

Effect of Adsorption of Long Chain Alcohol Molecules on Silica Particles on Toner Charging

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The adsorption of long chain alcohols on the surfaces of hydrophobic silicas has been studied using 1-hexadecanol on R972 silica as a model system. Both DSC and IR spectral data suggest that 1-hexadecanol is in the gaseous state on the silica surface at concentrations $\leq 4.8\%$ by weight. At 9.4% loading, which is equivalent to half of a theoretical monolayer on the silica surface, results suggest that the adsorbed 1-hexadecanol forms a hydrocarbon protective layer on the surface. The formation of the layer implies that the hydrocarbon chains in the adsorbed 1-hexadecanol are interacting with each other, presumably by folding the hydrocarbon chains back toward the silica surface. As the concentration of 1-hexadecanol increases, the space occupied by the folded hydrocarbon chains is replaced by the added 1-hexadecanol, up to one theoretical monolayer (17%). Beyond this concentration, crystallization of 1-hexadecanol occurs. The effect of the chain length of the adsorbed alcohol is studied at a theoretical monolayer coverage for a series of normal alcohols, from C_{12} to C_{22} . While protective hydrocarbon layers are formed for all the normal alcohols studied, IR spectral data suggest that the layers formed from 1-octadecanol, 1-eicosanol and 1-docosanol are less organized. The surfaces of these modified silicas may be more hydrophilic as compared to those from 1-dodecanol, 1-tetradecanol and 1-hexadecanol. The charging properties of alcohol-treated silicas were studied by first blending them with 9 μm unpigmented SPAR toner at 0.5% by wt. concentration, followed by charging the resulting toners with metal beads. The tribo data reveal that adsorption of long chain alcohols on the silica surface enhances the negative tribocharge of the resulting toner at both low (20%) and high (80%) relative humidity (RH). High tribo with minimal RH sensitivity, as judged from the tribo ratio from 20% to 80% RH, are obtained when R972 is covered with one theoretical monolayer of 1-hexadecanol. The attainment of optimal charging result is shown to correlate to the proposed molecular structure of the adsorbed alcohol layer. The important role of the hydrophobicity of the silica surface in toner charging is discussed.

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Introduction

Non-porous fumed silicas ranging from 5 to 50 nm in diameter are commonly used as flow-aids in xerographic toners.¹ In practice, they are performing a dual function. They enhance the flow while controlling the charging characteristics of the toner. One of the drawbacks of the approach is the humidity sensitivity of toner charging, e.g., the tribo of the toner decreases as the ambient humidity increases. We reported earlier that the charging of both hydrophilic and hydrophobic silicas are sensitive to humidity when they are incorporated into a toner; and expectedly hydrophilic silica is more humidity sensitive between the two.² The correlation between hydrophobicity of the silica surface and the degree of humidity sensitivity in toner charging is quite profound, however. We recently attempted to modify the surfaces of silica particles using conventional charge control additives (CCA). While the effect of the added CCA on toner charging is evident, the humidity sensitivity remains.^{3,4} It was concluded that a possible solution to eliminate or reduce humidity sensitivity is by modifying the surface of silica particles, rendering it

hydrophobic. We intuitively feel that this may be accomplished by encapsulating the silica surface with a hydrocarbon layer such that the fluctuation of water concentration on the surface is small as the ambient humidity is varying.

In this work, we report the use of a hydrocarbon layer, formed by adsorption of long chain alcohol molecules on the surface of a hydrophobic silica, as an encapsulating layer for the silica surface. Using 1-hexadecanol on hydrophobic silica R972 as a model, we systematically show that the adsorbed alcohol layer enhances negative charging and reduces the humidity sensitivity of the charging process when the alcohol-treated silica is incorporated in an unpigmented polyester (SPAR) toner. While both the chain length of the alcohol molecule and the concentration of the adsorbed alcohol on the silica surface are shown to have an effect on toner charging, the overall result can be rationalized in terms of an increase in hydrophobicity of the silica surface after the alcohol treatment. The origin of the increase is discussed.

