

A Mechanism for the Consolidation of the Structure of Clay-Latex Coatings

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Synopsis

Attempts have been made to follow the process of consolidation, during drying, of the structure of a paper coating based on clay and latex by the electron microscope observation, and the analysis, of coatings quenched by freezing at various stages and freeze-dried. Three phases are considered, separated by two critical concentrations. At the first critical concentration (FCC), a 3-dimensional network is formed, and particle motion is greatly restricted. The water-air interface recedes into the surface capillaries, creating a capillary pressure that causes a shrinkage of the 3-dimensional network until a second critical concentration (SCC) is reached at which the network is fixed and air enters the rigid structure. Latex stiffness and colloidal interactions influence the critical concentrations. The latex coalescence process has been observed to take place over a relatively narrow concentration range after the FCC and is completed at the SCC.

INTRODUCTION

Pigmented coatings, generally based on clay, are used to improve the optical and printing properties of paper. The coating is applied as an aqueous dispersion which is subsequently dried. The properties of the coated paper depend on the surface and bulk structure of the coating. For example, gloss is a function of the roughness of its surface; brightness, opacity, print density, and gloss are a function of its void structure. It is therefore quite important to understand how the structure of a paper coating develops and what are the important parameters that control its consolidation from the moment the wet coating is applied to the final drying stage.

In spite of its importance, the subject has not received much attention. Only a few investigators¹⁻⁴ have attempted to propose mechanisms for the development of this structure. These mechanisms were all inferred from measurements done on dry coatings. We wish here to describe the phenomena occurring during the consolidation process in a more quantitative manner. This has been made possible by the electron-microscopical observation, and the analysis, of coatings whose structure was "quenched" during the drying process by a quick-freeze method, followed by freeze-drying. On the basis of these observations and analysis, a mechanism for the consolidation of a clay-latex system is proposed. The first part of this study deals with the case of a nonfilming latex. In Part II the study is extended to the case of filming latexes and concentrates on the filming process and its influence on the structure development.

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PART I: NONFILMING LATEX

Experimental

Coating Preparation

A model system, consisting of clay, dispersant, and a nonfilming poly(styrene/butadiene) latex, without other additives, was used in this study. A No. 1 U.S. clay was dispersed at 70% solids in water containing 0.03 pph of clay of a polyacrylate dispersant. 20 pph latex (filming temperature 42°C) were then added and the diluted (60% solids) mixture was hand-coated using a wire rod on impervious polyester films. The coatings were dried at room temperature.

Freezing and Freeze-Drying

In order to observe a coating at various stages during drying, the clay-latex network existing in the wet coating has to be fixed. For this purpose a quick freezing (or quenching) method was used. The wet coatings were left to dry at room temperature for various given times, and then they were dipped directly into liquid nitrogen (196°C). The frozen coatings were then freeze-dried under reduced pressure.

Void Fraction, Gloss, and Reflectance Measurements

The void fraction of the freeze-dried coating was determined by the method described in Ref. 5. 75° gloss was measured with a Hunter glossmeter on both wet and freeze-dried coatings. Reflectance of wet coating was measured against a black background with a densitometer (Densichron).

Solids Volume Concentration

At the same time as they were frozen or as their gloss or reflectance were measured, a portion of the wet coatings was scraped with a razor blade and weighed, dried in an oven, and reweighed. The solids volume concentration in the wet coating was calculated from the solids content by weight and the known densities of clay and latex. It is simply expressed as a ratio of the volume of solids (clay and latex) to that of solids and water, times 100.

Results and Discussion

Gloss and Reflectance: Critical Concentrations

When a coating, applied on glass or plastic film, is left to dry, its gloss drops abruptly after some time. Shortly thereafter, its opacity, which was slowly decreasing, rises sharply. The phenomenon, which has been described earlier,⁴ is illustrated in Figure 1, where gloss and reflectance measured against a black background are plotted vs. drying time.

