

# The Critical Pigment Volume Concentration Concept for Paper Coatings: I. Model Coating Systems Using Plastic Pigments and Latex Binders for Paper Coating Applications

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## ABSTRACT

The immobilization and consolidation of the model coatings based on the plastic pigment and latex binder of known particle sizes were theoretically studied in terms of the dense random packing of binary spheres and varying extent of latex film shrinkage. The porosity of the model coatings was calculated based on three proposed latex shrinkage models: Maximum, Minimum, and Linearly Decreasing Latex Shrinkage. The increasing extent of latex shrinkage was calculated up to the critical pigment volume concentration (CPVC) as a function of plastic pigment volume fractions, and the maximum latex shrinkage was estimated from the CPVC. Also, the number of pores and the average equivalent spherical pore diameters were calculated based on those proposed models. The opacity and gloss of the model coatings on polyester films were measured and their porosity was also determined by a simple coat weight-thickness method. As expected, various coating structure-property-composition relationships, such as opacity, gloss, porosity, etc., were shown to exhibit sharp transitions near the CPVC. The CPVC values determined by the opacity, gloss, and porosity vs. PVC relationships, respectively, agreed very well with each other. Especially, the CPVC's determined by the opacity and porosity vs. PVC curves were identical. The comparison between the theoretically calculated and experimental porosity values showed that the intermediate value between the maximum and minimum latex shrinkage would best fit the experimental porosity data. The effect of plastic pigment particle size on the optical properties and porosity of model coatings was also studied and it was observed that the coating opacity and porosity increased with increasing plastic pigment particle size, but the gloss decreased. The ink gloss of the uncalendered model coatings applied onto commercial sheet offset coated papers was shown to be affected by both the coating gloss and porosity: the higher the coating gloss, the higher the ink gloss, but the higher the coating porosity, the lower the ink gloss. Their printability was also studied in terms of the number of passes-to-fail and the rate of ink setting as a function of both plastic pigment volume fractions and plastic pigment particle sizes. A minimum crack-free temperature (MCFT) of latex-bound coatings was proposed to better predict the behaviors of latexes as coating binders. The wet state of model coating dispersions, the surfaces of consolidated model coat-

ings, and their internal structure were examined by both electron and atomic force microscopy, and their micrographs were found to be consistent with our immobilization and consolidation models.

## INTRODUCTION

The Critical Pigment Volume Concentration (CPVC) concept was introduced for paint coatings by Asbeck and Van Loo (1) in 1949. Since then, it has been successfully used for the paint coatings as both theoretical and practical concepts. Although the concept is universally applicable to all coating systems, it has not been widely used for paper coatings. There are many reasons why this concept has not been widely adopted by paper coating specialists. For example, the original CPVC concept was mainly concerned with coatings below or slightly above the CPVC's, while paper coatings are mostly concerned with coatings much above the CPVC's. However, we are finding that the CPVC concept can provide better insight into the immobilization, consolidation, and structure development of paper coatings as well as their optical, mechanical, and printing properties. For this reason, this study has attempted to revisit the CPVC concept for paper coatings based on model coating systems using plastic pigments and latex binders used for paper coating applications.

The CPVC of a given coating system is the most important factor controlling the coating structure-property relationships as a function of pigment volume concentrations below and above the CPVC. It is well known that the CPVC is affected by many factors such as the immobilization volumes, the consolidation power of binders, the type of substrates, drying conditions, etc. In turn, the immobilization volumes which are the same as the packing volumes of wet coatings are dependent not only on the particle shapes, sizes, and size distributions of pigments and binders, but also their physico-chemical, colloidal, and rheological properties as well as their mutual interactions. Consequently, the CPVC can provide information on both the coating structure-property-composition relationships for the control coatings and the effects of

various additives such as alkalis, thickeners, water-retention aids, electrolytes, etc. Interestingly, it has been found in the present study that the CPVC's are relatively easy to determine by making coatings with varying pigment volume concentrations on polyester films or black substrates and measuring their opacity or by applying the same coatings onto coated papers and measuring their gloss. It is so easy to determine the CPVC's that the CPVC concept should be used more widely than before.