Experimental

Materials. The hydrophobic silica used in this work was R972 from Degussa. Long chain alcohols, 1-dodecanol, 1-tetradecanol, 1-hexadecanol, 1-eicosanol and 1-docosanol were of the highest commercial quality purchased from Aldrich Chemical Co. The coating solvents were low boiling hydrocarbons, e.g., pentane, hexane and cyclohexane; they were of spectral grade

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TABLE I. Physical and Spectroscopic Data of Silicas Formed by Adsorbing Various Concentrations of 1-hexadecanol on the Surface of R972 Silica

1-Hexadecanol concentration (% wt.)		C	H	Si	m.p. by DSC (degree C)	IR (cm ⁻¹) ^a
0	Found:	0.92	< 0.5	50.40	—	—
4.8	Calc'd:	4.68	0.69	48.08		
	Found:	4.74	0.59	48.33	—	2928.4
9.1	Calc'd:	8.05	1.29	45.81	41	
	Found:	8.18	0.94	45.52	(very broad)	2917.7
13	Calc'd:	11.11	1.84	43.85		
	Found:	10.88	1.64	43.64	41	2917.3
17	Calc'd:	14.00	2.36	44.98		
	Found:	13.45	2.11	43.60	41	2916.9
23	Calc'd:	18.94	3.25	38.81		
	Found:	18.84	3.30	36.85	50	2917.0
29	Calc'd:	23.33	4.04	35.99		
	Found:	22.78	4.17	35.93	50	2917.0
100	Calc'd:	79.27	14.14		54	2918.1

(a)CH₂ stretching in the hydrocarbon chain of 1-hexadecanol.

from Fisher Scientific. The toner resin was a linear polyester, SPAR, from Goodyear. The toner was unpigmented and was prepared by a melt-extrusion and jetting technique. It was classified to ~ 9 μ m. The metal beads for the charging experiments were made of steel core (~ 130 μ m) and were solution-coated by a carbon-black doped poly(methyl methacrylate) polymer on the surface at a total weight loading of ~ 0.8%.

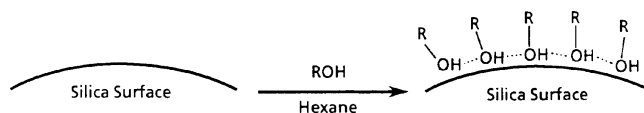
General Techniques. Infrared spectra were determined on a Perkin Elmer model 1750 FTIR. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC7 with a 2-stage inter-cooler and a IBM PS2 model 50z computer.

Preparation of Alcohol-Treated Silicas. A long chain alcohol was dissolved in ~ 100 mL of a hydrocarbon solvent inside a 250 mL round bottom flask. Silica R972 was added to the alcohol solution and the resulting suspension was subjected to an ultrasonic treatment for 2 h and then stirred overnight. The solvent was removed on an evaporator. The white residue obtained was dried in a force-air oven overnight at 70°C. The solid was 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 a fluffy white powder, the alcohol-treated silica.

Preparation and Evaluation of Experimental Toners. The above alcohol-treated silica (0.063 g), the SPAR toner (12.5 g) and 125 g of 1/4" steel shot were placed inside a 4-oz bottle and was rolled for 30 min to prepare an experimental toner. Developer was prepared by placing the above toner (1.25 g) and the metal beads (60 g) inside a 2-oz bottle. The entire content was conditioned inside a humidity-controlled glove box at a constant humidity, either 20% or 80%, overnight and was sealed. The tribo of the toner was generated by tumbling the toner and the metal beads inside the 2-oz bottle on a roll-milled for 5 min at a speed of 90 ft/min. The charge generated was determined by the standard blow-off technique inside a Faraday cage under lab ambient condition.⁵ Controlled experiments indicated that the charging process was leveled off after 5 min of roll milling and the tribo value was primarily sensitive to the ambient RH when the toner was charged up.

Results and Discussion

Alcohol-Treated Silicas. The Concept. The surface of hydrophobic fumed silica, such as R972, is quite polar even though it has been made hydrophobic by a silanating agent. There are residual silanol groups as well as siloxane groups on the surface.⁶ These functionalities are capable of forming H-bonding with the OH group in alcohol.⁷ The interaction would result in alcohol adsorption on the silica surface. At sufficiently high concentration, hydrocarbon chains of certain long chain alcohols start to interact with each other by the Van der Waals force, forming an encapsulating hydrocarbon layer. A schematic of the concept is shown in Scheme 1.



Scheme 1.

