Study of the Effect of External Additives on Toner Admix Performance

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Abstract

The charge-admix-exchange process happening in the xerographic developer between aged and fresh toner, as well as carrier particles carrying different electrostatic charges, is a complex and not well-understood process from a theoretical point of view. Fast electrostatic charging of fresh toner particles to a desired steady state in a developer is very important to achieve high quality prints, especially in the case of high speed printing devices. One common way that formulators try to improve toner admix is by adjusting the external additive package [1-3].

The goal of this study was to gain a better understanding of how different additive morphology and surface treatment influence admix. More specifically, we investigated what happens with the electrostatic charge of toner when aged and fresh developers are mixed in equal proportions and the mixture exercised over a short time period.

Results of the study of a simple model developer containing a positively charging toner, a single fumed silica surface treated with a silane containing an amino group, and a silicone coated ferrite carrier, will be presented. The collected data indicate that the carrier's ability to gain electrostatic charge quickly decreases as a result of the transfer of silica particles or molecules of the silica treating agent to the carrier's surface. This leads to an unfavorable performance in the admix test.

In the second part of the work, the effect of different types of spacer additives on carrier poisoning and admix was studied. The obtained results show that the formulations containing spacer particles have more stable charge vs. exercise time and better admix characteristics than the formulation containing only one silica additive.

Introduction

Rapid electrostatic charge pick up by fresh toner added to a developer which already contains charged toner (admix) is an important characteristic of a successful xerographic development system [1-5]. Despite significant technological importance, to our knowledge, there are few systematic studies of toner admix phenomenon and few reports dealing with this phenomenon at the materials level [2, 5].

Although, it is generally known in the field that external additives play an important role in helping to accelerate toner charging and to maintain a constant level of charge over time, selection of additives for optimization of toner charge pick up rate remains more of an art than a science. At the materials level, for example, effects of additive morphology, surface treatment, and electrical resistivity on toner charge pick up rate remain poorly understood. The overall goal of this study is to investigate the role of external additives in the toner admix process and learn how to design external additives to improve toner admix.

Experimental

Model toner and carrier. Commercial positively charging styrene-acrylic 9 μ m black toner containing no external additives was used in this study in combination with a commercial 80 μ m (BET surface area 0.16 m²/g) silicone coated carrier which has a complex metal oxide core (Mg, Mn, Fe oxide).

External additives. Four different external additives were used in this study: TG-7120 surface treated fumed silica manufactured by Cabot Corporation, JMT-150ANO surface treated fumed titania manufactured by Tayca Inc., and two types of spacer particles which are under development at Cabot Corporation. Characterization data for the external additives used in this study are summarized in Table 1.

Silica name	Base particle	Surface
or ID #		treatment
	115-145 m ² /g fumed	Cyclic silazane
TG-7120	silica, average	and hexamethyl-
	primary particle size	disilazane
	is 20 nm	
	50-80 m ² /g titanium	Silane coupling
JMT-150ANO	dioxide, average	agent
	primary particle size	
	is 15 nm	
	~30 m²/g colloidal	Cyclic silazane
Spacer #1	silica, average	and hexamethyl-
	particle size is ~100	disilazane
	nm	
	~60 m ² /g silica-	Cyclic silazane
Spacer #2	polymer composite,	and hexamethyl-
	average particle size	disilazane
	is ~80 nm	

Table 1. Characterization data for external additives used in this study.

Preparation of developers. A IKA M20 universal mill was used to mix external additives with the toner. Fumed silica and titania were loaded at 0.5 or 1.5 wt% while spacer additives were loaded at 1 wt%. To prevent toner from overheating and melting, mixing was performed in three 15 s pulses separated by 15 s cooling intervals. Developers were prepared by mixing toner formulated with external additives with the carrier. The developers contained 4 wt% of toner and 96 wt% of carrier.

Before the measurements of triboelectric charge, the developers were conditioned for several hours at 25 °C /50 % RH. After conditioning, electrostatic charge was developed by shaking glass jars with the developers for 0.5, 1, 5, 30 and 120 min using a TURBULA® Shaker-Mixer.

Q/m measurements. Triboelectric charge measurements were performed using a Vertex T-150 tester (Vertex Image Products, Inc.). 1 g of charged developer was placed in a Faraday cage and the toner blow off from the carrier was performed for 1 min using ~20 psi air jet. The electrostatic charge on the carrier remaining in the Faraday cage was measured by the electrometer built into the Vertex T-150 tester and the mass of blown off toner was determined as a difference between the weights of the Faraday cage before and after the blow off.

