# ASPECTS OF LATEX PARTICLE SIZE CONTROL FOR IMPROVED WATER BLUSH RESISTANCE

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Latex films have a tendency to blush when exposed to water. The swelling of trapped hydrophilic material, resulting in pockets with different refractive indices is proposed as a possible model for blushing. A pressure sensitive latex was developed based on this model. The blush was improved by choice of surfactant and control of particle diameter. The resulting latex has an unusual particle growth behavior, during polymerization. The particle size distribution was characterized by dynamic light scattering (DLS), methods of electron microscopy (SEM/TEM) and with the help of atomic force microscopy (AFM). AFM data are in a good agreement with our growth model. A possible explanation for the unusual particle growth behavior is proposed.

Introduction to Blush in Latex Films

As a latex film forms, the particles initially coalesce at the air interface as represented in Figure 1. Hydrophilic material is trapped in the interstices between particles. If the film composition is semi-permeable, when it is exposed to water,


Release liner
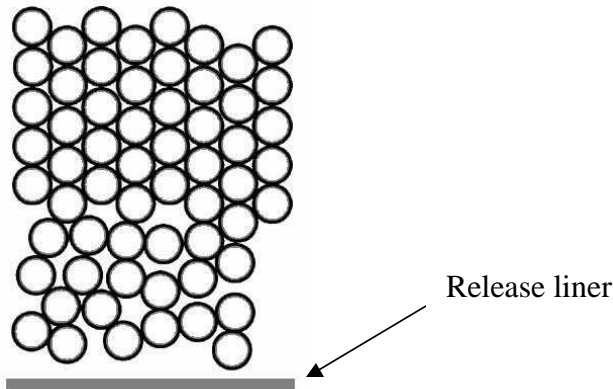
Figure 1.   Generalized drawing of latex particles during film formation.

the hydrophilic pockets will swell. The swollen pockets usually have a refractive index different from the polymer. As the pockets swell above 40nm, they scatter light, and the film becomes turbid. The degree of turbidity or blush depends on a number of factors. If the time frame of film formation is long enough, some hydrophilic material may follow the receding water phase. This may result in pockets with higher concentrations of hydrophilic material dispersed within the film. These pockets will swell more, and result in greater blushing. Perhaps because of this, air dried films have been measured to have more blush than oven dried films. Additionally, the blushing of an air dried film will not be improved by post oven treatment.

Water itself can impact blush resistance. In certain areas of the Northeast, where lead pipes are still in use, the pH of the water is lower than water in the Midwest. If the hydrophilic material is pH sensitive, a latex film that does not blush in the Northeast may blush in the Midwest.

Model to Improve Blush Resistance

Particle Size. One approach to improve blush resistance is to reduce the size of the hydrophilic pockets. If the pockets are small enough, even when they are fully swollen with water, they will stay small enough so as to not scatter light, and the film will remain clear. This can be done by lowering the average latex particle diameter to 80-90nm. The relative difference in the size of the interstices between 85nm and 300 nm particles is shown in Figure 2.
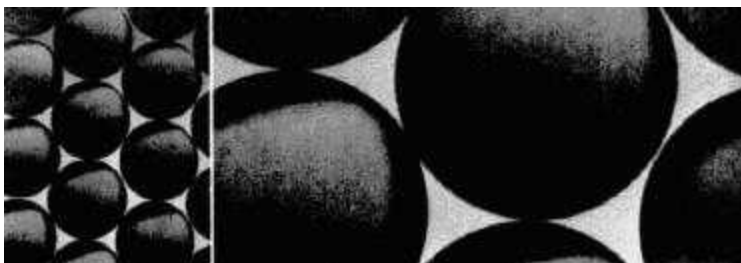
Figure 2. **A comparison of interstice size between 85nm and 300nm particles.**

