Weeping in blade coating

Part 2: SEM and X-ray analysis of microtome-sectioned weeps

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ABSTRACT: This paper reports results of SEM and X-ray microanalysis of microtome-sectioned weeps from a coater blade. The weeps shared a common structure, which was a bulbous crown on top of a comb of columns that join in their upper reaches. Cross-sectioned weeps contained a greater number of calcium carbonate lumps and large clay booklets in the trunks of the weeps at the point where they attached to the blade. This suggests that trunk growth is at least partly caused by blockage of large clay booklets and calcium carbonate lumps.

KEYWORDS: Analysis, blade coaters, blade coating, blades, bleeding, coaters, coating, electron microscopy, machine components, microframes, scanning electron microscopy, X-ray analysis.

This is the second of two papers on visualization of the bleeding phenomenon in blade coating known as "weeping." In Part 1,[1] we reported high-speed video (HSV) recording and still photographs of the dynamics of weeping. Now we report results of SEM and X-ray microanalysis of air-dried, microtome-sectioned weeps using three coating formulations containing precipitated calcium carbonate and kaolin.

Still macro-photographs in Part 1 showed that our weeps resemble mangrove trees, with several thin trunks and a large bulbous crown. The crowns range from 1–2 mm in diameter and have smooth surfaces. The trunks are thin (less than 100 µm across) and crooked. The side of the trunk facing the web has narrow, channel-like grooves, while the surface on the other side is smooth.

HSV data reported in Part 1 showed how weeps repeatedly initiate, grow, and detach. When we added a pigmented dye to the coating color after weeps had begun to grow, swirls of color appeared in the crowns, proving that they suffer from vortex flow of the sort produced by local, temporary contacts with a fast-moving surface. In addition, they acquire liquid during these contacts. In other words, our weeps grew by drinking from the coating on the moving web.

HSV also revealed how the crowns undergo frequent kicking away from the moving web. Kicking frequencies ranged from 30 Hz for small crowns to 300 Hz for large crowns. After most kicks, crowns rebounded towards the web. Sometimes, however, kicking was hard enough to detach weeps from the blade and propel them away. Our best estimate is that a strong air flow induced by the moving web blows against the weeps. The flow presses them against the web, causing them to rebound after most kicks. Sometimes ejected weeps fly in a curvilinear path partly back towards the web. This is proof that a strong air flow is present.

HSV recordings also showed merging of the crowns of adjacent weeps to form larger ones. As crowns grew, the trunks of the weeps dried partially, as judged from their reflectivity in HSV and from still photographs taken immediately after some of the trials ended.

The resolution of HSV and still macro-photography with the optics used for dynamic recording in Part

[1]Branston, R. E., Clark, P. C., Errico, M., *et al.*, *Tappi J.* 77(1):131(1994).

