Fluorescent Staining Technique for Visualizing Thin Films

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Abstract

Thin films can be observed by various microscopic interference techniques. Unfortunately these methods provide only a limited indication of the film coverage especially on irregular surfaces. Most films are invisible to more convention microscopy. By using a very simple staining technique, these films can be clearly observed by fluorescent microscopy. The technique is applicable to almost any polymeric film on any inorganic surface.

This technique was applied to a variety of xerographic carriers to visualize the coating. Changes in processing can be clearly observed. Film thickness down to hundreds of angstroms can be readily observed. Thin discrete films become apparent in this technique and it is ideal for observing powder-coating processes. The technique is applicable to a variety of other applications involving thin films on small irregular surfaces.

The technique was used to measure the coating available for charging on a carrier surface. The carrier charge was proportional to the fluorescent intensity of the polymer on the surface and not the total amount of polymer present.

Introduction

Visualizing thin films is a useful characterization method. Frequently complete coating coverage is not the primary characterization criteria and other properties such as uniformity or other morphological properties are most important. Characterizing uniform islands or discrete particles of material on an irregular surface is a difficult task. Visualizing the coating is one way of characterization.

Our original work focused on attaching chromophores to polymers and then using these polymers to prepare films. It is very difficult to prepare enough polymer for even a small scale-manufacturing run and our primary interest was in the processing of the materials. We also tried to attach chromophores to the processed material without much success. This is where we noticed the polymers would fluoresce without any exotic manipulation.

Procedure

It was found that the polymers could be made to fluoresce strongly simply by soaking the polymer in a dye solution. Laser dyes are the dyes of choice because they are pure and dissolve completely in solution and have greatly reduced fluorescence when not in solution. Typically 0.1 to 0.01% dye in methanol is added to our carrier beads in a small vial. After 5 minutes the mixture is filtered and the beads are dried. The beads are then observed by fluorescent microscopy.

The dyes diffuse into the polymer matrix with the methanol. After drying and removing the methanol, the dyes still retain the strong fluorescent behavior and do not revert to the weaker fluorescence they exhibit in the pure state. Dyes of choice are Coumarin 30 and Rhodamine 6G Perchlorate. The latter is especially useful for quantitative work since it is very stable to photodegradation. Generally no washing of excess dye from the surface or other means is necessary before observing the polymer films.

After staining the films were examined microscopically. A 100-watt Mercury light source with suitable fluorescent filters was used for observation.

Results

Figure 1 shows typical polymer coated carrier beads observed with reflected light microscopy. It is very difficult to make any inferences about the coating on these beads with conventional optical microscopy.

Figure 2 shows the same beads under fluorescent light. The bright areas are the coating. It is very easy to observe the coated areas of the beads. The dye used in these experiments was Coumarin 30. Again the standard simple staining technique is very effective and quick to use.

