Time Discrimination of Coulter Recount Artifact

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Abstract

The toning process has a strong size selectivity leading to filming of the carrier which can result in image fogging or high process control set points. Preparation of toners with minimal fines is needed to minimize these deleterious effects. The Coulter Counter technique has been the standard for characterizing toners because its ability to discriminate fines levels. It has been shown by using an internally purged aperture tube [1] that recounting of particles inside the aperture tube gives erroneously high fines measurements. The duration of the counting event is longer for particles inside the tube passing the aperture close enough to be recounted than it is for particles passing through the aperture. One can discriminate the recount artifacts from real counts using the pulse duration data available from measurements made the Multisizer 3.

Background

The size selectivity of the electrophotographic toning process results in fines accumulation in the developer with age and causes degraded performance. The increased surface area of toner in the aged developer decreases the charging rate and gives a broad charge distribution. These changes in the aged developer can cause contamination, background, decreased image uniformity, and charge levels may exceed the limits to which process control can compensate. It is desirable to eliminate toner fines during manufacturing by changes to the manufacturing process. Accurate assessment of the fines is required during development of a new manufacturing process.

Instruments that count individual particles can provide the necessary sensitivity to evaluate differences in fines levels for alternate toner manufacturing methods One commonly used counting technique is the electric sensing zone (ESZ) method where the resistance change in a conductive fluid (saline) displaced by a particle in an aperture is used to measure the volume of the particle [2]. The most commonly used instrument using this technique is the Coulter Counter which uses a constant current power supply and measures voltage to determine resistance change due to a particle and thus the particle size.

It was shown [1] that three factors influenced the level of fines detected:

1. Size selective flocculation,
2. Size asymmetric coincidence, and
3. Recount artifacts.

It was demonstrated that surfactant choices and counting concentrations could be optimized to minimize flocculation and coincidence. An internally purged aperture tube was demonstrated on a Multisizer IIE to reduce recount artifacts suggested in Atkinson and Wilson [3]. However, Multisizer IIE is obsolete with no parts or service available as of December 2005. The current model, the Multisizer 3, has most of the features automated making it difficult to develop an internal purge for the aperture tube.

A feature of the Multisizer 3 is the capture and download of both the peak height and duration of the count pulses. Built in software features include the ability to limit the counts by the pulse time. Göransson [4] observed that the pulse duration for the recount artifact is much greater than that for true measurement pulses. This paper investigates the use of the Multisizer 3 features to reduce the impact of the recount artifact on fines measurement.

Materials and Methods

A Multisizer 3 was purchased in late 2005 and installed in a lab having power with an isolation transformer having dedicated ground. A 1% saline solution filtered at 0.2 µm having a short chain ionic surfactant below its CMC in saline and a biocide was used for the electrolyte. Dry toners were dispersed in de-ionized water that had been filtered at 0.22 µm using a combination of short chain ionic surfactant and two nonionic surfactants having different polar characteristics.

Three classes of particles were used: latex calibrations beads from Beckman-Coulter, a dry melt pulverized toner (MPT) with a broad particle size distribution and high fines level, and a wet dispersion of nearly spherical polyester beads with a coating of silica made using evaporative limited coalescence (ELC) method [5] used to make chemically prepared toners (CPT). The ELC beads were made for various sizes from 4 to 17 µm. The ELC method was not optimized resulting in a low level of fines in bead samples much that were larger than typical CPT. These fines were removed by repeated cycles of washing and decanting after the beads had settled.

Results

It was found that setting an upper limit of 30 µS on counted pulses removed the recount artifact from a well-washed ELC bead. However, when this constraint was applied to broad particle size distribution (PSD), there was a drop out in the data (see Figure 1). A display of the pulse height versus widths showed a large shift for counts with peaks between 10 and 25 mV (see Figure 2), presumably from electronic circuit switching to obtain the dynamic range for the instrument. The same shift to longer times was found for this sample when measured with a different size aperture and on another Multisizer 3 instrument. Studies were conducted to determine how to minimize this switching lag and to optimize the discrimination of true particles counts from the recount artifact.

