

# Effect of Metal Oxide Surface Additives on Xerographic Toner Powder Flow Cohesion and Cohesion Aging Stability

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## Abstract

A systematic approach was used to select metal oxides with varying composition, surface chemistry and particle size, which were then blended on toner particles as surface additives. The Hosokawa Powder Flow tester was used to study the toner cohesion, both as initially blended, and with aggressive toner aging. The toner powder flow cohesion and aging was studied for two different base toner particles, based on a styrene/acrylate resin and a polyester resin. It is shown that selection of the metal oxide size, oxide type and chemistry is important to ensure stable flow with aging time.

## Introduction

Surface oxide particles control xerographic toner charge,<sup>1-5</sup> flow<sup>6-7</sup> and transfer.<sup>8</sup> Thus, while there have been previous studies of the effect of surface metal oxide additives on toner flow, none have studied the effect of the additive properties on flow stability with aggressive aging. This aspect of surface additive aging will be studied in this paper.

## Experimental

Cyan styrene/acrylate (St/Ac) and polyester (PE) 7.0 µm toners were studied, with silica surface additives of 30 nm and 40 nm primary particle size, titania of 40 nm primary particle size and alumina of 30 nm primary particle size. In some cases, additives were tested with both short- and long-chain hydrophobic alkylsilane treatment.

Toner (60 g) was dry blended with additives for 15 s at 15000 rpm. Additives were added based on an equal SAC\*size = 4000, where SAC is % surface area coverage,<sup>9</sup> and size is in nm. While 100% SAC gives optimal flow, for aging this is not the best loading to study. Correcting the SAC with the primary additive size gives the same additive layer thickness on the toner surface, which enables the study of any inherent differences of the additives. In other words, when all additives are loaded to the same coating thickness on the surface, are there differences in cohesion aging due to the chemistry and primary size of the additives?

For all cohesion aging studies, 40 g of blended toner and 200g of 1/8-inch steel shot were weighed into a 250g bottle, conditioned overnight at 50% RH and paint shaken for 5, 15, 30, and 60 minutes. At longer times toner particles showed fracture and fines generation, so 60 minutes was limit utilized in this study. Particle size was measured on a Coulter Counter for one hour samples, while SEM was done at t=0, 30 and 60 minutes. Cohesion was measured using a Hosokawa micron powder tester with screen sizes of 53µm and 45µm and 38 µm using 2 grams of toner. The % toner flow cohesion, was calculated in the usual manner.

$$\% \text{ Cohesion} = 50*A + 30*B + 10*C \quad (1)$$

In Formula 1, A is the weight of toner left on the top screen, B the weight on the middle screen, and C the weight on the bottom screen.

## Results and Discussion

Figure 1 shows the cohesion increase (flow loss) for the styrene/acrylate base toner without any surface additives and with a 40 nm primary particle size fumed silica, either untreated, or treated with a short-chain alkylsilane, or treated with a long-chain alkylsilane. The higher the cohesion, the worse is the toner powder flow. The base toner shows poor initial flow, which initially increases rapidly with aging to a relatively stable value. If there was increase in fines with aging, then this might make flow worse, since fine particles flow more poorly than larger.<sup>6</sup> However, no increase in fines content was noted over 60 minutes. Also, a change in toner morphology with aging might affect cohesion. However, SEM showed no apparent visible change in particle morphology. Presumably, the high points on a toner surface, the asperities, which control the inter-particle cohesion,<sup>6</sup> are flattened somewhat on aging, due to plastic flow of the toner resin. However, if these changes are occurring, it is not evident by SEM. On addition of untreated 40 nm silica surface additive, the flow improves dramatically, as does the flow cohesion aging. If the same 40 nm silica is surface treated with short-chain silane, flow is initially better, due to reduction of capillary and hydrogen bonding forces for the hydrophobic silica.<sup>6</sup> However, the short-chain treated silica

offers no advantages on toner cohesion aging, indicating that hydrophobic treatment does not improve or minimize the impaction of the additive into the toner. Making the silane chain longer shows little effect compared to the shorter chain, except that initial flow is somewhat worse.

Figure 2 shows cohesion aging with 40 nm silica, untreated, or treated with either long-chain alkylsilane or fluoro alkylsilane. It was anticipated that fluoro alkylsilane might show better cohesion aging due to lower surface energy. However, fluoro alkylsilane gives a rapid cohesion increase to a level that is close to that of base toner. Clearly additive chemistry is important to aging, but not understood.

Figure 3 shows aging of styrene/acrylate toner with long-chain alkylsilane treated 40 nm titania and short-chain alkylsilane treated 30 nm treated titania.