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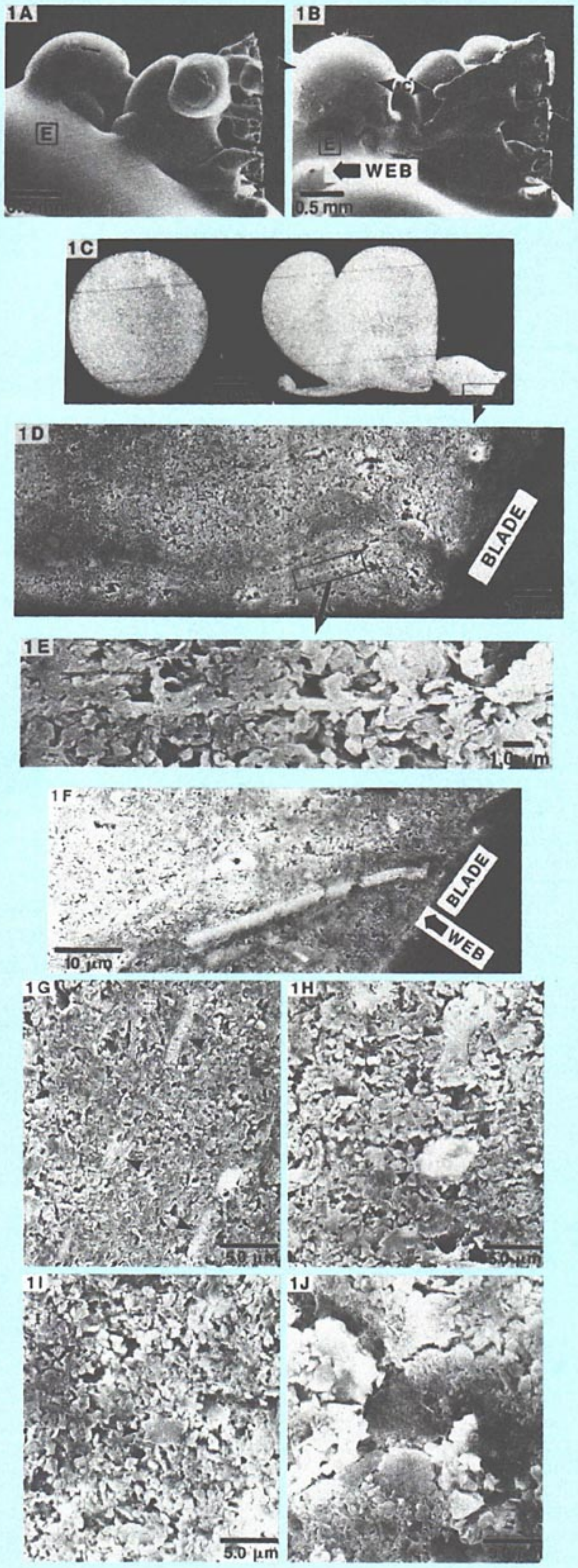
1. A-E: Standard formulation (60 parts No. 2 clay and 40 parts precipitated calcium carbonate). A and B: Weeps before microtome sectioning. Boxed E denotes epoxy resin used for mounting. C: Low magnification of sectional weep. D: Medium magnification of blade-web corner. E: Large clay booklet. 1. F-J: Standard formulation (60 parts No.2 clay and 40 parts precipitated calcium carbonate). F: Large clay booklet. G-I: High magnification of the trunk, crown, and air-dried formulation. J: Blade deposit from upstream side.



1 was only as low as 50 μm, obscuring the earliest stages of growth. By sectioning weeps and examining them microscopically, however, we found evidence about early as well as later growth. We now report SEM and X-ray microanalysis of weeps that were air-dried, embedded in epoxy resin, and sectioned with a microtome. High resolution down to about 4 nm with our microscope is an advantage of SEM, which clearly revealed the distributions of pigment particles. Observations recorded here include surface textures, shapes, internal distributions of pigment particles and binder, and distributions of consolidation in air-dried, microtome-sectioned weeps.

We first examined with SEM the shapes and surface textures of weeps air-dried and detached from the blade. Plates A and B of **Fig. 1** are typical. They indicate weeps resembling mangrove trees, with several thin trunks and a large bulbous crown as reported in Part 1. One side of each weep has a flat abrasion from the moving web, as in Plate B of this figure. Diameters of the crowns are often more than ten times that of the trunks. This implies that trunks and crowns grow by different mechanisms. If trunks and crowns grow by different mechanisms, we then supposed that interior microstructures of weeps would differ. To find out, we sectioned air-dried weeps with a microtome equipped with a diamond knife. We then examined the interior microstructures with SEM and X-ray microanalysis.

In the first sectioned weeps, we found huge booklets of clay in the trunks. Plate F of Fig. 1 shows the largest of these. It is a booklet of kaolin (36 μm across) in the trunk of a weep near the blade. This led us to hypothesize that trunks grow at least partly by blockage of large clay booklets. To prove this, we examined the distributions of oversized clay booklets and large calcium carbonate lumps in weeps of three different coating formulations. Two formulations had different-size clay particles, and one formulation contained no clay at all.

Experimental

Pilot coater

Experiments used a conventional coater with a roll applicator. Applicator roll speed was approximately 20% of line speed. The test used conventional blade geometry with a 0.50-mm-thick blade that was 76-mm wide with a 45° prehoned bevel. The coater head was at 46.5°. The blade load was 15–20°. Coating weight varied over the range 11–13 g/m^2.

Base paper

We applied coating formulations to the felt (top) side of a wood-free, 90-g/m^2 basestock. The base sheet had a low-solids, lightly pigmented precoating. Basestock sizing spanned the range 200–500 Hercules size test.

