

High-magnification cryogenic-scanning electron microscopy (cryo-SEMs) of wet coating microstructures

John G. Sheehan

M. Sc. candidate, chemical engineering, Dept. of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Ave., S.E., Minneapolis, Minn. 55455

Michael Whalen-Shaw

Consultant, 7041 Zane Trail Rd., Circleville, Ohio 43113

ABSTRACT *Fast-freeze, high-magnification, cryogenic scanning electron microscopy (cryo-SEM) is used to examine directly components in both dilute and concentrated coating pigments to deduce how components interact. We have examined wet microstructures in suspensions of kaolin clay, protein interpolymer styrene-butadiene (SB) latex with kaolin, four types of SB latex, and SB latex with carboxymethyl cellulose (CMC). Stacks of parallel plates are common in water-diluted suspensions of kaolin clay at coating formula concentrations. The microstructures of latex in suspension depend on ionic strength and on the water-soluble polymers present. The key to high resolution is a clean vacuum chamber attached to an SEM, where each frozen sample is fractured, etched, and then coated with an ultra-thin metal film before being transported into the SEM for examination.*

KEYWORDS

Analysis
Clay
Coatings
Cryogenics
Electron
microscopy
Latex
SEM

We used a high magnification procedure (up to 25,000X) for freeze-fracture, cryo-SEM to examine directly wet microstructures in suspensions of coating components. We obtained resolution high enough to observe associations between clay and latex pigments. Mechanisms of colloidal interactions and their relevance to paper coatings were discussed previously (1, 2). In addition, factors affecting the state of dispersion of coating clay have been measured (1, 2).

Here, we demonstrate with cryo-SEM how mechanisms of colloidal interactions can be deduced. We examined four suspensions of kaolin and water, four suspensions of water and styrene-butadiene (SB) latex, and suspensions of water and SB latex with carboxymethyl cellulose (CMC). Results demonstrate how freeze-fracture cryo-SEM provides the visual link between wet and dry microstructures.

Liquids must be fixed before they can be observed by electron microscopy; this calls for cryogenic techniques. Until recently, freeze-fracture transmission electron microscopy (FFTEM) was the only technique for imaging particle associations in suspensions (3-5). Fast-frozen samples for FFTEM are fractured, etched, and then coated with a thin, heavy metal film by electron beam evaporation, followed by a carbon coating for mechanical support. To produce a shadowing effect, the metal-coating source is usually placed at an angle of 30-45° from the surface normal. The carbon-supported metal films are cleaned with solvents and then imaged with transmission electron microscopy (TEM). Film thickness variations due to shadowing and surface roughness provide contrast in TEM. With FFTEM, the resolution is down to about 4 nm and is limited by the grain size of the metal coating. Rash and Hudson discussed further the

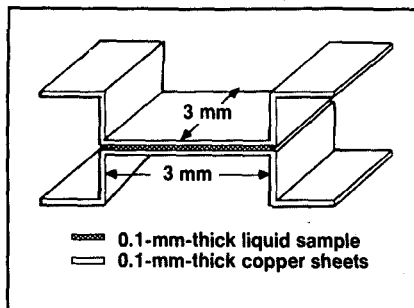
FFTEM procedure (6).

Recent improvements in cryo-SEM have made possible resolution down to 30 nm (7, 8). The sample preparation procedure for cryo-SEM is similar to FFTEM. A small drop of each sample is sandwiched between two copper sheets, fast-frozen in a liquid cryogen, and transferred to a vacuum chamber equipped with a cold stage. There, samples are fractured, etched, and then coated with ultra-thin, conducting metal films. The similarity with FFTEM ends here. Instead of removing the metal film and imaging it in TEM, the microscopist transfers samples to a cold-stage-equipped SEM and images them directly.

Requirements for high-magnification cryo-SEM

There are specific experimental requirements to freeze, transfer, fracture, etch, and coat samples for high-magnification cryo-SEM.

