

Microstructure evolution in latex coatings

Yaqiang Ming, Koichi Takamura, H. Ted Davis, and L. E. Scriven

ABSTRACT: *Experiments of rewetting latex films by water show that latex particle deformation in the film formation processes can be reversible under certain conditions. Water roughens latex films and raises their topographic contrast. Sodium dodecyl sulfate promotes redispersion of latex particles. Fronts of rewetting are observed. Water-soluble materials appear on rewetted film. The consolidation and pore-emptying or "dryout" fronts of dip-coated model latex-pigment coatings are recorded. Near the consolidation front, the suspension reaches the first critical concentration; near the "dryout front," the suspension passes through the second critical concentration. The microstructure development in latex-pigment coatings is continuous behind the consolidation front, although the dryout front has been observed there. The slightly carboxylated poly (styrene-butadiene) latex particles deform in seconds in coatings of precipitated calcium carbonate with latex binder. The highly carboxylated poly (styrene-butadiene) latex deformed only slightly in air-dried coating. The results indicate that latex particle deformation is not finished at the second critical concentration.*

KEYWORDS: *Coatings, coloring materials, deformation, dispersing, electron microscopy, film, formation, forming, latex, microstructure, mixing, pigment, rewetting, scanning electron microscopy.*

The early stages of latex film formation were studied with cryogenic scanning electron microscopy (cryo-SEM) (1). In this paper, a continuation of previous work, we report further applications of

cryo-SEM. Two aspects are studied: rewetting and redispersing of latex films, and microstructure evolution in model latex-pigment coatings.

When a latex coating is allowed to dry and anneal at a temperature higher than its glass transition temperature (T_g) or minimum film formation temperature (MFFT), a transparent continuous film is formed. This process of latex film formation is important in many applications, e.g., paper coating, paint, carpet backing, and adhesives. Although three stages (consolidation, particle deformation, and particle coalescence) have been identified, the mechanism of film formation is still not well understood. Past investigations were focused on the overall transition that takes place from wet latex suspension to dry transparent film. The preparation and properties of some redispersible latexes have been reported in the literature (2, 3). Here, we report further studies of the reverse process, i.e., from a dry transparent film, formed at earlier stages, to a wet suspension.

The microstructure development of latex-clay coatings was studied using freeze-drying SEM by Watanabe and Lepoutre (4). They proposed a consolidation mechanism of the structure. Further studies with cryo-SEM are reported here. We focus on latex particle deformation in the early stages of structure development.

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Experimental

Carboxylated latexes and pigments

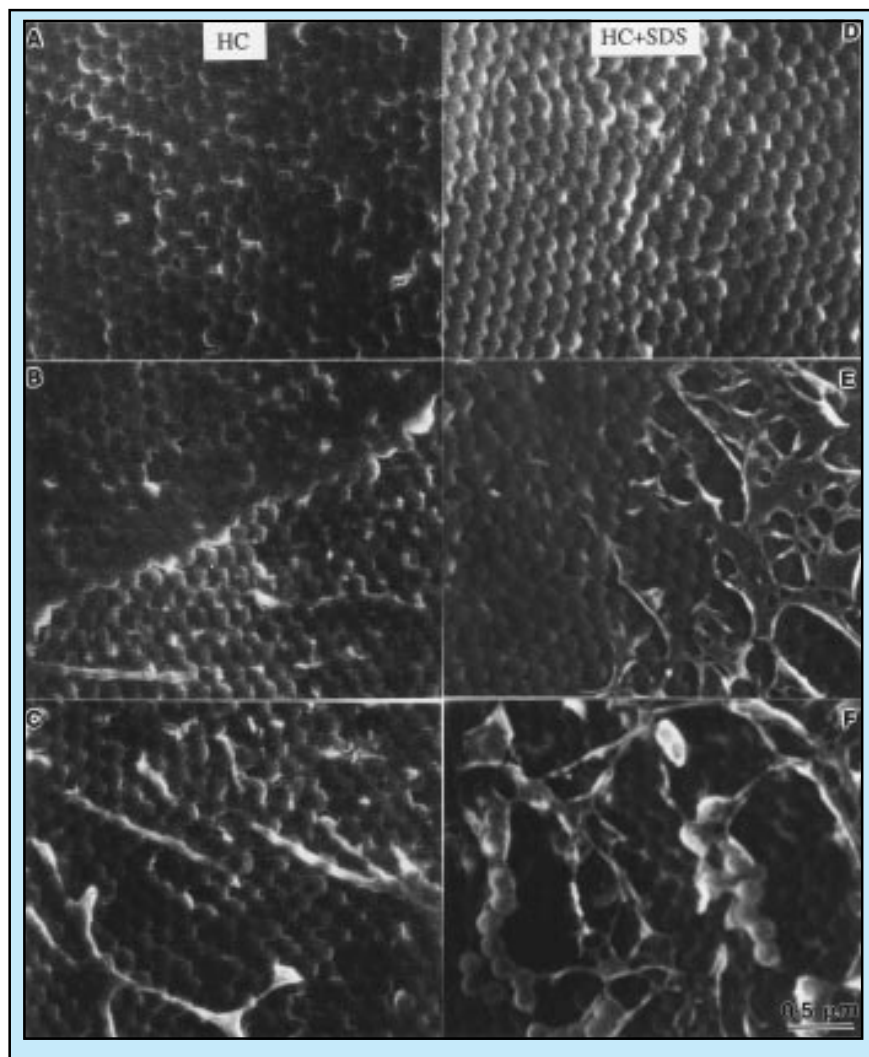
Two types of carboxylated poly (styrene-butadiene) (60:40) latexes were prepared: one had a low extent of carboxylation (LC), with a charge density of about $100 \text{ \AA}^2$ per carboxyl group, and the other had a high extent of carboxylation (HC), with a charge density of about $15 \text{ \AA}^2$ per carboxyl group. Other properties of the two latexes, such as the glass transition temperature, T_g , (about 0°C) and crosslinking degree, were the same. The mean particle size of both was 170 nm as determined by light-scattering measurement. Two more latex suspensions, HC+SDS and LC+SDS, were prepared by adding about 1 wt. % sodium dodecyl sulfate (SDS) (based on solid) to the LC and HC latexes, respectively. The pH of the latexes was adjusted to about 7.5 with a sodium hydroxide solution. One medium-carboxylated poly (styrene-acrylate) latex (AC), a commercial product, was also used. The glass transition temperature of this latex was also about 0°C , and the mean particle size was about 200 nm.

