The Physics and Chemistry of Metal Oxide Particles in Toners

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Introduction

In xerography, submicron metal oxide particles, such as SiO_2, TiO_2 and Al_2O_3, are commonly added to the toner particle surface. It is well known that these oxides improve the flow of toner,[1] have a large effect on charging levels and charging rates,[2] and can substantially reduce toner adhesion to substrate surfaces.[3] The purpose of this report is an initial systematic study of the role of: (1) the oxide physics, including particle size and toner surface coverage; and, (2) the oxide surface chemistry, including the effect of chemical surface modification. Key to these studies is the use of infrared spectroscopy (IR) to study adsorbed species on the oxide surface.

Table 1. Metal Oxides

Designation	Hydrophilic Base Oxide	Treatment
Al_2O_3	20 nm Al_2O_3	none
P25™	21 nm TiO2	none
R812™	7nm A300™	1)HMDS$_{(v)}$ {$(CH_3)_3$ Si NHSi$(CH_3)_3$} by Degussa
R8 12™/FTS	7nm A300™	1) HMDS$_{(v)}$ by Degussa 2) FTS$_{(sol'n)}$ {$CF_3(CF_2)_5$ $(CH_2)_2$ $SiCl_3$}
R972™	7nm A300™	1)DMDCS$_{(v)}$ {$(CH_3)_2$ $SiCl_2$)} by Degussa
A380™	7nm A380™	none
A380™/OTS	7nm A380™	1) OTS$_{(sol'n)}$ {$CH_3(CH_2)_{17}$ $SiCl_3$}
A380™/TEA/OTS	7nm A380™	1) TEA$_{(v)}$ {$(CH_3CH_2)_3N$: } 2) OTS$_{(sol'n)}$
A380™/TEA/OTS/washed	7nm A380™	1) TEA$_{(v)}$; 2) OTS$_{(sol'n)}$ 3) CH_3OH/H_2O washed 4) dried in vacuum
A380™/FTS	7nm A380™	1) FTS$_{(sol'n)}$

*the subscripts (v) and (sol'n) indicate vapor and solution phase reactions, respectively.

Materials and Methods

Metal Oxides

The untreated and treated metal oxides used in this study are shown in Table 1. FTS, DMDCS and OTS are from Huls (Petrarch). For solution treatment, the oxide was dispersed in CH_2Cl_2, silane was added, and after 3 hrs. stirring, the oxide was dried. For FTS, the weight of silane to silica was 0.35:1, which is the theoretical stochiometric amount needed to react FTS with all the silica surface SiOH groups. For OTS, the stochiometry was the same, at 0.28:1 to the silica. Vapour phase treatments were in vacuum as we have described previously.[4,5] IR spectra of oxides were recorded as described previously to monitor surface reactions.[5]

Charging and Flow Measurements

Toners with oxides were prepared by ball milling the oxide and 11μm Xerox Model 1075™ toner for 30 min. The oxide level was calculated as 100% coverage on the toner,[6] assuming perfect oxide dispersion. Scanning electron microscopy was used to monitor oxide coverage. In all cases 2 wt% toner and Xerox Model 9200™ carrier were blended on a roll mill for 15 minutes so that the toner reached its maximum triboelectric charge, measured by the standard total blow-off method. Toner flow (cohesion) was measured using the Hosokawa Powder Tester.[7]

