

# Shipping and Storage at Elevated Temperature: Studies of Toner Response

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## Abstract

Driven by a desire to reduce printer power demand by lowering the temperature requirements of the fuser, it has become common for lower softening temperature resins to be employed in toner. One consequence to the use of these resins is an increased risk of blocking during shipping or storage at elevated temperatures. By extended exposure of toner samples to elevated temperatures we propose to identify and evaluate the material characteristics most relevant to robust ship/store performance. As observed previously, low T<sub>g</sub> or onset of flow temperatures (Shimadzu) can contribute heavily to temperature induced blocking but are not necessarily a guarantee of ship/store failure. Failure can be accompanied by absorption of surface additives into the toner particle. High levels of additives can significantly improve blocking resistance.

## Introduction

The concept of 'blocking' or 'caking', the undesired fusion of toner during exposure to elevated temperatures exclusive of fusing, is not a new one. This vulnerability to elevated temperatures has been essentially a nuisance factor of concern during the shipping or storage of toner. It was demonstrated years ago<sup>1</sup> that there is a significant relationship between blocking behavior and toner glass transition temperature. It is perhaps tempting to consider the examination of blocking behavior uninteresting but several factors lead one to take a fresh look at the phenomenon.

Historically toner binders were first derived from resins used in coating applications. These resins exhibited poor fusibility by today's standards. Blocking behavior was appropriately low on the priority list and in reality a low risk factor. The art, however, has driven toner development to more highly engineered resins with lower T<sub>g</sub>'s and therefore better fusibility. This trend, driven by the desire for increased fusing speed, more transparent color, smaller printer size, less complex fuser configurations or decreased line power requirements is accompanied by an increased risk with respect to blocking. Not only so, but printers have become common and convenient and as such appear in less sophisticated environments than ever before – loading docks, store fronts, construction sites, and others – where the potential temperature variations are significant.

Blocking is no longer a shipping or toner storage issue alone but now includes concerns for the real time operation within a given printer.

Controlled environments, internal cooling, and sufficient space for heat dispersal were at one time all practical safeguards to blocking within the machine. The machines were generally more expensive and so cost was less of a restriction. The market, however, has driven the art to develop less expensive and less energetic devices, decreased developer sizes, and decreased energy input requirements, partially to accommodate the change in toner properties addressing fusibility. The implications for toner blocking within a dual component printer context remain largely a ship/store issue. An offending toner bottle can be discarded. Even lightly caked toner, once exposed to the high energy of a large developer mix, can still be dispersed, charged, conveyed and printed due to the conditions needed to churn the mix itself. The impact on printing due to caking, unless severe, is likely a charge effect with implications in powder flow. Reduction of toner flow within the developer is likely overwhelmed by the energetics of the mix. Actual problems due to caking in this context are minimal.

Once removed from the context of dual component printing, however, blocking can have much greater consequences to the actual function of the device. Unlike toner conveyance driven by carrier bead movement in a dual component printer, conveyance of toner in monocomponent non-magnetic printing is heavily, if not exclusively, dependent upon the powder flow of the toner itself. Agglomerates in a dual component developer mix are not devastating to toner movement due to the energetics of the mix and the strength of the driving mechanism of the carrier. Aside from paddle mechanisms designed to stir the toner, monocomponent systems have little internal remedy to even mild blocking. These stirring systems are easily defeated by a significant decrease in powder flow. Magnetic toner may provide some additional opportunity for mechanical conveyance, but it's force may still be insufficient to overcome blocking and allow continued printing.

Not only does blocking provide a risk to the mechanical functioning of the machine, but even at low levels the disruption in powder flow can have undesirable effects on image quality. Dual component printing depends upon a

reasonable control of the toner concentration for delivery of sufficiently charged toner to the latent image bearing member. The developer mix is recharged with virgin toner to maintain a constant toner concentration (TC). Monocomponent printing relies on doctoring or metering to deliver a uniform layer of charged toner to the developer roll and subsequently to the image bearing member. Disruption of powder flow or conveyance has a dramatic effect on the metering systems ability to create this uniform toner layer. Lack of uniformity in either toner charge or layer thickness results in non-uniform image production. This non-uniformity may manifest itself as streaking, blotching or mottling of the image.