Preparation, Characterization and Physical Properties. Hydrophobic silica R972 was chosen as a model for preparation and characterization studies. Basically, alcohol adsorption takes place when R972 is added to a hexane solution containing a long chain alcohol. After removal of the solvent, then drying, the alcohol-treated silica is prepared. Table I summarizes the results of the effect of 1-hexadecanol concentration on the physical and spectroscopic properties of the alcohol-treated R972 silicas. Elemental data show that there is a good agreement between the found values and the theoretical values based on the feed ratios. Evidence for the occurrence of alcohol adsorption comes from the hexane washing experiment. For instance, at 1-hexadecanol concentration \leq 17%, the alcohol molecules are found to be immobile and cannot be washed off by hexane. At 1-hexadecanol concentrations higher than 17%, part of the adsorbed 1-hexadecanol can be washed off by hexane and the resulting silicas generally consist ~ 17% by weight of 1-hexadecanol. The result suggests that up to ~ 17% of 1-hexadecanol can be tightly adsorbed on the surface of R972 silica.

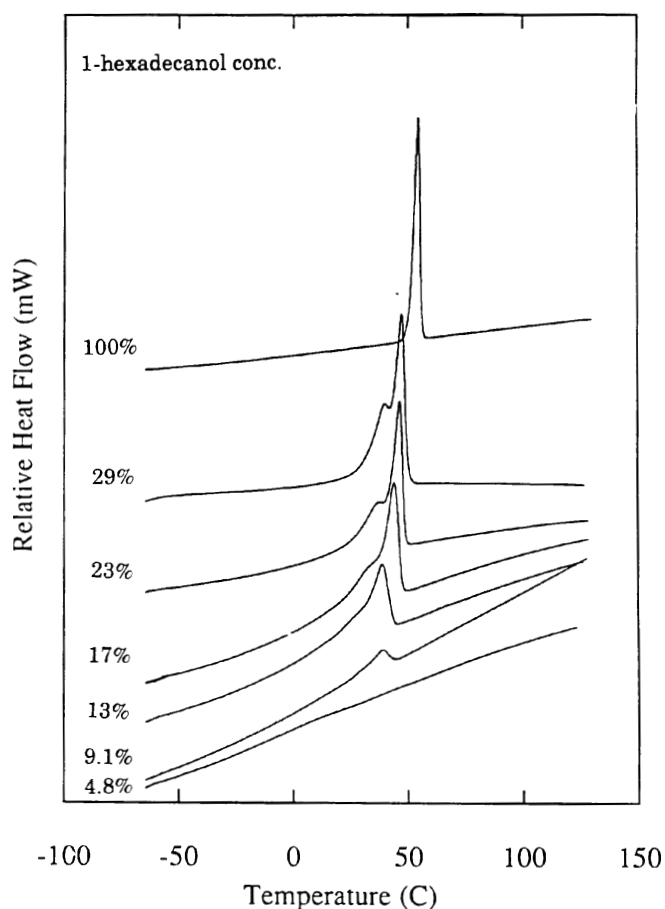
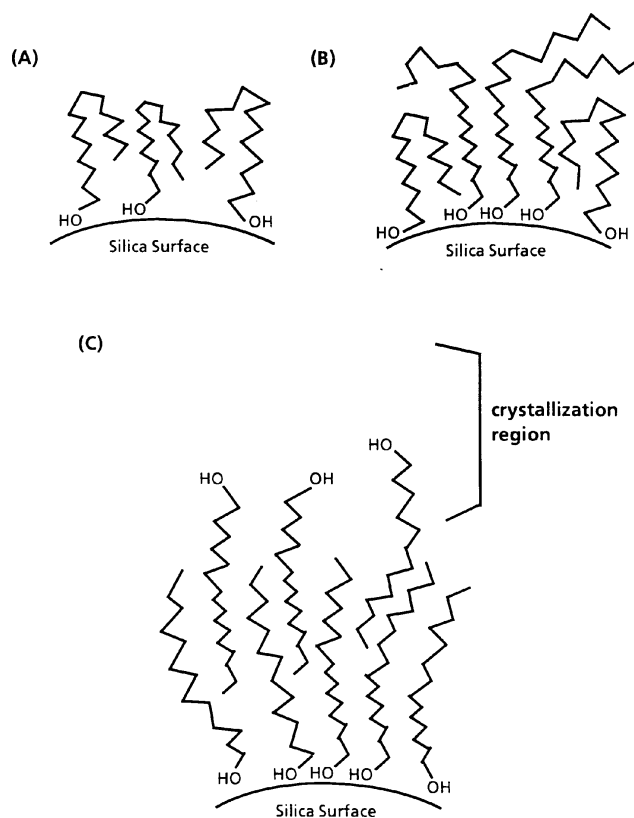


Figure 1. DSC isotherms of various 1-hexadecanol treated R972 silicas.