The model coatings based on plastic pigments have been investigated by many researchers in the past. Alinec and Lepoutre (2) have studied the light-scattering of plastic pigment coatings and their structure. Leskinen (3) has studied the layer structure of the model coatings based on the binary plastic pigments. Hoy and Peterson (4) have measured the critical particle packing in disperse systems by using a cantilevered-gravimetric beam (CGB) instrument mounted on a balance. Rennel, Eriksson, and Rigdahl (5) have studied the consolidation behavior and gloss of paper coatings based on plastic pigments. Toivakka, Salminen, Chonde, and Bousfield (6) have studied the consolidation and leveling of plastic pigment suspensions. In the present study, the literature on particle packings has been reviewed and the immobilization volumes of the model coatings have been calculated by one of the methods (7) available in the literature as a function of pigment volume fractions. Then, their consolidation volumes have been calculated from their calculated immobilization volumes based on three different latex shrinkage models (maximum, intermediate, and minimum latex shrinkage), leading to the theoretical calculation of the porosity of model coatings. Also, some theoretical considerations have been made to characterize their structure in terms of porosity, the number of pores and pore size, hydraulic circular diameter, etc. The CPVC of the model coatings and coating porosity have been experimentally determined. Then, the experimental porosity data have been compared with the theoretically calculated values.

The effect of plastic pigment particle size on the optical properties and porosity of model coatings has been also studied by measuring the coating opacity, gloss, and porosity of the model coatings applied onto

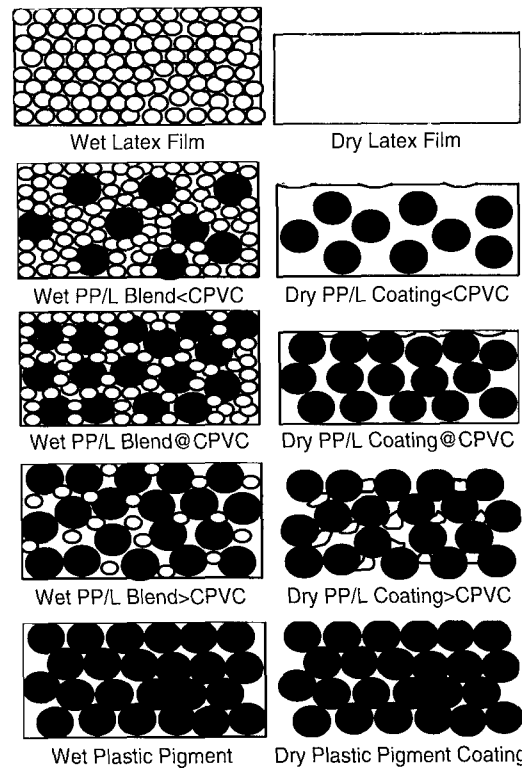
polyester films. Subsequently, the ink gloss and printability of the uncalendered model coatings applied onto commercial sheet offset coated papers have been investigated as a function of both plastic pigment volume fractions and plastic pigment particle sizes.

The present study has led to a proposal of determining a minimum crack-free coating temperature of latex binders in order to more accurately predict their behaviors as coating binders.

The wet state of the dispersions of plastic pigment and latex binder particles has been examined by a cryofixation technique, the surfaces of the model coatings by scanning electron microscopy, and their internal structure by looking at their fractured surfaces by scanning electron microscopy. Also, the topography of the coating surfaces has been examined by atomic force microscopy (AFM). These examinations have provided much better insight into the structure of model coatings and reinforced our immobilization and consolidation models.