Polymerizable Surfactant. Lowering the particle size creates a possible stability problem with the latex particles. If a 300nm particle latex is stable with 1.75% surfactant, an 85nm particle latex would require 6.2% surfactant just based on surface area, and ignoring the increase in collisions per unit time. Latex made with this level of surfactant will still blush because of the increased level of hydrophilic material causing the pockets to swell more. The 85nm latex needs to be made at the normal level of surfactant, to take advantage of the smaller hydrophilic pockets. Using a polymerizable surfactant improves the particle stability and reduces the amount of free hydrophilic material available. For example the combination of a nonionic / anionic hydrophilic tail on the Hitenol BC-10, shown in Figure 3, produces the desired particle diameter. The propenyl
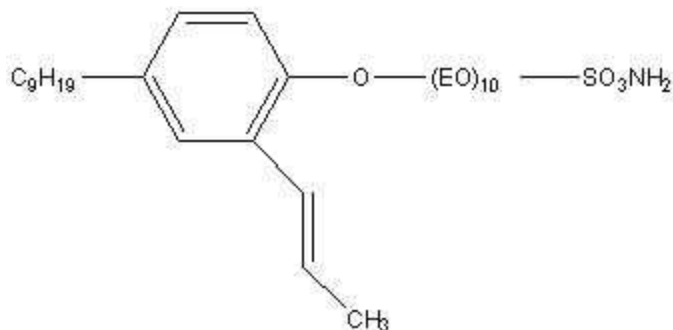

Figure 3. **Hitenol BC-10**

group works well since it does not readily homopolymerize. In comparison when methacrylate functional surfactants were used the amount of homopolymer formed was significant enough to increase the blush. The combination of small particle diameter and polymerizable surfactant has produced latex with good blush resistance over a range of testing conditions.
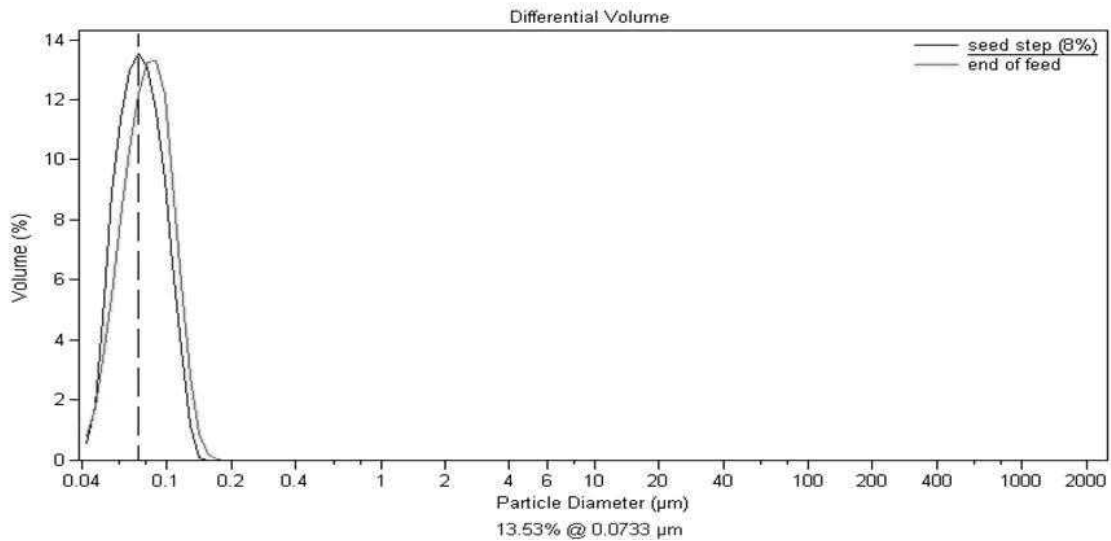
Particle Growth Behavior

During the polymerization of these latexes, samples were pulled and the particle size measured. The latexes were run under "starved" conditions with less than 1% unreacted monomer during the polymerization. Assuming that no particles were made or

lost, and knowing the amount of monomer that remained, a growth curve was calculated based on the particle diameter of a sample pulled early in the polymerization. The measured curve shown in Figure 4 shows the particle diameter growth to be much flatter than the predicted one. The average diameter could remain flat if new particles were created. The average particle diameter and