1. A small drop of sample is sandwiched to 0.1 mm thick between two copper sheets.



Freezing

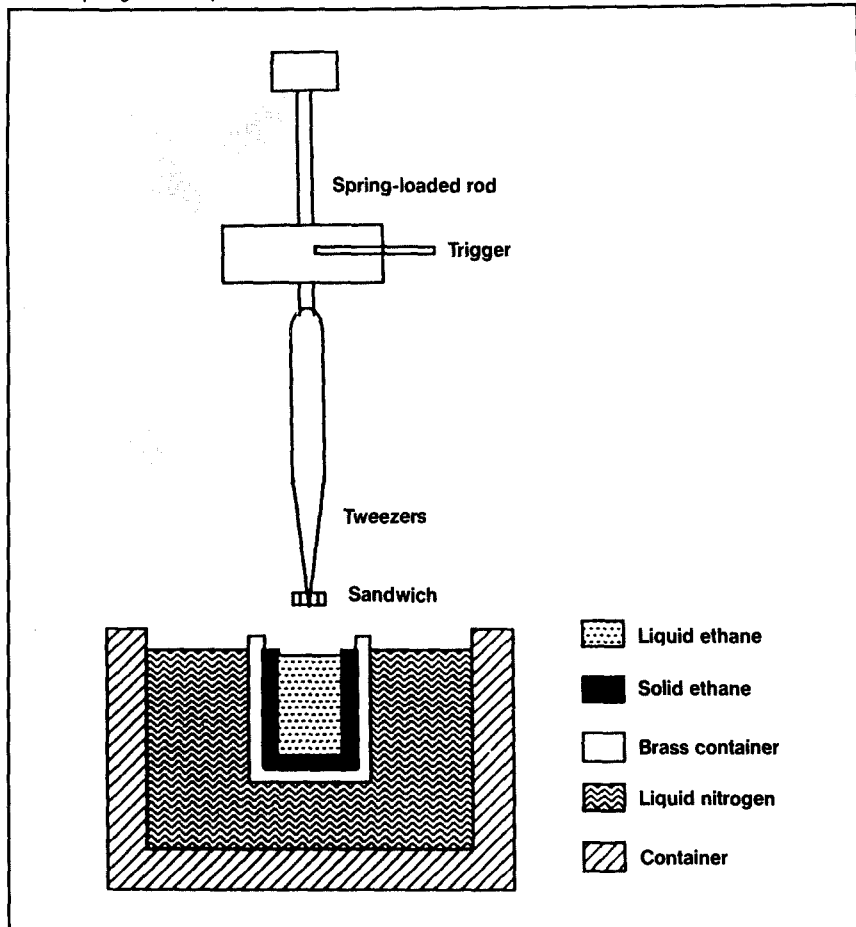
Freezing fixes water-based coating suspensions that are unstable in the vacuum of a scanning electron microscope. Fast-freezing suppresses the formation of ice crystals and prevents segregation of sample components at grain boundaries (9). The idea is to freeze fast enough to form noncrystalline or amorphous ice. Amorphous ice is formed by super-rapid freezing in liquid cryogenics (10) or by vapor condensation on cold surfaces in a vacuum chamber (11). Estimates of the cooling rate necessary to form amorphous ice range from 10^6 K/s to 10^{10} K/s (12). These cooling rates are difficult to achieve in practice. We found that ice crystal formation and grain boundary segregation is suppressed sufficiently when thin specimens are fast-frozen in liquid ethane.

Liquid cryogenics will boil when an ambient-temperature sample enters, creating vapor between the cryogen and the sample, which causes slow freezing. Boiling is minimized in cryogenics such as liquid propane and liquid ethane, which have a large difference between their melting and boiling points. Liquid ethane is a more efficient cryogen than liquid propane (13). Ryan showed that liquid ethane is the most efficient cryogen for plunge freezing, followed by propane, a propane-pentane mixture, Freon 22, and liquid nitrogen (14).

Vapor contamination and vacuum

Contaminant hydrocarbons (from vacuum pump oils) and water vapors can condense on cold (110 K) samples, blanket surface details, and cause decreased resolution. Water vapor is about one-half of the residual gas in an SEM vacuum chamber; it can condense on cold surfaces to form

2. Sandwiched specimens are attached to the tweezers, which is attached to the spring-loaded rod and plunged into liquid ethane.



amorphous ice (11). However, the vapor pressure of amorphous ice is high enough (12) that condensation will not be appreciable unless leaking vacuum feedthroughs cause surges in pressure during sample manipulation. The best solution to vapor condensation that we have found is to coat frozen samples with metal immediately after fracture (15).

Metal coating

High-magnification SEM at ambient conditions on nonelectrically conductive samples is possible only if they are coated with ultra-thin, continuous metal films that have the smallest possible grains. Films should be electrically conductive and continuous to prevent charge buildup during imaging. Films should be thinner than the size of the smallest surface details to be imaged. The thinnest, continuous films have the smallest grains, indicating high nucleation density during film formation.