A better way of describing the drying process is shown in Figure 2 where gloss and reflectance are now plotted vs. the concentration of solids (clay and latex) in the wet coating, expressed on a volume basis.

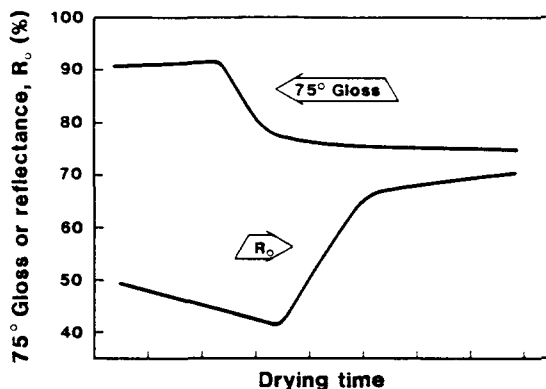


Fig. 1. Changes in coating gloss and reflectance during drying (nonfilming latex).

As long as the surface of the wet coating is a continuous water film, the specular reflection remains high. The slow rise observed at first is due to the slight increase in the refractive index of the medium as the concentration of clay and latex increases (refractive index of clay and latex is ca. 1.60 vs. 1.33 for water). The sudden drop in gloss indicates that the water film is no longer continuous. This happens at a first critical concentration (FCC) which is when menisci form at the coating surface.

The reflectance over black, R_o , decreases first. This is expected as the clay and latex particles get more crowded and are less efficient in scattering light. The phenomenon is well known in paints.⁶ At a second critical concentration (SCC), the reflectance rises sharply, an indication that the light-scattering process is suddenly considerably enhanced. The most likely explanation is that the largest of the water-filled spaces become filled with air creating a large difference in refractive index (refractive index of air is 1.0). Therefore, the SCC can be defined as the concentration at which air begins to enter into the coating structure. Furthermore, it is noted that the SCC so defined corresponds also with the point at which the gloss of the wet coating reaches a lower nearly constant value.

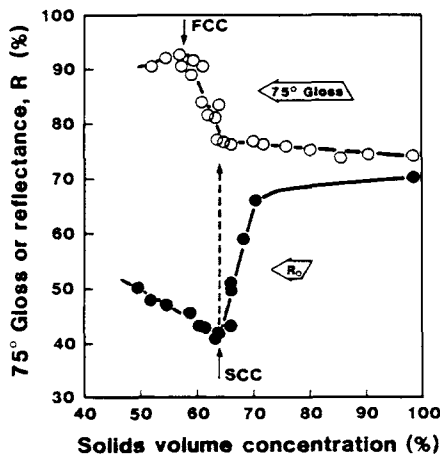


Fig. 2. Coating gloss and reflectance as a function of the solids volume concentration in the wet coating (nonfilming latex).

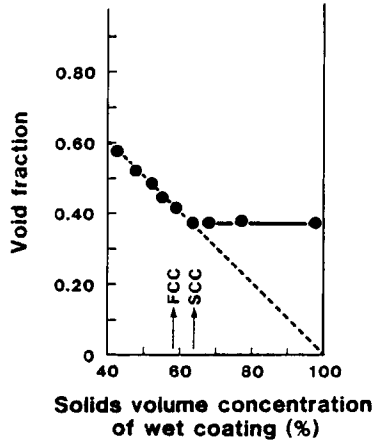


Fig. 3. Void fraction of coatings freeze-dried at various stages during drying. Dotted line shows the water volume content at which the wet coating was frozen.

Freeze-Dried Coatings

The void fraction of the freeze-dried coating is plotted in Figure 3 against the solids volume concentration at which the wet coating was frozen. Even in the freshly applied coatings, the void fraction is very nearly equal to the water fraction in the wet coating, evidence that the freezing and freeze-drying operations have preserved the structure existing in the wet coating. Note also that the void fraction becomes constant, meaning that shrinkage has stopped, when the volume concentration in the wet coating is around 63–64%, that is, around the SCC. Therefore, the structure is definitely fixed at the SCC. Beyond this point, there is no further structural change, and the water left in the coating is simply replaced with air.

