

Microstructure development in particulate coatings examined with high-resolution cryogenic scanning electron microscopy

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ABSTRACT: *The authors used cryogenic scanning electron microscopy to examine the early stages of latex film formation. They visualized the influence of ionic strength and extent of carboxylation in latex-calcium carbonate formulations and in latex-only formulations. Results demonstrated that latex particles deposited on calcium carbonate surfaces creating a suspension of carboxylic acid-stabilized calcium carbonate particles. Images of consolidation fronts showed that variation of ionic strength and extent of carboxylation dramatically change the way latex particles consolidate and form films.*

KEYWORDS: *Coatings, cryogenics, film, latex, microstructure, particles, scanning electron microscopy.*

Synthetic polymer latexes with carboxylic acid copolymers find use as binders for inorganic pigments in a wide range of applications that include paint, paper coating, and carpet backing. These latexes provide the desired rheology for pigment dispersions in wet latex and develop the desired binding strength upon drying. Film formation of the latex particles during drying of a pigment-in-latex formulation is the step most critical to development of binding strength. A review of the theories of latex film formation

indicates three main stages (1). In the first stage, the solvent evaporates, forcing latex particles close together. The second stage begins when latex particles crowd to the solvent surface and menisci form across the interstices between the particles. The third stage starts after solvent disappears from between the interstices and the latex particles begin to coalesce and fuse.

In this study, we examined how the colloidal stability of the latex particles through all three stages of film formation determines the properties of a

dried latex film. As solvent evaporates, the solutes concentrate, and latex particles come close together. The salt present in aqueous pigmented coatings concentrates during drying. The increased ionic strength weakens the electrostatic forces of repulsion. If there is too much weakening, the suspension flocculates. After menisci form and drying proceeds from them, the suspension must remain stable enough to allow the latex particles to order at the solvent surface without flocculating and coalescing. As they coalesce, the elastic deformation of the latex particles as they flatten against one another opposes the attractive van der Waals forces (2).

Previous studies of latex film formation have focused only on forces between latex particles. The objectives of this research are not only the examination of latex-to-latex interactions but also the investigation of the influence of pigment particles on film forming and pigment-to-particle binding in pigment-latex formulations. Past studies have paid little attention to effects of the extent of electrostatic and steric stabilization. Another objective is examination of these effects by changing the ionic strength of the suspending solution and the extent of carboxylation of the latex particles.

Using conventional electron microscopy, it is possible to examine *in situ* only the final stage of particle coalescence, fusion, and film formation (2, 3). Evaporation of solvent in earlier stages causes an electron beam to scatter and

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damages the vacuum pumps. Lowering vapor pressures by freezing the suspension and using cryogenic techniques will overcome this problem. Earlier work (4) showed that the colloidal forces operating in paper coating formulations can be deduced using cryogenic scanning electron microscopy (cryo-SEM).

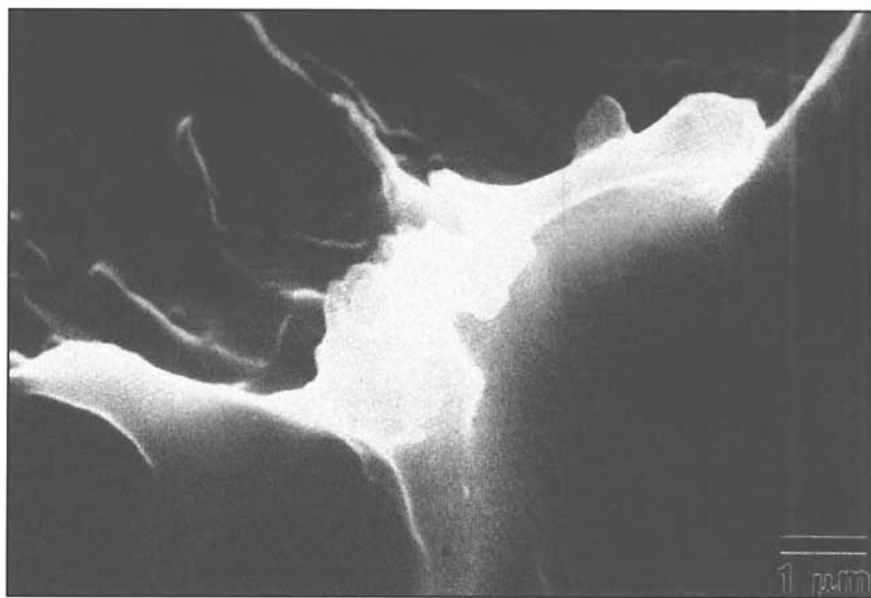
Resolution of samples by SEM should be at least as high as 10 nm to record sharp images of the latex and pigment particles used in coating formulations. The main barrier to high-resolution cryo-SEM is water-vapor condensation on cold samples. This blankets the surface details and reduces resolution. One way to prevent water vapor from condensing is to use sample temperatures high enough that ice sublimates from the sample instead of condensing on it. This is suitable for many biological materials that do not collapse after the ice sublimates. Microstructures in colloidal suspensions often collapse upon ice removal, however. In such cases, substrate temperatures low enough to stop sublimation are necessary. Unfortunately, vacuum systems always have residual water vapor, and low substrate temperatures cause that vapor to condense and blanket surface details. Thus the partial pressure of water vapor in the specimen chamber of the SEM must be low. The cryo-SEM system used for this research has cold traps throughout to reduce the partial pressure of water.