Q/d measurements. Q/d measurements were performed using charge spectrometer manufactured by Epping PES Laboratorium. The data collection settings were: developer activation time 1 s, toner deposition time: 3.0 s, electrode voltage: 4000 V, and air flow: 80 mL/min. Before the Q/d measurements developers were charged by shaking for 1 min, 30 min, or 120 min. Blends were prepared by adding together the same amounts of developers exercised for 1 and 30 min or 1 and 120 min and shaking these mixtures for 1 min. After that Q/d spectra were recorded.

Results and Discussion

The electrostatic charge (Q/m) for the three different toner formulations used in this work is plotted in Figure 1 as a function of toner/carrier mixture shaking time.



Figure 1. Electrostatic charge developed in the toner/carrier mixtures as a function of shaking time. Data for toner without external additives (circles) and for toners containing 1.5 wt% of TG-7120 surface treated fumed silica (squares) and 1.5 wt% JMP-150ANO surface treated titania (triangles) are plotted.

The data in Figure 1 indicate that none of the three developers reaches a steady state (state with equal charge-discharge rates) with bare toner being the closest to steady-state condition after \sim 30 min of shaking. This suggests that our model developers are far from being optimized. Nevertheless, we think that the results

collected in this study are still valid and applicable to other, better tuned, developers. Collected data show that, on one hand, addition of surface treated fumed silica or surface treated titania accelerates toner charging (points at 0.5, 1, and 5 min from the start) compared to toner without additives. On the other hand, in the system under investigation, the external additives clearly contribute to a decrease of toner charge after 30 min shaking.

The Q/d spectra for toners mixed with TG-7120 silica and JMT-150ANO titania and shaken with carrier for 1, 30 an120 min as well as spectra of the blends (1 + 30 min and 1 + 120 min) are shown in Figure 2. In these spectra, position of the blend peak with respect to positions of the peaks of blend components is the characteristics of admix which we are going to follow.

In the spectra for toner containing TG-7120 silica, position of the blend peak is shifted to the left with respect to the peaks for the blend components. While in case of 1 + 30 min blend, this shift to the left is relatively small (Plot A), in case of 1 + 120 min blend this shift is significantly more pronounced and even electrostatic charge polarity is reversed from positive to negative (Plot B).

The situation is different in case of toner containing JMT titania (Plots D and E). In this case maximum of the Q/d distribution for 1 + 30 min blend (Plot D) is located between the peaks for blend components. Peak for 1 + 120 min blend is shifted to the left from blend components (Plot E) but to a lesser extent than in the formulation with TG-7120 silica.

Comparison of the relative positions of Q/d peaks (Plots A, B, D, and E) with Q/m data (Plots C and F), suggests that position of the blend peak in the Q/d spectrum could be explained based on the Q/m data.

For example, in case of formulation with TG-7120 silica, $Q_1 > Q_{30} > Q_{120}$ and the difference between Q_1 and Q_{120} is ~30 μ C/g which is ~3X larger than the difference between Q_1 and Q_{30} . Also, it is important to note that Q_{120} is close to zero. When two developers exercised for 1 and 30 min or 1 and 120 min are combined, it is possible that some de-electrification of the like charged particles takes place. This process could result in reversal of polarity of electrostatic charge [6, 7]. Also, Q/m data suggest that electrostatic charge in developers exercised for 30 and 120 min could only decrease upon further shaking. Overall, it seems that in the combined developer (blend) there is no particle-particle interaction which could lead to increase of electrostatic charge.

The situation is different for formulation containing JMT-150ANO titania. In this case $Q_1 < Q_{30}$ and $Q_1 > Q_{120}$ and differences between Q_1 , Q_{30} , and Q_{120} are small, i.e. 5-6 μ C/g. Position of the peak for 1 + 30 min blend is shifted to the right from the 1 min peak because in this case, on one hand, toner and carrier which were exercised for 1 min still have significant capacity for further charge increase and, on the other hand, charging capacity of toner and carrier which were already exercised for 30 min doesn't decrease sharply upon further exercise. Peak for the 1 + 120 min blend is shifted to the left from 1 min because for such blend charge decay starts to overcome charge increase.

