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EMULSION/AGGREGATION TECHNOLOGY: A PROCESS FOR PREPARING MICROSPHERES OF NARROW POLYDISPERSITY

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INTRODUCTION: Processes of preparing microspheres that enable control of well-defined particle characteristics such as size, size distribution, and functionality are becoming increasingly important for a variety of applications. However, either the particle size range that is achievable, or the types of materials that can be utilized in the process limit some of the current methods of microsphere preparation. The development of new methods for the preparation of microspheres that broaden the design space would therefore be an asset.

Of particular interest for certain applications is the preparation of particles in the micron-size range. This size of particles is typically prepared via dispersion or suspension polymerization techniques [1]. For suspension polymerization, control of particle size distribution can be difficult range because of the mechanical factors that control the particle size. In dispersion polymerization limitations arise due to the types of materials that will work in the process, thus one is limited to using particular solvents, or monomer/solvent combinations. Thus, a less complicated and more controlled process for preparing microspheres of good size distribution would be beneficial.

This paper describes a new process for preparing micron-sized polymeric microspheres with narrow particle size distribution. It is called the Emulsion/Aggregation (EA) technology and was originally developed for the controlled growth of particles for electrophotographic applications. The process involves the growth of microspheres from nanometer size constituents, such as polymer and pigments, through careful control of chemical and physical conditions.

METHODS: The Emulsion/Aggregation process (Figure 1) begins with the preparation of nanometer sized polymer particles stabilized in water using various techniques. These particles are on the order of 10-300 nm in size. A variety of resin types are possible including styrene-based materials, acrylates, polyesters etc.

The second step involves the growth of the nanometer-sized particles by mixing in deionized water in the presence of an aggregating agent. It is at this stage that other ingredients can be incorporated into the particle by adding them as water based dispersions. All of the components are homogenized to ensure effective mixing and continuous mixing is utilized throughout the growth process. Once the desired particle size is reached, the growth process is terminated.

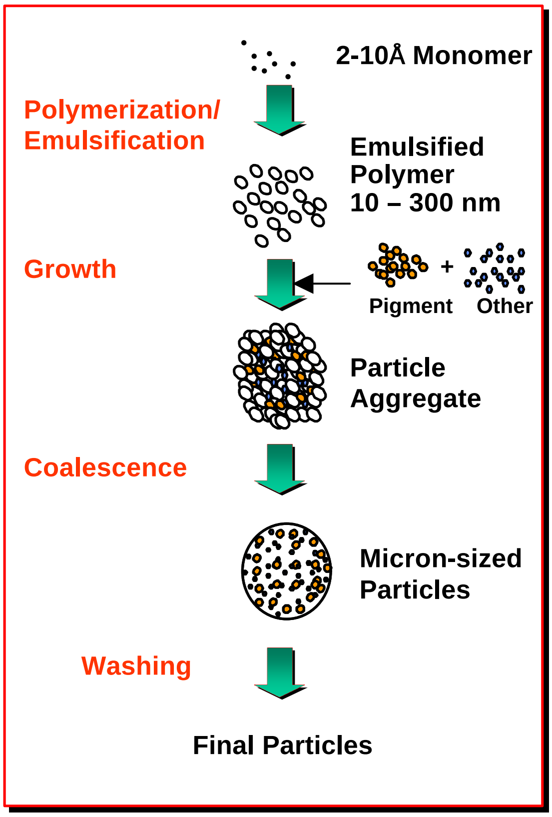

Fig. 1: Microsphere preparation by the emulsion aggregation process

Depending on the resin type utilized, the particles generated at this stage are either already spherical or require further treatment to coalesce into spheres. Once the microspheres are formed they can be isolated from the water and washed to remove the various ions and surfactants used in the process.

RESULTS: The EA process enables control of particle size and size distribution. As particles grow, the particle size increases with time as shown in Figure 2a. It is also during this phase that the particle size distribution narrows as illustrated in Figure 2b. A narrow particle size distribution is achieved using the EA process and a typical size distribution curve is shown in Figure 3. The geometric standard deviation based on volume is less than 1.25.

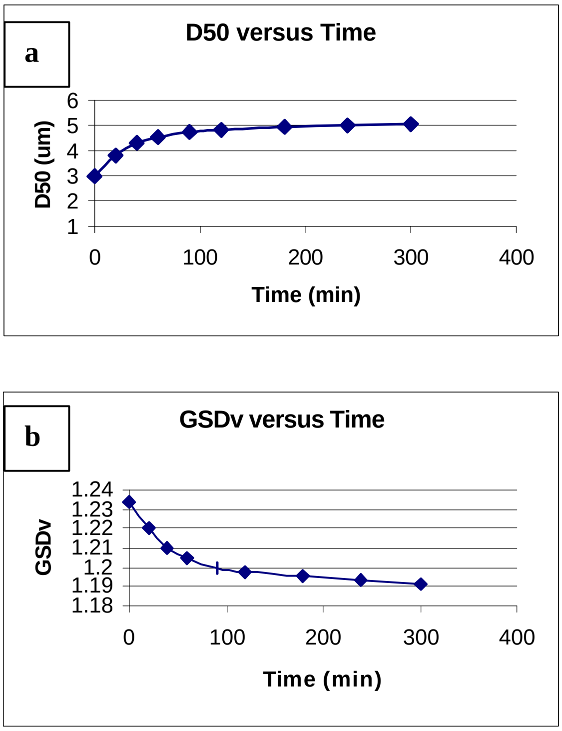

Fig.2: Particle Size (a) and Geometric Standard Deviation (b) as a function of growth time.