This study used two types of carboxylated styrene-butadiene latexes. One had a low degree of carboxylation and the other a high degree. We first flocculated each latex with CaCl_2 to demonstrate how the extent of carboxylation determines the resistance of each latex against coalescence and fusion when imaged with cryo-SEM after freezing and fracturing. Then we prepared formulations of carboxylated polystyrene-butadiene latex and ground calcium carbonate with varying degrees of carboxylation, ratios of latex to calcium carbonate, and ionic strengths. We examined wet microstructures with cryo-SEM after freez-

1. Cryo-SEM of fractured, frozen floc of carboxylated polystyrene-butadiene HC latex



2. Cryo-SEM of fractured, frozen floc of carboxylated polystyrene-butadiene LC latex



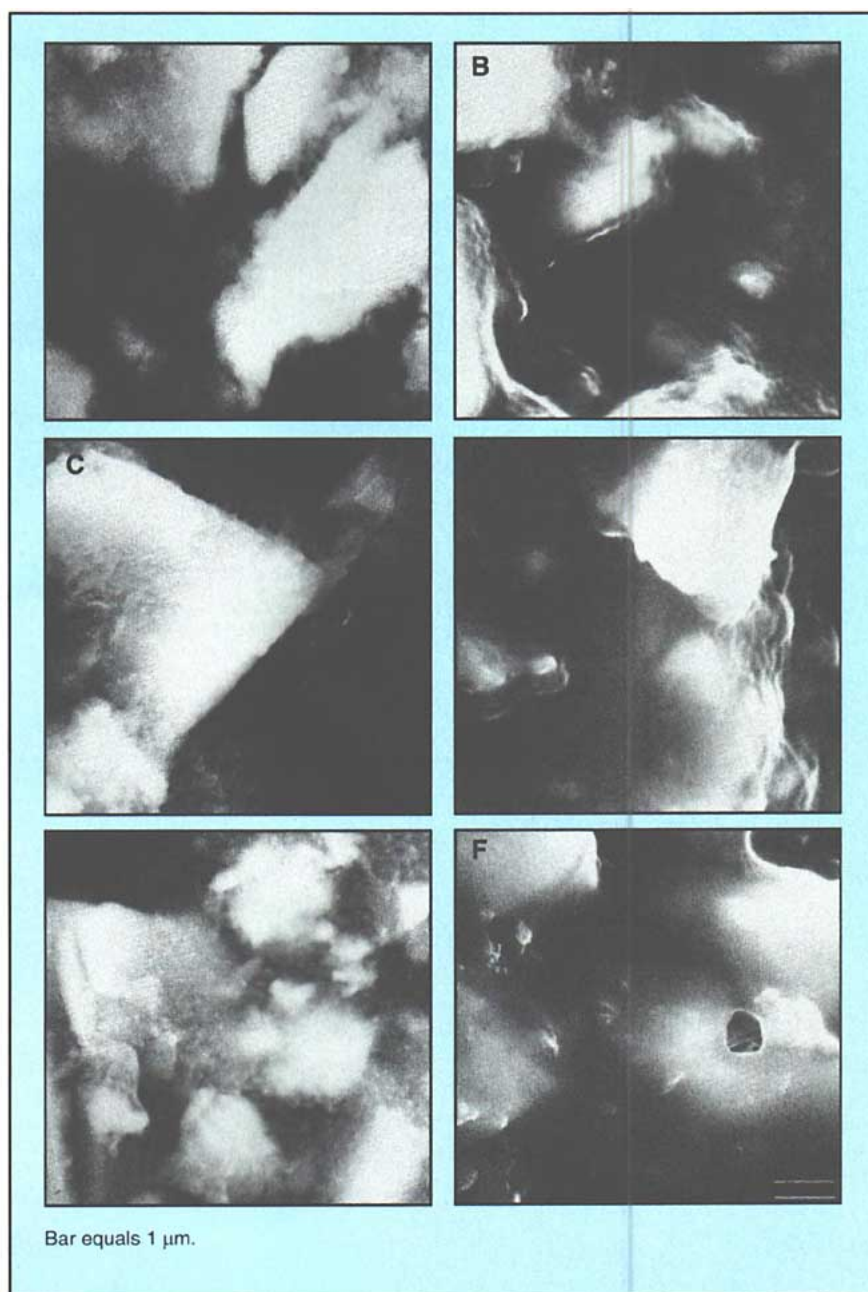
ing and fracturing and compared them with microstructures in air-dried films examined at ambient temperature with conventional SEM. Finally, we examined consolidation fronts of latex suspensions at various ionic strengths after dip-coating on films of polyethylene terephthalate (PET), partly drying, and then fast-freezing with cryo-SEM.

Experimental

Carboxylated latex

We used two types of carboxylated styrene-butadiene latex—one with low extent of carboxylation (LC) and the other with high extent of carboxylation (HC). The glass-transition temperature ($T_g \approx 0^\circ\text{C}$) and the cross-linking density were the same. The

3. Microstructures of one part latex to six parts CaCO_3 suspensions at 80% solids by weight examined with cryo-SEM after freezing and fracturing (A, C, E) and with conventional SEM (B, D, F)



mean particle size of both was 140 nm.

Flocculated latex

We placed drops of HC latex (50% solids by weight) into a beaker containing about 20 mL of 0.1M CaCl_2 and drops of LC latex (50% solids by weight) into a beaker containing 20 mL of 0.02M CaCl_2 . We scooped out the flocculated latex from each beaker

and sandwiched the material between two copper sheets. Using tweezers, we attached the sandwiches onto the end of a spring-loaded rod equipped with a trigger (5). After release of the trigger, we fast-froze each sandwich by plunging it at approximately 1.5 m/s into liquid ethane at its freezing point (89.9 K). This freezing of samples occurred within 30 ± 10 min after floccu-

lation. The authors estimated the freezing rate to be about 3000 K/s, which was not fast enough to vitrify the ice. We only detected ice crystals when the solids content was low, however. We stored frozen samples in liquid nitrogen until examination by cryo-SEM.