A similar conclusion can also be reached via the filtration experiment. For example, by adding 3 g of R972 into a 100 mL hexane solution containing 1.2 g of 1-hexadecanol, one would yield an alcohol-treated silica containing 29% of 1-hexadecanol if one prepares the sample by the solvent evaporation method. Instead, if one isolates the alcohol-treated silica by filtration followed by a gentle hexane wash, the silica is shown to contain ~ 17% by wt. of 1-hexadecanol as indicated by the weight up-take. This finding confirms that the maximum amount of 1-hexadecanol that can adsorb on the silica surface of R972 is ~ 17%. Incidentally, in a typical preparation of an alcohol-treated silica containing 17% by wt. of 1-hexadecanol, 3 g of R972 and 0.6 g of 1-hexadecanol are used. The total surface area in the silica sample is $3.3 \pm 0.6 \times 10^{22} \text{ \AA}^2$ based on the BET surface area of R972.⁶ The total molecular area for 0.6 g of 1-hexadecanol is estimated to be $\sim 3.7 \pm 0.6 \times 10^{22} \text{ \AA}^2$, assuming that 1-hexadecanol forms a Langmuir-Blodgett film structure with a molecular area of $25 \text{ \AA}^2/\text{molecule}$.⁸ The matching of surface area between the silica and 1-hexadecanol suggests that R972 can adsorb as much as one theoretical monolayer of alcohol on the surface.

The DSC scans for various 1-hexadecanol treated R972 silicas are depicted in Fig. 1. The melting peaks and the IR spectral data are tabulated in Table I. The results show that melting peaks only become observable at 1-hexadecanol concentrations $\geq 9.1\%$. Controlled experiments suggest that the absence of a melting peak at concentrations $\leq 4.8\%$ is not due to the low alcohol con-

centration on the surface. We hypothesize that the adsorbed alcohol is in a gaseous state at these low concentrations. At concentrations $\geq 9.1\%$, the hydrocarbon chains interact with each other on the silica surface, forming a hydrocarbon layer. It is important to note that at 9.1% of 1-hexadecanol, there is only half of a theoretical monolayer of 1-hexadecanol on the surface. The fact that the hydrocarbon chains start to interact and form a hydrocarbon layer indicates that hydrocarbon chains may be folding back toward the silica surface (Scheme 2A). Between 9.1 to 17%, the space occupied by the folded hydrocarbon chains is replaced by the incoming alcohol as the concentration of 1-hexadecanol is increasing (Scheme 2B). At concentrations above one theoretical monolayer, the excess alcohol may simply crystallizes on the alcohol-treated silica surface (Scheme 2C).



Scheme 2.

The hypothesis in Scheme 2 is supported by IR spectral data that show that the hydrocarbon chains are indeed interacting with each other when the alcohol concentration is higher than half of a monolayer. For example, the aliphatic C-H stretching of the methylene group is known to be sensitive to the packing density of the hydrocarbon chain, with a lower stretching frequency for CH_2 group in the crystalline phase.^{9,10} This frequency shift has been used to characterize the packing of the hydrocarbon chains in self-assembled monolayers and Langmuir-Blodgett films.¹¹ In Table I, we show that the C-H stretching frequency decreases from 2928.4 cm^{-1} at 4.8% of 1-hexadecanol on R972 to $\sim 2918 \text{ cm}^{-1}$ for 1-hexadecanol concentration $\geq 9.1\%$. The data clearly suggest that 1-hexadecanol molecules are interacting with each other at concentrations $\geq 9.1\%$ and there is certain degree of hydrocarbon chain packing analogous to that occurs in pure 1-hexadecanol. A simi-

TABLE II. DSC and IR Spectral Data of Silicas Formed by Adsorbing Various Alcohols on the Surface of R972 at a Theoretical Monolayer Coverage

Alcohol	m.p. by DSC (degree C)		IR (cm ⁻¹) ^a	
	neat	on R972	neat	on R972
1-dodecanol	29	14	2926.1	2925.9
1-tetradecanol	40	31	2919.9	2919.9
1-hexadecanol	54	41	2918.1	2916.9
1-octadecanol	62	55	2917.0	2917.9
1-eicosanol	68	63	2917.8	2918.0
1-docosanol	72, 74	69	2917.0	2917.6