Coating techniques for SEM include thermal evaporation, d.c. plas-

ma sputtering, electron beam evaporation, Penning sputtering, and ion beam sputtering. Thermally evaporated films are formed when metal is heated to its melting point in a high vacuum. Films formed by thermal evaporation have large grains compared to other techniques, but grain size decreases with decreasing substrate temperature (16), an advantage for cryo-SEM. With d.c. plasma sputtering, films are formed when ionized, inert gas atoms strike a metal cathode to eject metal atoms, which strike the sample. Ionization efficiencies and, hence, sputtering rates are increased with an annular magnetic field that surrounds the cathode to concentrate electrons in the cathode area (17). Films made with d.c. plasma sputtering have smaller grains than thermally evaporated films. However, grain size is sensitive to contamination (18), and artifacts are often present (19). In another type of plasma sputtering, Penning sputtering, the target is inside a chamber that is separate from the specimen. Metal atoms and

charged particles exit through an aperture. Charged particles are deflected by electrodes so that only neutral metal atoms strike the sample. Peters (20) used Penning sputtering for high-resolution SEM.

To coat with electron beam evaporation (21, 22), the anode, which is the evaporant material, is heated by bombarding electrons. Mean grain sizes smaller than 2 nm are obtained. For nearly 20 years, electron beam evaporation has been the standard metal-coating technique for FFTEM, but it has rarely been used for SEM. Total coating times are very short (about 10 s), an advantage for coating frozen specimens that are subject to impingement rates of vapor contaminants that can be greater than rates of metal coating with other techniques.

Films are formed by ion beam sputtering when a collimated ion beam strikes a metal target to eject metal atoms (23). Mean grain sizes of 1 nm have been obtained for both gold and platinum (24)—too small to be resolved with SEM. Dislodged metal atoms have about 100 eV of kinetic energy. It is speculated that metal atoms of high kinetic energy implant themselves into sample surfaces, causing increased nucleation density and small grains. Ion beam sputtering is becoming widely used for ultra-high resolution SEM. Owing to its slow coating times (3–6 min), ion beam sputtering is not practical for cryo-SEM.

Metal film thickness should be measured to ensure that only enough metal is deposited on the sample to form a continuous film. The quartz microbalance is the most widely used instrument to measure film thickness on electron microscopy specimens. Film thickness sensitivity is equivalent to about 0.05 nm of gold. Flood discussed methods of determining film thickness (25).

The best method of metal coating for cryo-SEM should be fast—i.e., the sample should be coated with a continuous film in less than 30 s to preempt contaminant vapor condensation during coating. This need excludes sputtering techniques, which take at least 2 min to deposit continuous films. We obtained high-resolution images with d.c. plasma sputter-coated samples, but reproducibility was dismally low, owing to long sputtering times and to the small

coverage area of our sputtering source, which makes film thickness measurements impossible. We found that high-resolution cryo-SEM images were reproducible when samples were coated by thermal evaporation with chromium, which was also used by Echlin (26).

Equipment and procedures

Freezing

A small drop of each sample is squeezed to about 100 μm thick between two copper sheets (Fig. 1) (Balzers BU 012 054-T and BU 012 056-T) to form a sandwich. Each sandwich is attached to a spring-loaded rod (Fig. 2) (27, 28) and is plunged at about 1.5 m/s into melting ethane. The sandwiches travel about 25 mm through the liquid ethane before coming to rest. Measured cooling rates under similar plunging conditions into liquid propane are 4500 K/s (29).

While submerged in liquid nitrogen, each sandwich is slid into a hinged fracture module (Fig. 3) (30). Next, the hinged fracture module is transferred into the metal-coating chamber (Figs. 4 and 5). To minimize vapor condensation, frozen sandwiches are not fractured until the best possible vacuum is reached in the metal-coating chamber.

Metal-coating chamber

The modified Hexland CT1000A metal-coating chamber (Fig. 5) is attached to the SEM specimen chamber, separated by a gate valve. It is evacuated from atmospheric pressure with a rotary pump. Higher vacuum is reached with the SEM's diffusion pumps when the gate valve (Fig. 4, Valve 2) is opened. To improve vacuum, several modifications were made to the Hexland CT1000A, shown in Fig. 5. To reduce the volume of the chamber and improve vacuum, an extra valve was added between the rotary pump hose and the chamber.

To prevent frost deposition on the stage during sample transfer, a pre-pump chamber (removed from a JEOL CRU-40 cryo-SEM chamber) was added to the entry port. It is therefore not necessary to bring the coating chamber to atmospheric pressure during each sample transfer. To allow us to measure metal-film thickness, a quartz microbalance (Maxtek

model TM-100) was installed on a side port. The metal film thickness could be measured only for thermally evaporated films. Film thickness from the sputtering source could not be measured because of the small coverage area by the sputtering source.

Transfer

The fracture module is quickly removed from liquid nitrogen with a transfer rod and placed in the pre-pump chamber (Fig. 4), which is evacuated for 20 s with a rotary pump. The pre-pump valve (Fig. 4, Valve 1) is opened, and the fracture module is placed on the cold-stage (87 K) in the metal-coating chamber.