The gloss of the freeze-dried coatings is plotted in Figure 4 vs. the solids volume concentration at which the wet coating was frozen. The curve rises, goes through a maximum around the FCC, and finally joins the curve for the wet coating. A

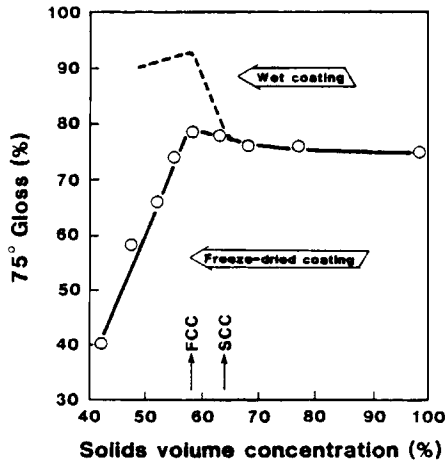


Fig. 4. Gloss of freeze-dried coatings as a function of the solids volume concentration at which the wet coating was frozen.

difference in gloss between the wet and the freeze-dried coatings is expected since the water film is absent in the latter. After the SCC, the values are similar indicating that the water-air interface has receded below the surface. The initial increase in gloss in the freeze-dried coatings, as the concentration rises, was first thought to reflect the increasing parallel orientation of the clay particles near the surface in the wet coating, until the electron micrographs were obtained. It is now believed that the lower gloss of the early samples is due to the undulations of wavelength 5–10 μm (whose origin is not known), which are present in samples frozen at a low concentration rather than to clay orientation. Figure 5 combines reflectance, gloss, and composition changes as drying proceeds.

PART II: FILMING LATEXES

From a practical point of view, it is necessary to extend the study to the case of filming latexes since these are used as binders for the pigment. This is done in this second part which concentrates on the process of coalescence, or filming, of the latex and its effect on the development of the structure.

Experimental

Latexes Used

The following latexes, typical of commercial usage, were added to the clay dispersion at the level of 20 pph:

(a) A carboxylated 60/40 poly(styrene-butadiene) latex. This latex is identical in composition to that used in the first part except for a lower styrene content which makes it film-forming at room temperature.

(b) A polyvinylacetate latex.

(c) An acrylic latex which may interact with clay depending on the pH.

In addition, the following systems were also examined:

(d) An oxidized starch.

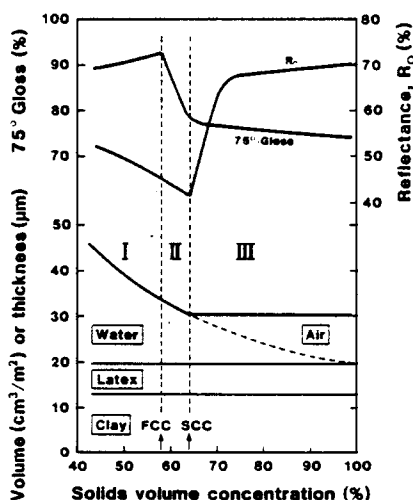


Fig. 5. Changes in gloss, reflectance, and dimension during drying of coatings containing 20 pph of a S/B nonfilming latex. Coat weight: 40 g/m², application solids: 60% by weight (42% by volume).

(e) A 50/50 blend of the 60/40 S/B filming latex and of the oxidized starch.

Preparation for Observation of Latex Coalescence in the Electron Microscope

If the glass transition temperature of the latex polymer is below ambient temperature, the latex particles of the freeze-dried coating will coalesce once the coating is brought to room-temperature. It is thus impossible to follow the coalescence process, when and how it happens, and a special technique, described elsewhere,⁷ was developed. It essentially consists of coating the sample with Au—Pd immediately after the freeze-drying has taken place and while the sample is still cold. The Au—Pd-coated samples can then be stored and examined at room temperature.