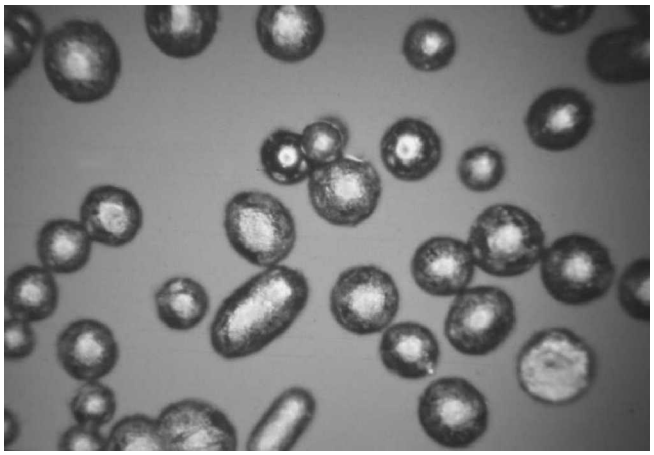

Figure 1. Optical microscopy

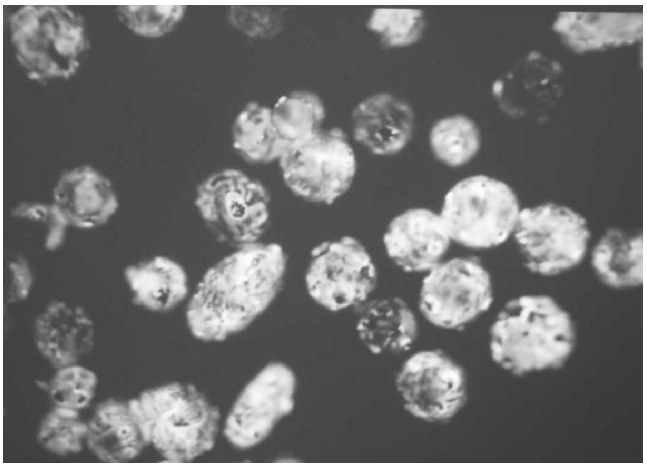

Figure 2. Fluorescent microscopy

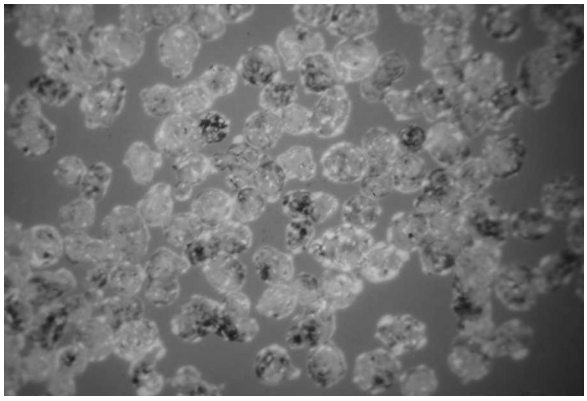

Figure 3. Well coated carrier

Figures 3 and 4 show solution coated carrier particles. The beads in figure 3 are relatively well coated while the beads in figure 4 are poorly coated, showing a significant number of beads that have less then 50% polymer coating.

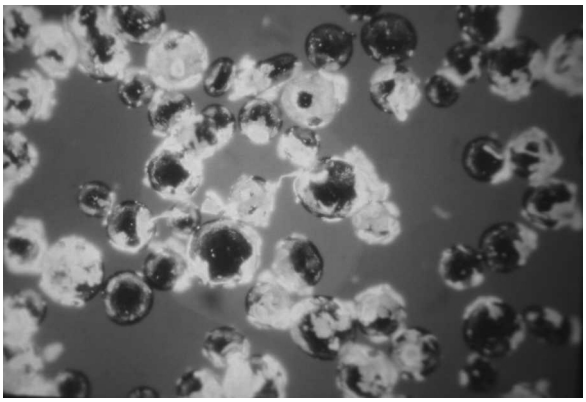

Figure 4. Poorly coated carrier

Fluorescent staining provides a very quick way to examine carrier coatedness. This method works on any coated carriers and has the advantage that it can be used after the carrier is prepared. The staining is done after the carrier is made so it is applicable even to large scale manufacturing batches of material.

Powder Coated Carrier

Powder coating can also be used to coat carriers. The mixing and dispersion of the powders can be observed with fluorescent microscopy. Powder coating can be used to completely coat the carrier beads or to introduce a small amount of polymer on the bead surface to effect the charging behavior. Both these methods have been used commercially in out products.

Figures 5, 6, 7, and 8 show how the polymer coating coverage changes with mix time. The coating polymer and core are mixed before fusing. It appears that five minutes provides the best overall coverage. Longer time result in agglomeration of the polymer and poorer coating coverage. Fluorescent staining provided a very simple method to determine the optimum mix time for the best coating coverage.

