Improvements in Toner Fines Characterization

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Abstract

The extreme size selectivity of the toning process presents a unique challenge of preparing toners with minimal fines. The Coulter Counter technique has been standard for characterizing toners because its ability to discriminate fines levels. The advent of chemically prepared toner with no fines and processes such as multiple classification steps in ground toners has revealed needed improvements in the characterization method. Dispersion stability and count rate were found to have the opposite effects on the measured fines level. A simple modification was discovered that could overcome the artifact of recounting coarse particles as fines due to turbulence inside the aperture tube. Investigation using this modification found that a simple mathematical model with one tuned parameter for each aperture size could be applied to simulate the modification.

Background

The toning process is very size selective causing the accumulation of fines in the developer leading to lower charge levels and charging rates and broader charge distributions as the developer ages. These changes in the aged develop can cause contamination, background, and decreased image uniformity. Often, the low charge levels exceed the limits to which process control can compensate.

The toning process can be thought of as a size separator with the undersize returned to the feed. In such a process, the fines accumulate until their population times the selectivity for removal by toning equals the input rate. At this point, equilibrium for that size is achieved. Often, the size selectivity can be modeled as a power function with the typical value of 3. For powers of 3, the number distribution of the feed toner is equivalent to the volume distribution of the developer at equilibrium.

For development systems that are sensitive to fines, measurements methods for quantifying fines in the feed size distribution need to be sensitive to fines in the presence of larger particles. Instruments that count individual particle 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. The most commonly used instrument using this technique is the Coulter Counter. While different theoretical models give both linear and nonlinear response of the resistance change to the particle volume, experimental results find a linear response for latex spheres of diameters up to 60% of the aperture size.[1]

As with any counting technique, presentation of a single particle to the sensing zone is critical. Accurate characterization requires achieving a completely dispersed stable suspension of particles, controlling dilution to present a single particle to the sensing zone, and designing flows that prevent particles from being counted multiple times. Conditions for stable dispersion and appropriate dilutions vary with the material and need to be optimized by the user.

Dispersion is often achieved using surfactants and ultrasonic energy. The time and amount of energy needed to obtain a good dispersion can depend upon the age of the sample and the surfactant and dispersant used. The critical micelle concentrations (CMC) of common surfactants used to disperse particles are a strong function of salinity[2] and it is much more difficult to obtain dispersion in saline than in deionized water. Even when a good dispersion is obtained, dilution into saline can cause flocculation.

Flocculation is a size selective process and will change the ratio of fines to coarse particles measured. The rate of flocculation for a given size is proportional to the stirring rate and the concentration of that size times the square of the sum its hydrodynamic radius with that of another particle times the second particle's concentration integrated over all sizes for the second particle. The hydrodynamic radius is smaller than the actual radius and is much smaller for very small particles that following the flow lines around a larger particle rather than a straight-line trajectory.[3] Hence dispersion stability is enhanced by stable surfactant saline systems, low stirring rates, and low concentration of large particles.

Concentration of particles should also be low to prevent more than one particle being in the sensing zone at a time. When more than one particle is in the sensing zone, the signals from the particles are coincident and only the first peak will be counted. Primary coincidence occurs when the size of the counted particle is not shifted to a large size bin due to overlap of the signals. Secondary coincidence occurs when there is enough overlap of signals to push the measured size into a large bin. Primary coincidence affects concentration measurements but concentrations are not of concern in measuring particle size distributions. Secondary coincidence affects particle size distributions by removing counts from the fines side of the main mode and adding counts to the coarse tail. In an ideal system, primary coincidence is symmetric and has no influence on the size distribution. Coincidence is often discussed only in the context of loss of counts per unit volume for concentration measurements.