Particle Diameter, nm
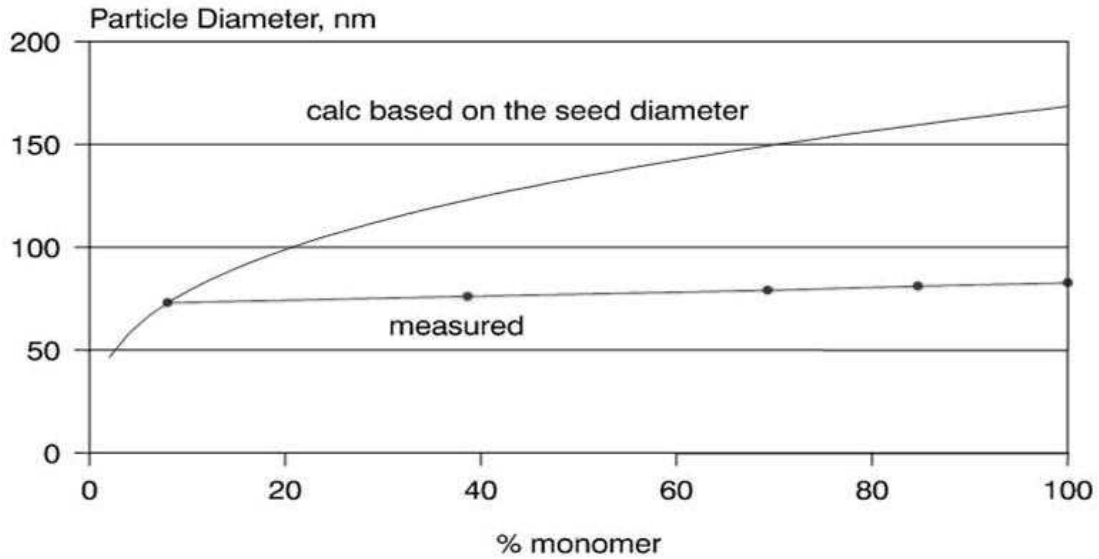
Figure 4.   Measured versus calculated particle growth

distribution were measured by light scattering on a Coulter LS230 for a sample with 8% monomer added versus a final sample. Figure 5 shows the results were unexpectedly close in average diameter and distribution.


Figure5.   Particle size results for 8% monomer versus 100%

Particle Growth Models

To try to explain the unusual particle growth behavior Competitive Growth and Surfactant Control models are proposed. If the particle growth can be understood, it has positive implications for continuous polymerization of narrow particle size distribution latexes.

Competitive Growth Model. To verify the data samples were sent for analysis on several different light scattering instruments, with basically the same results. So then the assumption was that the technique did not measure all the particles. The cut off for detection on the LS230 was around 40-50nm, and perhaps there was a significant population of smaller particles. Just to see if this was feasible a competitive growth model was used, where the monomer was absorbed as a function of particle surface area. So if for each 68.1nm particle, there were twenty-eight 25nm particles, then the larger diameter particle would grow along the measured line. The 25nm particles would also grow, but not get big enough to be detected, as shown in Figure 6. So while the numbers are not expected to be accurate, it would be expected if this idea is valid there should be a large number of small diameter particles.
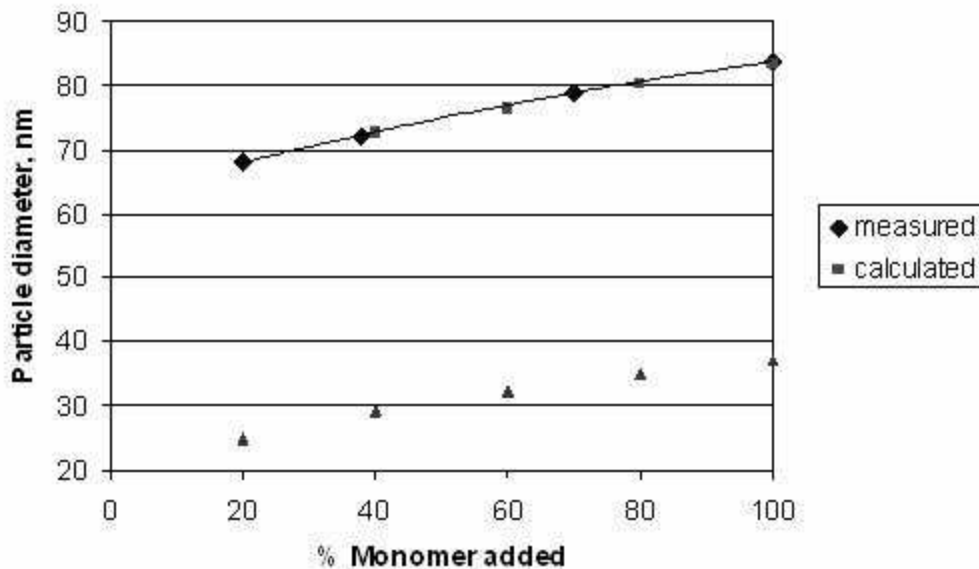
**Figure 6. Results of competitive growth model**

