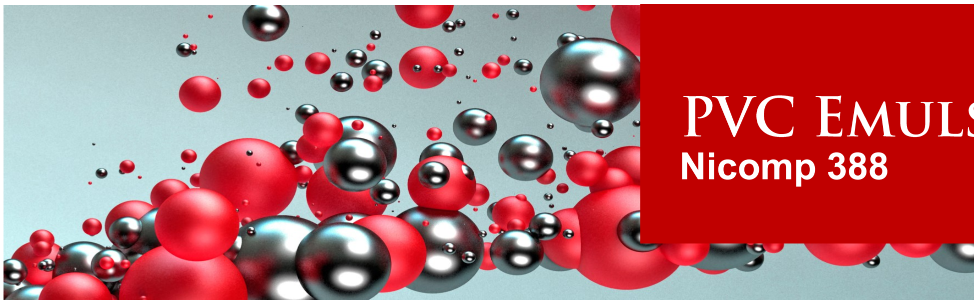

PVC EMULSIONS

Nicomp 388

AN–162

Application Note

The Analysis of PVC Emulsions with the Nicomp 388

In analyzing the particle size distributions of polymer emulsions, it is common to employ one of the various light scattering methods. Generally, they fall into two categories: Static and Dynamic. Static light scattering, also known as Laser Diffraction, employs the use of spatially arrayed detectors that record the scattered light patterns as a function of angle. Dynamic light scattering measures, over a period of time, the amplitude of the scattered light at one angle. In both techniques, specialized mathematical algorithms are needed to invert either the scattered light patterns or scattered light time profiles to arrive at particle size distributions (PSDs). As a consequence of the ensemble nature of both these light scattering methods, they are low resolution and low sensitivity techniques and they can be susceptible to artifacts and instabilities. The data in this paper demonstrates that the Nicomp algorithm, used only in the Nicomp 380, can provide accurate and realistic PSDs for emulsion samples which have relatively wide distributions and would give other light scattering instruments trouble.

Light scattering techniques, by virtue of their ensemble nature (i.e. where the measured signal results from the simultaneous contribution of many particles of different size), require mathematical algorithms to "invert" the raw data so as to yield a simplified estimate of the true, underlying particle size distribution or PSD. Because all of these algorithms are "ill-conditioned" to one degree or another, the corresponding measurements are necessarily lacking in resolution and accuracy, so the more complex, or "polydisperse", is the PSD of the emulsion being analyzed. Specifically, Dynamic Light Scattering (DLS) requires the interpretation of an autocorrelation function. This smooth, monotonically decreasing curve is usually analyzed by obtaining the best fit to a pre-chosen analytic function derived from a well-defined particle size distribution. It is possible to invert the correlation function to a particle size distribution (using, for example, a LaPlace Transform) after choosing reasonable initial conditions. Particle counting methods, on the other hand, like the AccuSizer 780 (see AN 156 and 157) have an inherent advantage over light scattering methods, given that they are capable of providing much more accurate and unambiguous results for the portion intimately related to emulsion safety and stability – i.e. the largest globules in the emulsion.

Emulsions present an interesting problem for light scattering techniques. Generally, the manufacturing goal is to produce an emulsion of a specific mean diameter and a relatively narrow width or polydispersity. Unfortunately, the manufacturing techniques (homogenization, see AN 706) cannot be relied on to always produce a constant product. The specific properties of the raw materials can change, requiring constant adjusting of the process parameters. This requires that the emulsion be characterized during and after the process. It is important not only to establish that the mean diameter is within specification but that the homogenization process has sufficiently reduced amount of large particles, which will cause stability problems later on. The measurement of the mean diameter can be done quickly and accurately by light scattering methods except in the case where the emulsion has considerable amounts of large particles. Such polydisperse systems can be difficult for light scattering instruments to handle (see AN 168). The result could be answers that do not stabilize or artifacts that do not represent actual particle sizes. Large particles have a tendency to "jerk" the distribution to larger mean diameters thus producing an inaccurate picture of the true distribution.

The more common situation is when the homogenization process has reduced the size of the vast majority of the solids fraction (99%) to within specification but there is 1-2% of the solids fraction in particles greater than 1 micron. It has been shown by numerous studies that such particles present in a small amount can still cause stability problems (see publication list, AN155). Yet, the amount of material in the tail is not enough to be observed by light scattering techniques.