Characterization of the Coatings

Even though, as discussed above, film formation took place as soon as the freeze-dried samples were brought to ambient temperature for testing, at the latex addition level used (20 pph) the fusion process does not significantly change the gloss nor the void fraction.⁸ This was confirmed by submitting freeze-dried coatings containing a nonfilming latex to a heat-treatment above the T_g of the latex (Table I).

TABLE I
Effect of Latex Fusion on Gloss and Void Fraction of Freeze-Dried Coatings

Solids vol concn at which wet coatings were frozen (%)	Void fraction (%)		Gloss (%)	
	Before fusion	After fusion	Before fusion	After fusion
48.0	52.6	51.1	62.0	60.5
54.8	45.5	44.6	76.5	74.5
60.9	39.2	38.8	78.0	75.5
Air-dried	36.5	36.2	74.5	72.0

Note: The first three coatings were frozen at various stages during drying followed by freeze-drying and then heated in an oven (100°C, 5 min) to fuse the latex particles.

Analysis for Latex Content at the Coating Surface

Coatings were applied at four different solids levels (55%, 60%, 65%, and 70% solids by weight) and dried in an oven at 100°C. The top layer (approximately 10%) of the dry coating was scraped gently with a razor blade. The scrapings were collected, and their latex content was then determined by ashing.

Results and Discussion

Critical Concentrations

Effect of Polymer Stiffness. Figure 6 shows the gloss of the wet coating as a function of its solids volume concentration and compares it to that of the freeze-dried coatings. The change in reflectance, R_0 , of the wet coating measured against a black background is also shown. The behavior is basically the same as observed with the nonfilming latex coating. Therefore, coatings containing a film-forming latex can be also considered to have two critical concentrations: that is, a first critical concentration (FCC) defined as the concentration at which the first menisci form at the coating surface and cause a drop in gloss and a second critical concentration (SCC) defined as the concentration at which the structure of the clay-latex network is fixed and air voids begin to appear in the coating structure. However, when comparing the results shown in Figure 6 with those of Figure 2, the following are noted.

(1) The FCC of the film forming latex coating is higher than that of the nonfilming latex (61.5% vs. 58%).

(2) The SCC of the filming latex coating is substantially larger than that of the nonfilming latex (79% vs. 64%).

(3) The final constant gloss value is considerably lower (46.5% vs. 75.5%).

(4) The air void fraction of the film-forming latex coating after air-drying is about 20%, while that of the nonfilming latex coating was about 37%.

The difference in the FCC observed between these two coatings can be explained in terms of the rigidity of the latex polymer. As the surface tension of water acts as a compressive force, the soft latex particles which are squeezed between clay platelets can absorb the compressive force through deforming, as shown in Figure 7. As a result, the continuous water film (and therefore the glossy surface) can be kept a little longer. After the FCC, as more water leaves, the capillary forces grow and compact the clay-latex network. For the nonfilming latex coating, the network becomes fixed when the friction between particles is such that it resists the compressive force. This happens at the SCC (64%). However, for the filming latex coating, the capillary forces act as the

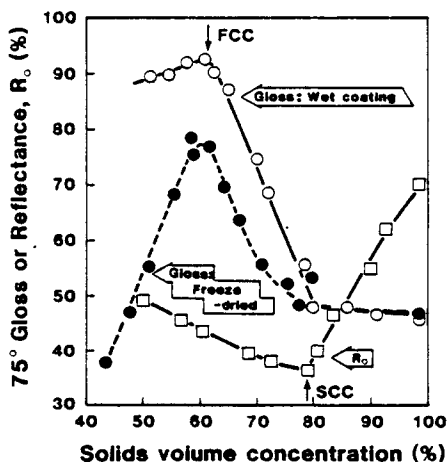


Fig. 6. Changes in 75° gloss of wet and freeze-dried coatings and in reflectance as a function of the composition of wet coating (filming latex).