Surfactant Control Model. The Competitive Growth model requires a large population of ~20nm particles with a set number of 70-85nm particles. It does mimic the growth of the larger diameter particles as a function of conversion, but doesn't explain their initial formation, so another model is now proposed. For a particle to grow

monomer needs to be absorbed and polymerized. If the monomer fails to be initiated in the particle it may migrate out initiate in the water phase or be absorbed into another particle.   Smith & Ewart states that two free radicals cannot co-exist (except momentarily) in a very small particle. So in the particles there is either a single growing radical chain, or no polymerization. The structure of the chosen polymerizable surfactant is such that abstraction of an allylic hydrogen may occur in preference to attack of the double bond. This is shown in Figure 7.
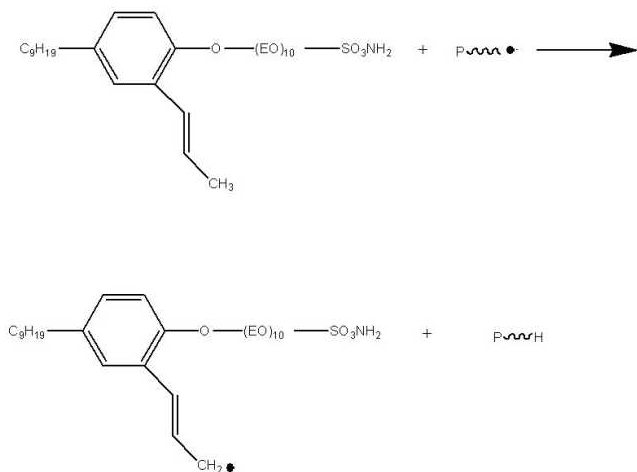
Figure 7. Possible allylic hydrogen abstraction

It may be that the surfactant acts as a chain terminator, preventing the entry of free radicals into the particle. It is interesting to note that the particle diameter of the latex is in the transition region to more than 0.5 radicals per particle as predicted by Smith & Ewart kinetics.   This is shown in Figure 8, taken from Turner Alfrey's 1976 notes.
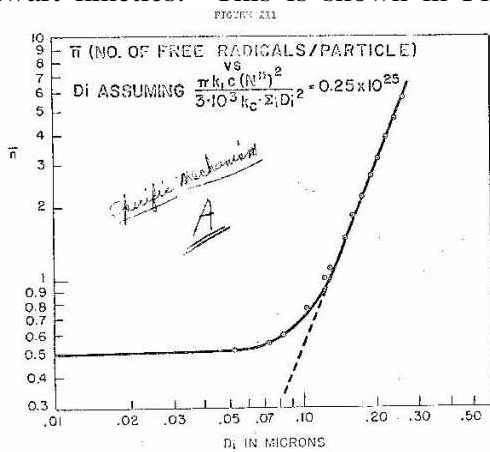

Figure 8. Number of free radicals versus particle diameter

If the surfactant does produce a dead particle, then the newly formed particles will not be competing for the monomer with the existing larger diameter particles. The newly initiated particles would rapidly grow to the limiting diameter due to the leveling effect. There are articles in the literature to support the use of inhibitors to reduce particle diameter. Japanese patent 2003335807 uses 1-chloro-2,4-dinitrobenzene to limit the average particle diameter of a styrene, methyl methacrylate, acrylonitrile, butadiene latex to less than or equal to 60nm. Carolino Quintero has also published on allylic hydrogens reduction of polymerization rates in latexes. With this model, the number of possible small particles would be limited to those formed over the final stage of conversion.