Etching

Some samples were etched to expose more microstructure before metal coating. Samples for etching were moved to the cold-stage-equipped SEM at 173 K for 3 min to remove about 1 μm of ice. A cold-trap (about 110 K) was placed 3 mm above the fracture surfaces to condense subliming vapors. After etching, samples were cooled back to 110 K and were transferred to the metal-coating chamber. Cooling back to 110 K is necessary for d.c. plasma sputter-coated samples.

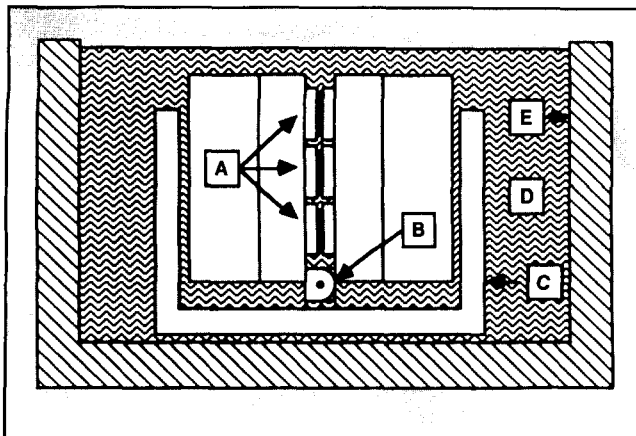
Coating artifacts were seen on ice samples that were coated by d.c. plasma sputtering at 173 K (7). Unfortunately, the effects of etching were reversed during cool-down and transfer to the coating chamber. Results for etched samples were not reproducible. The best procedure that we have found is to omit the etching step and metal coat immediately after fracture.

Results

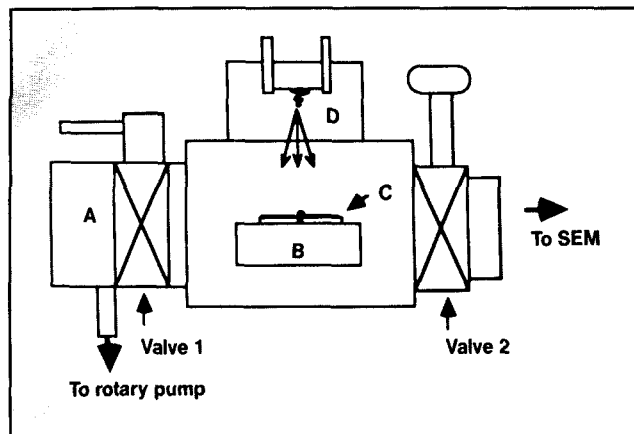
Kaolin and water suspensions

Anisometric clay particles are oriented to a position parallel to the paper substrate in the dried coating, even when applied at low shear (31). Gane and Coggon, in studying the effects of blade geometry (32), provided evidence that the upstream flow regime of a blade coating may discipline clay to achieve a state of parallel-plate alignment. Lepoutre proposed that the order of clay platelets in a dry coating already exists in the aqueous coating formula and may be accentuated during the coating process (33).

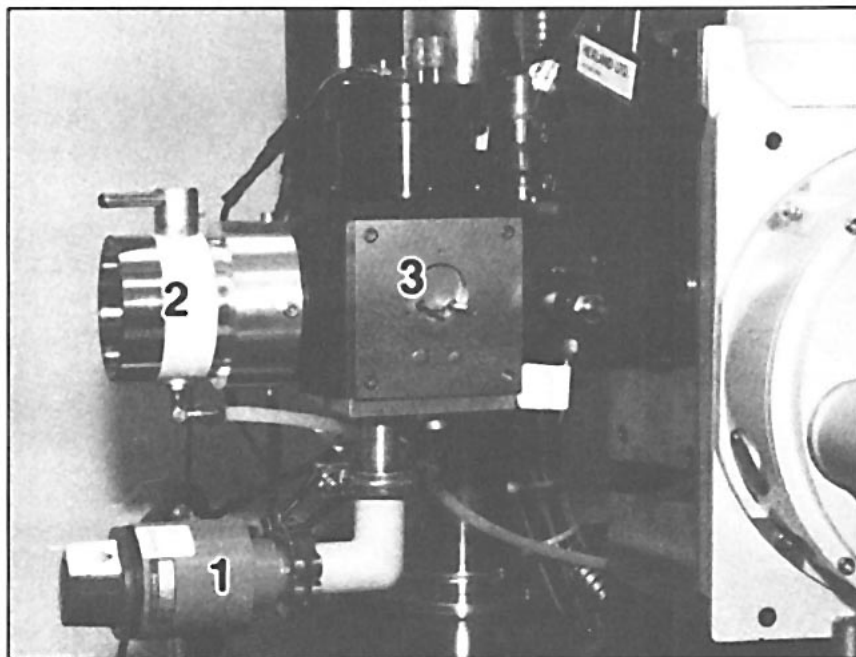
3. Fracture module with a hinge (B) and three sandwiches (A) in a holder (C) immersed in liquid nitrogen (D) in a container (E)



4. Metal-coating chamber with pre-pump chamber (A), cold-stage (B), fracture module (C), and evaporation source (D). High vacuum is reached with the SEM's diffusion pumps when Valve 2 is open.