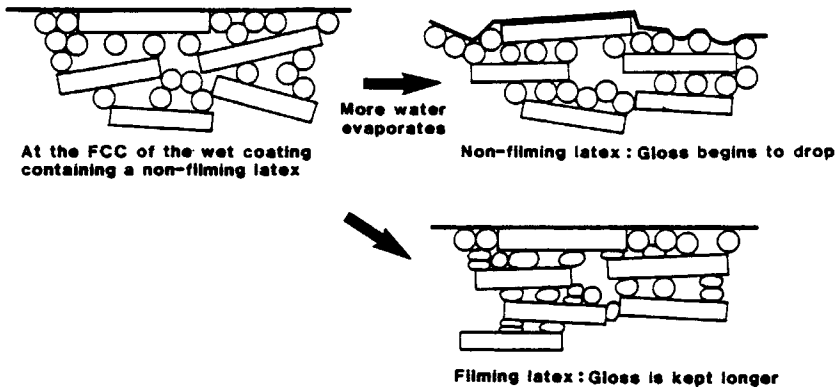


Fig. 7. Schematic representation of a clay-latex network at the FCC.

driving force for the coalescence and flow of the latex, and therefore the shrinkage continues and the SCC is greater (79%).

The shrinkage that occurs between the first and the second critical concentrations was much larger for the filming latex (46% vs. 12% for the nonfilming latex) because it is associated with the phenomenon of coalescence and flow of the latex polymer. The lower gloss results from this larger shrinkage which brings about surface roughening.⁹ Therefore, out of the 30 points drop in gloss from the value of 78 at the FCC (see Fig. 6), ca. 28 points are attributable to the shrinkage caused by this coalescence and flow. The large difference in the air void fraction between two coatings is a direct result of the difference in shrinkage.

Type of Binder. Gloss and reflectance curves were also obtained with the other binder systems. The results shown in Figures 8 and 9 indicate that all the binder systems used in this study behave basically in the same manner, and their FCC and SCC, determined by gloss and reflectance measurements, are shown in Table II. Note that when starch is used as the only binder, shrinkage proceeds beyond the SCC.

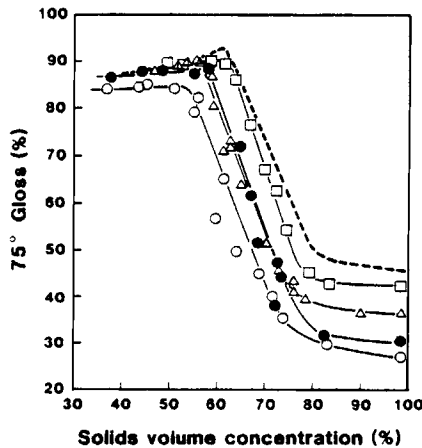


Fig. 8. Change in 75° gloss as a function of solids volume concentration for various types of binders: (---) filming S/B; (Δ) PVAc; (\square) acrylic, pH 9.5; (\circ) oxidized starch; (\bullet) 50/50 S/B oxidized starch.

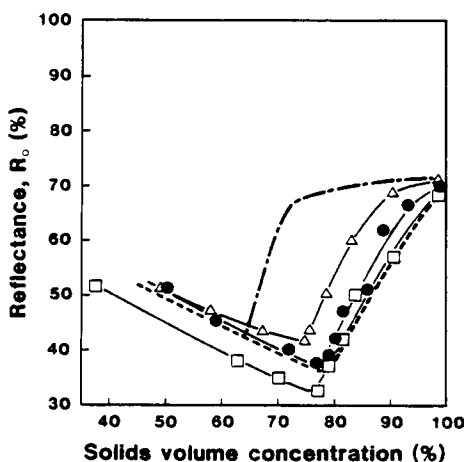


Fig. 9. Change in reflectance as a function of the solids volume concentrations in the wet coating for various types of binders: (---) filming S/B; (Δ) PVAc; (\square) acrylic, pH 9.5; (\bullet) 50/50 S/B oxidized starch; (- · - ·) nonfilming latex.