Pigments used in the study were precipitated calcium carbonate (PCC) and No. 1 clay. Relevant properties are given in **Table I**.

Rewetting and redispersing of latex films

Suspensions of 30 wt. % HC, LC, HC+SDS, and LC+SDS latexes were prepared in filtered (Millipore) water. Each suspension was dip coated on a PET (Mylar) film of about $4 \times 10 \text{ mm}$ in area, air dried for 4 min (the film had become transparent), and turned horizontally. A drop of filtered water was placed in the middle of the film with a pipette. After 1 min, the center of the water droplet was touched with a piece of filter paper, which absorbed some of the water. The remaining droplet, with the Mylar film, was fast-frozen

1. Cryo-SEM micrographs showing the unwetted parts (A, D), wetting fronts (B, E), and wetted parts (C, F) of HC and HC+SDS latex films, respectively. Redispersed latex particles are shown in F.



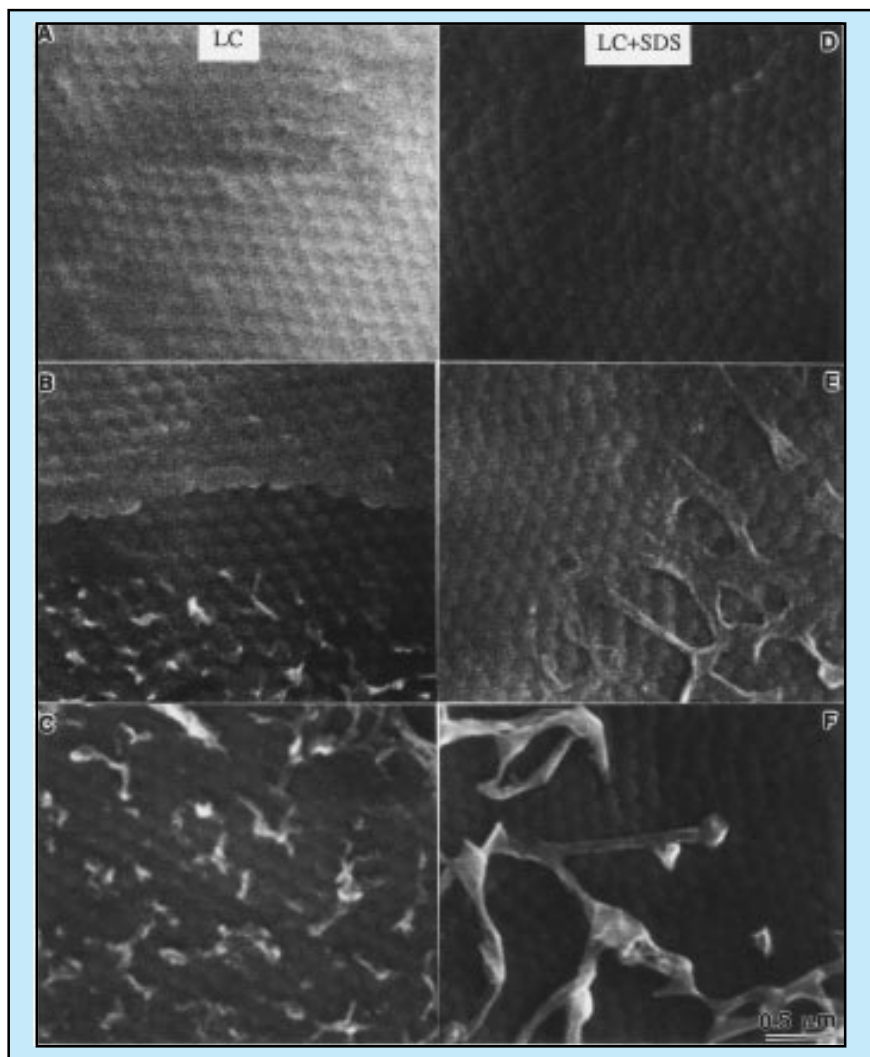
by plunging it by hand into liquid ethane (**Figs. 1, 2**).

The suspension of HC latex was dip coated by hand onto three pieces of PET films coated with colloidal graphite to reduce charging. The pieces were then laid horizontally and air dried for 1 hour, 1 day, and 1 week, respectively. The films were immersed halfway into Millipore water and the lower part soaked for 1 hour. After each film was removed from the water, its bottom side was touched to a piece of filter paper, which absorbed some of the water. The film was then fast-frozen by hand plunging into liquid ethane (**Fig. 3A–C**). Frozen samples were stored in

liquid nitrogen until cryo-SEM examination. Before samples were viewed by cryo-SEM, they were etched 10 min at 163°K to remove the water film and any ice that condensed on them during transfer from the liquid nitrogen. The samples were coated with about 6 nm of chromium as measured with a quartz microbalance.