Model Validation
For the Competitive Growth model to be correct, a larger number of small particles need to be present. The Surfactant Control model would also require smaller diameter particles to be found, but at much lower numbers. Several microscopy techniques were tried, including AFM, SEM, and TEM. Possibility because of the low T_g of the polymer, these images did not give conclusive evidence that small particles did, or did not exist. A TEM is shown in Figure 9.
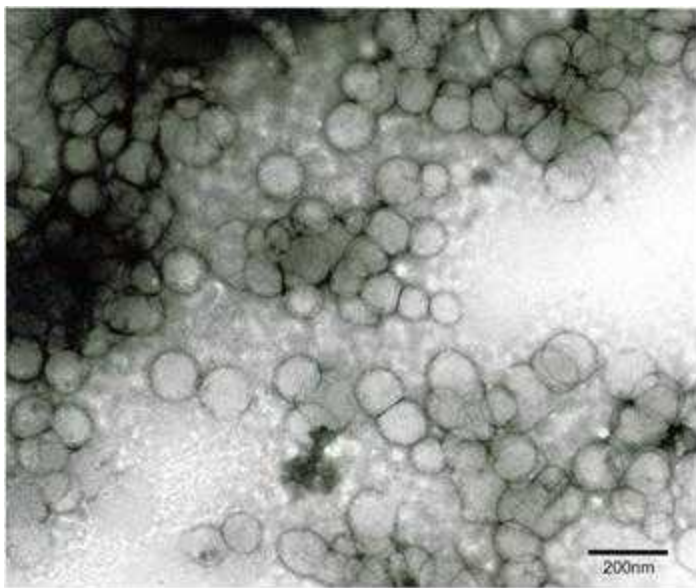

Figure 9. TEM of latex

Cryo-SEM. The latexes were analyzed using Cryo-SEM by Debra Sherman of Purdue University. This is a freeze drying technique in which the latex is not diluted, but a drop is flash frozen with liquid nitrogen. The frozen drop is fractured to expose ice crystals, as shown in Figure 10. The crystals were then sublimed while keeping the particles frozen as shown in Figure 11. The images of the particles show close to the

same diameter measured by light scattering. Hexagonal packing is also clearly shown in Figure 12. No evidence was shown for a significant population of smaller diameter particles.
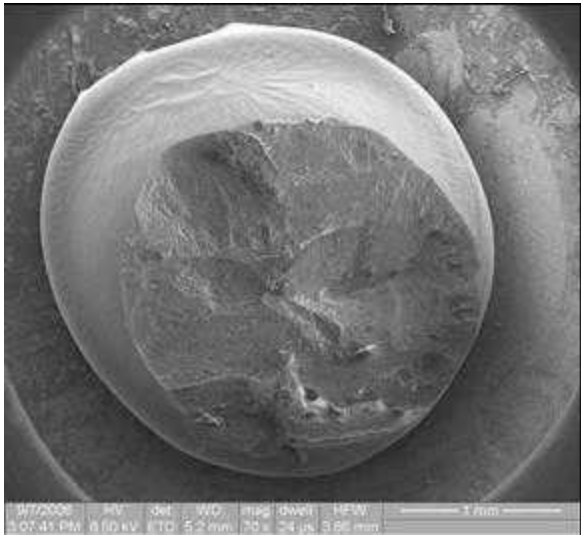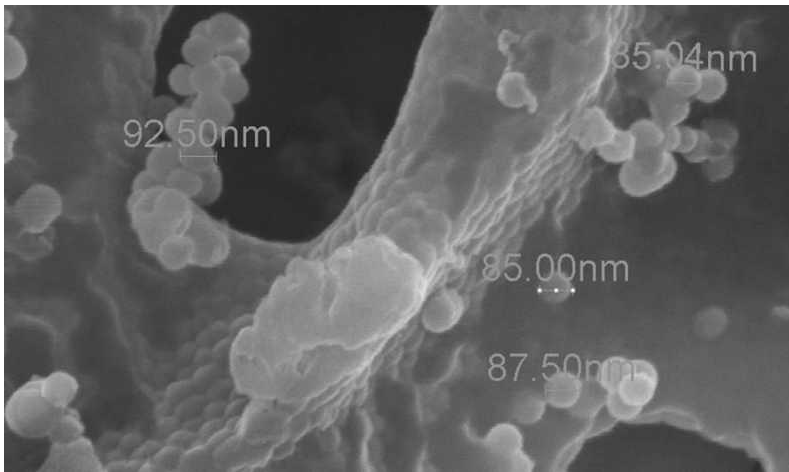