Calcium carbonate suspensions in latex

We prepared suspensions of latex and ground calcium carbonate at 80% particulate solids by weight with ratios of one part latex to six parts CaCO_3 . There were three suspensions with calcium carbonate using HC latex in 0.02M CaCl_2 . There were three more suspensions prepared in the same way except at 64.4% solids by weight with ratios of one part latex to 33 parts CaCO_3 . Approximately 30 min after preparation, we fast-froze a drop of each suspension as described previously and stored it in liquid nitrogen. We air-dried a drop of each of the suspensions (80% solids by weight) and coated them with about 5 nm of a gold and palladium mixture in a dc magnetron sputter coater before SEM examination at ambient temperatures.

There were two more suspensions of latex and calcium carbonate at 85% solids by weight with ratios of one part latex to 10 parts CaCO_3 . One used HC latex, and the other used LC latex. Again we air-dried a drop of each, coated them with the gold and palladium mixture as described previously, and examined them at ambient temperature with SEM.

Consolidation fronts

We prepared suspensions of HC latex (20% solids by weight) in water and in 0.02M, 0.03M, and 0.05M CaCl_2 . We also prepared one suspension of LC latex at the same solids content (20% solids by weight). Each suspension was dip-coated on a PET film, air-dried for 20s, and fast-frozen by hand plunging into liquid ethane. Frozen samples were stored in liquid nitrogen until cryo-SEM examination.

Cryo-SEM

Earlier work details the cryo-SEM system used in this research (6, 7). The system consists of two main parts: a vacuum chamber attached to the SEM specimen chamber with a gate valve and a cold-stage in the SEM specimen chamber. The vacuum chamber itself contains two parts: a pre-pump chamber and a metal-coating chamber. Each chamber has a conduction-cooled sample stage at approximately 100 K. During sample transfer, only the pre-pump chamber vents to atmospheric pressure. This protects the metal-coating chamber from contaminants. The metal-coating chamber has three tungsten baskets for thermal sublimation of chromium, a shutter that protects samples from thermal radiation during warm-up of the tungsten baskets, and a quartz microbalance that measures the thickness of deposited chromium.

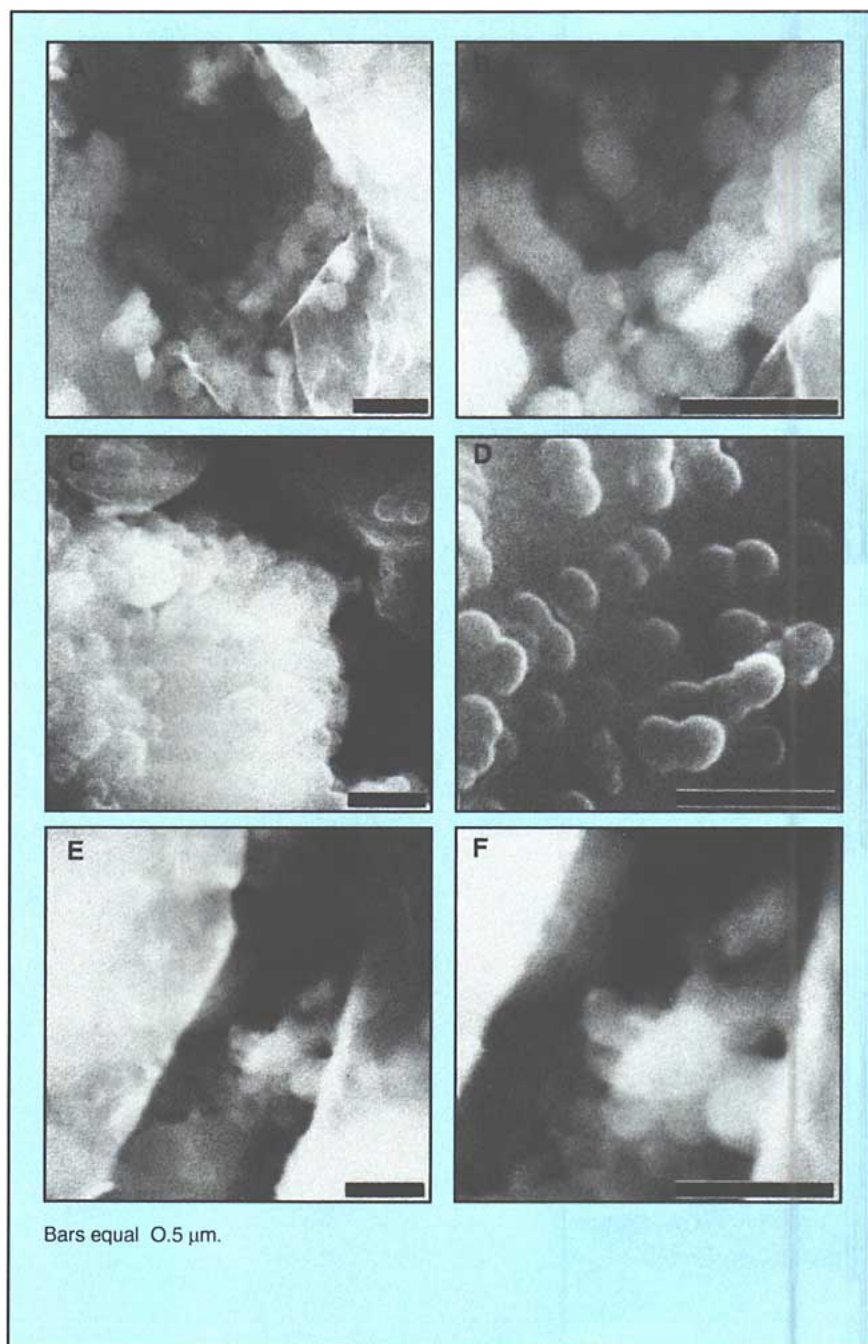
Each sample transfers from liquid nitrogen to the cold-stage in the pre-pump chamber. Here we fractured the sandwiched samples after evacuating the pre-pump chamber to approximately 10^{-6} torr. We etched only dip-coated samples at 175 K for 10 min to remove ice that condensed on them during transfer from liquid nitrogen. The sandwiched samples did not require etching because we fractured them in high vacuum. We coated all the samples with approximately 3 nm of chromium as measured with a quartz microbalance. The final transfer was through a gate valve to the cold stage (ca. 100 K) in the SEM specimen chamber.