The HC latex suspension was also dip coated on a glass substrate, air dried, and stored in a desiccator for 36 hours (**Fig. 3D**). The sample was examined with low-voltage SEM (LVSEM) at 2 kV (tilted 20°).

2. Cryo-SEM micrographs showing the unwetted parts (A, D), wetting fronts (B, E), and wetted parts (C, F) of LC and LC+SDS latex films, respectively.



Microstructure evolution in latex-pigment coatings

The suspensions of LC, HC, and AC latexes with PCC were prepared at 60 wt. % with ratios of 15 parts latex to 100 parts PCC (**Figs. 4, 5A–D, and 6**). A suspension of HC latex and No. 1 clay was also prepared at 45 wt. % with a ratio of 15 parts latex to 100 parts clay (**Fig. 7**). Each suspension was dip coated on a PET film, air dried for about 30 seconds, and fast-frozen by hand plunging into liquid ethane. Frozen samples were stored in liquid nitrogen until cryo-SEM examination. Each sample was etched 10 min at 173°K to remove ice

that condensed during transfer from the liquid nitrogen. It was also coated with about 6 nm of chromium before cryo-SEM examination.

The suspension of HC and PCC was also dip coated on two glass substrates; one was air dried for 4 hours (**Fig. 5E–F**), and the other was air dried and stored in a desiccator for about 3 days (**Fig. 8A–B**). The suspension of LC and PCC was also dip coated on a glass substrate, air dried, and stored in a desiccator for about three days (**Fig. 8C–D**). All coatings were stained with osmium tetroxide vapor before LVSEM examination.

Cryo-SEM

The cryo-SEM system used in this research was developed by Sheehan (5). There are 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 prepump chamber and a metal-coating chamber. Each chamber has a conduction-cooled sample stage at about 100°K. Only the prepump chamber is vented to atmospheric pressure during sample transfer, thereby protecting the metal-coating chamber from contaminants. This chamber is equipped with three tungsten baskets that are used for thermal sublimation of chromium, a shutter that protects samples from thermal radiation during warmup of the tungsten baskets, and a quartz microbalance that measures the thickness of deposited chromium. Each sample is transferred from liquid nitrogen to the cold stage in the prepump chamber. Dip-coated samples were coated and etched in the metal-coating chamber.

Low-voltage SEM

All LVSEM images, both secondary and backscattered, were made with the Hitachi S-900 SEM. The secondary electron images were always made first to reduce contamination, charging, and radiation damage. The SEM microscope has an immersion lens, a field emission (FE) source, an Everhart-Thornley (ET) secondary electron (SE) detector, and a scintillator/photomultiplier tube (PMT) backscattered electron (BSE) detector (6). All samples were sputter coated with 1–2 nm of platinum just before they were placed into the microscope.

Normal-speed video

A normal-speed video of drying and consolidating an HC-PCC (60 wt. %) coating, made with a dip coater, was recorded with a Panasonic AG-7300

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S-VHS videocassette recorder. The substrate was a PET film.

Results

Rewetting and redispersing of latex films

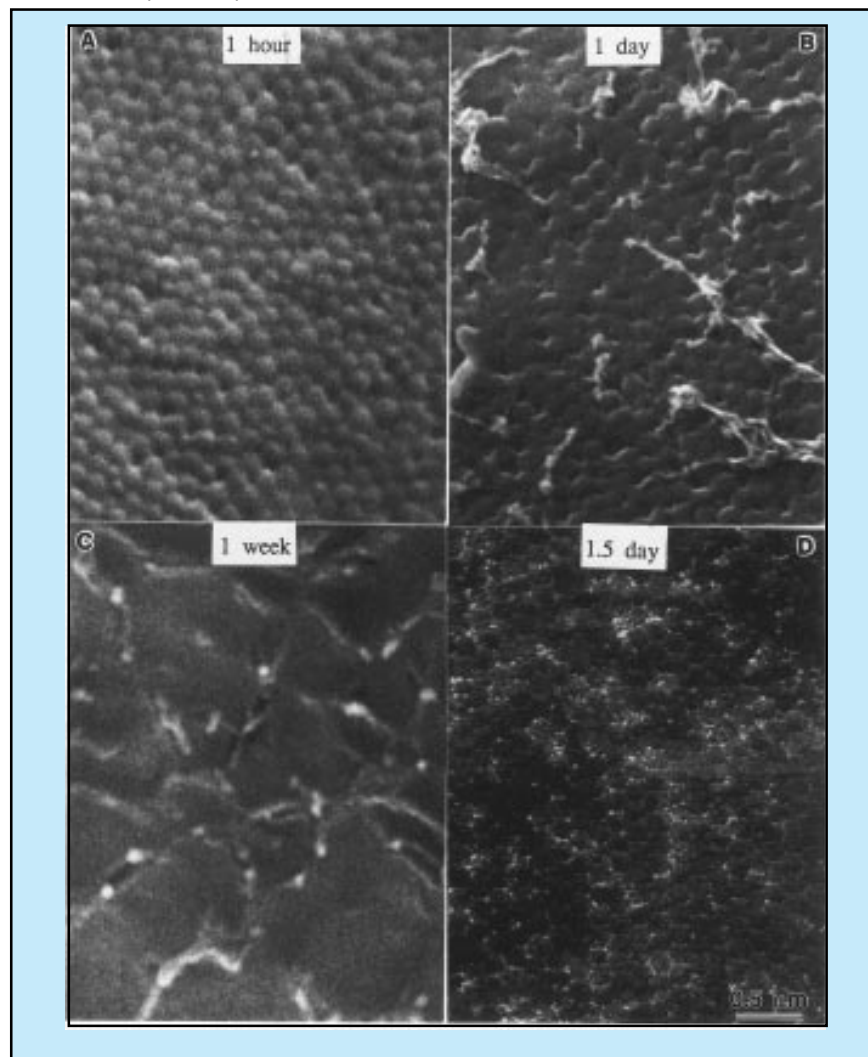
Redispersibility of latex films depends on several factors (2):

- Number of carboxyl groups on the latex particle surface
- Amount of surfactant in the latex
- Aging time of the cast film
- pH of the latex used to cast a film
- Type of base used to neutralize the latex
- Composition of the latex
- Time water was allowed to rewet a film.