Formulations

We examined weeps of three formulations, each of which used different pigments. In the first, hereafter referred to as "standard" formulation, we mixed No. 2 clay and precipitated calcium carbonate in a 60/40 ratio. The second, called the "calcium carbonate" formulation, consisted of only precipitated calcium carbonate. In the third, designated as "fine-clay" formulation, we mixed ultra-fine clay and precipitated calcium carbonate in a 60/40 ratio. On the basis of pigment content, we added 12 parts carboxylated styrene butadiene latex and 3 parts low-viscosity ethylated starch to each formulation as binder.

Microtomy and SEM examination

We removed air-dried weeps of each of the three formulations from the blade and glued them intact with epoxy resin to aluminum stubs. We examined shapes of the weeps and their surface textures using SEM. Plates A and B of **Figs. 1–3** are micrographs. Then we embedded each weep in the epoxy resin and sliced it in a plane perpendicular to both the web and the blade with a microtome equipped with a diamond knife. Plate F of Fig. 1 is an exception. The surface is a cut in a plane parallel to the web.

To compare microstructures in weeps with those in the original formulations, we air-dried a drop from each of the three formulations, embedded it in epoxy, and sectioned it with the microtome. Plates I in Figs. 1–3 are micrographs of the air-dried drops.

We first coated all samples examined by SEM with 5–7 nm of gold/palladium in a dc magnetron sputter coater equipped with a rotating–tumbling stage. We examined all samples with SEM.

Results

Surface textures and shapes

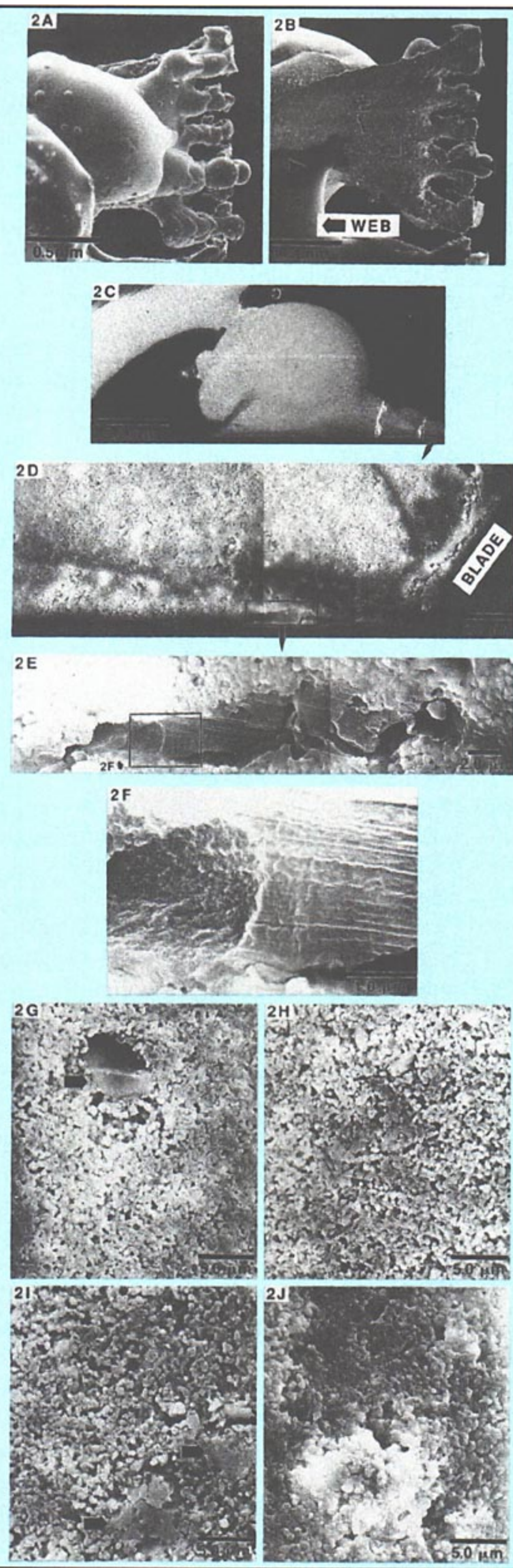
Plates A and B of Figs. 1–3 show surface textures and shapes of weeps of the standard, calcium carbonate, and fine-clay formulations, respectively. Plates B of each figure indicate the web direction. The boxed E in Plates A and B indicates the epoxy resin used for mounting. Plates A show the side of the weep facing away from the web, while Plates B show the opposing side facing the web. In each figure, the viewing aspect of Plate B is a reflected, 180° rotation from that of Plate A.