What is needed is an extremely sensitive technique that can detect small amounts of large particles. Single Particle Optical Sizing (SPOS) is a particle sizing tool that can supply this capability. SPOS, as utilized by the AccuSizer 780, is a single particle counter with the ability to count particles as small as 0.5 microns. The AccuSizer 780 has found considerable utility in applications where the coarse particle tail of a primarily sub-micron distribution needs to be quantified (see AN157, 164, 168, and 706). Unlike light scattering ensemble methods, the AccuSizer 780 does not assume a PSD shape. The PSD is built up by counting and sizing hundreds of thousands of particles and placing them into very narrow size bins. Since SPOS is not an ensemble method, broad distributions are not problematic and since the distribution is not computed, no artifacts are produced.

Consider the data in Figure 1. Figure 1a contains the Volume-Weighted PSD obtained from the Nicomp 380 on a PVD emulsion. The result of the analysis was a single Gaussian peak with a mean diameter of about 0.68 microns and width of 18%. Figure 1b contains the Volume-Weighted results from the same sample obtained by the AccuSizer 780. The first thing to point out is that the results from the 380 and 780 qualitatively

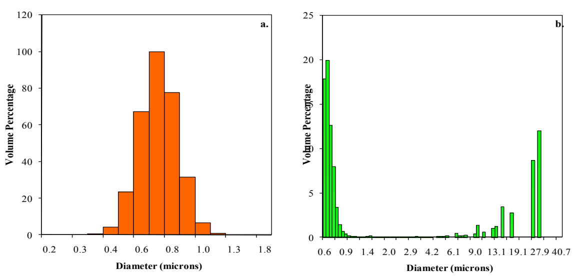

Figure 1: a. Volume-Weighted PSD of PVC Emulsion from Nicomp 380;
b. Volume-Weighted PSD of PVC Emulsion from Accusizer 780.

agree. They both produced the mean diameter of the main peak. Of course, the main peak was slightly broadened by the 380, which is a consequence of the poorer resolution. Notice, however, that the 780 was able to detect particles as large as 30 microns while no such particles were seen by the 380. This is due the low sensitivity inherent in light scattering techniques. As a matter of fact, based on the 780 results it was determined that the particle greater than 1 micron only contributed 0.5% of the solids volume. The emulsion that produced this data is an example of a sample that should be analyzed easily by light scattering devices. The distribution was narrow and the number of large particles relatively small. Figure 2, on the other hand, contains the results from a unstable emulsion with a broad distribution. Figure 2a contains the Volume-Weighted 380 results from the second emulsion. The analysis produced two peaks, one at 0.27 microns and another 1.3 microns. The first peak represents the main emulsion peak and the second is a proxy peak for the aggregate tail. It is important to point out again that such a distribution can cause problems for an ensemble measurement. The larger particles tend to obscure or shift the contribution from the main peak. But the Nicomp algorithm has the capability of "separating" out the contribution from the larger particles allowing the main peak to stabilize to the correct mean diameter. The mean diameter obtained from the analysis correlated to the expected value. As can be seen in Figure 2b, which contains the Volume-weighted PSD obtained from the AccuSizer 780, the second peak observed by the 380, actually represents a true particle size. This further validates the accuracy of the Nicomp algorithm and its

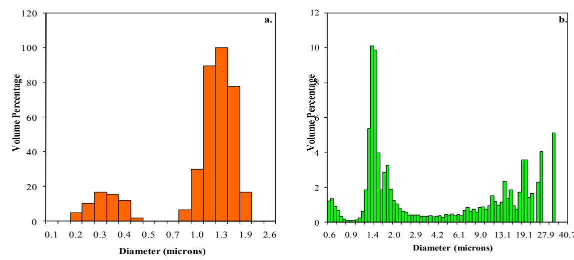

Figure 2: a. Volume-Weighted PSD of Broad PVC Emulsion from Nicomp 380;
b. Volume-Weighted PSD of Broad PVC Emulsion from Accusizer 780.

ability to handle difficult distributions. Of course, the 780 observed large particles (out of 20 microns) that were not seen by the 380 but again this is due to sensitivity. The significant issue is that the 380 alone was able to produce an accurate representation of the emulsion PSD, something that most light scattering devices would not be able to do. It was able to determine the correct mean diameter of the main peak and also accurately describe the aggregate tail.

In conclusion, the Nicomp 380, using the patented Nicomp fitting algorithm, was able to accurately size both narrow and polydispersed PVC emulsions. It was able to correctly identify the two modes present in the polydispersed emulsion. But only the AccuSizer 780, a single particle counter, was able to detect the largest particles present and produce quantitative information about them.

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