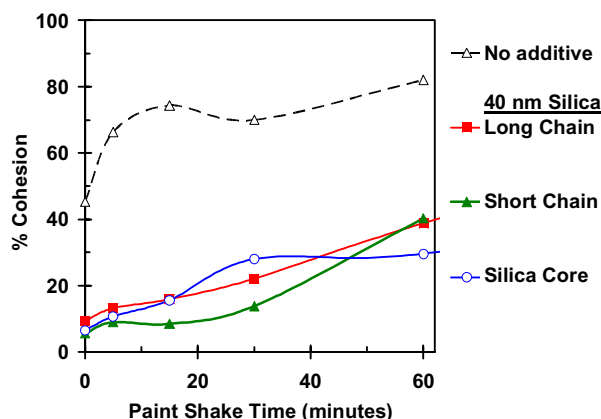


Figure 1. Cohesion aging of styrene/acrylate toner without additives; and with 40 nm silica, either untreated, or treated with a short- or a long- chain alkylsilane.

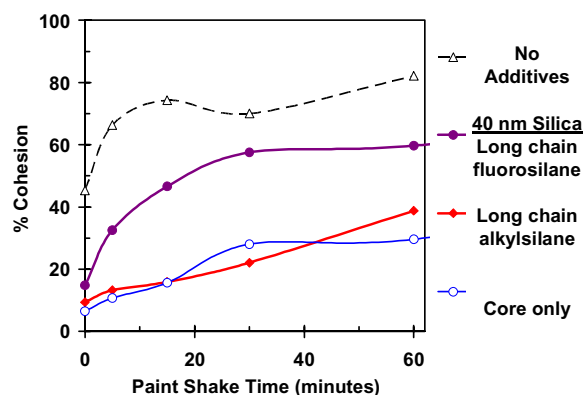


Figure 2. Cohesion aging of styrene/acrylate toner with 40 nm silica, with either alkyl- or fluoro- alkylsilane treatment.

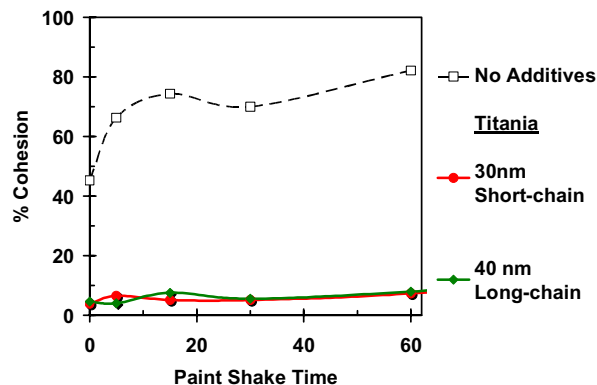


Figure 3. Cohesion aging of styrene/acrylate toner with titania of different sizes and alkyl chain lengths.

Both additives gave identical initial lower and very stable cohesion, showing no cohesion aging over the full 60 minutes. It would appear that the neither the size nor the length of the alkyl silane chain treatment had a significant effect on cohesion aging with  $\text{TiO}_2$ . Both titania additives show excellent aging performance.

Figure 4 shows the effect of the base oxide Si, Al and  $\text{TiO}_2$  with long-chain alkylsilane treatment. The 30 nm silica and alumina, and 40 nm titania, all had low, stable cohesion with aging. Thus, there was no effect of base oxide but an effect with the additive size. However, the large 40 nm silica did show a cohesion increase with aging. The initial cohesion for this large silica was also higher than the smaller silica. The higher initial cohesion with large silica, is expected based on previous work,<sup>6</sup> but on aging the smaller silica core aged much better than the larger. Since the additive layer thickness on the surface was equal for all oxides, and since the chemistry of the small and large silicas were the same (they had the same surface treatment), other factors must be important.

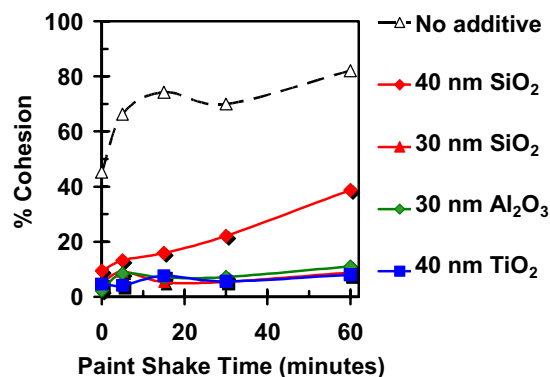


Figure 4. Cohesion aging of styrene/acrylate toner with silica, alumina and titania, all with the long chain alkylsilane treatment.