The effect of colloidal interactions between latex and clay on the FCC was briefly examined with the acrylic latex which interacts with clay when pH is reduced due to a charge reversal. As the pH of the clay slurry was reduced, the FCC occurred earlier as expected (Fig. 10). In the case of PVAc, whose FCC is considerably less than that of the S/B and acrylic latexes, it is not known whether the effect is due to colloidal interactions or to the higher stiffness of the polymer (T_g is around 30°C), or both.

The latex content in the top 10% layer of coatings dried in an oven immediately after application is plotted in Figure 11 against the concentration of solids (by volume) at which the coatings were applied. The results show that the movement of latex particles towards the surface gradually becomes restricted and almost ceases when the concentration is over 50% by volume. That is, latex migration during the drying period can be considered to take place before the FCC and is negligible after.

TABLE II
Coating Composition at the Critical Concentrations and Dry

Binders (20 pph)	Critical concn (vol %)		Void fraction of clay coatings	Shrinkage ^a (%)	75° Gloss (%)
	FCC	SCC			
S/B nonfilming latex A	58.0	64.0	0.37	11.9	75.0
60/40 S/B filming latex B	61.5	79.0	0.21	45.5	46.5
Vinylacetate latex C	57.0	75.0	0.26	39.5	36.0
Polyacrylic latex	62.0	77.0	0.24	36.8	42.0
60/40 S/B filming latex/oxidized starch 10/10	58.0	77.0	0.22	47.6	30.5
Oxidized starch	53.5	74.0	0.20	57.0	26.5

^a This is the shrinkage between the FCC and the SCC calculated as: shrinkage = $(W - V)/W \times 100$, where W = volume fraction of water at the FCC and V = void fraction of dry coatings.

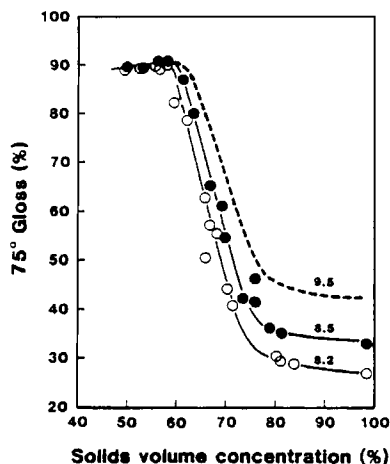


Fig. 10. Change in 75° gloss of coatings containing 20 pph of a clay reactive acrylic latex as a function of pH. Numbers refer to pH of clay at the time of latex addition: (○) (●).

The Latex Coalescence Process

At what stage of the drying does the coalescence of the latex start? In order to answer this question, a scanning electron microscope study was undertaken using the special sample preparation procedure described in the experimental section. Figure 12 shows the surface of the coating at five stages of the latex coalescence process.

The latex particles at the surface keep their spherical form until the wet coating reaches a solids volume concentration of about 67%, i.e., well after the FCC. However, as drying proceeds further, the coalescence has partially taken place at 68.5% solids volume concentration, and at 74% the spherical form of the latex particles disappears. Therefore, coalescence takes place over a relatively narrow range of concentration after the FCC and is probably finished at the SCC.