## THEORETICAL CONSIDERATIONS

It is well known to paper coating specialists that paper coatings are formed by two steps: coating immobilization and consolidation followed by the further coalescence of latex particles (8-11). Now, let us take a look at the model coatings using plastic pigments and latex binders of known particle sizes. Their coating immobilization volume fractions can be estimated by the packing volume fractions of the binary or multi-component mixtures of spheres as a function of plastic pigment volume concentrations (2, 3, 7, 12-18), which have been extensively studied in the past. It is also known that an immobilized film-forming latex film consolidates to form a continuous film, resulting in a significant shrinkage (8) during drying, whereas an immobilized plastic pigment (non-filming latex) coating dries without much shrinkage, as depicted in Figure 1 (top and bottom). Based on the above-described behaviors of a film-forming latex film and a non-filming plastic pigment coating, it is expected that their blends below and at the CPVC, respectively,

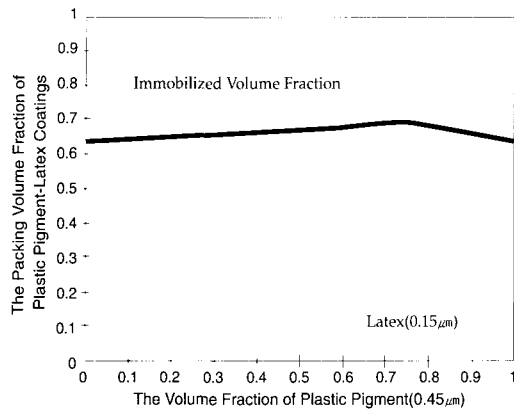


**Fig. 1. Schematics for the immobilization and consolidation of a latex (L) film and plastic pigment (PP)/latex (L) blend coatings below, at, and above the CPVC of plastic pigment under study, respectively, and a plastic pigment coating**

would form nonporous coatings, while the blends above the CPVC would form porous coatings, as shown in Figure 1 (top middle, middle, and bottom middle). From these qualitative understandings on the immobilization and consolidation of the model coating systems based on the plastic pigment and latex binder of known particle sizes, this paper will attempt to estimate their immobilization volume fractions and characterize their coating structure in terms of their porosity, average pore size, and number of pores.

## Immobilized Coating Volumes

On the assumption that film-forming latex and plastic pigment particles would behave like hard spheres in the wet state up to the immobilization, one can use the



**Fig. 2. The dense random packing volume fraction of the binary mixtures of spheres as a function of the volume fraction of large spheres with the diameter ratio of large (0.45  $\mu\text{m}$ ) to small (0.15  $\mu\text{m}$ ) equal to 3 as a parameter**

dense random packing volume fractions of binary spheres (7, 12-17) to estimate the immobilized coating volume fractions of plastic pigment and latex particles from their particle size ratios and compositions. Figure 2 shows the dense random packing volume fraction of the binary mixtures of spheres as a function of the volume fraction of large spheres with the diameter ratio of large(0.45  $\mu\text{m}$ ) to small(0.15  $\mu\text{m}$ ) equal to 3 as a parameter by using a methodology developed by Lee (7) in 1970. The following information was used:

The volume fraction of uniform spheres:  $\phi_p(\text{uniform small})$  or  $\phi_p(\text{uniform large}) = 0.639$

The maximum packing volume fraction of the binary mixtures of spheres with a diameter ratio of 3:

$$\phi_p(\text{max}) = 0.69 \text{ from Figure 1 of Reference 7}$$

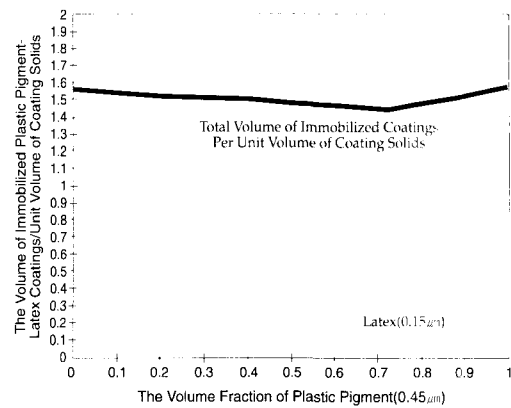
The volume fraction of large spheres for the maximum packing:  $X(\text{max}) = 0.735$