To extend the generality of results with the styrene/acrylate, some additional experiments were done using a base polyester toner. Figure 5 illustrates the cohesion aging with short-chain alkyl silane treated 40 nm silica with short-chain silane, on both the styrene/acrylate and the polyester base toners. For comparison, the base toners without additives are also shown.

The two base toners have remarkably similar cohesion aging profiles, although the polyester has higher cohesion at nearly all ages. With the short-chain silane treated 40 nm silica, the cohesion and cohesion aging for both styrene/acrylate and polyester base toners were nearly identical. Slight differences in base toner cohesion did not appear to affect final toner cohesion with oxide additives.

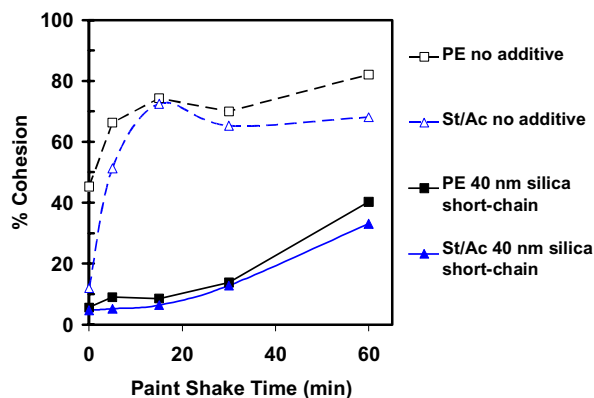


Figure 5. Cohesion aging of styrene/acrylate and polyester toner, both base toners and with short-chain silane treated 40 nm silica.

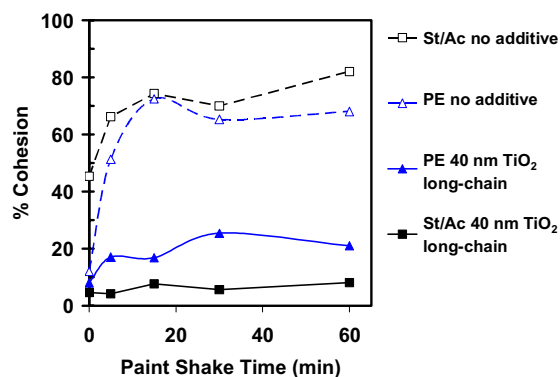


Figure 6. Cohesion aging of styrene/acrylate toner with 30 nm silica and alumina, both with the same long alkyl silane treatment.

Figure 6 shows a comparison of the cohesion aging with the styrene/acrylate and polyester base toners, both with the 40 nm silica, with a long-chain silane treatment. While both show similar initial cohesion, there is a rapid initial increase in cohesion for the polyester, which then also shows stable flow on continued aging. Thus, there is some difference in cohesion with the two base toners, with this initial increase in cohesion, but the overall aging in both cases shows similar stability. Thus, in Figure 5, both show some instability, while with the additives in Figure 6, both show relatively stable performance. On either base toner, the cohesion and cohesion aging is reasonably similar.

## Conclusions

Toner flow was studied as a function of aggressive aging on styrene/acrylate and polyester toner particles, varying metal oxide surface additives. Overall, on styrene/acrylate particles, 30 nm silica, 30 and 40 nm titania, and 30 nm alumina, with short- and long-chain alkylsilane treatments, gave similar low initial cohesion, with little loss of flow on aggressive aging. However, with a larger 40 nm silica core, either untreated or treated with a hydrophobic long-chain silane, there was considerable loss of flow on aging. Long-chain fluoro alkylsilane treatment of the same 40 nm silica gave worse aging, although initially flow was also very good.

Overall, both oxide surface chemistry and oxide size can be important in cohesion aging, although inherently both 30 and 40 nm oxides, with either short- and long-chain alkylsilane treatment can show similar excellent aging. The polyester base toner replicated the styrene/acrylate results, suggesting the base toner surface was not critical.

## References

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### **Biography**

**Mrs. Maria McDougall** has a B.Sc. in Industrial Chemistry, specializing in Organic Chemistry. She started her professional life as a researcher in the heart of the Amazon forest working with natural products doing extractions, isolation, purifications and identification of alkaloids and other compounds found in trees and small plants used by natives of this region.

She has been with Xerox for over 15 years; and for the last 10 years has been working in the Developer Physics Area on new toner evaluations and toner design. Areas of interest are related to the chemistry of metal oxides and interactions with xerographic toners, and the physics of nanoparticles and fine powders. Maria enjoys travel, old civilizations' history, and meeting interesting people from all over the world.