Weeps of all three coating formulations have the same surface textures and shapes, as reported in the still photographs in Part 1 of this paper. Plate A of Fig. 2 shows what evidently had been small droplets (small arrows). The HSV recordings reported in Part 1, however, revealed that droplet addition is not the main growth mechanism.

Interior microstructures

Plates C of Figs. 1–3 show the sectioned weeps at low magnification. Arrows on Plates A and B of each figure indicate the sectioning position of each weep.

2. A-E: Calcium carbonate formulation (precipitated calcium carbonate only). A and B: Weeps before microtome sectioning. Boxed E denotes epoxy resin used for mounting. Arrows show where the weep was sectioned by microtomy. C: Low magnification of sectional weep. D: Medium magnification of blade-web corner. E: Large calcium carbonate lump. **2**. F-J: Calcium carbonate formulation (precipitated calcium carbonate only). F: High magnification of lump. G-I: High magnification of the trunk, crown, and air-dried formulation. J: Blade deposit from upstream side.



The relative sizes of the bulbous crowns and the trunks are plain in Plates C of Figs. 1–3. The bulbous crowns have diameters sometimes more than ten times larger than the trunks. This is an indication that trunks grow by one mechanism and bulbs grow by another.

We found many large clay booklets and calcium carbonate lumps in the trunks of microtome-sectioned weeps. Plate E of Fig. 1 shows at high magnification a clay booklet that spans about 13 µm. Plate F of Fig. 1 shows another clay booklet that spans more than 36 µm. This booklet was in the trunk of a weep sectioned in a plane parallel to the web. X-ray microanalysis confirmed the presence of aluminum in the booklet. This is evidence that it was indeed kaolin clay and not some contaminant.

The appearance of large clay booklets in weeps of the standard formulation led us to infer that large clay booklets could be responsible for blockage events that initiate weeping. If this were so, we reasoned, a formulation of ultra-fine clay should produce weeps with fewer or no large booklets. In addition it should be easier to run, i.e., less prone to weeping. Yet we knew that formulations lacking clay and containing only calcium carbonate can weep. We decided to compare the microstructures in weeps of the standard formulation with weeps of the calcium carbonate and ultra-fine clay formulations.

For the calcium carbonate formulation, weeps formed when the solids content exceeded 71% and web speed exceeded 700 m/min. We found a huge lump of calcium carbonate in the trunk of the sectioned weep shown in Plates D–F of Fig. 2. Plate D shows its location about 50 µm from the blade and 1–2 µm from the web. The 30-µm-long lump has an orientation parallel to the web and a width of 2–3 µm. The diamond knife sliced across the weep from the bottom to the top of Plate E of Fig. 2. Parallel lines in the lump are perpendicular to the cutting direction. The parallel lines and the crack below the lump are indicators that the lump pushed upward as the diamond knife cut through it. X-ray microanalysis confirmed the presence of calcium in the lump. This is evidence that it was indeed calcium carbonate and not some contaminant. The lump comprises smaller particles shown at high magnification in Plate F of Fig. 2.

Even more surprisingly, we found many large clay booklets in the trunk of the weep of the fine-clay formulation. This is shown in Plate D of Fig. 3.

Comparison of trunks, crowns, and air-dried formulations

If trunks of weeps initiate and grow partly by blockage of large particles, and if crowns grow by drinking from the web, then there should be fewer large booklets and lumps in the crowns as well as in the formulation before it enters the coater (represented by the air-dried drops of formulation). The occurrence of large booklets and lumps in randomly chosen areas of the trunks, crowns, and air-dried drops of the three formulations are compared in Plates G–I of Figs. 1–3, respectively. Plates G of Figs. 1–3 show, respectively, the trunks of the standard, calcium carbonate, and fine-clay formulations. Plates H of Figs. 1–3 show, respectively, the crowns of the standard, calcium carbonate, and fine-clay formulations. Plates I of Figs. 1–3 show, respectively, air-dried drops of the standard, calcium carbonate, and fine-clay formulations. Plate J of each figure shows upstream blade deposits of each formulation, as discussed later in this report.