The following equations were used to construct Figure 2:

$$\phi(\text{small-large}) = 0.639 + (\phi_p(\text{max}) - 0.639) / X(\text{max})$$

$$\phi(\text{large-small}) = 0.639 + (\phi_p(\text{max}) - 0.639) / (1 - X(\text{max}))$$

$$\phi_p(\text{small}) = 0.639 \times X(\text{small}) + \phi(\text{small-large}) \times X(\text{large})$$



**Fig. 3. The total volumes of the binary mixtures of spheres per unit volume of spheres as a function of the volume fraction of large spheres, which are equal to the reciprocals of the dense random packing volume fractions shown in Figure 2**

$$\phi_p(\text{large}) = \phi(\text{large-small}) \times X(\text{small}) + 0.639 \times X(\text{large})$$

$$X(\text{small}) + X(\text{large}) = 1.0$$

where  $\phi(\text{small-large})$  and  $\phi(\text{large-small})$  are the binary coefficients of small and large sphere mixtures,  $\mu\text{m}$  the smaller values of  $\phi_p(\text{small})$  and  $\phi_p(\text{large})$  are the packing volume fractions of the binary mixtures of spheres, and  $X(\text{small})$  and  $X(\text{large})$  are the volume fractions of small and large spheres in the binary mixture.

Figure 3 shows the total volumes of the binary mixtures of spheres per unit volume of spheres as a function of the volume fraction of large spheres, which are equal to the reciprocals of the dense random packing volume fractions shown in Figure 2. As already discussed above, the wet latex alone and the blends of plastic pigment and latex at immobilization below and at the CPVC, respectively, consolidate to form non-porous latex film and coatings, respectively. This means that up to the CPVC of plastic pigment, no air-voids would be present so that the immobilized volumes would shrink to the unit volume of coating solids. Figure 4 shows the schematics for the extent of the volume loss during consolidation per unit volume of coating solids throughout the whole plastic pigment volume concentrations and the air-voids which would be contained in the coat-

ings above the CPVC. The line AB in Figure 4 is an arbitrary linear connection between A and B. However, it would be highly desirable to be able to predict or estimate the relationship between the immobilized and consolidated coating volumes above the CPVC's from the theoretical considerations.

### Coating Porosity

In order to estimate the relationship between the immobilized coating volume and the final consolidated coating volume as a function of plastic pigment volume fractions above the CPVC, three possibilities have been considered: (1) Latex binders will shrink to their maximum shrinkage even in the coatings beyond the CPVC, (2) Latex binders will shrink only to their minimum shrinkage, and (3) Latex binders will shrink to the linearly decreasing value from the maximum to the minimum shrinkage above the CPVC. The maximum shrinkage values of latex binders can be determined from both the immobilized coating volumes and CPVC values. For example, suppose that the CPVC of a mixture of a plastic pigment and a latex is 0.6, then the maximum shrinkage of the latex at the CPVC can be calculated as follows:

From Figure 4, the total coating volume shrinkage ( $\Delta V$ ) and the latex volume concentration ( $X(\text{latex})$ ) at the CPVC (the critical pigment volume concentration ( $X(\text{plastic pigment}) = 0.6$ ) can be found as follows:

$$\Delta V(\text{total coating volume shrinkage}) = V(\text{total immobilized coating}) - V(\text{total consolidated coating}) = 1.469 - 1 = 0.469$$