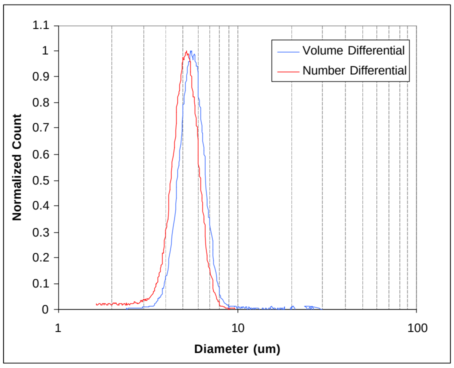

Fig.3: Particle Size of final particle as measured on a Coulter Counter instrument.

The ability to obtain narrow particle size distributions is driven by the growth kinetics and balance between the forces binding the particles together and the shear forces that erode aggregated particles. Figure 4 illustrates how the growth process proceeds from individual particles, to a gel network, to individual aggregates that continue to grow with time.

The particles produced in this process can vary in shape depending on process conditions. For the styrene-based case, the conditions can be adjusted such that a non-spherical or completely spherical particle is obtained. Figure 5a shows final particles with an irregular morphology. In 5b the particles are completely spherical.

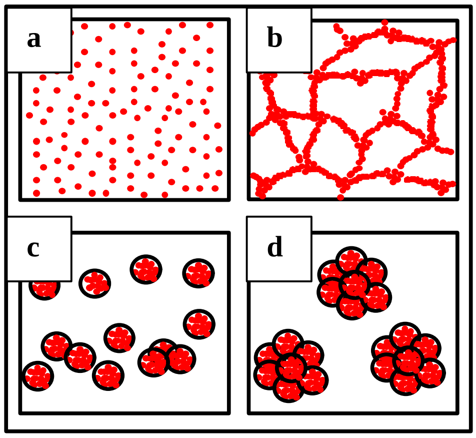

Fig.4: Mechanism of growth. a) Emulsified resin particles. b) Nucleation of Primary Particles. c) Primary particles. d) Final particles.

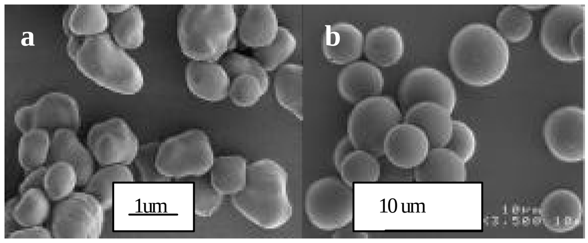

Fig.5: SEM of particle during EA process. a) Final irregular particles. b) Final spherical particles.

The Emulsion/Aggregation process is particularly suited to the incorporation of nanometer-sized pigments. This has been demonstrated in the application to toner materials for electrophoto-graphic applications. Dispersions of pigments in water are mixed with the emulsified resin and the process is carried out in the same manner.

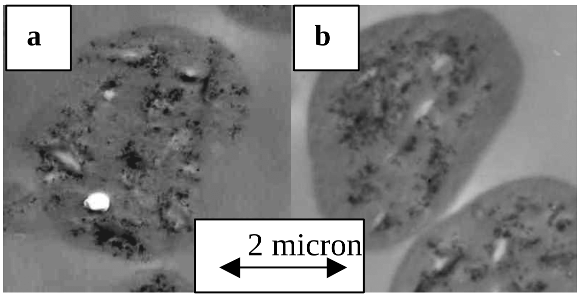

Fig. 6: TEM images of a) particle containing pigment throughout the particle, and b) particle with surface pigment covered by resin.

Cross sections of particles that contain pigment show that the pigment is fairly evenly distributed throughout the particle. It is possible to add additional latex to cover surface pigment. Figure 6 shows TEM's of particles with and without additional latex added to cover surface pigment.

CONCLUSIONS: The Emulsion/Aggregation technology is a process which has been developed for the preparation of micron-sized polymeric particles that enables the control of particle size, shape and size distribution. This process offers an alternate route to microspheres of narrow polydispersity. The process yields particles with geometric standard deviations of below 1.2 with well-controlled structures. A variety of resin types can be used in this process and other materials such as pigments can be incorporated into the particles.

REFERENCES: [1]R. Arshady, (1992) *Colloid Polym Sci 270:717-732.*

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