We found clay booklets up to 5 µm across in the trunk of the standard formulation shown in Plate G of Fig. 1. We found particles several micrometers across in the crown and in the air-dried drop of standard formulation. The arrows of Plates H and I, respectively, of Fig. 1 indicate these. It is not clear, however, if they are composed of calcium carbonate or kaolin clay.

We found a calcium carbonate lump about 5 µm across in the trunk of calcium carbonate formulation, shown by the arrow in Plate G of Fig. 2. There were no oversized lumps in the crown (Plate H of Fig. 2). However, the air-dried drop contained two lumps—one 4 µm across and the other 8 µm across—as indicated by the two arrows in Plate I of Fig. 2.

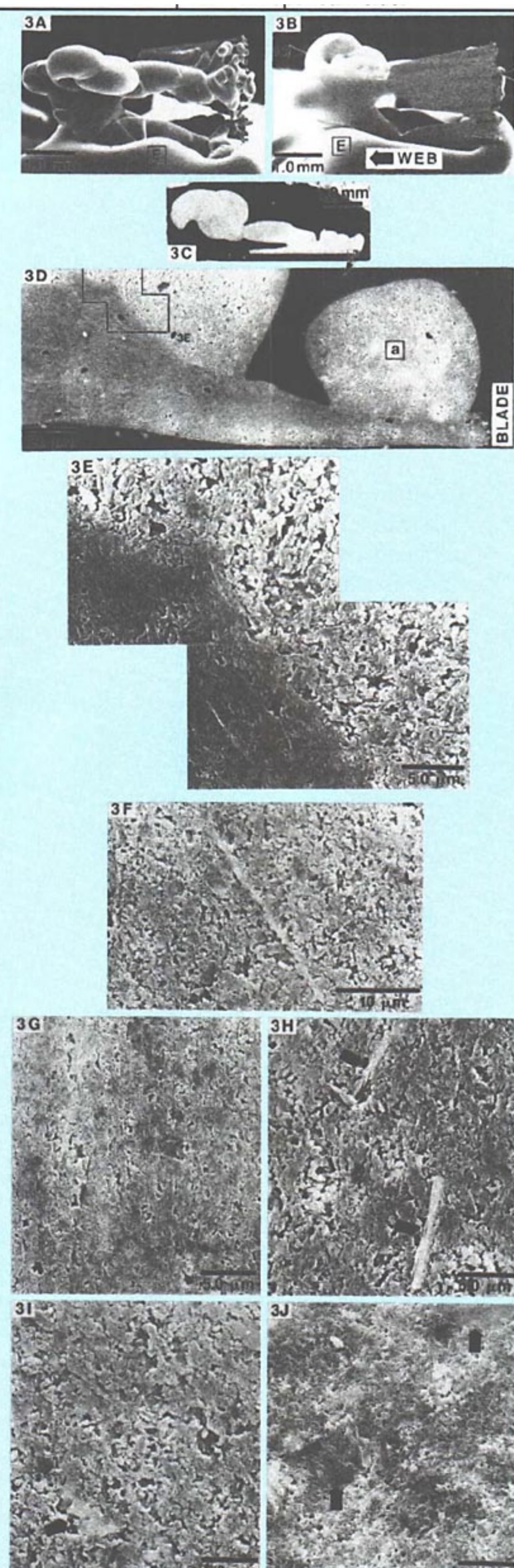
In contrast, there were no oversized clay booklets in the trunk of fine-clay formulation shown in Plate G of Fig. 3. There were clay booklets up to 10 µm across in the crown, as indicated by the arrows in Plate H of Fig. 3. The air-dried drop contained a 6-µm calcium carbonate lump, as seen in Plate I of Fig. 3.

In summary, we saw no pattern of occurrence of clay booklets or calcium carbonate lumps up to 10 µm across in the randomly chosen areas of the trunks, crowns, and air-dried drops of the three formulations shown in Plates G–I of Figs. 1–3. However, there is a pattern in the occurrence of clay booklets and calcium carbonate lumps larger than 10 µm. We sectioned a total of five weeps. Three of these were from the standard formulation (only one is shown), a fourth was from the calcium carbonate formulation, and the fifth was from the fine-clay formulation. All five had an excess of booklets, lumps, or both larger than 10 µm in their trunks. Micrographs of these are in Plates E and F of Fig. 1, Plate E of Fig. 2, and Plate D of Fig. 3. The bulbs contained no booklets or lumps larger than 10 µm.