The sensing zone extends beyond the aperture and gives rise to the opportunity for large particles to be counted without passing through the aperture. Thom suggested to Atkinson and Wilson[4] that the fines appearing in Coulter Counter measurements of very narrow distributions using hydrodynamic focusing (HDF) cells were artifacts due to the recirculation of the particles back into the electric field that extends beyond the orifice once the particles have passed through the orifice. This artifact type was observed by Göransson to have long duration pulses.[5]

Results
Flocculation
Time dependant changes were observed for several methods practiced. It was noted that the total counts decreased, the volume median increased, and the fineness index (number median divided by the number 15.78%) increased with the length of time that the sample was in saline. The rates of changes for these effects were observed to be a strong function of the concentration. Studies revealed that flocculation occurred for particles greater than 6 microns by 2 minutes. Also, the nonionic surfactant used was not stable and formed flocs in the 1.5 to 2 micron size range after about 5 minutes. Experiments showed that short chain ionic surfactants could stabilize the nonionic surfactants in saline. However, an interaction between short chain ionic surfactants and the nonionic surfactants can cause slow crystallization in deionized water unless the concentration of the short chain ionic surfactant well below its CMC when the nonionic surfactant concentration is above the its CMC.

A key to obtaining stable dispersions was to disperse samples in deionized water rather than saline since the CMC's of surfactants are about 10 times lower in 1% saline. For measurement times longer than 2 minutes, additional surfactants can be added to the saline at the same level as that used in dispersion step when extra short chain ionic surfactant is added to the saline. Results equivalent to the initial measurement may be had after 15 minutes of stirring in the saline.

Coincidence
It was found that coincidence was asymmetric in Coulter Counters. For electric sensing zone instruments, the size of the sensing zone is determined by point at which the second particle causes a rise in signal just before the peak detector is reset. Large particles have a greater signal and push this point further out, expanding the sensing zone from which second particles must be excluded. Additionally, instruments run with a constant current power supply, the sensing zone expands more for larger particles. As the distance between a larger particle following a smaller particle is closed, secondary coincidence is observed in counting the smaller particle and then the peak for the small particle is hidden by the larger particle signal giving rise to primary coincidence. Thus, fines are shadowed by the larger particles and missed in primary coincidence or binned into larger size more frequently than coarse particles.

It was found that asymmetric coincidence effect was significant at lower concentrations than those that cause significant secondary coincidence. The effect of the sensing shadow on the PSD is to reduce the measured fines. Concentrations to avoid significant shadowing of fines are at much lower count rates than is typical in the industry. The count rates for samples depend upon the particle size and the aperture size. The count rates recommended in the Coulter operator's manual apply to unclassified particles ground from brittle material that contain mostly fines in the number distribution. Very stable dispersions are required for the accumulation times needed to obtain the total counts for good PSD statistics at low count rates.

Recounting Artifact
During experiments to define appropriate count rates, it was noticed that there were no fines for the first 5 seconds of a measurement for a sample that had been classified three times to remove fines. Comparing the combined results from twelve 5 second runs compared to one 60 second run showed a significant difference in fines level. It was noticed that accumulation of particles inside the aperture tube took 20 to 30 seconds after adding the sample to come to equilibrium suggesting the effect hypothesized by Thom and observed Atkinson and Wilson[4] and by Göransson.[5]

The edit board would remove long duration pulses and would eliminate this artifact. However, on the Multisizer IIE model, the edit is only enabled for the narrow mode and only about ½ the log diameter range of the full scale mode is available in the narrow mode. Additionally, the artifact reported by Atkinson and Wilson[4] in the narrow mode is not removed equally for all sizes. This other artifact is caused by the particles near the edge of the aperture where the field gradient is higher.[6] Hydrodynamic centering[7] and power supply lag are greater for larger particles so that the edit mode may not equally remove the same percentage of large and fine particles. For toner PSD's, the edge artifact represents one or two channels shift in full mode for about 10% of the particles and should be included in the PSD analysis.

A better solution is to remove the stream of counted particles by capturing the jet leaving the orifice and eliminating any back eddies that bring particles into the field that extends inside the aperture. This was accomplished by reversing the flow in the rinse tube, forming a jet scoop on the rinse tube with a Pasteur pipette broken higher on the side facing the jet, and adding a rinse line through a manometer port. It was found that a continuous rinse drip of 2 to 3 drips per second was required to fully capture the jet. This was accomplished with a needle value in parallel with the plug value on the rinse. The position of the jet scoop was optimized using chemically prepared toners that were about 35% of the aperture size and had what little fines removed by multiple cycles of settling, decantation and resuspension. No fines were observed for this cleaned toner proving that the recounted particles were all internal to the aperture tube.