Color printing only serves to compound the risks discussed. A color image requires uniform transparent toner layers for the production of a vibrant color gamut; such uniformity strongly depends upon charge, uniform metering and a lack of streaking or blotching defects. Without layer transparency the colors are muddy and dull. Without uniformity the image has sporadic color development resulting in color defects easily detected by the human eye. The increased sensitivity to non-uniformity makes color printing especially vulnerable to any disruption in powder conveyance and doctoring that may result from toner blocking.

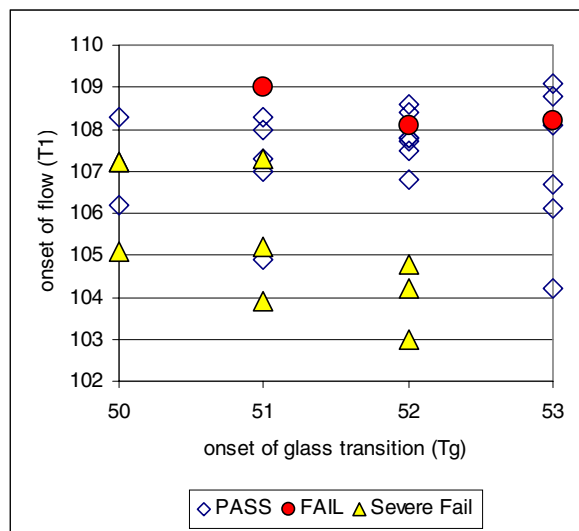


Figure 1 Caking failure as measured by slope of cohesion change over time noted with respect to onset Tg and T1 of toner tested.

O'Reilly noted that there was a clear correlation between glass transition temperature and blocking failure temperature. We have chosen to examine the caking response more explicitly by defining not simply a caking failure temperature but a rate of failure. By looking at the behavior of a variety of toners we have found that, at a given storage temperature, the blocking failure rate is not so easily traced to Tg alone. Figure 1 above shows the observed relationship between Tg, T1 (softening temperature) and blocking failure as measured at 50°C.

Failure rate was measured by monitoring the change in powder cohesion. The approximate slope of the cohesion versus time trend was determined and the slope used to estimate severity of failure. Toners with a slope  $<0.5$  were rated 'pass'. Toners with slope  $<1.5$  were rated 'fail' and were heavily caked by 35 days. Toners with slope  $>2$  were rated 'severe fail' and solidly caked within 7 days.

The challenge for the determination of caking failure is the definition of the conditions of the test. Success or failure in the caking response is heavily dependent upon the conditions of the test. What temperature is sufficient but not excessive for the extended test? What expectations are not devastating to competing technical goals and yet remain accurate predictors of the blocking risk a toner represents? Should the test involve vibration to simulate shipping? For this study we have chosen moderate conditions believed to yield a reasonable risk assessment for toner.

## Blocking Test

Blocking tendency was determined by measuring the change in powder cohesion effected by storage at 50°C in a 100 mL covered beaker. No vibration or other agitation was employed. The toners used in this study exhibited glass transition (onset) temperatures between 51 and 53°C, somewhat less than a conventional toner Tg. The binder resin was not varied. Each toner sample was stored at temperature for 35 days or until failure. Failure was noted when powder cohesion exceeded a value of 20. A cohesion value of 20 was typically a lightly fused powder easily broken up with moderate pressure, but of sufficiently low flow that printing would likely be disrupted. Cohesion values in excess of 50 were typically brick-like and could not be broken except under heavy pressure or grinding conditions. Cohesion was measured on a Hosokawa Micron Corporation Powder Tester using a standard procedure with 6 gram samples, a vibration time of 90 seconds, and nested screens (150 $\mu$ , 75 $\mu$ , 45 $\mu$ ).

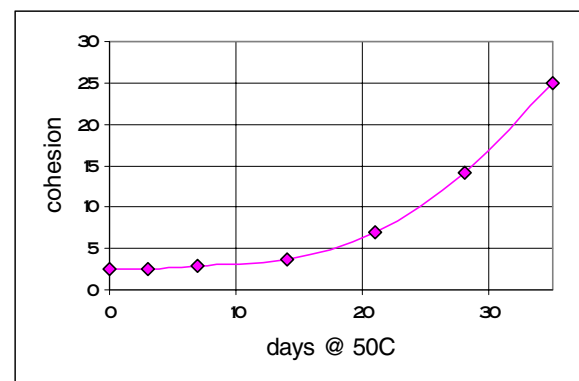


Figure 2 Typical line shape of blocking failure. Note initial 'induction' period (no change in powder cohesion).