The effects of the first three factors are examined here.

Figures 1 and 2 compare the redispersibility of latex films of HC, LC, HC + SDS, and LC + SDS. Views A, B, and C in Figs. 1 and 2 show the unwetted part, wetting front, and wetted part of an HC film and an LC film, respectively. The unwetted part, the wetting front, and the wetted part of the HC + SDS film and the LC + SDS film are given in Views D, E, and F in Figs. 1 and 2, respectively. The redispersed latex particles are seen in Fig. 1F. Sodium dodecyl sulfate (SDS) promotes the redispersion of HC latex particles but not LC latex particles. Therefore, the redispersibility of the latex films is influenced by both the number of carboxyl groups on the latex particle surface and the amount of surfactant in the latex. The wetting fronts are seen in all the latex films (Views B and E). Water-soluble materials, which are present in a higher percentage in HC + SDS and LC + SDS than in HC and LC, accumulate on the surface of wetted parts of the films (Views C and F). These materials could be acrylic acid (oligomer and low-molecular-weight

3. Effect of aging time on latex film redispersibility (A-C). Latex: highly carboxylated poly (styrene-butadiene) (pH 7.5). A-C: cryo-SEM micrographs. D: low-voltage SEM micrograph taken at 2 kV (tilted 20°).



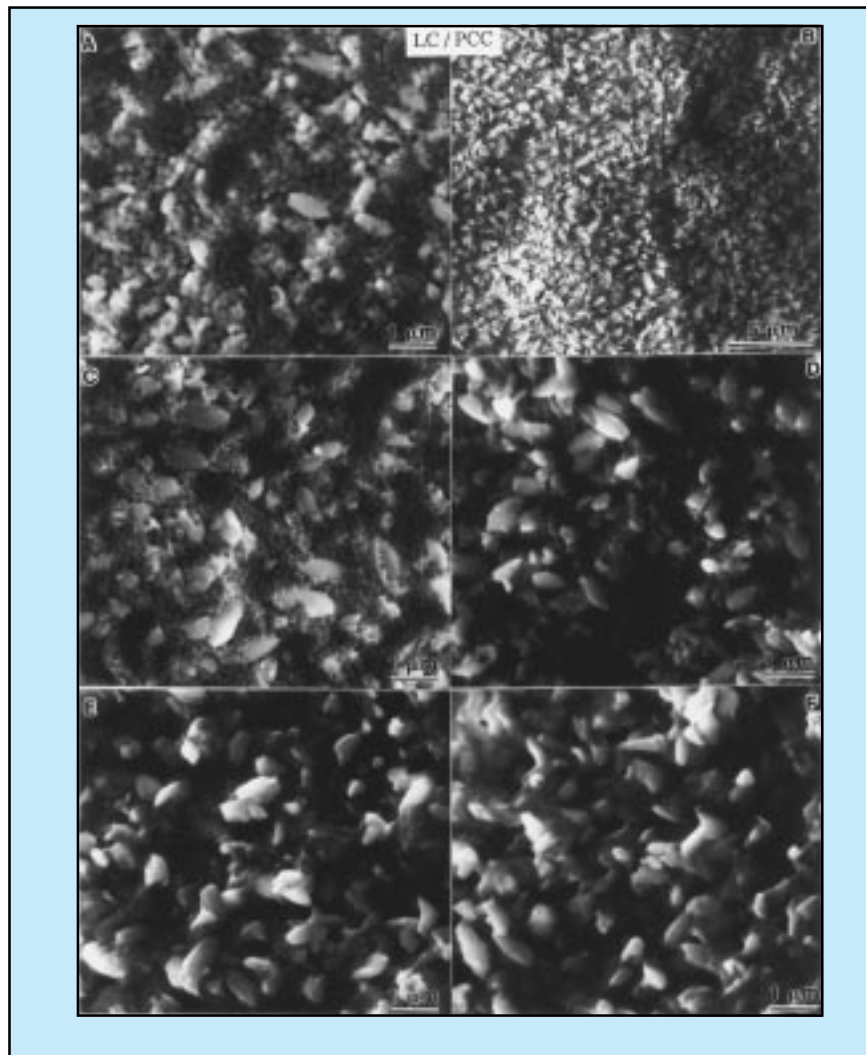
polymer) and surfactant. Views A and D of Figs. 1 and 2 show that the latex particles are least deformed in the HC + SDS film and most deformed in the LC film. This demonstrates that carboxylate layers and SDS retard latex particle deformation.

Figures 3A–C show the HC films that were dried and aged 1 hour, 1 day, and 1 week, respectively, before being immersed in water for 1 hour and then withdrawn and fast-frozen by hand plunging into liquid ethane. The spherical latex particles, which are randomly packed together, are obvious in View A, aged 1 hour. The deformed latex particles are

seen in View B, aged 1 day. The latex particles cannot be identified in View C, aged 1 week. Water-soluble materials are also seen in View B (white spots). The images show that the redispersibility and water sensitivity of the HC latex film decrease with aging time.