Table 2. Toner Triboelectric Charge and Flow

Metal Oxide Additive	Toner Q/M* (μC/g)		Toner Flow** (% Cohesion)	
	20%RH	80%RH	20%RH	80%RH
none	-7.0	-0.7	13.4	12.8
Aluminum Oxide C™	0.0	0.0	3.4	2.7
Aluminum Oxide C™/HMDS	-7.1	-5.0	1.5	1.3
P25™ TiO_2	-7.7	-1.0	9.8	8.7
P25™ TiO_2/HMDS	-13	-8.9	4.8	4.5
A380™ SiO_2	-28	-5	4.6	6.7
A380™ SiO_2/ HMDS	-95	-24	2.2	2.0
R812™ (A300 SiO_2/HMDS)	-60	-22	2.0	1.8
R972™ (A300 SiO_2/DMDCS)	-62	-31	2.6	2.0
A380™ SiO_2/OTS	-25	-20	4.7	5.0
A380™ SiO_2/TEA/OTS	-36	-14	11.2	13.7
A380™ SiO_2/TEA/OTS/washed	-64	-40	6.1	6.8
A380™ SiO_2/FTS	-75	-65	3.7	2.6
R812™ SiO_2/FTS	-51	-29	2.0	1.7

* measurement precision <5%, sample reproducibility error <10%
**measurement precision <10%, sample reproducibility error < 10%

Results and Discussion

Triboelectric Charging

The charge of all toners, with and without surface oxides, are shown in Table 2. Compared to the negative toner charge without added oxide, the charge with untreated

Al_2O_3 drops to zero, becomes slightly more negative with untreated TiO_2, and much more negative with untreated silica. Charge is always lower at 80% than at 20% relative humidity (RH), and the difference in the charge between 20% and 80%RH increases with charge. At either RH extreme, charge does not correlate with oxide pH values, which are not very different: pH = 4.5 to 5.5 for Al_2O_3, 3-4 for P25 TiO_2, and 3.6 to 4.3 for A380 SiO_2.[8] However, the charge does correlate with the oxide point of zero charge (pzc), which occurs at a pH = 9 for Al_2O_3, 6 for TiO_2 and 2-3.7 for silica,[9] with the most acidic pzc correlating with the most negative charge.

Treatment of oxides with HMDS makes them hydrophobic, by capping the M-OH (M = metal atom) groups of the oxide with $-Si(CH_3)_3$.[8] This increases the charge of all oxides at both RH extremes. However, the charge of the treated oxide is not determined by just the surface treatment, as the charge clearly depends on the nature of the base oxide (increasing charge with more acidic pzc). As with untreated oxides, the difference in charge between 20% and 80% RH increases with increasing charge. The hydrophobic oxides also impart much better flow compared to hydrophilic oxides. This is reasonable, as we observed that hydrophilic silicas alone clump together at high RH, indicative of increased interparticle adhesion. It is known that water can increase interparticle adhesive forces.[10]

Two commercial hydrophobic treated oxides are shown, one treated with HMDS (capping the SiOH groups with $-Si(CH_3)_3$ and one treated with DMDCS (capping with $>Si(CH_3)_2$).[8] The toner charges with these oxides are nearly identical, although charge with R972 is slightly higher at 80%RH, somewhat surprising, as R812 is more hydrophobic than R972.[8] It is also surprising that neither oxide is as negatively charged as HMDS treated A380, since the latter treatment is done on aged silica, while the former is done at high temperature on silica *in stata nascendi*, where it is more reactive.[8]

It is clear from Table 2 that making oxides hydrophobic with short alkyl chain silanes does not prevent a large and undesirable RH sensitivity in charging. To make these oxides more resistant to RH changes, Table 2 shows the results of our treatment of silica by either of two long chain hydrocarbons: OTS with a Cl8 chain, and FTS with a fluorinated C9 chain. Our IR investigations show that OTS does not attach to the silica surface,[5] unless the silica is first treated with a base (TEA) to promote the reaction.[4,11] In the latter case, a TEA chloride salt is formed, which must be first removed by washing to obtain the optimal charge. The difference in toner charging between OTS and TEA/ OTS treated silicas is striking, with the TEA/OTS showing much higher charge, at both 20% and 80%RH, while OTS alone is not very effective in increasing charge. In contrast to OTS, FTS without added base does react effectively with the silica SiOH groups, as can be shown by IR.[11] The FTS treatment gives the highest toner charge, particularly at high RH. The improvement over the OTS is presumably due to the more hydrophobic nature of the fluorohydrocarbon over pure hydrocarbon.