Results

Flocculated latex

The extent of carboxylation determines the resistance of a latex to deformation by van der Waals forces. **Figure 1** shows a fractured floc of HC latex flocculated in 0.1M CaCl_2 . **Figure 2** uses the same magnification to show a fractured floc of LC latex flocculated in 0.02M CaCl_2 . Many of the

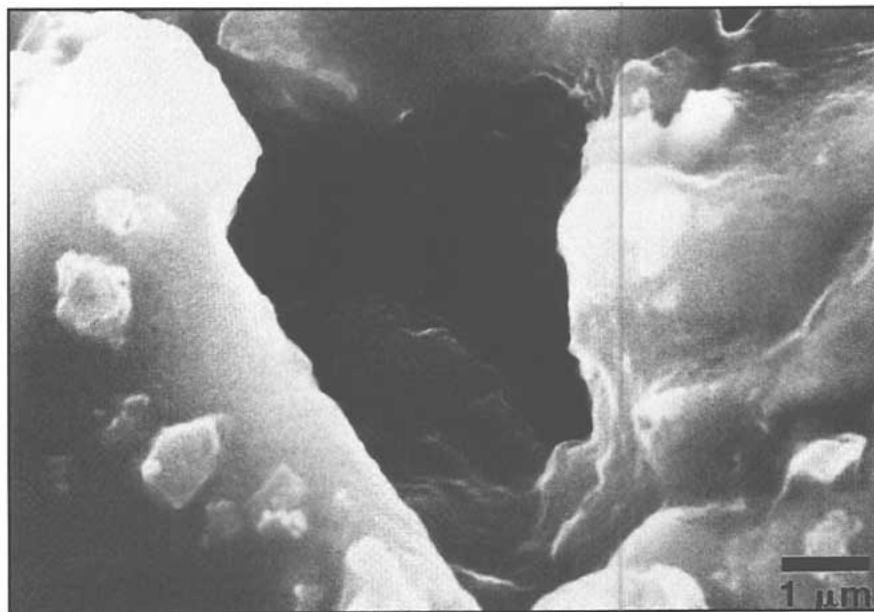
4. Wet microstructures of one part latex to 33 parts CaCO_3 suspensions at 64% solids by weight examined with cryo-SEM after freezing and fracturing



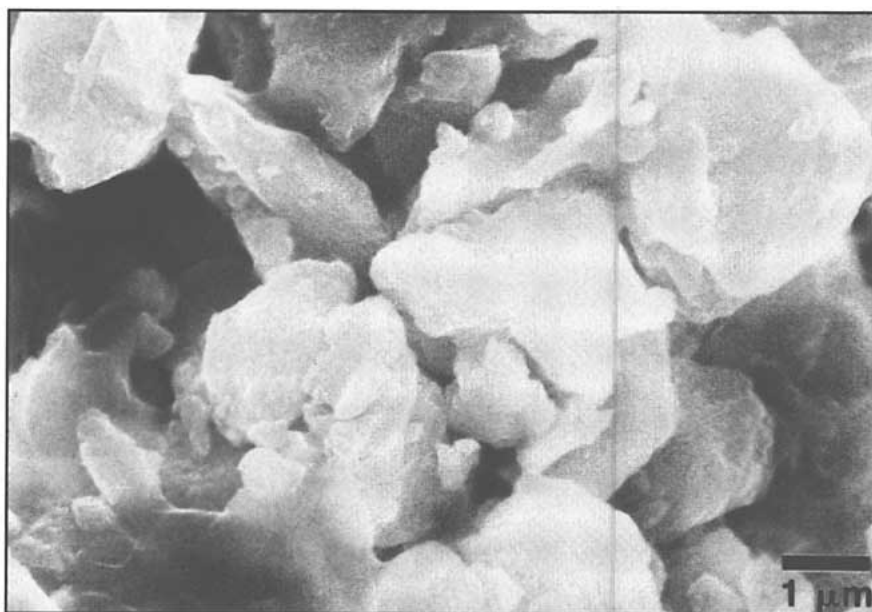
140-nm HC latex particles in Fig. 1 do not show deformation. In contrast, the LC latex in Fig. 2 at one-fifth the ionic strength shows not only deformation but also complete fusion. Electrical double-layer theory predicts that electrostatically stabilized latex should flocculate when the concentration of the divalent cation reaches $10^{-2}M$. The

HC latex in Fig. 1 had flocculation at approximately 10 times that concentration, yet many particles did not exhibit deformation. This demonstrates that, at least in the first 30 min after flocculation, our HC latex was stable against deformation by van der Waals forces even after eliminating electrostatic repulsion.

5. Conventional SEM micrograph of a suspension of one part HC latex to 10 parts CaCO_3 air-dried from 85% solids by weight



6. Conventional SEM micrograph of a suspension of one part LC latex to 10 parts CaCO_3 air-dried from 85% solids by weight



Latex/calcium carbonate suspensions

Figure 3 shows six different variations of microstructures of the suspensions of one part latex with six parts CaCO_3 at 80% solids by weight. In this figure, A and B show wet and dry microstructures, respectively, with HC latex. C and D show wet and dry mi-

crostructures, respectively, with LC latex. Finally E and F show wet and dry microstructures, respectively, with HC latex in 0.02M CaCl_2 . Wet samples were examined with cryo-SEM after freezing and fracturing. Dry samples were examined with SEM at ambient temperatures after air drying.