Figure 3D shows the surface of an HC film aged 36 hours in a desiccator. This surface appeared to have no contrast in conventional SEM. The image here was taken at 2 kV and a tilt angle of 20°. Comparing Views B and D reveals that water roughens the latex film and raises its topographic contrast.

4. Microstructure development of LC-PCC coating examined with cryo-SEM. A: unconsolidated, B: consolidation front, C: consolidated, D: latex particles slightly deformed, E: rough surface structure and latex particles more deformed, F: latex particles continue to deform.



Microstructure evolution in latex-pigment coatings

Consolidation and pore-emptying (dryout) fronts. The drying and consolidating of a dip-coated HC-PCC coating were recorded. One frame of the video is given in **Fig. 9**. Two fronts are identified there: They are called the consolidation front and the pore-emptying, or dryout, front. Near the former, the solid concentration is close to the first critical concentration (FCC), which was defined by gloss measurements; near the latter, the solid concentration is approaching the second critical concentration (SCC), which was defined

by reflectance measurements (4). Drying and consolidating started from the top and two sides of the substrate. The drained suspension accumulated at its bottom. The white spot in the center is due to undispersed PCC. Other latex-pigment coatings, e.g., LC-PCC, HC-clay, and AC-PCC, have similar drying and consolidating behavior as the HC-PCC coating.

The microstructures of latex-pigment coatings, from top to bottom and dried only seconds (Fig. 9), were imaged by plunging specimens in liquid ethane and examining them in the cryo-SEM. The dryout front cannot be discerned in the cryo-SEM

images because of the continuous change of structure and topographic contrast.

LC-PCC coating. Figure 4 shows the microstructure development of LC-PCC coating. The consolidation front appears in View B at a relatively low magnification. The left, brighter side of the image is an unconsolidated region; the right, darker side is a consolidated region. Views A and C are higher magnifications of unconsolidated and consolidated regions, respectively. The space between particles in the consolidated region (C) is much smaller than that in the unconsolidated region (A). The particles closely pack together in the consolidated region, where the coating gloss reaches a maximum. The gel point or perhaps the first critical concentration (FCC) is reached at the consolidated region. As water continues to evaporate, menisci start to form, capillary pressure begins to deform the latex particles, and the coating continues to shrink (View D). The surface of the coating becomes rougher, and its gloss decreases.

As more water is evaporated, the menisci descend into interior pores, the latex particles deform more, and a porous structure forms on the coating surface (View E). The coating gloss continues to decrease. Figure 4F shows the surface structure of the coating after the second critical concentration (SCC) (top in Fig. 9). The latex particles in this image have almost completely lost their identity. From Views A to F, i.e., from wet suspension to almost dry coating, it takes only seconds; in that interval, the latex particles deformed and the coating structure developed. The coating structure development and the latex particle deformation are continuous beyond the consolidation region. Figure 8C–D show the surface structure of the LC-PCC coating after it was aged about 3 days at room temperature. The latex particle contours are hardly discernible, even in LVSEM. The

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sample was stained by osmium tetroxide vapor before LVSEM examination at 4 kV.

HC-PCC coating. The microstructure development of the HC-PCC coating is shown in Fig. 5, where View B (low magnification) and View C (high magnification) show the consolidation front. The left, brighter region is unconsolidated; the right, darker region is consolidated. View A, an unconsolidated region, shows individual latex particles. These particles start to deform in the closely packed consolidated region as water continues to evaporate, as shown in View D. View E, a secondary electron image, and View F, a backscattered electron image, show a completely air-dried (4 h) HC-PCC coating. Although the consolidation process of HC-PCC coating is similar to that of the LC-PCC coating, HC latex particles are only slightly deformed in the course of completely drying. This is quite different from the behavior of LC latex particles, which deform dramatically within seconds. The HC latex particles can be clearly seen, even in the coating that was aged about 3 days at room temperature (Fig. 8A–B). These results agree with a previous report (1). A comparison of Fig. 5E–F and Fig. 8A–B confirms that HC latex particles deform slowly with time. The samples were stained by osmium tetroxide vapor before LVSEM examination at 4 kV.

AC-PCC coating. Figure 6 shows the microstructure development of AC-PCC coating. An unconsolidated region appears in View A. View B shows a consolidated region in which menisci began to descend into the pore space, and the latex particles started to deform. As water continues to evaporate, menisci descend into interior pores, the latex particles continue to deform, and a surface porous structure starts to form. The coating surface becomes rougher and gloss decreases (View C). View D shows the surface structure at the top of the coating (see

5. Microstructure development of HC-PCC coating examined with cryo-SEM and LVSEM. A: unconsolidated; B and C: consolidation front; D: consolidated and latex particles slightly deformed; E and F: air-dried (4h), latex particles are clearly visible. A–D: cryo-conventional SEM secondary electron images; E: secondary electron image; F: backscattered electron image. E and F were taken with LVSEM at 4 kV. The sample was stained with osmium tetroxide vapor.