The reason why toner charge decreases over the longer exercise times (30 and 120 min) is that upon shaking of



Figure 2. Plots A and B show Q/d spectra of model toner formulated with 1.5 wt% of TG-7120 silica while Plots C and D show spectra of toner formulated with 1.5 wt% JMT-150ANO titania. Experimental data are fitted with Gaussian functions and positions of the Gaussian peaks are shown on the plots as x0. The Gaussian functions don't provide a good fit for shoulders which are observed in many cases on the right hand side of the peak and should be considered only as a first approximation of the experimental data. Q/m data for formulations with TG-7120 silica and JMT-150ANO titania are shown on Plots C and F, respectively. Electrostatic charges (Q/m) after 1, 30, and 120 min of shaking are marked as Q₁, Q₃₀, and Q₁₂₀.

toner/carrier mixture, the carrier surface becomes contaminated with particles of positively charging external additives mixed with toner resin. This contamination of the carrier surface decreases the carrier's ability to gain negative charge. At the same time external additives become embedded into the toner surface, decreasing toner's ability to gain positive charge. These phenomena are illustrated on SEM images shown in Figure 3.



Figure 3. SEM images of the model toner mixed with 1.5 wt% of TG-7120 silica before (A) and after (B) shaking with the carrier for 120 min.

Comparison of images A and B clearly shows that shaking for 120 min results in partial impaction of fumed silica into toner. Also, some clumps attributed to fumed silica/polymer mixture could be seen on the surface of aged toner (white arrows on image B). Images C and D are SEM images of surface of fresh and aged carrier from the same experiment. White arrows on image D show small clumps of toner/silica mixture present on the surface of aged carrier. Scale bars on all images correspond to 400 nm.

One possible way to slow down impaction of fumed silica into toner and transfer of material from toner to carrier surface is to introduce spacer additives. In this study, two types of positively charging spacer additives were used (see details in Table 1). Q/m data for formulations containing spacer particles are shown in Figure 4. The data indicate that substituting 1.0 wt% of fumed silica by spacer particles reduces the initial toner charge (0.5, 1 and 5 min) but helps to slow down charge decay after 30 and 120 min of exercise with the carrier.

The Q/d spectra for toners containing spacer particles are shown in Figure 5. Positions of all three peaks, i.e. 1 min, 30 min and 1 + 30 min blend, are very close for both formulations. These data suggest that presence of 80-100 nm spacer particles may reduce rate of transfer of material between toner and carrier surfaces and, therefore, help to maintain toner charge and fast admix. Comparing Figures 5 and 2 shows that the admix stabilty

with the fumed silica and spacer particles is significantly better than fumed silica or titania alone.



Figure 4. Electrostatic charge of toners mixed with 1.5 wt% of TG-7120 silica and with 0.5 wt% TG-7120 and 1.0 wt% of Spacer #1 or #2 as a function of shaking time.

In case of formulation with TG-7120 silica (Figure 2, Plot A), the position of the blend peak is shifted by -1.8 and 1.0 fC/10 μ m with respect to positions of 1 and 30 min peaks, while in case of formulations containing Spacer #1 and #2, these shifts are only - 0.2 and -0.1 fC/10 μ m and +0.4 and -0.3 fC/10 μ m, respectively (Figure 5). Further and more detailed studies are necessary in order to understand the effect of spacer particles on material transfer between toner and carrier surfaces.



Figure 5. Q/d spectra for model toner mixed with 0.5 wt% of TG-7120 silica and 1.0 wt% of Spacer #1 (Plot A) and 0.5 wt% of TG-7120 and 1.0 wt% of Spacer #2 (Plot B).

Conclusion

Electrostatic charge exchange processes taking place when new and aged developers are mixed are complicated from two points of view: (1) multiple interactions between toner and carrier particles present at different charging states contribute to the admix process - some of these interactions are shown in Figure 6; (2) interaction between charged particles involves transfer of electrostatic charge and transfer of material (i.e., external additives, polymer) which, in turn, affects toner and carrier charging properties. One way to maintain fast admix for fresh and aged toners is to introduce spacer additives which may be able to slow down degradation of charging properties of toner and material transfer between toner and carrier surfaces.



Figure 6. Scheme illustrating some of the interactions between the particles of fresh (1 min) and aged (120 min) toners and carriers. Electrostatic charge on fresh toner is designated as $+Q_{1,0}^{t}$, on fresh carrier as $-Q_{1,0}^{c}$, on aged toner as $+Q_{120}^{t}$ and on aged carrier as $-Q_{120}^{c}$. Six interactions are labeled as i - vi. If $Q_1 > Q_{120}$ as in Figure 2 (Plot C), than it's likely that five interactions (ii-vi) result in decrease of electrostatic charge upon further shaking of the blend and only one (i) can lead to increase of charge.

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