Latex associates with calcium car-

bonate in all three frozen-fractured samples of Fig. 3: A, C, and E. Only LC latex in C of Fig. 3 shows deformation on CaCO_3 surfaces (note arrow). There appears to be less free LC latex in the ice between the CaCO_3 particles than there is of free HC latex (A of Fig. 3) and of free HC latex in 0.02M CaCl_2 (E of Fig. 3). Deformation of the LC latex particles on CaCO_3 surfaces and the appearance of fewer free LC particles in the ice are both consequences of the lower colloidal stability of the LC latex compared with HC latex.

By comparing only the wet microstructures, it appears that the HC latex formulation in water (A of Fig. 3) and in 0.02M CaCl_2 (E of Fig. 3) is more stable against van der Waals attraction to CaCO_3 surfaces than the LC latex formulation (C of Fig. 3).

Comparison of the extent of ordering and deformation in the dried films of each formulation indicates, however, that HC latex in 0.02M CaCl_2 is the least stable, not the LC latex. The dried formulation of HC latex (B of Fig. 3) shows mostly areas of hexagonal close packing. The roundness of the latex particles is plain. Both of these factors indicate latex stability. The dried formulation of LC latex (D of Fig. 3) shows only a few areas of hexagonal close packing. The roundness of the latex particles is less distinct. These two factors indicate that the formulation of LC latex is less stable than the formulation of HC latex. The dried formulation of HC latex in 0.02M CaCl_2 (F of Fig. 3) has no areas of ordered packing, and there is no evidence of any roundness of the particles. This indicates even less stability than the LC latex formulation. The addition of 0.02M CaCl_2 had its strongest destabilizing effect as it concentrated during evaporation of water.

To reduce the crowding of latex seen in Fig. 3 and make it easier to see where latex and CaCO_3 are associating, we prepared suspensions of one part latex to 33 parts CaCO_3 at 64.4% solids by weight. Figure 4 shows wet

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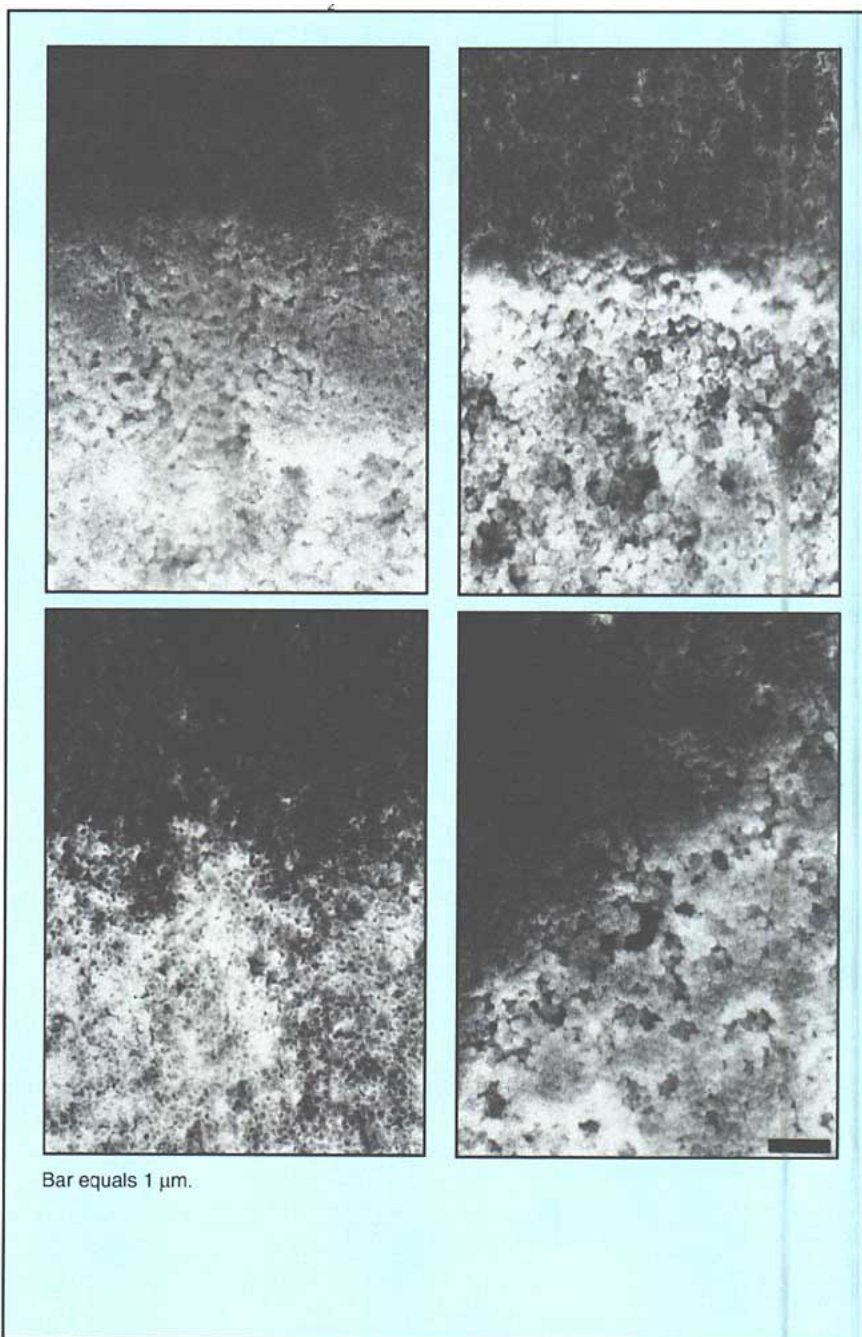
microstructures with three degrees of latex stability imaged with cryo-SEM after freezing and fracturing. A and B of this figure show the HC formulation at medium and high magnifications, respectively. C and D show the LC formulation at medium and high magnifications, respectively. E and F show the HC formulation with 0.02M CaCl_2 at medium and high magnifications, respectively. Latex covers the CaCO_3 surfaces of all three formulations. Only the LC latex formulation has deformed latex on CaCO_3 surfaces, however, and no free latex in the ice between CaCO_3 particles. D of Fig. 4 shows this. Adding 0.02M CaCl_2 to the HC latex formulation did not affect colloidal stability. It did cause complete coalescence of the latex in the dried film shown in F of Fig. 4. This is presumably because calcium ion concentrated enough during drying to erase the stabilizing effect of the carboxylic acid layer, thereby causing latex to deform.