Switching Time Lag

It was discovered that the shift due to switching lag could be reduced by increasing the aperture current at constant gain or by increasing the gain at constant current. The upper edge of the real counts with peaks between 10 and 25 mV is 40 µs for the standard

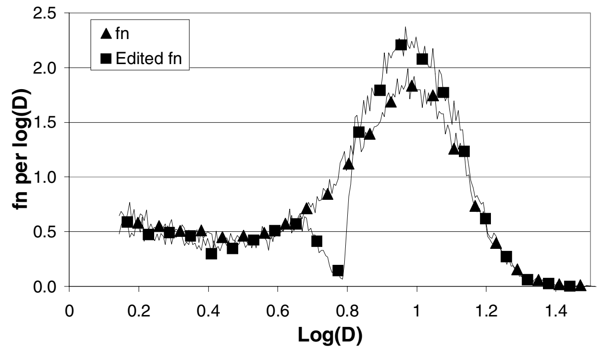

***Figure 1**. Comparison of a toner with a broad PSD edited for pulse times between 10 and 25 µs.*

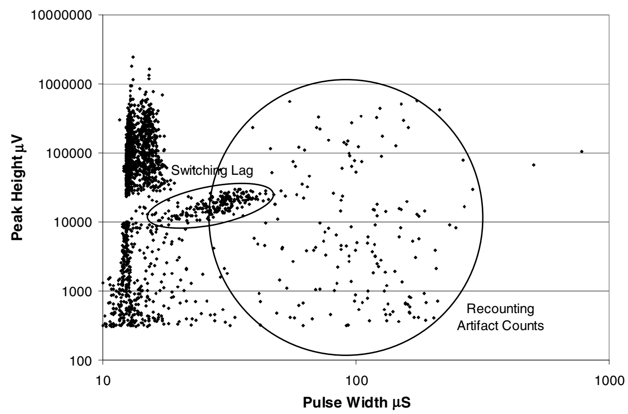

***Figure 2**. Pulse width versus height for the measurement in Figure 1.*

conditions. This is reduced to 29 µS for a doubling of either the gain or the current and to less than 20 µS for a factor of 4 in the current.

The strategy for selecting the current and gain to reduce the shift depends upon the user requirements and the state of the instrument. The gain can only be changed by factors of 2 while the current can be set in increments of 1 µV. Changing either may require recalibration. Increasing the gain at constant current will lower the noise threshold when electronic noise post amplification dominates the threshold. This may allow lower size thresholds at the cost of reduced maximum size and movement of the switching shift to lower sizes. Increasing the current will tend to increase the noise threshold for systems limited by connection and power supply noise. Linearity in the low range should also be evaluated at the selected operating conditions.

Alternately, the pulses can be saved and read into a worksheet and values between the threshold of 10 and 25 mV rescaled to the appropriate times. One can also adjust the linearity by changing the offset removed before converting pulse heights to particle sizes. Changing this offset is equivalent to the changing preamp restore module adjustment on the Multisizer IIE. This method allows flexibility in changing conditions to maximize the accuracy of each sample type but requires a high level of programming skill to manage and interpret the data.

Recount Artifact and Coincidence

Accurate interpretation of particle size distributions requires a map of the recount artifact and switching shift effects. The effects were mapped for a 70 µm aperture using pulse width distributions of seven calibration beads of sizes from 2 to 43 µm. The recount artifacts were found to have increasing times at lower peak heights with a 3rd order power law up to about 700 µS and intercepting the real count peak height at about 35 µS (see Figure 3). A possible second switching shift region was found around 250 to 500 mV although this was not seen in Figure 2 and may be caused by coincidence of recount artifact events.