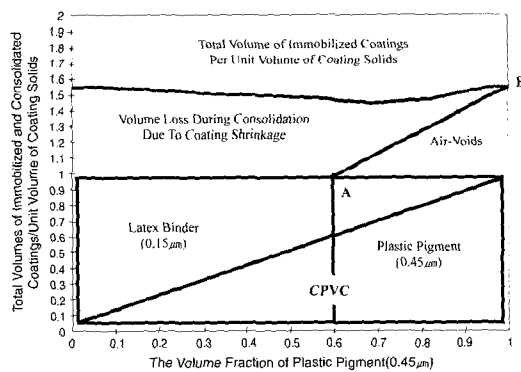
$$X(\text{plastic pigment}) \text{ at the CPVC} = 0.6$$

$$X(\text{latex}) = 0.4$$

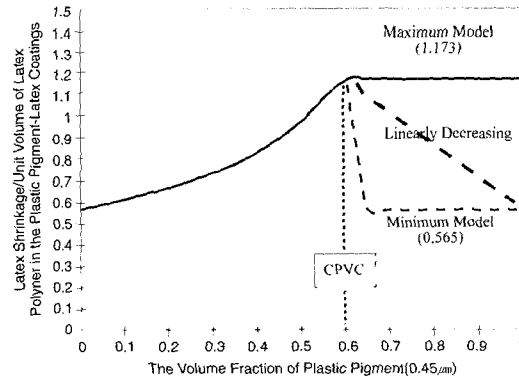
Because the plastic pigment particles do not have any capability to shrink, the total coating volume shrinkage must be taken up by the latex. The total coating volume shrinkage at the CPVC corresponds to the maximum shrinkage of a given latex per unit volume of latex for the coating system under study,  $\Delta v_{\text{max}}$ , and its value is calculated as follows:

$$\Delta v_{\text{max}}(\text{latex shrinkage}) = 0.469/0.4 = 1.173$$

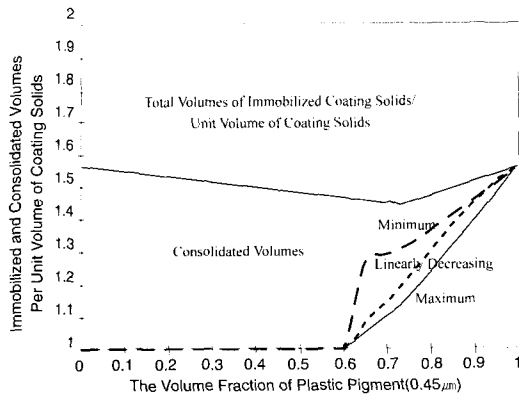
On the other hand, the *minimum* latex shrinkage corresponds to the shrinkage of pure latex films, and its value is:



**Fig. 4.** The schematics for the extent of the volume loss during consolidation per unit volume of coating solids throughout the whole plastic pigment volume concentrations and the air-voids which would be contained in the coatings above the CPVC upon the consolidation



**Fig. 5.** The extent of latex shrinkage per unit volume of latex polymer as a function of plastic pigment volume concentrations up to the CPVC, along with three models of Maximum, Minimum, and Linearly Decreasing Latex Shrinkage above the CPVC



**Fig. 6. The immobilized and consolidated volumes per unit volume of coating solids above the CPVC calculated based on three proposed approaches: Maximum latex shrinkage ( $\Delta v_{\max}=1.173$ ), Minimum latex shrinkage ( $\Delta v_{\min}=0.565$ ), and Average latex shrinkage, ( $\Delta v_{\text{linearly decreasing}}=1.173-(1.173-0.565) \times ((X(\text{plastic pigment}-\text{CPVC})/(1-\text{CPVC}))$ ), as shown in Figure 5**