In this work, since the latex particles inside the coating could not be observed, it is still unknown when overall coalescence is finished. However, considering that (1) the capillary forces and the polymer-water interfacial tension which induce the coalescence act evenly throughout the water-filled coating and (2) the change in volume of the wet coating which is brought about by the coalescence and flow of the latex is finished at the SCC, one should expect that the deformed

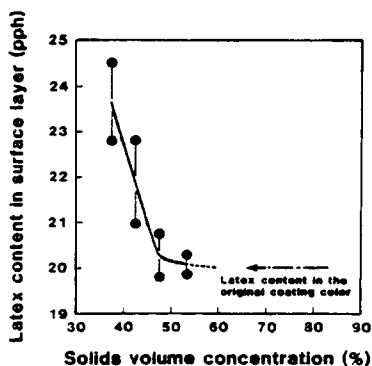


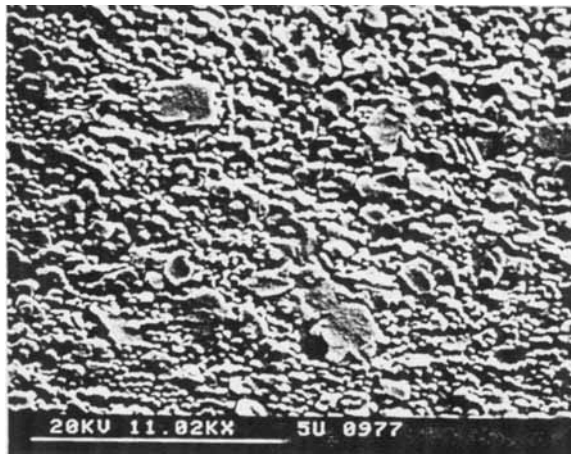
Fig. 11. Latex content in surface layer as a function of the solids volume concentration at which coatings were applied. Latex: 20 pph of a 60/40 S/B filming latex.

latex particles present inside will begin to fuse at the same time as latex particles at the surface do and overall coalescence and flow are completed around the SCC.

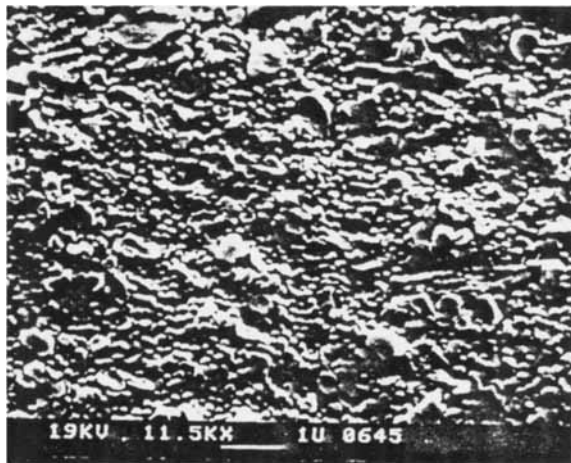
GENERALIZED MECHANISM OF THE CONSOLIDATION OF A CLAY-LATEX COATING STRUCTURE

On the basis of the observations discussed above, the following mechanism for the consolidation of a clay-latex coating structure can be proposed.

Basically, the consolidation of a clay-latex coating can be considered to proceed in three phases. In the first phase, clay and latex particles can move about freely in the aqueous dispersion; latex particles tend to migrate towards the surface along with the evaporating water (and towards the paper substrate if it is ab-

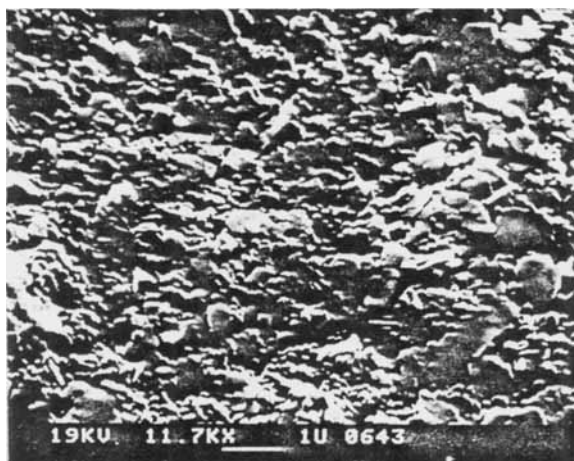


(a)



(b)

Fig. 12. Scanning electron micrographs of the coatings freeze-dried at various stages during drying: (a) SVC = 42.5%, initial stage (immediately after application); (b) SVC = 67%, latex particles are still spherical; (c) SVC = 68.5%, coalescence has partially occurred; (d) SVC = 74%, latex particles at the surface have disappeared; (e) air-dried.