5. Modified Hexland CT1000A metal-coating chamber attached to the SEM specimen chamber. An extra valve (1) was added to isolate the rotary pump hose. A pre-pump chamber (2) (JEOL CRU-40) was added to prevent frost from depositing on the cold stage during sample transfer. A quartz microbalance (3, reverse side of flange) was added to measure film thickness.



6. Aqueous suspension of 70% by wt. kaolin. Parallel-plate alignments are common. Etched and then sputter-coated with platinum. (Bar = 1 μm)



Cryo-SEM images of suspensions of kaolin in water, at 70% by wt. in Fig. 6 and 50% by wt. in Fig. 7, support Lepoutre's hypothesis. High crowding and substantial parallel plate alignments are obvious. Of course, the order of clay in a coating formula may be different from that seen in Figs. 6 and 7, since salts and binders are added. Dilute aqueous suspensions of kaolin clay were examined to determine clay platelet associations not influenced by crowding. Aqueous suspensions of kaolin were examined

with cryo-SEM at 12% by wt. (Fig. 8) (7) and 7% by wt. (Fig. 9). Edge-to-edge, edge-to-face, and face-to-face associations are seen in both samples.

Frozen samples in Figs. 6-9 were etched for about 3 min at 173K before coating by d.c. plasma sputtering. Metal film thickness was not measured. Platinum was deposited for Figs. 6 and 7, and gold was deposited for Figs. 8 and 9. Note that platelets partly beneath the ice surface are visible in Fig. 8 but not in Fig. 9. This indicates that a thinner film

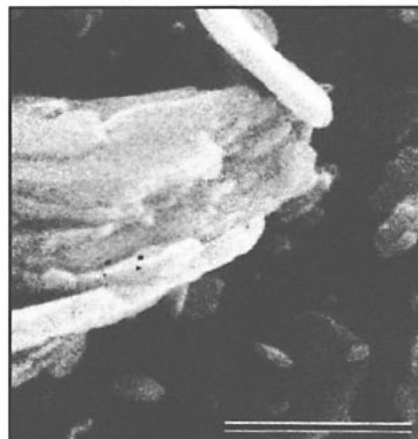
deposited for the sample in Fig. 8 than for the one in Fig. 9, where too much metal was deposited.

The absence of ice in Figs. 6 and 7 has three possible explanations. First, excessive etching left only kaolin platelets and no ice. Second, metal coating that is too thick reduced the atomic number contrast, which is required to differentiate between ice and clay platelets. Third, high crowding of clay made ice invisible. Tabular clay platelets in Fig. 8 are visible in all orientations, which is an advantage

7. Aqueous suspension of 50% by wt. kaolin. Parallel-plate alignments are common. Etched and then sputter-coated with platinum. (Bar = 1 μm)



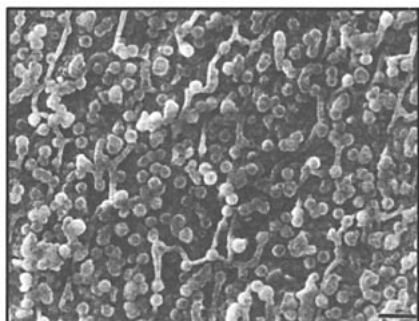
9. Aqueous suspension of 7% by wt. kaolin. Edge-to-edge, edge-to-face, and face-to-face alignments are seen. Etched and then sputter-coated with gold. (Bar = 1 μm)



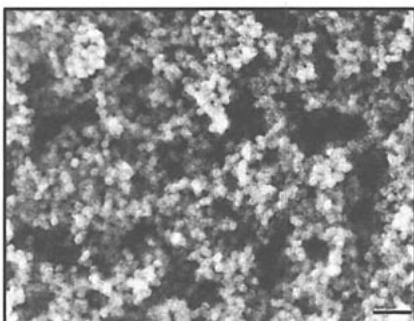
8. Aqueous suspension of 12% by wt. kaolin. Edge-to-edge, edge-to-face, and face-to-face alignments are seen. Platelets are visible partly beneath the ice (7). Etched and then sputter-coated with gold. (Bar = 1 μm) (7)



10. Standard nonreactive latex (Latex A) at 5% by wt. in water, etched and then coated with chromium by thermal evaporation. (Bar = 1 μm)



11. Latex sensitive to pH (Latex B) at 5% by wt. in water, etched and then coated with chromium by thermal evaporation. (Bar = 1 μm)



that cryo-SEM has over indirect observation by means of FFTEM.