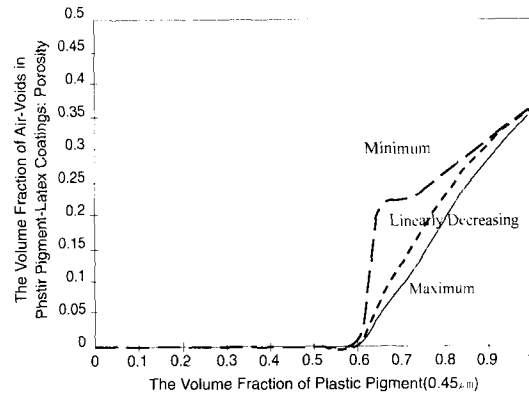
$\Delta V$ (total coating volume shrinkage) at the zero plastic pigment =  $V(\text{immobilized latex}) - V(\text{latex film})$   
 $= 1.565 - 1 = 0.565$

$$\Delta v_{\min}(\text{latex shrinkage}) = 0.565/1 = 0.565$$

Figure 5 shows the increasing extent of latex shrinkage per unit volume of latex polymer as a function of plastic pigment volume fractions up to the CPVC, along with three proposed models of Maximum, Minimum, and Linearly Decreasing Latex Shrinkage above the CPVC. It is interesting to see how the extent of latex film shrinkage changes with the pigment volume concentrations below and above the CPVC.

Figure 6 shows the immobilized and consolidated volumes per unit volume of coating solids above the CPVC calculated based on the above-discussed three latex shrinkage models: Maximum latex shrinkage ( $\Delta v_{\max}=1.173$ ), Minimum latex shrinkage ( $\Delta v_{\min}=0.565$ ), and Average latex shrinkage ( $\Delta v_{\text{linearly decreasing}}=1.173-(1.173-0.565) \times (1-\text{CPVC})$ ), as shown in Figure 5. Figure 6 has been constructed as follows:

$V(\text{consolidated coating volume})$  at  $X(\text{plastic pig-$



**Fig. 7. The calculated porosity values of the model coatings above the CPVC as a function of plastic pigment volume fractions**

ment) above the CPVC

$$= V(\text{immobilized coating volume}) - (1-X(\text{plastic pigment})) \times \Delta v_{\max}, \Delta v_{\min}, \text{ or } \Delta v_{\text{linearly decreasing}}$$

The volume fraction of air-voids contained in the dry coatings above the CPVC, which is the coating porosity, has been obtained by dividing the differences (total air-void volumes) between the consolidated coating volumes and the unit volume of coating solids by the consolidated coating volumes shown in Figure 6. The calculated porosity values of the model coatings above the CPVC are shown against the volume fraction of plastic pigment in Figure 7. These calculated porosity will be later compared with the experimental porosity data in the Experimental Section.

## The Number of Pores and Pore Size

To characterize the structure of coatings, the number of pores and pore size are needed in addition to coating porosity. We have attempted to calculate the number of pores and the average equivalent spherical pore diameters in the plastic pigment-latex binder coatings for optical properties as well as the average hydraulic circular diameters for flow properties such as air permeability and capillary penetration through the coat-

ings in the z-direction. In order to estimate the number of pores in the plastic pigment-latex coatings, we had to first estimate how many pores would be associated with a single plastic pigment particle in the coatings. Although the average dense random packing volume fraction of uniform spheres was experimentally determined (7, 14, 17, 19, 20), its value(0.639) agrees very well with the average value(0.632) between the cubic packing(0.5236) and the closest(tetrahedral or hexagonal and pyramidal or face-centered cubic) packing(0.7405), suggesting that the number of pores and the average pore volume/size in the dense random packing would be intermediate between those of the cubic and closest packings (21). For this reason, the number of pores associated with a single sphere and the average pore volume/size in the cubic and closest packings (22) have been first reviewed, then the number of pores in the dense random packing has been assumed to be the average of the two values. Table 1

shows the packing and void volume fractions of uniform spheres, the number of unit voids per sphere, the unit void volumes associated with a single sphere and the diameters of spheres to fit into unit voids, the average equivalent spherical pore diameters, and the average hydraulic circular diameters with respect to the different packing types.

