Influence of Colloidal Stability on the Uniformity of Drying in Waterborne Colloidal Coatings

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Polymer colloids that are used in coatings and adhesives are often chargestabilised. The basic physics of their colloidal interaction energy is often well described by the DLVO theory.¹ The colloidal dispersion is initially stable when cast to make a film. But during drying, two things happen: (1) particles get closer together as the water evaporates; and (2) the salt content steadily increases, such that it approaches very high concentrations in the "last drops" of water within the film. Both of these processes can potentially affect the colloidal stability of the particles. As the particle density increases, the particles might be pushed together into the attractive regime leading to flocculation. Simultaneously, with increasing salt concentration in the water phase, the Debye screening length, κ^{-1} , and the energy barrier to flocculation both decrease. In some cases, we predict that the barrier height will be sufficiently low so as to induce flocculation before drying is complete.

This lecture will report our investigations of how changing colloidal stability, during the drying of charge-stabilized latex films, leads to the development of non-uniformities in the water concentration in the vertical direction. Routh and Russel,² have argued that the extent of uniformity of the profile can be considered to be determined by the ratio between two characteristic times: the time for evaporation of water, τ_{dry} , and the time for the self-diffusion of particles in the wet film, τ_{diff} , setting how long it will take for the particles to re-distribute themselves. The ratio of the time for particles to re-distribute themselves is longer than the time for drying, and vertical non-uniformities will develop. We propose that particle flocculation will increase τ_{diff} , and hence lead to drying non-uniformities, as shown schematically in Figure 1.



Figure 1. (left) Schematic diagram of non-uniform drying in the vertical direction within a waterborne colloidal film and (right) the corresponding water concentration profile showing the water concentration gradient between the packed region at the top and the underlying dilute region.

To determine the variation of the water concentration in the direction normal to the wet film, $\phi_w(z)$, we use the GARField magnet³ to perform magnetic resonance (MR) profiling. Further insight into the effects of salt on the dynamics of colloidal particle motion has been obtained from *simultaneous* dynamic light scattering (DLS) and MR profiling experiments on a drying latex film using the apparatus shown in Figure 2. The presence of additional salt decreases the screening length, which then decreases the effective particle volume. In the early stages of drying, the DLS data indicate an increase in the particle diffusivity with salt addition.

When the as-received latex is dried, a shallow and linear water concentration gradient, $d\phi_w/dz$, is observed throughout the drying process. There is an increase in $d\phi_w/dz$ when the salt concentration is increased via the addition of NaCl, as illustrated in Figure 3. The results are broadly consistent with our DLVO simulations that predict the onset of flocculation during drying at higher concentrations of salt in the later stages of drying. For particles having a low viscosity, it is predicted² that vertical drying non-uniformities result in the creation of a coalesced surface layer or "skin," which has been observed experimentally in some colloidal films.⁴ We propose that water entrapment - and associated problems with film formation and properties - could be caused by film additives that raise the electrolyte level.



Figure 2. Schematic diagram of experimental set-up showing light passing from the laser (A) and scattering from the drying film sitting above an RF coil (B) within a magnetic field gradient created by the pole-pieces (C) on the GARField magnet. The light then passes into an optical fiber connected to a photomultiplier tube and an autocorrelator (D).



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