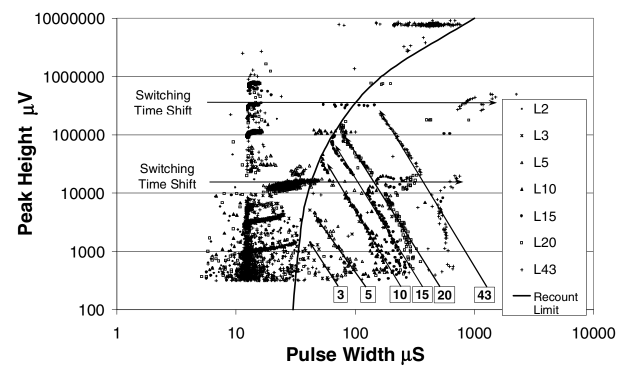

***Figure 3**. Pulse peak height versus pulse width for calibration beads.*

The coincidence of real counts with the recount events leads to counts at the true size but at longer times. The region for these coincident events overlaps the recount artifact region of the map. Also noted was a greater gap between the real counts and the largest of the recount artifact. This allows one to collect more of the counts for larger particles that are coincident. In fact, all of the 43 µm counts appear to be coincident with recount artifact events but fall outside the region

The latex calibration beads are not particularly clean of fines. Washed ELC beads where used to further investigate the mapping. Increasing concentrations of a 17.5 µm bead were measured to find the coincidence interactions between real and artifact counts. The rate of recount artifact was found to be nearly constant at 15% of the total counts up to about 400 pulses per sec showing that the recirculation of counted particles is at equilibrium in the aperture.

Mapping effect requires and understanding of how coincidence affects the pulses. The peak height for a coincident event between equal size particles will be $2^{1/3}$ higher than that for the individual particles. The coincident event peak height rapidly becomes that of the larger particle as the difference in particle size increases. The pulse duration will be between that of the longest pulse and the sum of the pulse times. The long duration of recount artifacts from larger particles with peak heights higher than fines causes size asymmetric coincidence events that reduce the observed fines at lower counting rates than where coincidence of total counts is significant. Because of this, coincident events with the recount artifacts should be excluded from the data accumulation to reduce the size asymmetric effect of coincidence.

With this knowledge, one can map the regions where the beads are coincident with other beads separately from recount artifacts (see Figure 4). Since the rate of the recount artifact is constant percent of the total counts, a second order relationship is expected for coincidence events. This relationship was found for events between the particles and the recount artifact but was somewhat less for primary coincident events between pairs of particles (see Figure 5).

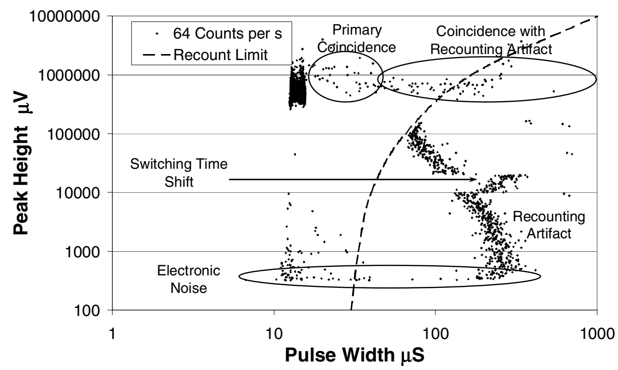

Figure 4. Pulse peak height versus pulse width for washed beads.

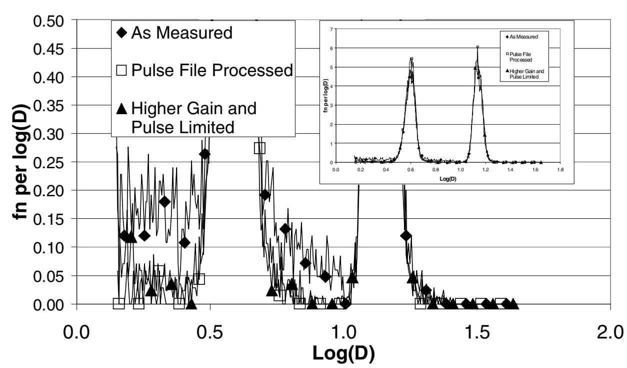

Figure 5. Coincident counts versus counting rate.