Binder demand is defined here as the amount of latex binder required to glue together and coat all the pigment particles. **Figures 5 and 6** show the dependence of binder demand on the extent of carboxylation. The SEM micrographs in these two figures are of air-dried formulations prepared at 85% particulate solids by weight with a ratio of one part latex to 10 parts CaCO_3 . In Fig. 5, HC latex particles bind together and completely coat all the CaCO_3 particles. In Fig. 6, however, the latex particles of the LC formulation neither bind together nor completely coat the CaCO_3 . In Fig. 6, the darker particles have a latex coating, and the bright particles with visible sharp edges do not have a latex coating. This illustrates that less latex is necessary to bind together the pigment particles, if the latex has a higher extent of carboxylation.

Consolidation fronts

As discussed previously, the second stage of latex film formation begins when latex particles crowd to the solvent surface and menisci form across

7. Cryo-SEM micrographs of consolidation fronts of HC latex (20% solids by weight) in water with varied concentrations of CaCl_2

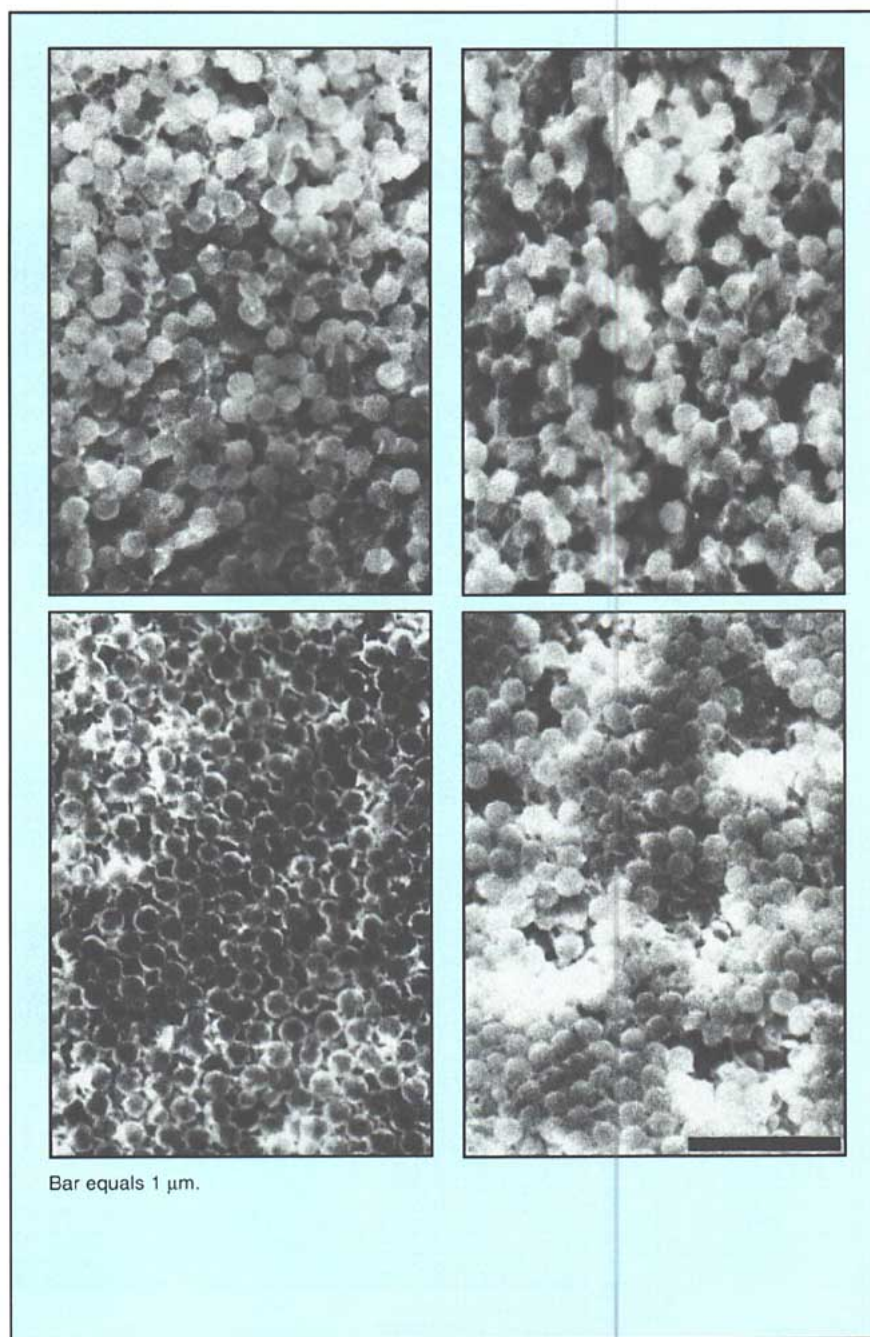


the interstices between the particles or both. Consolidation fronts develop during drying of latex at boundaries between the latex crowded near the solvent surface and the latex with menisci across the interstices between the particles.

Figure 7 shows the consolidation fronts of HC latex in water as well as 0.02M, 0.03M, and 0.05M CaCl_2 as A,

B, C, and D, respectively. Each sample in Fig. 7 was dip-coated on PET, air-dried for 20 s, and plunge-frozen. The darker, upper area of each micrograph in the figure shows consolidated latex particles and the brighter, lower region of each shows unconsolidated latex particles. In A of Fig. 7 there are three distinct regions. Unconsolidated latex is in the lower, brighter area.