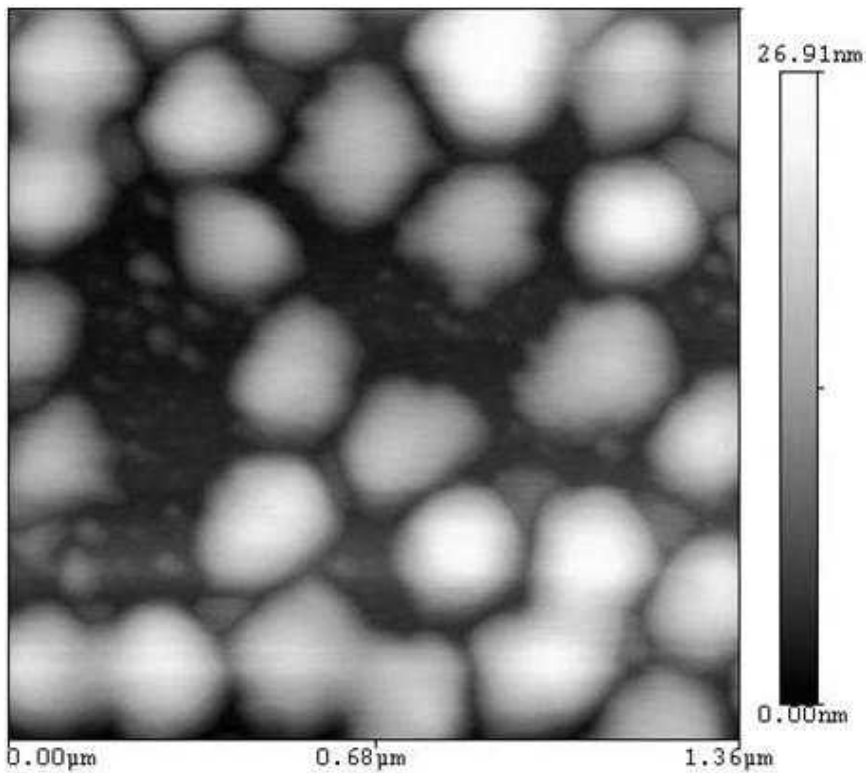**Figure 10.   Fractured latex drop**
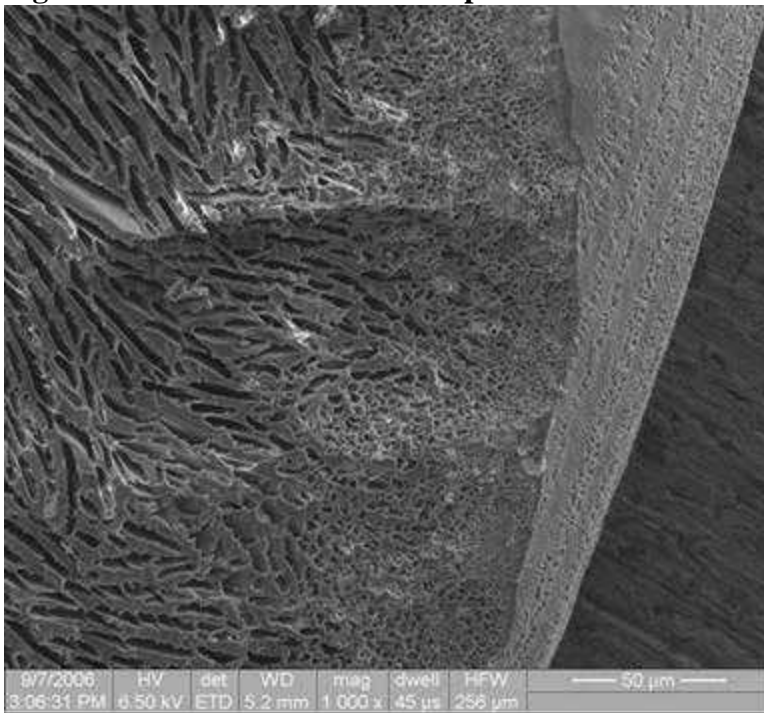
Figure 11.   Voids from ice crystals

Figure 12.   **Cryo-SEM image for latex particles**

      AFM. Samples were also sent for AFM analysis by Pacific Nanotechnology. Using this technique small particles were found. As shown in the Figure 13.

Figure 13.   **AFM micrograph.**

Software analysis of the number and size of particles show a small population of ~20nm particles. .

Conclusions

A model to explain blush has led to a practical solution. The use of a small particle diameter combined with a polymerizable surfactant has been shown to improve blush resistance.

The flat particle diameter growth curve during polymerization does not seem to be due to a significant population of particles small enough to be undetected by light scattering. AFM has found a small population of ~20nm particles which seems to support the model that this surfactant may limit the particle growth by being a growing radical chain terminator.