(a) CH₂ stretching in the hydrocarbon chain of various alcohols.

lar conclusion has also been reached by solid state ¹³C NMR spectroscopy in a complimentary study. In that study, in addition to the packing information, ¹³C NMR data clearly show that the OH groups in the adsorbing alcohol are interacting with the silica surface.¹²

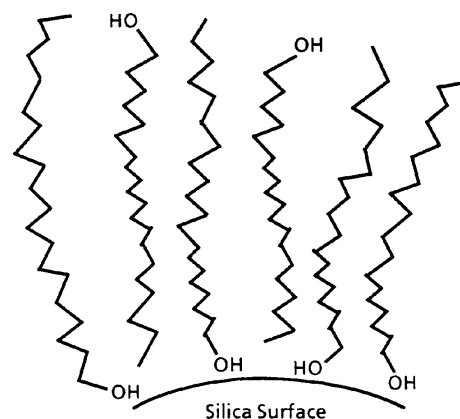
Effect of Chain Length. By making the assumption that each aliphatic hydrocarbon occupies ~ 25 Å²,⁸ a series of alcohol-treated R972 silicas of varying alcohol chain length were prepared. The DSC and IR results along with the data of the pure alcohols are tabulated in Table II. Both DSC and IR data in Table II suggest that alcohol molecules are adsorbing on the surface of R972 and that hydrocarbon layers are also formed through Van der Waals interactions of the hydrocarbon chains. For 1-dodecanol, 1-tetradecanol, and 1-hexadecanol, the CH₂ stretching frequencies are either equivalent or lower than those of the pure materials, implying that a significant packing for the hydrocarbon chains has occurred on the silica surface as compared to the neat materials. The contrary is observed for 1-octadecanol, 1-eicosanol, and 1-decosanol; relatively speaking, the hydrocarbon layers in these systems are less organized on the silica surface. We suspect that as the chain length in these long chain alcohols is increased, hydrophobic interaction may become more and more important, the thermal stability gained by having the OH group interacting with the silica surface is no longer dominating. A schematic of the possible interactive state is given in Scheme 3. If this molecular model is true, the surfaces of the 1-octadecanol, 1-eicosanol and 1-decosanol treated silicas will be relatively hydrophilic. Incidentally, we find that these silicas are less effective in imparting negative charging on SPAR toner and their charging is relatively humidity sensitive as compared to silicas treated by 1-dodecanol, 1-tetradecanol and 1-hexadecanol. The schematic provided in Scheme 3 is internally consistent with these observations.

Tribocharging of Alcohol Treated Silicas in Unpigmented SPAR Toners. The tribocharging properties of the prepared alcohol-treated silicas were examined by first blending them with a 9 μm unpigmented SPAR toner and then determining their tribo values against the metal beads at 20% and 80% RH at room temperature. The charging of the unpigmented SPAR toner and the R972/SPAR toner were also studied as controls. The results for the modified R972 silicas containing varying concentrations of 1-hexadecanol are summarized in Table III. The tribo results can qualitatively be rationalized based on the molecular models shown in Scheme 2. For example, the humidity sensitivity for the SPAR toner and the SPAR toner containing R972 is between

TABLE III. Effect of 1-Hexadecanol Adsorption on R972 on the Charging of SPAR Toner

Concentration of 1-hexadecanol	Toner tribo		Humidity sensitivity ^a
	20% RH	80% RH	
SPAR resin only	-15.4 μC/g	-2.2 μC/g	7.0
0% (R972 only)	-24.1 μC/g	-4.9 μC/g	4.92
4.8%	-30.4 μC/g	-8.9 μC/g	3.41
9.1%	-30.4 μC/g	-12.3 μC/g	2.47
13%	-30.4 μC/g	-12.8 μC/g	2.36
17%	-32.1 μC/g	-12.9 μC/g	2.49
23%	-27.9 μC/g	-11.5 μC/g	2.43
29%	-27.5 μC/g	-11.9 μC/g	2.31

(a) ratio of tribo value at 20% and 80% RH.



Scheme 3.