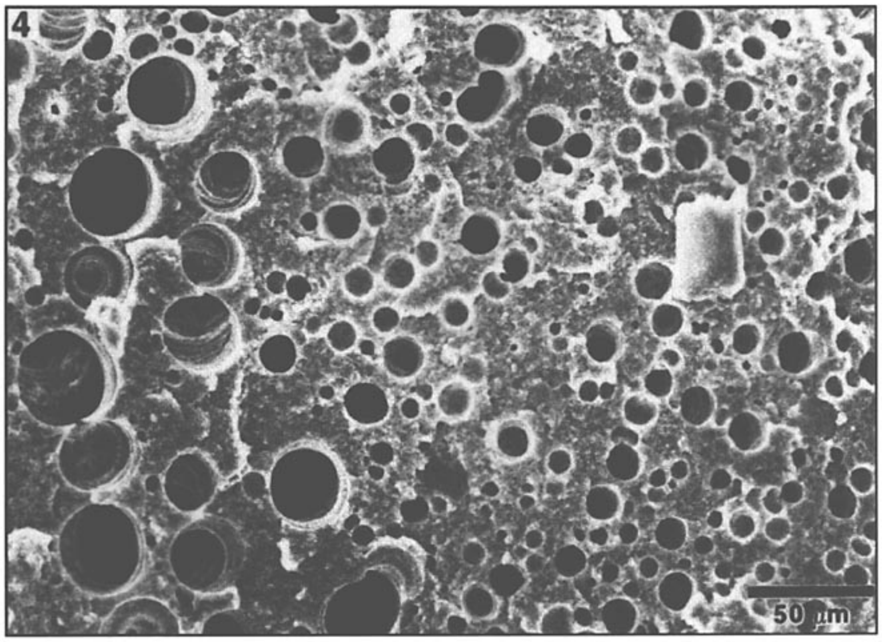
We did find one booklet 25 µm across in another area of the air-dried drop of the fine-clay formulation. Plate F of Fig. 3 shows this. The implication is that the largest booklets and lumps, i.e., those larger than approximately 10 µm, preferentially incorporate in the trunks.

The trunks in weeps of all three formulations are less porous than the

3. A-E: Fine-clay formulation (60 parts ultra-fine clay and 40 parts precipitated calcium carbonate). A and B: Weeps before microtome sectioning. Boxed E denotes epoxy resin used for mounting. Arrows show where the weep was sectioned by microtomy. C: Low magnification of sectional weep. D: Medium magnification of blade-web corner. E: Trunk-crown boundary. **3**: F-J: Fine-clay formulation (60 parts ultra-fine clay and 40 parts precipitated calcium carbonate). F: Large clay booklet in air-dried formulation. G-I: High magnification of the trunk, crown, and air-dried formulation. J: Blade deposit from upstream side.



4. Air bubbles in blade deposit of standard formulation from the upstream side.



I. Maximum runnable speeds and solids contents of three formulations

Formulation	Solids, wt. %	Maximum runnable speed, m/min ±50
Standard	67.3	800
	68.4	600
	68.7	600
Calcium carbonate	69.2	>900
	71.1	700
Fine clay	68.7	500

crowns and the air-dried drop of each formulation. The evidence is in the relative amounts of dark areas, which indicate pore space, in Plates G–I in each of Figs. 1–3. In each figure, Plate G (trunk area) has the least amount of dark area and thus the least porosity. The trunks might be less porous than the crowns and the air-dried drops because their mechanism of growth entails greater consolidation. Another possibility is that the trunks tend to trap binder from liquid that subsequently migrates through them, so that binder more nearly fills the space between particles.

The trunks of standard formulation (Plate G of Fig. 1) and calcium carbonate formulation (Plate G of Fig. 2) have more porosity than the trunk of fine-clay formulation (Plate G of Fig. 3). There seems to be more latex and starch binder in the pore space between the particles of fine-clay formulation than in the pore space of the other two formulations. Plates D and E of Fig. 3 show more evidence of this. The left side of Plate D shows a sharp boundary between the trunk and the crown. Plate E is a magnification of the area outlined in Plate D. The contrast in SEM images depends on both the sample's surface roughness and its distribution of average atomic number. Extra binder in the lower left of Plate E in Fig. 3 masked the surface roughness of particles and lowered the average atomic number. Together, these effects make the binder-rich trunks in the SEM micrographs appear darker than the crowns.

