. Because contact charging is a surface phenomenon,[11] the attainment of a higher tribo value from the molecularly adsorbed sample, that has the largest surface area, is rational.

Along with the high tribo values, shorter admix times are also obtained for the molecularly adsorbed samples. While the mechanism of charge exchange in toners prepared from these surface modified silicas remain to be understood, the correlation in Table II suggests that it may also correlate to the surface area. We suspect that the short admix time may be a consequence of rapid charging or efficient direct charge exchange between CCA sites. Undoubtedly, further work is needed to elucidate the charge exchange mechanism in these toner systems.

Relative Humidity Sensitivity. A notable shortfall for toners employing silicas is the decrease of toner tribo at high RH.[2] One of the intentions of this work is to examine whether the RH sensitivity can be reduced when the CCA is molecularly adsorbed on the silica surface. The RH data for the three molecularly adsorbed (with t-BSA,

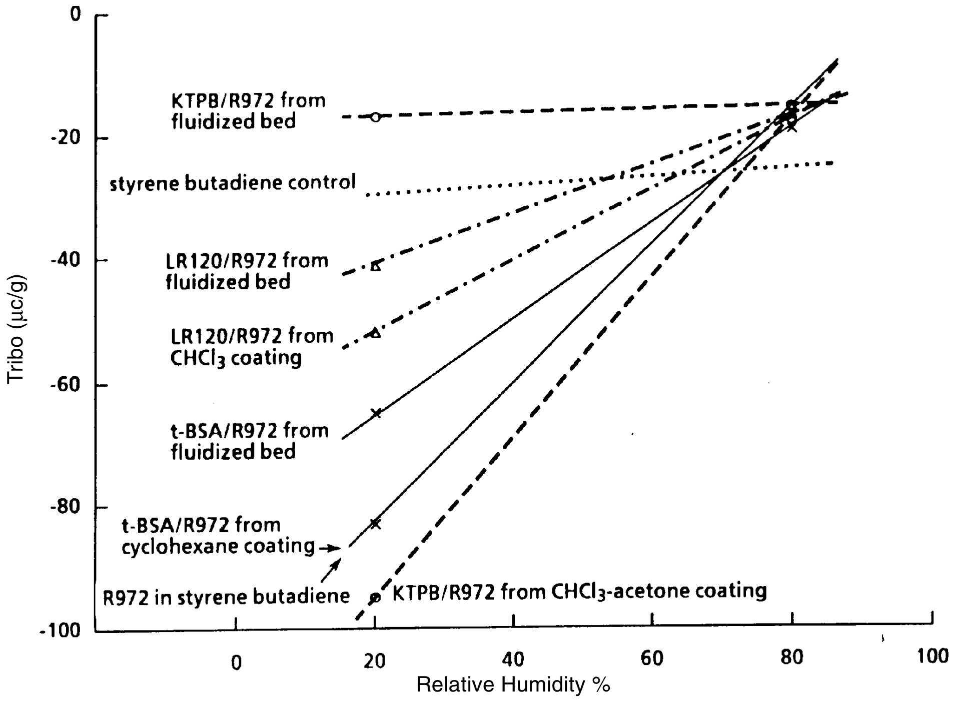

Figure 6. A plot of the effect of RH on the tribo of various styrene-butadiene toners containing t-BSA-, LR120-, and KTPB-modified silicas.

LR120, and KTPB) silica samples are tested by conditioning the developers at 80% RH prior to tribo evaluations. The three corresponding surface-modified silicas that were prepared by the fluidized bed method are studied in parallel. A comparison of the RH effect is given in Fig. 6. Again, the RH effect of the two controls, the styrene-butadiene toner and the styrene-butadiene toner containing the R972 silica, are included. The data show that the tribo values for toners containing surface-modified silicas are extremely sensitive to RH variation. At 20% RH, there is a wide spread in tribo values (from –90 to –18 μC/g) and these values merge into a very narrow range, from –14 to –19 μC/g, at 80% RH. The results suggest that at 20% RH, the added CCAs control the charging properties. At 80% RH, due to the water uptake, the water-rich silica surfaces dominate the charging in all the silica samples. This results in nearly constant low tribo values.

Concluding Remarks

We modeled and studied the deposition of molecular CCAs on the surface of silica R972. Our results demonstrate that CCAs of different physical states in the silica sample can be prepared by selection of an appropriate solvent (or solvent system) during the solution coating step. For a given CCA surface modification, the physical state of the CCA in the silica sample is found to have a profound influence on the charging property. Higher tribo values and shorter admix times are obtained when the CCA is molecularly adsorbed on the silica surface. The results are attributable to a surface area effect.

By comparing the charging properties of surface-modified silicas prepared by the solution-coating method with those by the fluidized bed spray method, we conclude that CCAs usually form a particulate mixture with the silica particles when they are prepared by the second process. The charging results are complemented by fluorescence emission data in the case of t-BSA, that show t-BSA exists as fine powder in the fluidized bed sample.

We also showed in RH experiments, that the charging properties of surface-modified silicas are dominated by the water-rich silica surfaces at 80% RH, regardless of the original physical state of the CCA in the silica sample. In other words, the “hydrated” silica surface dominates the charging at high RH. Any further attempt to improve the RH sensitivity of toners incorporating silicas should be focused on the silica surface *directly*. ▲

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References and Notes

1. R. J. Gruber and P. C. Julien in *Handbook of Imaging Materials*, A. S. Diamond, Ed., Marcel Dekker, New York 1991.
2. K. Y. Law and I. W. Tarnawskyj, *J. Imaging Sci. Technol.* **41,** 550 (1997).
3. R. J. Gruber, R. A Yourd, III, P. C. Julien, S. B. Bolte, and J. F. Knapp, U.S. Patent 4,965,158 (1990).
4. K. Y. Law, I. W. Tarnawskyj, P. J. Julien, and F. Lee, *J. Imaging Sci. Technol.* **42,** 459 (1998).
5. L. B. Schein, *Electrophotography and Development Physics*, Springer-Verlag, New York, 1988.
6. K. Y. Law, *J. Photochem. Photobiol. A: Chem.* **107,** 115 (1997).
7. A. J. Gordon and R. A. Ford, *The Chemist's Companion*, John Wiley & Sons, New York, 1972, p. 375.
8. Molecular modeling study suggests that the molecular area of t-BSA is ~ 30 Å^2. Assuming that these molecules lie flat on the silica surface, they will occupy ~ 2 x 10^{22} Å^2. The total surface area for 3 g of R972 Aerosil is ~ 3.6 x 10^{22} Å^2.
9. K. Y. Law and J. Shoham, **99,** 12103 (1995).
10. We have also studied the charging behavior of R972 silicas that are treated with pure solvent (cyclohexane, benzene, and methanol) and found that the solvent effect on charging is very small if there is an effect.
11. J. Lowell and A. C. Rose-Innes, *Adv. Phys.* **29,** 974 (1980).