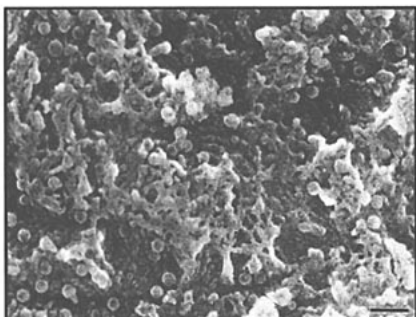
SB latex and water suspensions

Aqueous suspensions of four types of SB latex were observed at 5% by wt. Type A is standard nonreactive latex. Type B is pH-sensitive latex that can associate with clay (34). Type C is non-pH-sensitive latex that can destabilize clay. Type D is protein interpolymer latex containing 20% protein bound to the SB latex. Type D can associate with clay (35).

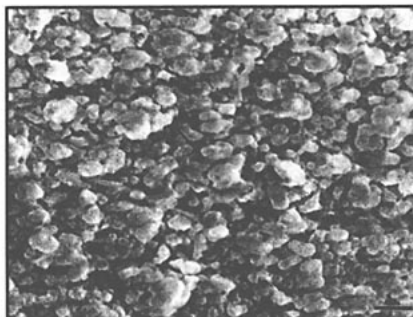
Cryo-SEM images are in Figs. 10–13. Nonreactive Latex A (Fig. 10) has mostly monomodal spheres. Many particles are bridged, possibly with surfactant, or oligomeric water-soluble material, or coagulum. Latex B (Fig. 11) has smaller particles than Latex A, and there are clusters of many spheres. Latex C (Fig. 12) is comparable in particle size to the standard Latex A, but it contains considerably more of the bridging material seen with Latex A. Type D, the interpolymer latex, appears quite different from the others (Fig. 13). Out-of-round particles are seen with a size distribution from 0.1 to 1.0 μm . Protein present during polymerization apparently modulates the formation of spherical particles.

Eklund compared the appearance of SB, acrylic, ester, and polyvinylacetate latices in dilute form when dried on a glass slide (36). Some latex particles appeared to be bridged by an undefined material. Cryo-SEM images in Figs. 10 and 12 suggest that bridges seen by Eklund are not necessarily a drying artifact.

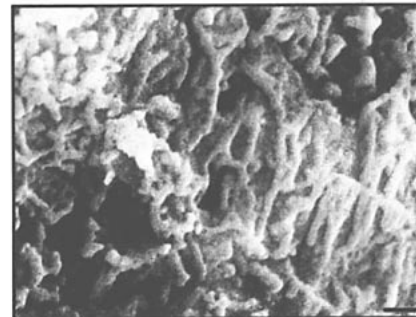
12. Latex not sensitive to pH (Latex C) at 5% by wt. in water, etched and then coated with chromium by thermal evaporation. (Bar = 1 μm)



13. Protein interpolymer latex (Latex D) at 5% by wt. in water, etched and then coated with chromium by thermal evaporation. (Bar = 1 μm)



14. Kaolin diluted to 5% by wt. with 12% by wt. protein interpolymer latex based on clay. The invisibility of clay suggests that protein latex interpolymer encapsulates clay. Etched and then coated with chromium by thermal evaporation. (Bar = 1 μm)