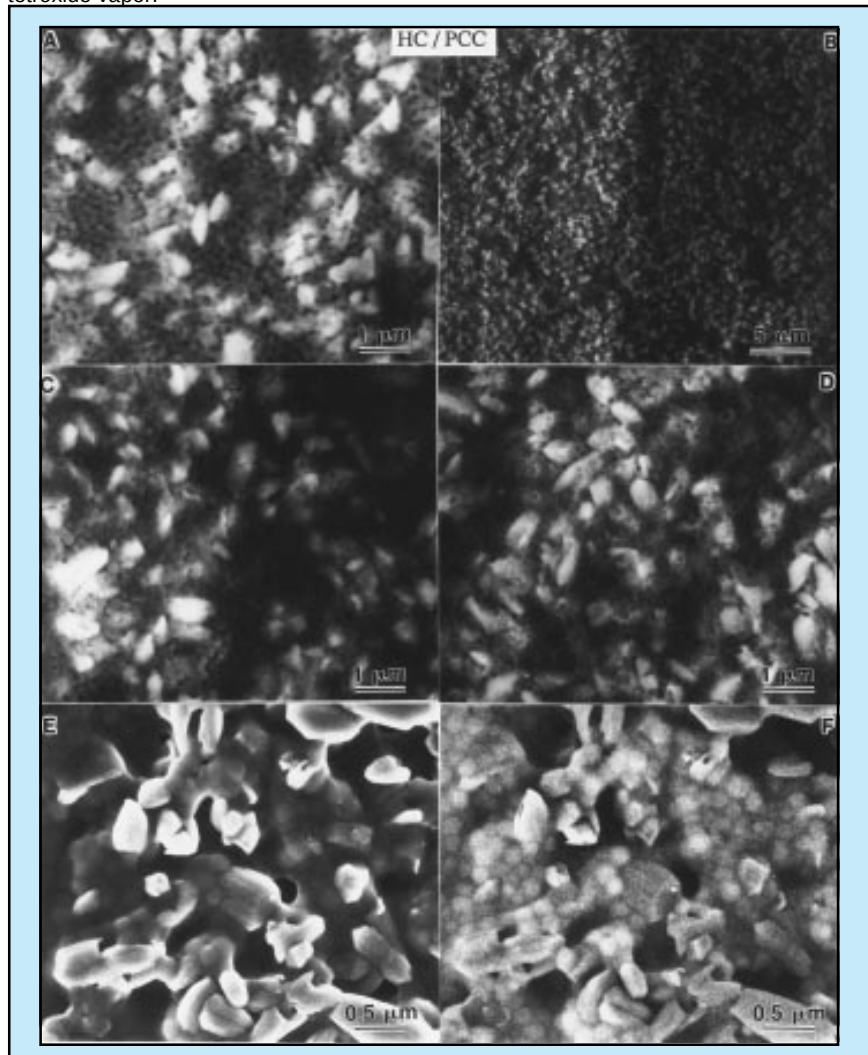
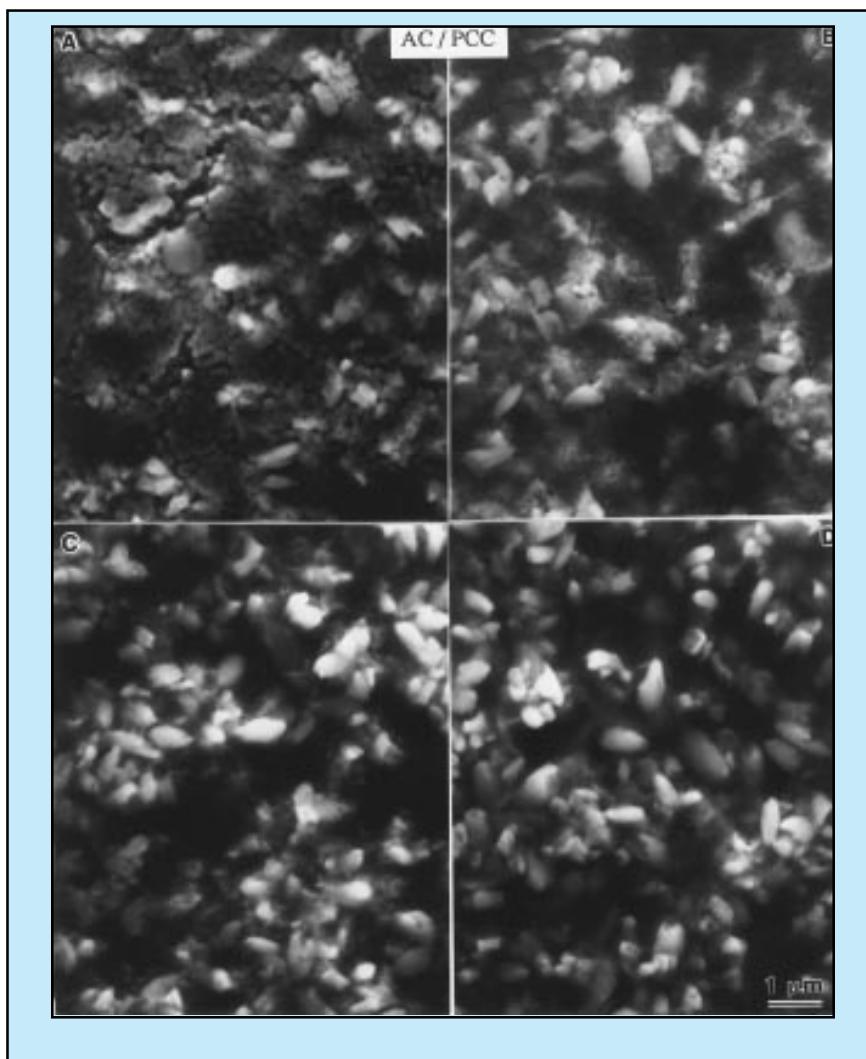


Fig. 9); there, the latex particles are greatly deformed and have lost their identity. Although the AC latex particles are medium carboxylated, they deform as quickly as the LC latex particles during drying. This is probably due to water's plasticizing effect. Water is more soluble in AC latex particles than in HC latex particles, because it is more soluble in acrylate than in butadiene. The drying, consolidating, latex particle deformation, and microstructure development in AC-PCC coating are similar to those in the LC-PCC coating.