8. Higher magnification of each lower, brighter, unconsolidated region of Fig. 7



More consolidated latex is in the middle region, presumably because of capillary pressure-induced flow of latex from the unconsolidated region to the consolidated region. Consolidated latex is in the upper region because there has been enough water evaporation so that the capillary forces in the menisci between the particles draw them together.

Conversely, B–D in Fig. 7 have only two distinct regions. Electrostatic repulsive forces are weak at $0.02M$ CaCl_2 in B. Evidently there is not enough repulsion to hold particles apart in the region of capillary pressure-induced flow near the consolidation front. Therefore the consolidation front is narrow compared with A in this figure.

Figure 8 shows higher magnification of the lower, brighter, unconsolidated regions of Fig. 7. The figure shows HC latex in water as well as in $0.02M$, $0.03M$, and $0.05M$ CaCl_2 as A, B, C, and D respectively. In A and B of the figure, there appears to be no difference in interparticle distances. The small interparticle spacings in C, however, indicate that electrostatic force has weakened at $0.03M$ CaCl_2 . The flocs in D are the result of even weaker repulsive force at $0.05M$ CaCl_2 . A possible explanation is that the carboxylic acid chains became mutually attractive in $0.05M$ CaCl_2 , collapsed against the particles, and left no barrier against van der Waals attractive forces.

There are also areas of hexagonal close packing in D of Fig. 8. One explanation is that flocs protruded from the water surface, and capillary forces in the menisci between the particles of each floc caused ordered packing before the consolidation front moved across.

Figure 9 shows higher magnification of the higher, darker, consolidated regions of Fig. 7. Again, the figure shows HC latex in water as well as $0.02M$, $0.03M$, and $0.05M$ CaCl_2 as A, B, C, and D respectively. The density of packing in A and B of this figure is approximately the same, and there is no orderliness of packing. This indicates that electrostatic repulsion more than offsets capillary forces at concentrations up to $0.02M$ CaCl_2 . Packing is more dense, and there are also areas of close hexagonal packing in C of Fig. 9, indicating that electrostatic forces could no longer offset capillary forces at $0.03M$ CaCl_2 . One can best understand D of Fig. 9 by comparing it with the unconsolidated region of D in Fig. 8. It appears that flocs in D of Fig. 8 consolidated as they moved across the front.

A of Fig. 10 is a consolidation front of a suspension of LC latex at 20% solids by weight in water. B and C of the same figure show high magnification of the unconsolidated and consolidated regions for the same material, respectively. Unlike the fronts in Fig.

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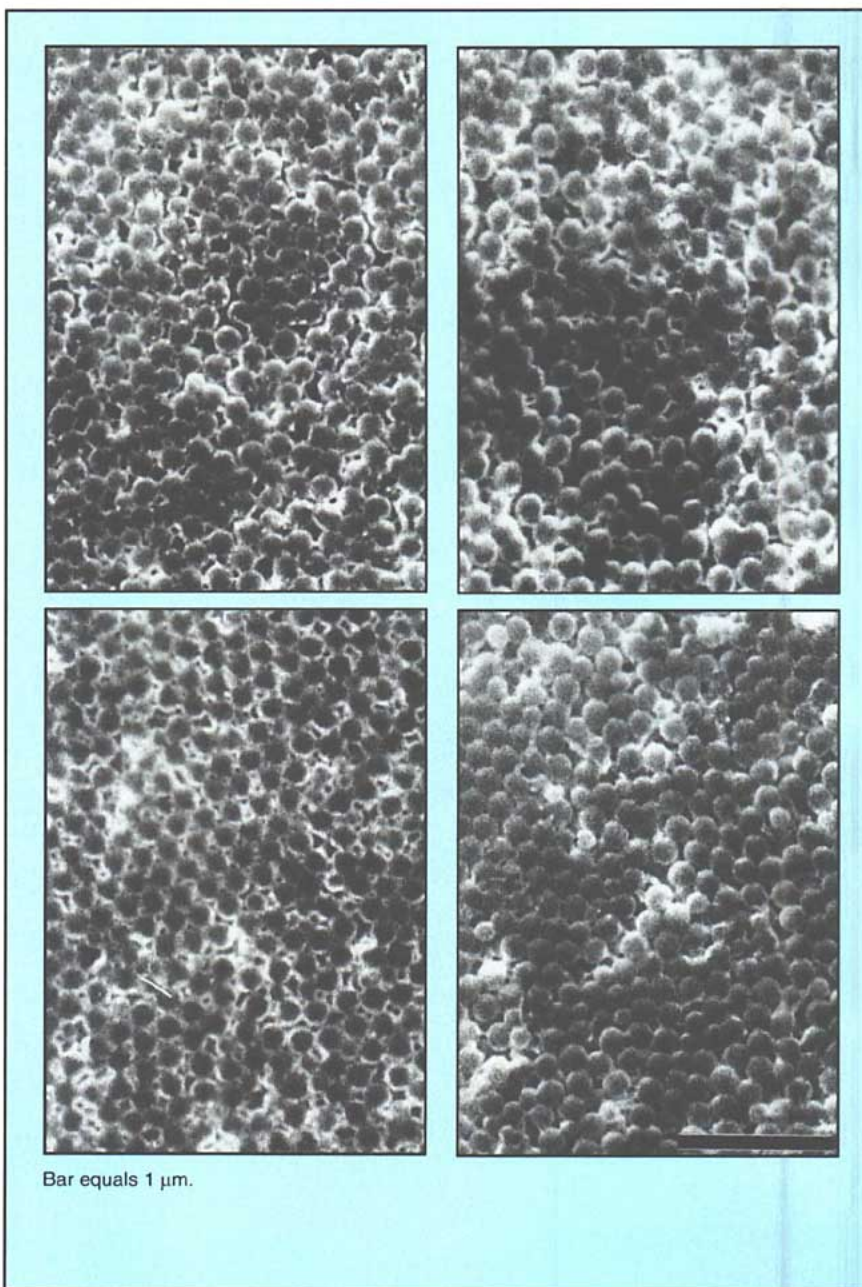
7, the consolidated region in the upper half of A of Fig. 10 appears brighter than the darker, unconsolidated region. We etched all the dip-coated samples (by sublimation at -100°C for 10 min to remove approximately $1\text{ }\mu\text{m}$ of ice) before coating with chromium and examining with SEM. Etching rates were difficult to control, however, because they vary by an order of magnitude per 10 K. Low contrast from the latex particles in the unconsolidated region indicates that only enough etching occurred to remove water vapor that condensed during sample transfer. The ice between latex particles remained behind.