Interpolymer latex and clay

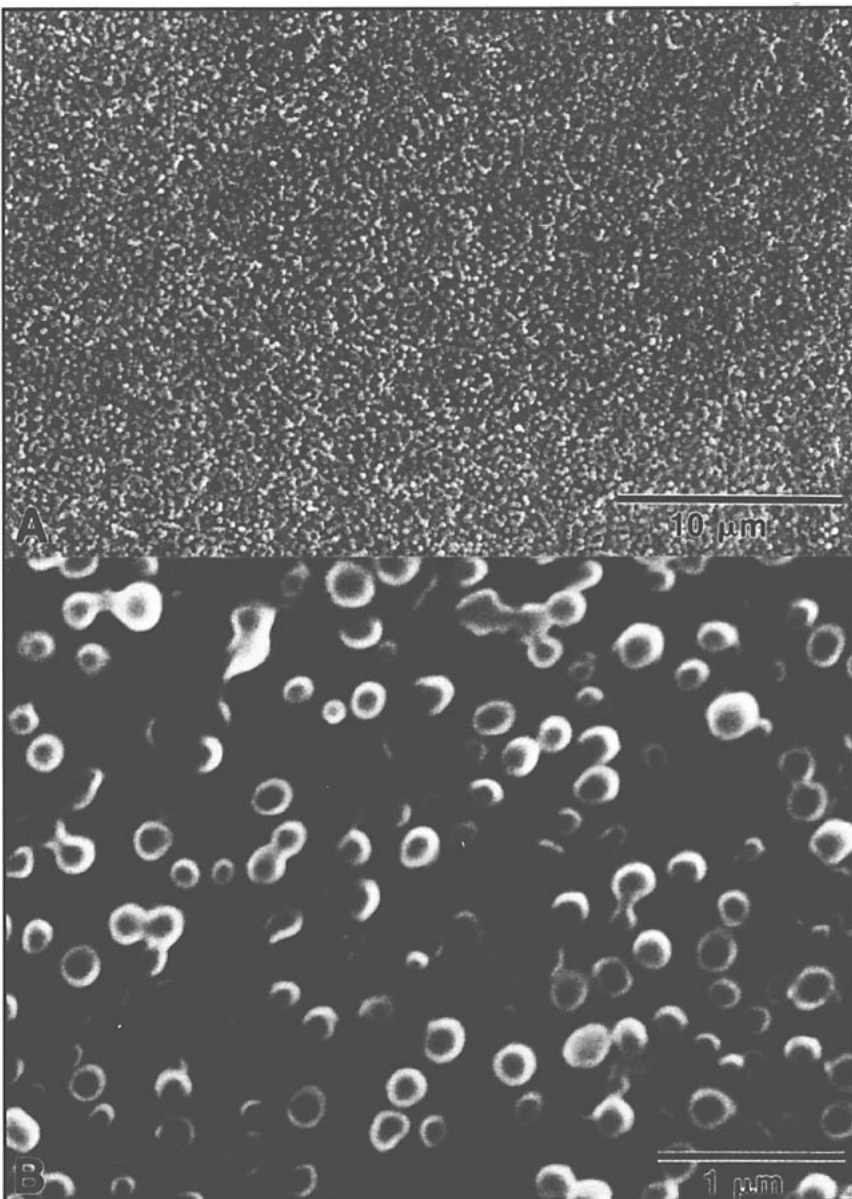
Coco suggested that protein latex interpolymer (Latex D) deposits on clay and encapsulates it during drying (35). To test this hypothesis, a coating formula containing 12% interpolymer latex based on No. 1 coating clay at 60% by wt. was diluted to 5% by wt. and examined with cryo-SEM. The presence of latex and protein and the invisibility of clay (**Fig. 14**) suggests that protein interpolymer latex encapsulates clay in suspension.

Latex A and CMC

Davis noted an increase in yield stress on adding CMC to a clay suspension (37). Fadat demonstrated that the relative viscosity of CMC latex blends at paper coating formula concentrations is independent of CMC concentration when water is the solvent (38). He argued for the absence of specific interactions between CMC and latex. To deduce latex-CMC interactions, suspensions of 13.7% by wt. of Latex A with 1.3% by wt. of CMC were examined with cryo-SEM. This concentration is about the same as found in a 60% by wt. coating formula.

Water was the diluent for one sample (**Fig. 15**), and clay supernatant was the diluent for the other (**Fig. 16**). Low magnification of the water-diluted sample (**Fig. 15A**) shows evenly dispersed particles, indicating a stable suspension. Low magnification of the clay supernatant-diluted sample (**Fig. 16A**) shows what is perhaps loose flocculation and areas of ice devoid of particles, indicating that clay supernatant destabilized the latex. Bridged particles are plain at high magnifications of both the water-diluted sample (**Fig. 15B**) and the clay

15. Water-diluted standard nonreactive latex (Latex A) at 13.7% by wt. with 1.3% by wt. CMC. The suspension appears evenly dispersed at low magnification (A). Bridges are seen at high magnification (B). Coated by thermal evaporation of chromium immediately after fracture.



supernatant-diluted sample (Fig. 16B). However, particles are out-of-round in Fig. 16B, perhaps owing to CMC adsorption in the presence of clay supernatant.

Samples for Figs. 15 and 16 were fractured and immediately coated by thermal evaporation with about 2 nm of chromium, measured with a quartz microbalance. The etching step was omitted, and sample temperatures were below about 120K during the entire procedure. There are two advantages to omitting the etching step. First, an uncertainty is eliminated because etching depth is difficult

to control. Second, the morphology of the fracture can be imaged; round (Fig. 15B) and out-of-round dark spots (Fig. 16B) are from latex particles that pulled away during fracture. Figures 15B and 16B show less bridging than Fig. 10, probably because etching made more bridges visible in Fig. 10.