(c)

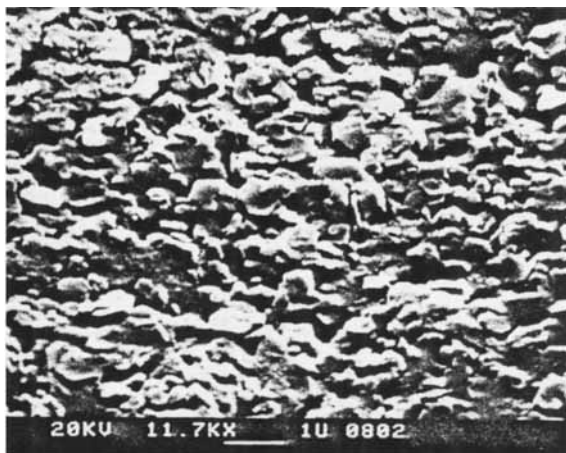


(d)

Fig. 12. (Continued from previous page.)

sorbent). At one point, free motion ceases and a bulky and deformable 3-dimensional network forms with latex particles trapped between clay platelets. The first meniscus forms, and the gloss drops immediately after this point if the latex particles are hard enough to resist the compressive force arising from the water surface tension. On the other hand, if the latex particles, which act as spacers for the clay platelets, can deform, the formation of the first meniscus is retarded, and the value of the FCC will be larger. The FCC was shown to depend on the latex stiffness, but also on the colloidal interactions that exist between clay particles and binder. Presumably, other factors such as latex particle size and size distribution and latex content will also affect the FCC.

During the second phase, the wet coating shrinks under the increasing capillary forces. Only when these capillary forces become sufficient to initiate it, the coalescence of latex particles finally begins. This does not take place immediately after the FCC but, as the SEM observation indicates, at a later stage (68.5% vs. 61.5%). At the SCC, overall latex coalescence and flow appear to be complete,



(e)

Fig. 12. (Continued from previous page.)

and structural changes both inside and at the surface stop. From this time on, capillaries empty until drying is completed. Like the FCC, the SCC will be dependent on latex stiffness and latex content. For filming latexes, however, the latex type has only a small influence.

CONCLUSIONS

It has become apparent in a more quantitative manner how the structure of a clay-latex coating develops during the drying process. From the proposed mechanism that the coatings consolidate through three phases, it can be considered that the first (before the FCC) and the second (between the FCC and SCC) phases are regions where latex redistribution (migration) in the coating and the void structure, respectively, could be controlled.

References

1. J. L. Burke, Ph.D. thesis, The Institute of Paper Chemistry, Appleton, WI, 1966.
2. D. R. Grafton, Ph.D. thesis, The Institute of Paper Chemistry, Appleton, WI, 1968.
3. J. W. Vanderhoff and E. B. Bradford, preprints, TAPPI Coatings Conference, 1972.
4. P. Lepoutre, *Pulp Paper Can.*, **80**(2), 98 (1979).
5. P. Lepoutre and A. Rezanowich, *TAPPI*, **60**(11), 86 (1977).
6. W. D. Ross, *J. Paint Technol.*, **43**(563), 51 (1971).
7. J. Watanabe, G. Seibel, and M. Inoue, *J. Appl. Polym. Sci.*, to appear.
8. P. Lepoutre and B. Alince, *J. Appl. Poly. Sci.*, **26**, 791 (1981).
9. Do Ik Lee, preprints, TAPPI Coating Conference, 1974.

Received April 5, 1982

Accepted May 13, 1982