Comparison of the consolidation front of LC latex in Fig. 10 with those of consolidation fronts of HC latex at various ionic strengths in Fig. 7 shows that LC latex behaves like HC latex in CaCl_2 at concentrations between $0.02M$ and $0.03M$. The unconsolidated region of LC latex in B of Fig. 10 has interparticle spacings similar to the unconsolidated regions of HC latex in water and in $0.02M$ CaCl_2 , as seen in A and B of Fig. 8, respectively. The consolidated areas of both LC latex in C of Fig. 10 and HC latex in $0.03M$ CaCl_2 in C of Fig. 9, however, are the most similar, except that order is more long range in the LC latex, indicating that LC latex in water has slightly stronger repulsive electrostatic force than HC latex in $0.03M$ CaCl_2 .

Conclusion

Cryo-SEM of flocculated latex suspensions indicates how carboxylation stabilizes latex against coalescence and fusion, even at ionic strengths that far exceed what is necessary to remove electrostatic repulsion. Results from calcium carbonate suspensions in latex demonstrated that latex particles deposited on calcium carbonate surfaces, creating a suspension of carboxylic acid-stabilized calcium carbonate particles. This was true for latexes with both low and high extent of carboxylation. However, only latex particles with a low extent of carboxy-

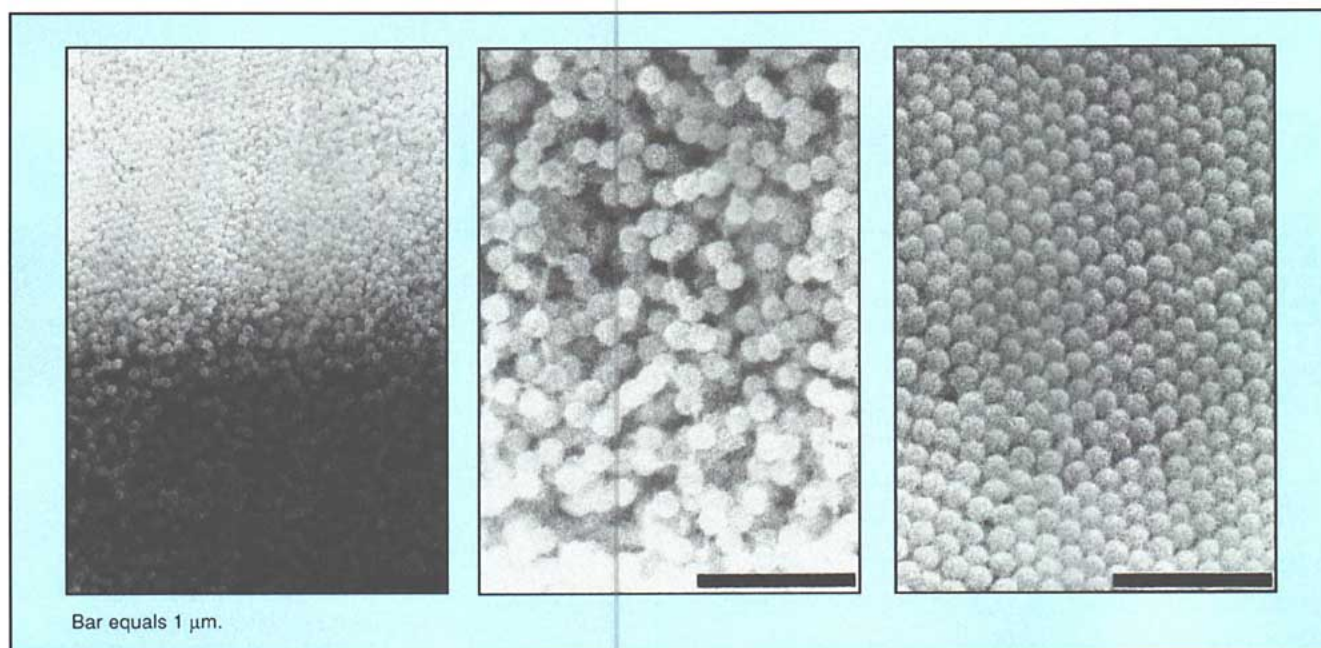
9. Higher magnification of each upper, darker, consolidated region of Fig. 7



lation succumbed to van der Waals forces and deformed on calcium carbonate surfaces. Latex particles of high carboxylation developed dense hexagonal packing and formed uniform continuous films during drying.

Although the latex particles with low carboxylation formed continuous films, there was disordered packing. Cryo-SEM of consolidation fronts showed how LC latex particles at low

ionic strength consolidated near the wet side of the front and left behind a hexagonal, closely-packed film on the dry side of the front. HC latex particles at high ionic strength, however, flocculated before the consolidation front moved across. Flocs, instead of individual latex particles, consolidated at the drying front and left behind a polycrystalline, hexagonal, closely-packed film on the dry side. LC latex



particles in water behaved about the same way as HC latex at 0.02–0.03M CaCl_2 , demonstrating again the strong colloidal stability of the HC latex.

This work demonstrated for the first time that one can deduce colloidal forces present in all stages of latex film formation with high-resolution cryo-SEM. $\square$

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