HC-clay coating. The microstructure development of the HC-clay coating is shown in Fig. 7. View A is an unconsolidated region in which only a few clay particles can be seen; this is quite different from the unconsolidated HC-PCC coating (Fig. 5A). This is probably due to the plate-like shape of the clay particles. The consolidation front can be seen in View B (low magnification) and View C (high magnification). The upper, brighter region is unconsolidated; the lower, darker region is consolidated. A consolidated region also appears in View D, and in it the par-

6. Cryo-SEM micrographs showing the microstructure development of AC-PCC coating. A: unconsolidated, B: consolidated, C: latex particles slightly deformed, D: latex particles have almost lost identity.



ticles pack closely. Interestingly, more clay particles are discernible and appear to be oriented parallel to the coating surface in the consolidated region than in the unconsolidated region. The latex particle deformation and microstructure development at later stages in the HC-clay coating are similar to those in the HC-PCC coating.

Discussion

Three stages of latex film formation have been imaged (7): consolidation,

latex particle deformation, and latex particle coalescence. It is generally believed that latex particle consolidation and deformation are irreversible (8). The redispersion of HC+SDS latex particles demonstrates that the first two stages of latex film formation can be reversed under certain conditions. The rewetting and redispersing of latex films are complicated, especially when the latexes are not pure. The fact that sodium dodecyl sulfate (SDS) promotes the redispersion of HC latex particles could be due to its joining with the carboxylate-rich

surface regions to form a hydrophilic layer between latex particles.

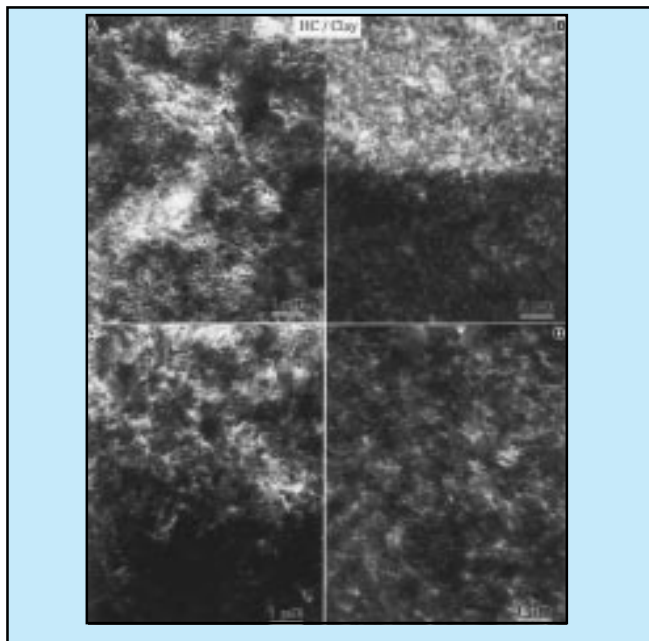
Microstructure evolution in latex-pigment coatings is continuous after the consolidation front passes through it, even though the second critical concentration (SCC) has been detected by reflectance measurement during that stage (4). How strongly the latex particles deform depends on their properties. The slightly carboxylated poly (styrene-butadiene) latex (LC) particles begin deforming within seconds at room temperature, but the available evidence does not establish how soon they finish. The medium carboxylated poly (styrene-acrylate) latex (AC) particles deform similarly to the LC latex particles. This could be attributed to the plasticizing effect of water. The highly carboxylated poly (styrene-butadiene) latex (HC) particles deform only slightly, even in air-dried (4 h) coatings, although the consolidation of HC-PCC coatings is similar to that of LC-PCC coatings. The contours of HC latex particles can still be discerned in a coating aged about 3 days at room temperature, even though the particles continue to deform with time. Our results are not consistent with a previous report that indicates the coalescence and flow of the latex particles are finished at the second critical concentration (SCC) (4).

The microstructure evolution of HC-pigment coating can also be divided into three stages:

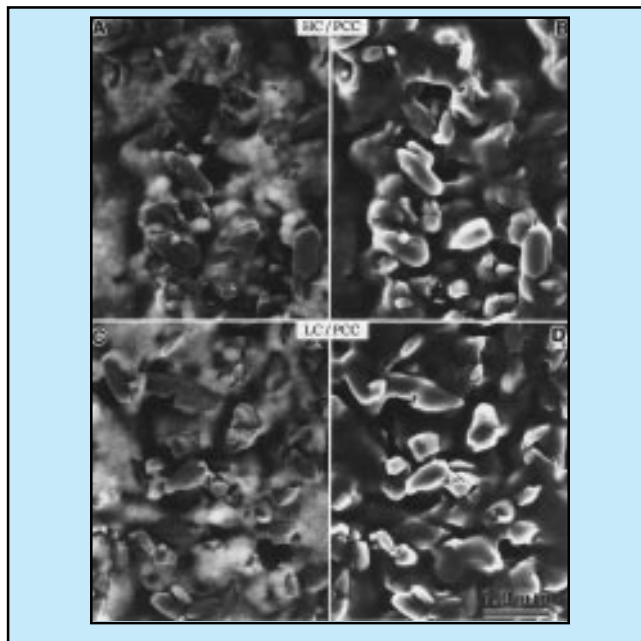
1. Water evaporation and consolidation, that is, the transformation from a suspension to a porous medium that can support stress. This stage is similar to the first stage of latex film formation (7). By the end of this stage, the solid concentration of the coating reaches the first critical concentration (FCC).
2. Pore-emptying and latex particle deformation, that is, water continues to evaporate, menisci descend into interior pores, the

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7. Microstructure development of HC-clay coating examined with cryo-SEM. A: unconsolidated, B and C (higher magnification): consolidation front, D: consolidated.