A typical curve shape for the cohesion versus time relationship was observed. This shape is shown in Figure 2 and is characterized by an initial period where no change in

powder cohesion is observed, followed by the rise in cohesion associated with blocking failure. Once this increase began and powder cohesion exceeded a value of 20, toner powder was transformed to a brick-like state independent of rate of change. Examination of blocked toner powder shows the particles clearly fused to one another yet still suggestive of the single particle shape. The irregular fracture surfaces normally associated with conventionally milled toner also appear rounded in the blocked toner (Figure 3 & Figure 4). This smoothing of the surface and fusing of the particles shows clearly the occurrence of flow of the binder resin during the blocking test. It is also notable in Figure 4 that the numerous surface additives visible on the virgin toner (Figure 3) are apparently absent from the surface of the blocked toner. EDS analysis of the virgin toner and the blocked toner surfaces shows that the fumed silica is not absent but merely obscured. One must assume that the surface additives were absorbed into the surface of the toner particles when they were softened by the elevated temperatures of the blocking test.

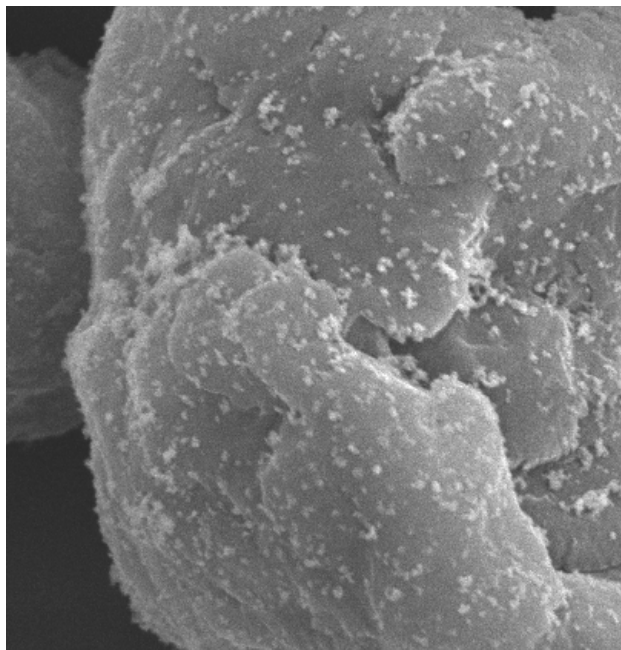


Figure 3 SEM of virgin toner prior to caking test. 10.0kV image magnified 15,000X.

Though nominally set below the glass transition temperature of the toners tested, the oven temperature sporadically exceeded the  $T_g$  during the course of the test due to temperature drooping and spiking in the heating cycle of the oven. It is estimated that the temperature was at or nominally above the  $T_g$  of the toner 10% of the time. Over the duration of the 35 day test this excursion above the  $T_g$  was presumably sufficient to cause the flow responsible for absorption of the additives, rounding of the surface roughness and fusion of the toner particles.

### Extraparticulate Additive Level Effects

One can imagine additives on a toner particle surface acting as small spacers that prevent the contact of particle surfaces with one another. Without contact, the particles cannot fuse or coalesce even when very soft. Given sufficient flow, however, the toner resin should wet the surface of the hydrophobic additives and result in their absorption into the soft particle. Once absorbed, the additives can no longer act as spacers. This absorption takes a finite amount of time. Once the toner particles are free to contact one another, continued exposure to elevated temperatures results in particle-particle fusion and therefore toner blocking. It is believed that the flat portion of the cohesion versus time curve shows the time it takes for a given toner to absorb surface additives at a given temperature, characteristic of the materials employed.