Upstream blade deposits

Plates J of Figs. 1–3 and **Fig.** 4 show deposits collected from the edge of the upstream side of the blade. We chipped the deposits from the blade with a knife after air drying. We mounted the chips blade-side down on SEM stubs with conductive paint. Only the standard formulation had noticeably more clay booklets larger than 5 µm across in its upstream blade deposit (Plate J of Fig. 1) compared with the trunk, crown, and air-dried drop of formulation (Plates G–I, respectively, of Fig. 1). We did not microtome-section the blade deposits before SEM imaging. This is one reason for the different appearance of Plate J in comparison with Plates G–I of Figs. 1–3.

The blade deposit of the standard formulation differed from those of the other formulations in another way. The blade deposit of standard formulation contained air bubbles, as seen in Fig. 4. Examination of the formulation as fed to the coater revealed that it was abundantly laden with small air bubbles. Introduction of these evidently occurred during mixing beforehand and recirculation during the trials. We collected formulation from the coater, froze it in nitrogen slush, fractured it, and examined it at –173°C in an SEM with a cold stage. Whether the presence of air bubbles has anything to do with the initiation or early and late growth stages of weeping remains an open question.

Maximum runnable speeds

The term "maximum runnable speed" means the minimum speed required for noticeable weeping. **Table I** records this speed and the solids contents of the formulations used in each trial. Maximum runnable speeds depended strongly on solids content of the standard and calcium carbonate formulations. Because we only tried the fine-clay formulation once, there was no rating for it. The calcium carbonate formulation was the more runnable of the two. Web speeds and solids contents higher than in the trials of standard formulation were necessary to induce weeping.

Conclusion

SEM micrographs of shapes and surface textures of weeps corroborate the still photographs reported in Part 1. With few exceptions, the weeps all share a common structure. They have a bulbous crown on top of a comb of separate columns or "trunks" that join, two-by-two, in their upper reaches. In some cases, what evidently had been small droplets were attached to the legs, but there were not enough of these to support the previously proposed mechanism of growth through droplet addition.[2] The crowns are about 1–2 mm in diameter and have smooth surfaces. The trunks are thin (less than 100 μm across) and crooked, with narrow channels on the sides that face the web. Other sides have smooth surfaces.

The (HSV) recordings reported in Part 1 showed how weeps initiated and then appeared to oscillate rapidly against the web as they grew. The weeps partially solidified, often merged, and finally detached. HSV recordings also showed that our weeps grew in at least two ways, as indicated by addition of dyed formulation to the coating pan after weeping had begun. Trunks acquired coating formulation that flowed up their web sides. Crowns acquired formulation during temporary contacts with the moving web, as evidenced by swirls of dye in the crowns. It also appeared that the weeps initiated at preferred sites, although only beyond critical limits of web speed, blade angle and loading, and solids content.

The two lines of evidence we report in Part 2 from SEM of microtome-sectioned weeps and dried drops of coating formulation point to growth of trunks by a different mechanism than growth of bulbous crowns. The trunks have lower porosity than the crowns and seem to grow at least partly by blockage of large clay booklets and calcium carbonate lumps. Weeps of the three coating formulations had an excess number of booklets and lumps larger than 10 μm across in their trunks compared with crowns of the weeps and drops of air-dried formulation. We do not know if blockage of large booklets and lumps is the event that initiates weeping, but we cannot eliminate it from any of the evidence at the time scales and length scales reported here. **T**

This research is a joint project of the Real-Time Imaging Initiative and the Coating Process Fundamentals Program of the Center for Interfacial Engineering (CIE) at the University of Minnesota, the research and development laboratories of the Potlatch Corp., and the dispersions research and development laboratory of BASF Corp. Potlatch Corp. provided the pilot coater, operating staff, and coating materials. BASF funded the microscopy, which was carried out at the CIE's High Resolution Microscopy Center. Microtomy was done in the laboratory of Prof. S. Erlandson, Dept. of Cell Biology and Neuroanatomy. Thanks are due to C. D. Frethem for assistance with microtomy. Thanks are also due to Prof. E. Nater, Department of Soil Science, for loaning us the diamond knife.

Received for review Dec. 11, 1992.

Accepted June 10, 1993.

Presented at the TAPPI 1993 Coating Conference.