The internal purging drip highlighted a source of noise in the tee tube where air is introduced to the waste line to regulate vacuum. As the waste drips from the end of the tube in the bulb, pressure fluctuations are transmitted back through the aperture momentarily changing the flow rate through the orifice. Since charge is being conducted through the aperture, the change in flow rate creates a voltage spike that is counted. This type of noise is too low in most measurement to notice but is significant at 2 to 3 drips per second. Adding a ground after the tee tube connected to the signal return and to platen ground focused the noise into a few channels. Adding a RC low pass filter with a time constant of about 10 microsecond removed the noise.

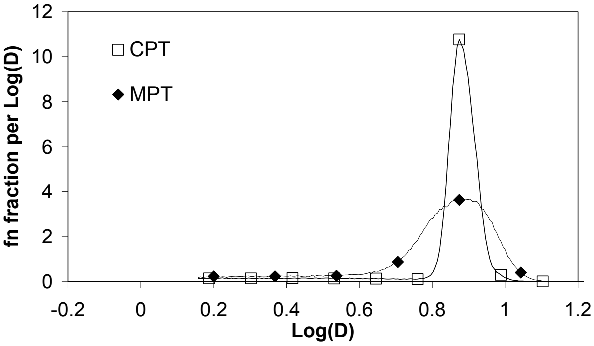

Figure 1. PSD of chemically prepared and melt-pulverized toners.

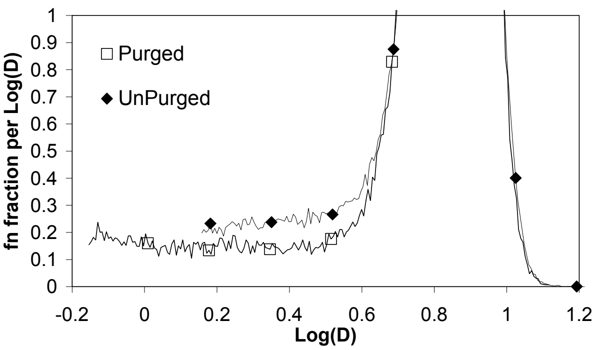

Figure 2. Enlargement of fines for of MPT showing the effect of capturing the jet on fines measurement where the purged measurement is scaled by 1.05 to account for the greater range of the measurement.

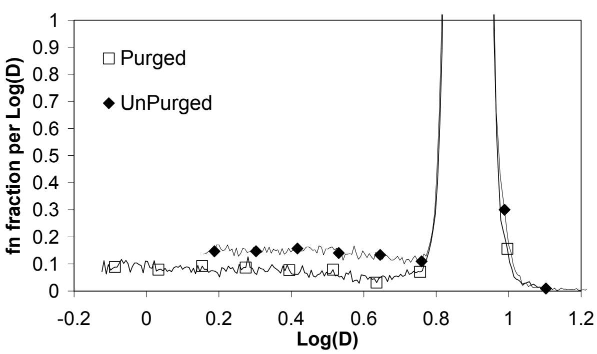

Figure 3. Enlargement of fines for of CPT showing the effect of capturing the jet on fines measurement where the purged measurement is scaled by 1.03 to account for the greater range of the measurement.

The effectiveness of this internally purged configuration was evaluated using a melt-pulverized toner (MPT) and a chemically prepared toner (CPT) made by NexPress's limited coalescence process (see Figure 1). The data in Figure 1 was taken with a 70 micron aperture at about 1300 counts per second without surfactants in the saline or a short chain ionic surfactant to improve stability. Expansion of the scale reduced the fines by 30% for the MPT (see Figure 2) and 50% for CPT (see Figure 3) when measured with a 30 micron internally purged aperture. The CPT has only 40% of the fines of that seen in the MPT classified with a single rotor forced vortex classifier.