A decrease was noted in the electronic noise and residual fines not removed by washing with increasing concentration. This occurred at much lower counting rates than expected. To test the size asymmetric coincident reduction of real fines by large particle recount artifacts, a 3.8 µm bead was measured with increasing amounts of a 17 µm bead. No loss in counts of the smaller bead was observed up to 300 counts per second for the larger bead. This combination was also run at a gain of 4 with pulses limited to 10 to 30 µS (see Figure 6). The standard measurement conditions resulted in 5.6% fines below 3.0 µm while the higher gain with time discriminated pulses had 2.2% fines and processing the pulse file reduced the fines to 1.0%. The major difference for the fines for the conditions of higher gain with time discriminated pulses compared to the processed pulse file occurred below 1.8 µm and was most likely due to increased noise amplification at higher gain.

It has been shown that the recount artifact error can be nearly eliminated by counting time discriminated pulses under higher gain or current or by processing the pulse date using the pulse width information to eliminate. Good agreement has been found using this method with that of an internally purged aperture. However, the size asymmetric coincident limit is increased with the purged aperture and high counting rates could be used. Additionally, the accuracy of the purged aperture is greater because of influence on noise of methods to overcome the effect of switching lag for pulse time discriminated methods. Designs that eliminate the switching lag and have internally purged apertures can allow lower noise measurements at high counting rates.

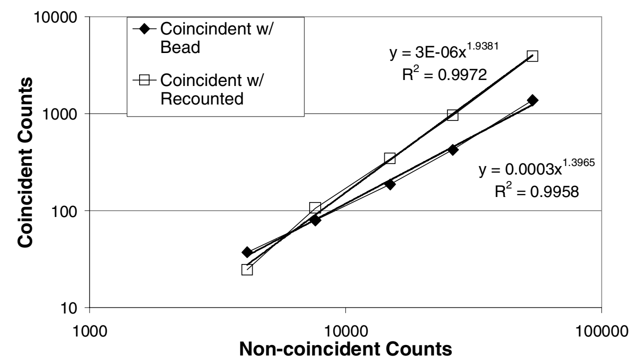

Figure 6. Comparison of methods to correct for the recount artifacts.

Mathematical Estimation of Recount Artifact

The consistent time and peak distributions seen for the recount artifact validate the mathematical approach [1] to removing the artifact given only the number distribution and a single calibrated factor. This factor is the concentration of recount artifacts and was found to 10% per log(D) for bead sizes from 3.8 to 17.0 µm (see Figure 7). This level of recount is lower than that found earlier for a previous bead of 17.5 µm. The recount artifact level is determined by the recirculation rate inside of the aperture tube and aperture to be sensitive to changes in orifice position and vacuum level. However, the rate is does not appear to be constant for the 3.8 and 5.5 µm beads because the pulse width varies much more as the peak height approaches the noise threshold size. The regions of real particle and electronic noise pulses overlap with the recount artifacts region (see Figure 3) so that the recount artifact is overestimated when a constant time is used to discriminate the artifact pulses. An improvement is possible by using longer times for the low peak heights. This can be accomplished using a constant value in the mathematical model or by using longer times at lower peak heights for when processing the pulse data file.

In the previous development, the onset of the recount artifact less than 0.15 Log(D) smaller than the actual size or 0.71D and was assumed uniformly distributed over the sizes less than the onset size. The number distribution can be corrected by a two-step transformation (see Equation 1).

$$n^*(d) = n(d) - \sum_{x>1.41d} an(x)$$

$$f_n(d) = \frac{n^*(d)}{\sum_{x=all\,d} n^*(x)} \tag{1}$$

The larger narrow ELC beads used in this study showed that the onset was not a constant fraction of the particle size for very large sizes. The onset of the recount artifact for the measurements in Figure 7 was found to be a linear function of the particle size (see Figure 8). One could also derive a function for the recount limit line in Figure 3. Modifying the limit on the summation in Equation 1 to the maximum of (d-1.02)/0.5545 and d caused a reduction in the relative height of the 3.8 µm peak. The recount artifact could be eliminated from the lower sizes by increasing the estimate of the recount rate (constant a in Equation 1 divided by the bin width) to 18% per log(D) but this gave a 2% shift downward in the partition of the small beads. The recount artifact rate is double the expected value and reflects the non-constant nature seen for the 3.8 µm bead in Figure 7. The fit to the tail below the 3.8 µm bead dominates the error and this would give higher recount artifact rates. A linearly decreasing recount rate did not improve overall fit and resulted in parameters similar to those for the 3.8 µm bead in Figure 7.