Flow

The flow of all toners are also shown in Table 2. Lower % cohesion indicates better toner powder flow. In all cases but one, flow improves with surface flow additives present. The exception is silica that has been treated by TEA/OTS, where the treated silica was not washed to remove the TEA salt. The salt presumably attracts water to the silica surface, increasing the cohesion between silica particles. The role of water in decreasing toner flow, is also supported by the general flow improvement with hydrophobic treatment of the oxide by short chain hydrocarbon silanes (HMDS or DMDCS). The flow is nearly equal for silica treated by any of the short chain hydrocarbon silanes. Water is implicated in decreasing flow, but the untreated hydrophilic oxides are not very sensitive to RH (neither are the oxides treated by any of the short chain hydrocarbon silanes). The exception is untreated hydrophilic A380 silica, which flows more poorly at 80% RH than at 20%RH. Silicas treated by long chain hydrocarbon and fluorohydrocarbon silanes behave quite differently from oxides treated with short hydrocarbon chain silanes. Thus OTS treatment of A380, where OTS does not effectively attach to the silica surface, does not improve flow at 20% RH, but does improve flow at 80% RH. OTS/TEA treatment of silica (with washing), where the long chain hydrocarbon silane is attached to the silica, gives poorer flow than if the OTS chains are not surface attached. Thus, it appears that long hydrocarbon chains on the silica surface make flow worse, compared to short chains. However, long chains do ameliorate the decrease in flow with RH. Again, the unwashed TEA/OTS treated silica is a special case, due to the presence of the hydrophilic salt. Flow with this unwashed silica is much poorer than with the washed silica, and becomes even worse going from 20% to 80%RH. The silica treated with the long chain fluorohydrocarbon gives better flow than the hydrocarbon chain, and does improve flow compared to untreated silica. Indeed, the flow even improves somewhat at 80% RH.

Conclusions

The negative charge of toners covered with high surface area metal oxides, whether hydrophobic after silane treatment, or hydrophilic without treatment, correlate with the oxide pzc, with a more acidic pzc corresponding to a higher charge. Charge is always lower at 80%RH than at 20%RH. Treatment with short hydrocarbon chain silanes, which react with the oxide surface M-OH groups, increases charge in all cases, but is not effective at improving RH sensitivity. Silanes with long hydrocarbon chains do not effectively increase the toner charge with the oxide, unless the silane is attached to the oxide surface M-OH groups. For silanes with long hydrocarbon chains this attachment only occurs effectively with a two-step base promoted reaction. When the long chain hydrocarbon silane is effectively attached to the oxide surface, the RH sensitivity is improved, and the toner charge increases. In contrast, fluorohydrocarbon chain silanes are more reactive than pure hydrocarbon chain silanes, so that the former react effectively without base promotion. Treatment with fluorohydrocarbon silanes result in the highest charging, and the lowest RH sensitivity. The improvement in RH sensitivity with the long chain silanes is ascribed to the increased hydrophobicity of the oxide.

The flow of toners improves with the surface addition of high surface area metal oxides, and with oxide treatment

by short chain hydrocarbon silanes. Flow is not sensitive to RH, except that untreated hydrophilic silica shows poorer flow at high RH. Longer chain fluoro and hydrocarbon substituted silanes are not as effective as short chain hydrocarbon substituted silanes for silica treatment to improve toner flow. This might be due to entanglement between long chains on different silica particles, or to increasing the conformability of the surface, which would increase the contact area between silica particles. They are effective, however, in reducing the sensitivity of flow to RH changes. The long chain fluorohydrocarbon silane treated silica showed better flow than the long chain hydrocarbon silane treated silica. This is ascribed to a shorter chain length, and lower surface energy due to the fluorine content, with the former treatment.

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