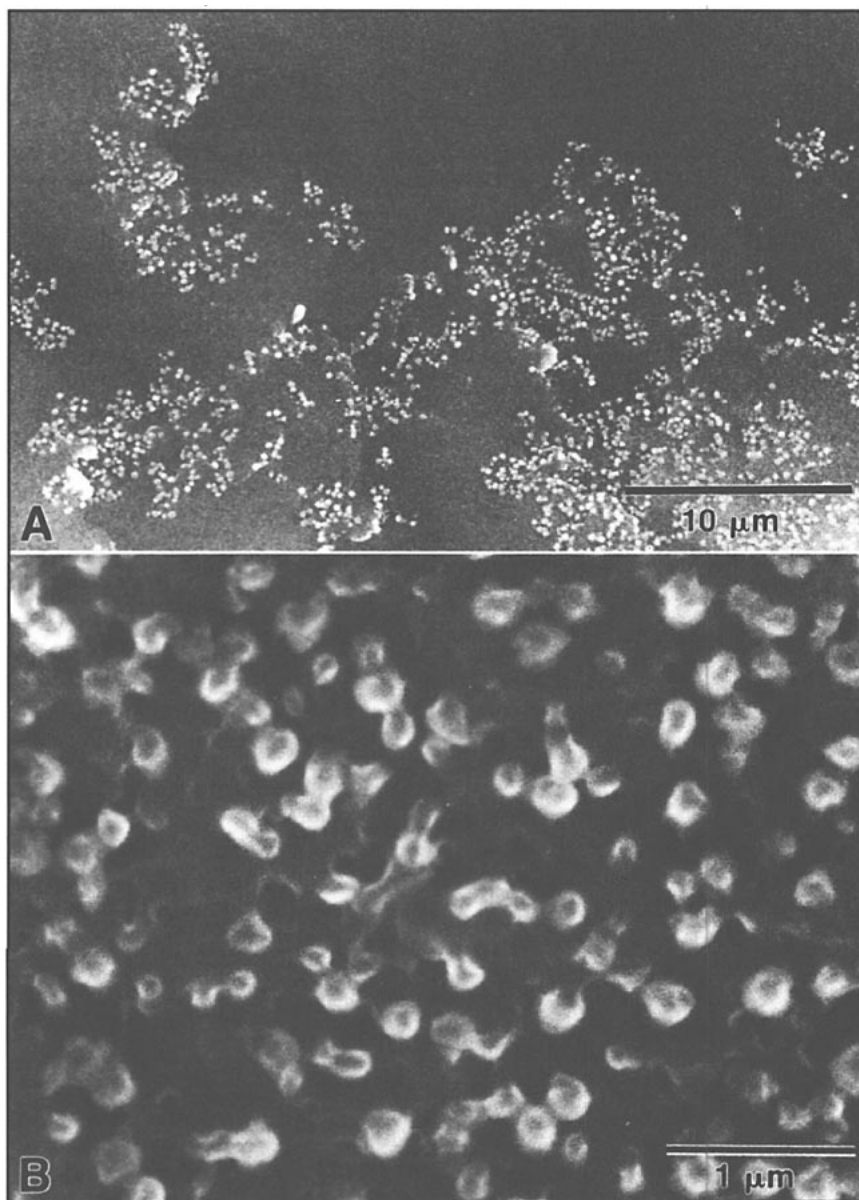
Conclusions

Interactions of latex and clay particles in pigmented wet coatings can be inferred from observing at high magnifications with fast-freeze cryo-

SEM. High-magnification images are obtained when samples are fractured and then coated by thermal evaporation with about 2 nm of chromium. Face-to-face, edge-to-face, and edge-to-edge alignments can be seen in water-diluted suspensions of kaolin clay. At coating formula concentrations, stacks of parallel plates are common.

In suspensions diluted with water containing protein interpolymer SB latex, the invisibility of the platelets indicates that protein interpolymer SB latex encapsulates them. Some nonreactive SB latex particles are bridged when diluted in water, water with CMC, or clay supernatant with CMC. But nonreactive SB latex particles are aspherical in the clay supernatant-CMC diluent. With these examples, we have demonstrated that high-magnification cryo-SEM provides new access to microstructures in coating pigments, binders, and formulations.□

16. Clay supernatant-diluted standard nonreactive latex (Latex A) at 13.7% by wt. with 1.3% by wt. CMC. The suspension appears weakly flocculated at low magnification (A). Bridges and out-of-round particles are seen at high magnification (B). Coated by thermal evaporation of chromium immediately after fracture.



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