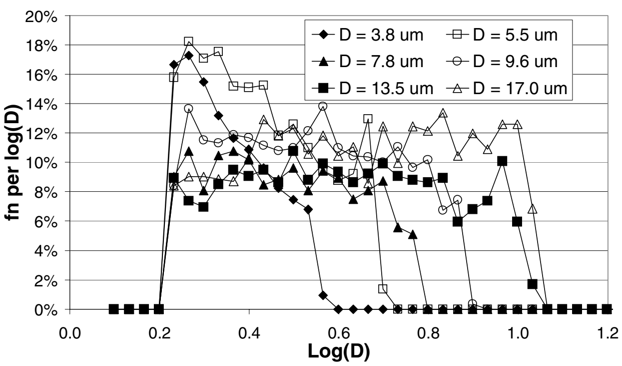

***Figure 7**. Recount artifact rates in a 70 µm aperture versus bead size.*

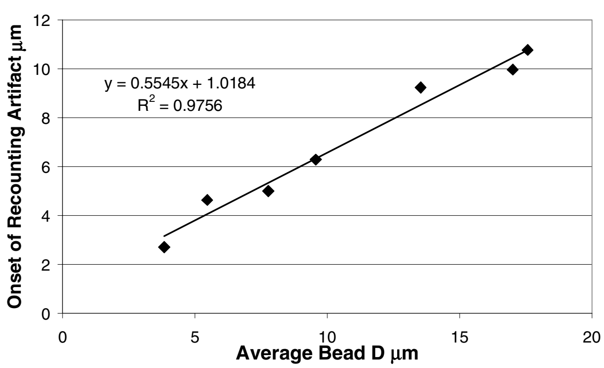

***Figure 8**. Onset of recount artifacts in a 70 µm aperture versus bead size.*

The shift in the partition of the smaller bead was caused by the coincidence of the larger beads with the recount artifacts. A new model was developed having the coincidence with the recount artifacts removed (see Equation 2). The constant b in Equation 2 should be related to the scaling factor of the fit in Figure 5 by the bin width. Least squared error fit of the model to the data from the processed pulse file found b to be 84% of this scaling factor.

$$n_r(d) = \sum_{x>\max(d,(d-1.02)/0.5545)} a n(x)$$

$$n^*(d) = \left(n(d) - n_r(d)\right) \times \left(1 - b\sum_{x<d} n_r(x)\right) \qquad (2)$$

$$f_n(d) = \frac{n^*(d)}{\sum_{x=all\ d} n^*(x)}$$

Conclusions

It is possible to remove the recount artifact using pulse width times to discriminate the artifacts from the particle pulses. An apparent lag in switching amplifier electronic gives rise to long pulses between 10 and 25 mV. This lag and the broadening of the pulses by electronic noise for the smaller peaks result in an overlap of particle and recount artifact regions. Increasing the gain or current can reduce the overlap caused by the switching lag.

The longer pulse times for recount artifact gives rise to the size asymmetric coincidence as well as decreased threshold concentration at which coincidence is significant. Excluding the pulses coincident with recount artifacts using a pulse width discrimination technique removes the coincidence size asymmetry.

The recount artifact may also be removed with mathematical models. This requires the evaluation of two parameters for the instrument using calibration beads. Once these parameters are established, the pulse width times no longer need to be analyzed.

The long durations of the recount artifacts and the switching lag reduce the rate at which particles can be accurately counted. A redesign of the Multisizer to include an internal aperture purge and the removal the switching lag would make accurate measurements with time discrimination of the pulses more effect.

References

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Author Biography

Kevin Lofftus received a B. S. in 1982 and a M. S. in 1984 for Mineral Process Engineering from Montana College of Mineral Science and Technology and a Ph. D. in 1989 from The University of California Berkeley for Mineral Processing with minors in Chemical Engineering and Statistics. He joined the Copy Products Division of Kodak in 1989 and is currently a Research Scientist at Eastman Kodak Company.