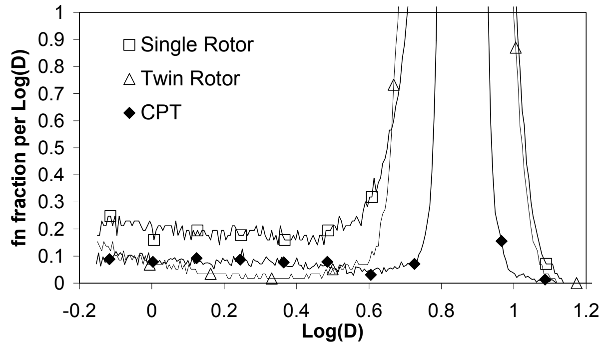

Figure 4. Enlargement of fines for single rotor and twin rotor MTP and CPT measured on 30 micron internally purged aperture

A comparison of single and twin rotor classifier performances shows a reduction in fines (see Figure 4). The twin rotor classifier produces a lower fines level that is equivalent or better than the CPT. Also, the sharpness of cut by the twin rotor is nearly as good as the lower edge formation of the CPT but the mode is broad to achieve a high yield.

The low count rates and dispersion stability require to obtain accurate fines measurement also improved the characterization of grade-efficiency curves for classifiers. One can generate a grade-efficiency curve by dividing the classified toner PSD by the feed in either number or volume distribution and normalizing the upper end of the curve to 1. A problem with industry standard count rates is that the greater concentration of coarse particles in the classified product needed to achieve the same count rate as the feed increases flocculation rates and the amount of asymmetric primary coincidence. With these differences, the upper end of the curve has a positive slope.

Mathematical Simulation of Internally Purged Apertures

A review of results from various PSD's and conditions indicated that the probability of a particle being recounted was uniformly distributed in log diameter space over all the channels about 0.15 log microns smaller than that for the actual particle size. Figure 5 shows a simulation of the purged aperture for CPT measured on an unpurged 70 micron aperture by subtracting the sum over sizes greater than 0.15 log micron for a recount rate of 0.05% per 0.00602 log microns (256 channel mode) and then renormalizing. The recount rate is different for different conditions and can be estimated by accumulation of many initial measurements compared to the standard unpurged run. Only toner with very narrow PSD such as CPT's are sensitive to the size below which the recounting occurs.

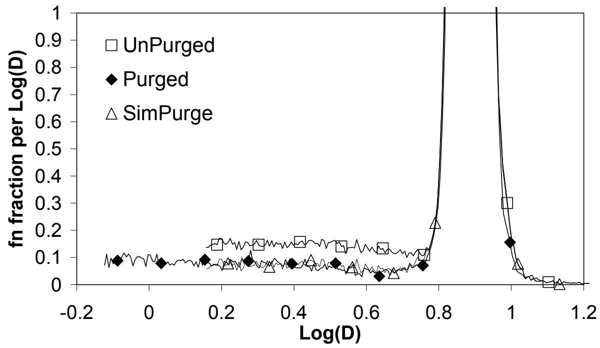

Figure 5. Enlargement showing the simulation of purged aperture using a recount rate of 0.05% per channel for channels less than 0.15 log microns below actual size. The purged measurement is scaled by 1.03 to account for the greater range of the measurement.

Conclusions

The accuracy of estimating fines is important in evaluating effects of toner manufacturing method changes on developer life. Three processes in the Coulter Counter technique affect the accuracy of fines measurement. Unstable dispersions in saline preferentially flocculate above 6 microns increasing the apparent level of fines and can be overcome with combined surfactants and proper dispersion techniques. Asymmetric primary coincidence reduces the apparent level of fines and is minimized with low count rates for long times in very stable dispersions. Counted particles moving past the inside of the aperture are recounted as fines and may be removed by constructing an internally purge aperture system or by simulation with a single calibrated parameter. These improvements allow easy construction of grade-efficiency curves for classifiers facilitating evaluation of manufacturing process effect on developer life.

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 Associate at NexPress Solution Inc., a fully owned subsidiary of Kodak.