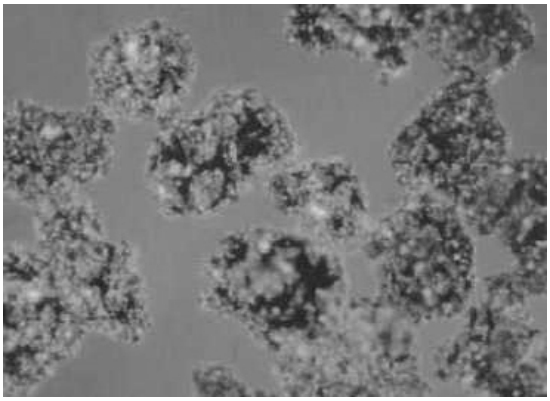

Figure 5. One-minute mix time

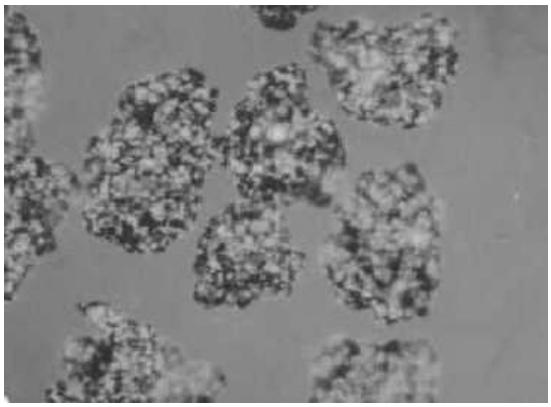

Figure 6. Five-minute mix time

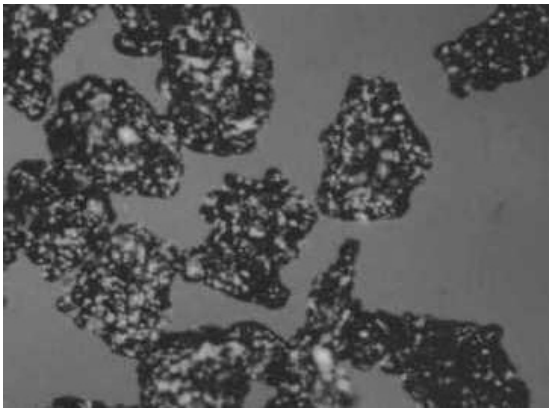

Figure 7. Ten-minute mix time

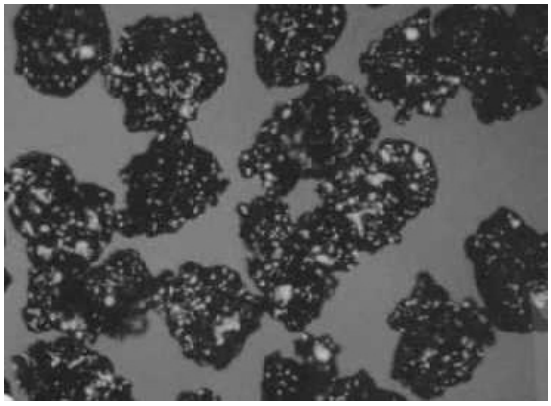

Figure 8. Thirty-minute mix time

Mechanism Studies

Fluorescent staining can also be used to follow toner impaction in machine tests. Toner containing carbon black does not stain nearly as intensely as a polymer coating without carbon black. Impacted toner shows up as very dark particle on the bright polymer surface. Figure 9 and 10 show impacted toner on a carrier bead. The toner used in figure 9 was non-classified and much of the impaction appears to be smeared toner particles composed of toner fines. The toner in figure 10 was classified and the impacted toner appears bigger in size then the toner in figure 9.

It should also be noted that the impaction with the unclassified toner occurs faster then with the classified toner.