8. LVSEM (4-kV) images showing the deformation degree of HC and LC latex particles in PCC coatings. The coatings, aged about 3 days at room temperature, were stained with osmium tetroxide vapor. A and C: backscattered electron images, B and D: secondary electron images.



coating continues to shrink, and capillary pressure deforms latex particles slightly. By the end of this stage, water has completely evaporated except for residual pendular deposits in equilibrium with the local humid air, and the HC latex particles are not completely deformed.

3. Final coating properties development, that is, the target gloss, opacity, and brightness, are formed by heat, pressure (calendering), and aging. During this stage, the latex particles continue to deform. A study of Stages 1 and 2 is reported in this work. A detail examination of Stage 3 is given elsewhere (7).

Conclusion

Cryogenic scanning electron microscopy (cryo-SEM) has been used to study rewetting and redispersing of latex films and microstructure development in latex-pigment coatings. Low-voltage SEM (LVSEM) and

I. Coating pigments

Property	PCC	No. 1 clay
Percent finer than 2.0 μm	79	91
Percent finer than 1.5 μm	72	87
Percent finer than 1.0 μm	47	79
Percent finer than 0.5 μm	9	59
Percent finer than 0.3 μm	0	44
Median size, μm	1.0	0.38
Surface area, m^2/g	6.4	19.1

normal video recording have also been used. Experiments of rewetting latex films with water show that latex particle deformation in film formation processes can be reversible under certain conditions. Water roughens latex films and raises their topographic contrast. Sodium dodecyl sulfate (SDS) promotes the redispersion of latex particles. The redispersibility of latex films diminishes with film-aging time.

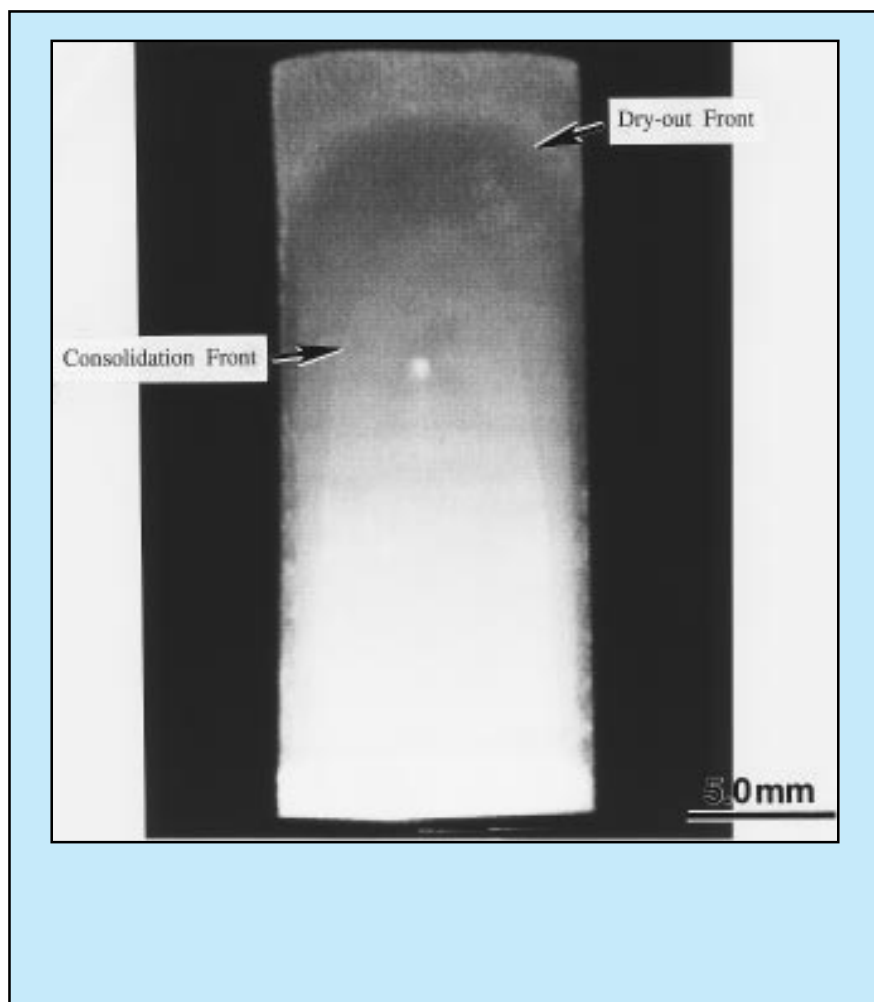
The consolidation and pore-emptying (dryout) fronts of dip-coated latex-pigment coatings have been recorded. Microstructure development in latex-pigment coatings is continuous behind the consolidation

front although the pore-emptying front has been observed there. The slightly carboxylated poly (styrene-butadiene) latex (LC) particles deform in seconds in latex-PCC coatings. The highly carboxylated poly (styrene-butadiene) latex particles deform only slightly in air-dried coatings. The results indicate that the latex particle deformation is not complete at the second critical concentration. $\square$

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9. Video frame showing the consolidation and dryout fronts. The HC-PCC coating was made with a dip coater. The white spot in the center is due to undispersed PCC.



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