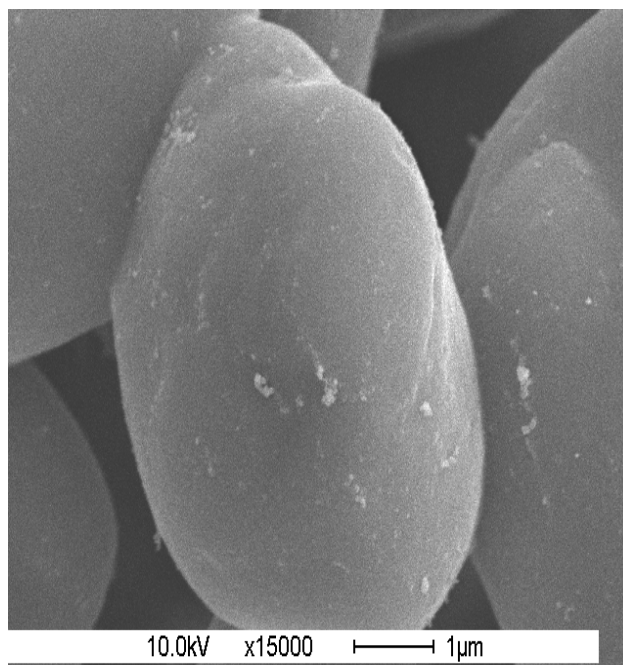


Figure 4 SEM of toner after caking failure. 10.0kV image magnified 15,000X.

Correlation of the induction period with additive absorption into the surface of the toner should lead to a relationship between blocking performance and the amount of additive on the surface of the toner. Intuitively it should take longer to absorb more surface additives given the same toner base powder and identical testing conditions. A standard toner powder was treated with approximately 1.5% hydrophobic surface additive. The additive level was increased to 150% and 200%. These toners were measured for blocking performance. Figure 5 shows the dramatic effect of increased additives on a common toner powder. Increasing the additive level significantly suppressed the blocking tendency of the standard toner without any modification to the  $T_g$  or flow temperature. High additive

levels to avoid caking are obviously independent of any charge, powder flow or printing characteristics vital to the usefulness of the powder as a toner.

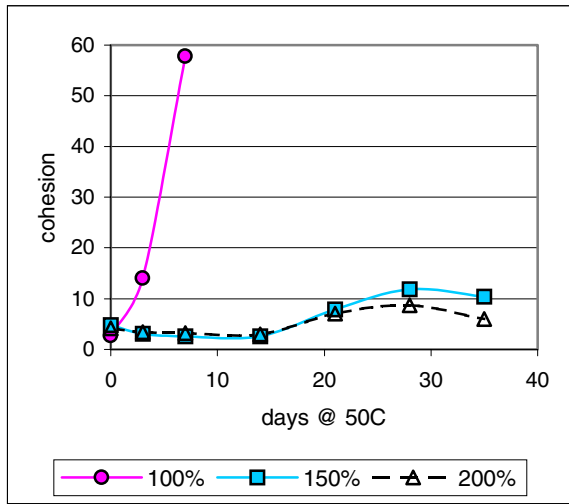


Figure 5 Cohesion versus time for standard toner with increasing levels of surface additives.

To further test the hypothesis that surface absorption of additives is related to the blocking failure, a toner with moderate resistance to blocking was ball milled for 10 hours in an effort to physically impact the additives into the surface of the toner without exposure to elevated temperatures. This impacted toner was compared to a virgin sample (unmilled standard toner with additives) and an unfinished version of the powder. Impaction of the additives into the surface of the toner was demonstrated by charge measurements (Figure 6) and high magnification pictures. Particle size distribution measurements were taken to verify a minimal change in the particle median and indicated minor changes in distribution (Figure 7).

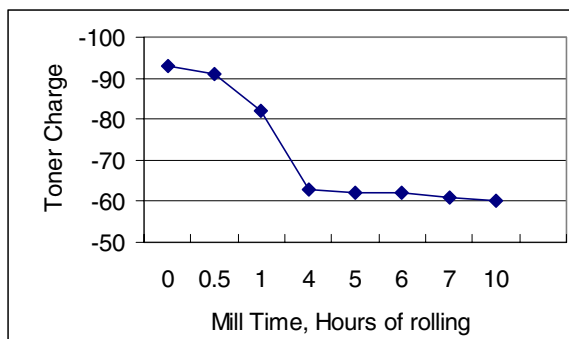


Figure 6 Charge measurements as a function of milling time in a ball mill. Decreasing charge theoretically indicative of impaction of additives into the surface of the toner.