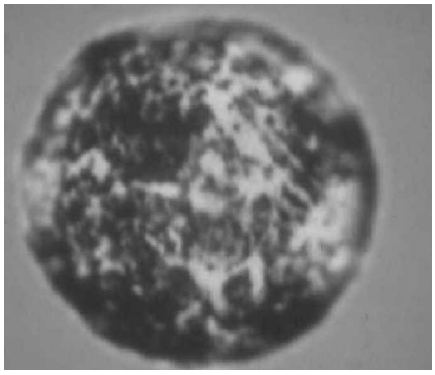

Figure 9. Unclassified toner impaction

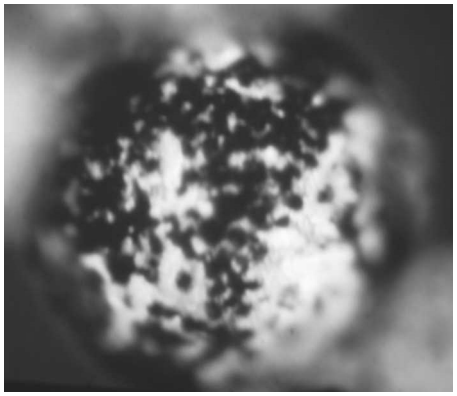

Figure 10. Classified toner impaction

Fluorescent staining can also determine where impaction occurs on carrier particles. In magnetic brush development, elongated beads will align with their longest axis following the lines of magnetic flux. Figure 11 shows an elongated ferrite bead with extensive impaction on the ends of the bead. There are not many techniques available that can illustrate this phenomenon as quickly, easily and dramatically.

We have also observed the carrier and toner orientation in a magnetic brush. The brush can be stopped and a heat lamp applied to the developer with just enough heat to fix the carrier and toner in place. Pieces of the brush can then be broken apart and stained. One can then observe the toner residing mainly between the carrier beads.

One last technique of interest was the use of fluorescent staining to observe the coating thickness. Carrier beads can be stained and then embedded in epoxy and polished to obtain a cross section of the bead. The stained coating shows the coating thickness and continuity as shown in figure 12.

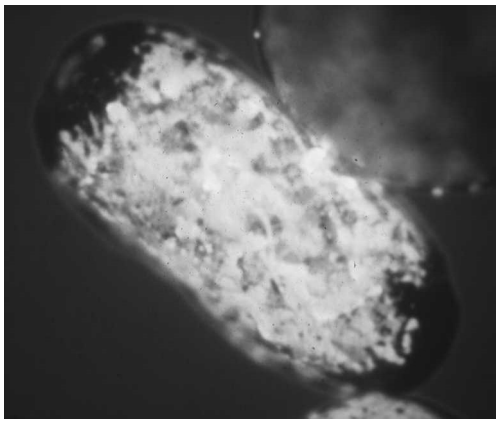

Figure 11. Elongated ferrite bead impaction

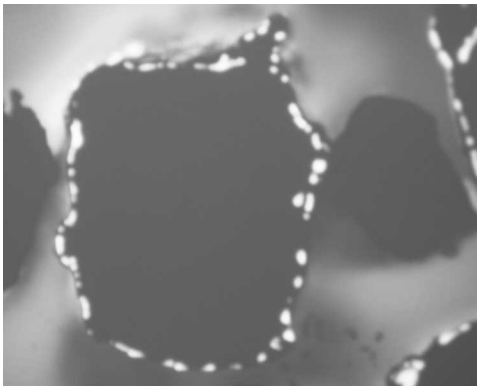

Figure 12. Bead cross section

We have also tried various methods to quantify the coating observed by fluorescent microscopy. The powder coating mixing experiment in figures 5 through 8 show that the amount of fluorescence decreases with mix time. These were all taken with the same exposure time. A photometer can be used to measure the decrease to obtain a quantitative value for the coatedness. It was found that the tribo decreased with excessive mix time and this correlated with the decreased fluorescence. Image analysis can also be used on the carriers to obtain quantitative numbers.

Conclusions

Fluorescent staining is an interesting technique to observe coatings on carrier particles. It is a quick simple method that can be used on almost any sample of carrier. The carrier is stained after coating so it can be used with any coating process. It is also useful for various mechanistic studies and allows observation of the processes.

Biography

Thomas Budny received his BS in Chemistry from Stevens Institute of Technology in 1969 and a Masters in Chemical Engineering from the University of Rochester in 1984. He has been at Xerox Corp. for 33 years in materials characterization, development and product delivery.