4.9 and 7. At 1-hexadecanol loading between 4.8% to 17%, we show that a hydrocarbon layer is formed due to chain folding. In our charging study, we observe a gradual increase in tribocharge at both 20% and 80% RH. Simultaneously, the humidity sensitivity is also reduced. Maximum tribo value and minimum humidity sensitivity (ratio of the tribo values obtained at 20% and 80% RH) are obtained when the R972 silica is treated with 17% 1-hexadecanol. This optimal performance corresponds to the adsorption of 1 monolayer of 1-hexadecanol on the surface of R972. We suggest that adsorption of 1-hexadecanol on R972 renders the silica surface more hydrophobic, leading to an increase in negative charging and a reduction in humidity sensitivity in the charging process.² This rationalization is supported by a water up-take study. We found that the water uptake for R972 treated with 17% of 1-hexadecanol is 0.17% from ~ 0% to 80% RH. The water uptake is less than that of the control (R972 silica), which adsorbs 0.26% by weight of water under an identical condition.

At 1-hexadecanol loading beyond 17%, both negative charging and humidity sensitivity fall off from the optimal value. The results can be rationalized using the model in Scheme 2C. For instance, when more than one monolayer of 1-hexadecanol is placed on the surface of R972, crystallization of 1-hexadecanol occurs. We assume that due to the more random orientation of 1-hexadecanol molecules on the silica surface (Scheme 2C), hydrophobicity of the alcohol-modified surface will be less than optimal, leading to the inferior charging results.

TABLE IV. Tribocharging Properties of Various Alcohol-Treated R972 Silicas at a Monolayer Coverage

Alcohol	Toner tribo		Humidity sensitivity ^a
	20% RH	80% RH	
1-dodecanol	- 28.5 $\mu\text{C/g}$	- 9.3 $\mu\text{C/g}$	3.06
1-tetradecanol	- 29.3 $\mu\text{C/g}$	- 11.7 $\mu\text{C/g}$	2.50
1-hexadecanol	- 30.4 $\mu\text{C/g}$	- 12.3 $\mu\text{C/g}$	2.49
1-octadecanol	- 26.9 $\mu\text{C/g}$	- 8.4 $\mu\text{C/g}$	3.20
1-eicosanol	- 26.2 $\mu\text{C/g}$	- 6.1 $\mu\text{C/g}$	4.30
1-docosanol	- 24.8 $\mu\text{C/g}$	- 5.6 $\mu\text{C/g}$	4.43

(a) ratio of tribo value at 20% and 80% relative humidity.

Table IV summarizes the results of the effect of the chain length of the adsorbed alcohol on the charging in SPAR toner. A chain length effect is observed and optimal tribos at 20% and 80% RH are obtained for 1-hexadecanol. Theoretically, the number of alcohol molecules that are on the silica surface is identical. The variation in tribo suggests that the formed hydrocarbon layers are different among all the alcohols studied. The increase in tribo from 1-dodecanol to 1-tetradecanol to 1-hexadecanol seems to suggest that the protection from the hydrocarbon layer increases as the chain length increases in this regime. The tribo decreases as the chain length increases for 1-octadecanol, 1-eicosanol and 1-docosanol. The decrease in tribo and the increase in humidity sensitivity on toner charging suggest that the surfaces of these modified silicas are more hydrophilic relative to their shorter chain analogs. We suggest that the packing of the hydrocarbon chains for these long chain alcohols is less ordered on the silica surface. Specifically, due to the increased hydrophobic interaction (through the CH_2 groups) between the hydrocarbon chains, these long chain alcohols may have been incorporated into the hydrocarbon layer with the OH group pointing to both directions (Scheme 3). Again, hydrophobicity of the modified silica surface is a determining factor for tribocharging and humidity sensitivity.

Conclusions

This work demonstrates that hydrocarbon layers are formed when long chain alcohols are adsorbed on the

surface of silica particles. The formed hydrocarbon layers increase the hydrophobicity of the silica surfaces. As a result, higher tribo values and reduction in humidity sensitivity in toner charging are obtained when the silica is incorporated in SPAR toner. For R972 silica, optimal charging results are obtained when one theoretical monolayer of 1-hexadecanol is adsorbed on the silica surface. Both alcohol concentration and chain length are shown to have an effect on toner charging. The results can be rationalized based on the molecular structure of the adsorbed alcohol layer on the silica surface. As it turns out, depending on the structure of the adsorbing layer, the hydrophobicity of the alcohol-modified silica surface does vary. The charging performance correlates well to the hydrophobicity of the silica surface, the higher the hydrophobicity, the better the charging results. \blacktriangle

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