Figure 8 shows the cohesion variation with time in the oven for the virgin toner, the impacted toner and the unfinished toner. Impaction of the additives into the toner

surface or the absence of surface additives had a predictable effect on the initial powder cohesion. Though not directly comparable with respect to the initial plateau of the cohesion value, a statement about the relative blocking failure rate is easily made. The standard toner took approximately 28 days to show a change of 20 units in its cohesion. The impacted toner showed the same change in less than 7 days. The unfinished toner changed from a highly cohesive unfused powder to a solid block of fused toner during the duration of the test.

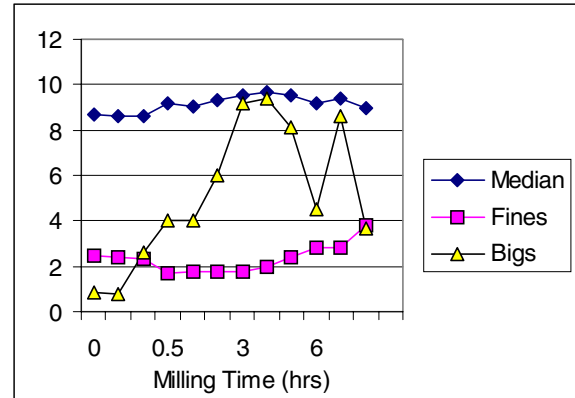


Figure 7 Particle distribution changes as a function of milling time in a ball mill. Median ( $\mu$ ). Fines (% <  $5\mu$ ). Bigs (% >  $16\mu$ ).

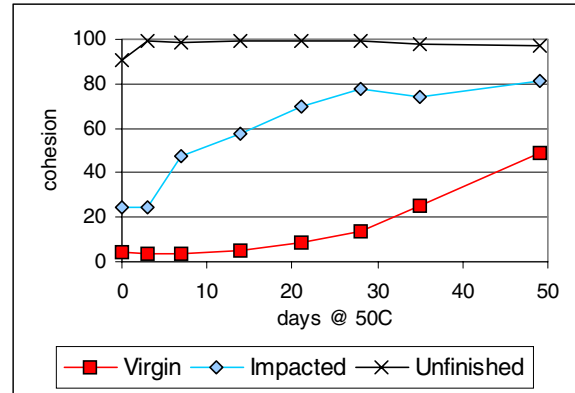


Figure 8 Cohesion as a function of time at  $50^{\circ}\text{C}$  for unfinished, impacted and standard toner. The base toner powder is identical in all three cases.

### Conclusion

A toner must be judged against a wide variety of performance criteria. Among these criteria is a toner's resistance to blocking during shipping and storage under moderately elevated temperatures. We have demonstrated that, independent of a change in the basic melting characteristics of a toner, blocking behavior can be heavily influenced by surface additives. It has been observed that blocking can be accompanied by absorption of the additives into the surface of the toner particle. This absorption can

delay the fusion of adjacent particles under near-T<sub>g</sub> temperature conditions and therefore inhibit blocking. It is also likely that the additive absorption can have a notable effect on the charging characteristics of the toner imparted by the surface additives and will therefore have an impact on the print performance of the toner.

Increased levels of surface additives can dramatically decrease a toner's vulnerability to blocking but may also be devastating to its charge and flow characteristics which may compromise use as a printing ink. The task for the toner formulator is to properly balance inter-related and frequently complex performance requirements with the formulation latitude for the optimum working material.

### **Acknowledgements**

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### **References**

1. J.M.O'Reilly, P.F.Erhardt, Physical Properties of Toner Polymers, Proc. NIP 2, pg 95. (1974).

### **Biography**

Dr. Walsh was born and raised in Pittsburgh, PA. She received a B.S. in Chemistry from Wheaton College (Illinois) in 1990. She earned a PhD. in Physical Organic Chemistry from Northwestern University (Illinois) in 1994. She spent time as a postdoctoral associate at the University of Colorado (Boulder) in 1995-96. She has been employed with Lexmark as a toner formulator in the Development group in Boulder, Colorado since 1996.