Based on the above assumption that there are two unit voids associated with each sphere in the dense random packing of uniform spheres, as reviewed in Table 1, we can estimate the average equivalent spherical diameter of the pores in the coating made with a plastic pigment of  $0.45\mu\text{m}$  in diameter in the absence of latex binders. It is estimated to be  $0.30\mu\text{m}$  by using the value of  $0.66D$  shown in Table 1. This value is a little larger than the value reported by Alinec and Lepoutre (2). As shown in Table 2, they reported that the average porosity and void diameter of plastic pigment coatings were 0.331 and  $0.586D$ , respectively,

**Table 1. Characteristics of the structure of uniform sphere coatings with respect to different packing types (packing and void volume fractions, the number of unit voids/unit void volumes/diameter of a sphere to fit into unit void, average equivalent spherical void diameter, and average hydraulic circular diameter)**

Packing Type	Packing Volume/Unit Volume of Uniform Sphere Coatings	Void Volume /Unit Volume of Uniform Sphere Coatings (Porosity)	Number of Unit Voids /Sphere of Diameter D	Unit Void Number & Volumes /Sphere of Diameter D (Diameter of a Sphere to Fit into Unit Void) (22)	Number of Spheres/Unit Volume of Coatings( $\text{cm}^3$ ) and Average Equivalent Spherical void Diameter	Average Hydraulic Circular Diameter (3, 22)
Cubic	0.5236	0.4764	1	$1 \times 0.4764D^3$ (0.732D)	$1.0 \times 10^{12} / D^3$ 0.97D	0.607D
Dense Random	0.639	0.361	2	$1/2 \times 0.4764 D^3$ (0.732D) $1 \times 0.037D^3$ (0.225D) $1/2 \times 0.186 D^3$ (0.414D)	$1.221 \times 10^{12} / D^3$ 0.66D	0.377D
Closest	0.7409	0.2591	3	$2 \times 0.037 D^3$ (0.225D) $1 \times 0.186 D^3$ (0.414D)	$1.416 \times 10^{12} / D^3$ 0.49D	0.233D

**Table 2. Characteristics of plastic pigment coatings by Alinec and Lepoutre (2)**

Particle Diameter ( $\mu\text{m}$ )	0.10	0.20	0.31	0.37	0.50	1.01	Average
Porosity	0.328	0.330	0.329	0.319	0.331	0.350	0.331
Void Diameter ( $\mu\text{m}$ )	0.08	0.11	0.14	0.20	0.30	0.58	
D(Void)/D(Particle)	0.8	0.55	0.452	0.541	0.6	0.574	0.586D

**Table 3. The critical packing fractions of polystyrene latexes by Hoy and Peterson (4)**

Particle Diameter ( $\mu\text{m}$ )	0.18	0.215	0.28	0.43	Average
Critical Packing	0.629	0.663	0.644	0.644	0.645
Porosity	0.371	0.337	0.356	0.356	0.355

for a series of plastic pigments having a wide range of particle sizes from  $0.1\mu\text{m}$  to  $1.01\mu\text{m}$ . In view of the fact that their average porosity value is a little smaller than that of the dense random packing, it is not surprising that their average void diameter is intermediate between those of the dense random and closest packings:  $0.66D$  and  $0.49D$ , respectively. Eski and Bousfield (18) reported that the peak void diameter of their model computational particle packings was  $0.61D$  with a void fraction of  $0.4$  for a series of spheres having the particle diameters of  $0.1\mu\text{m}$  to  $0.5\mu\text{m}$ . As shown in Table 3, Hoy and Peterson (4) determined the average critical packing and porosity for a series of monodisperse polystyrene latexes ranging from  $0.18\mu\text{m}$  to  $0.43\mu\text{m}$  to be  $0.645$  and  $0.355$ , respectively. Rennel et al. (5) reported that the porosity of the coating layers based on a plastic pigment of  $0.2\mu\text{m}$  was about  $0.3$ . Toivakka et al. (6) reported that the packing fractions of the plastic pigment coatings ranged from  $0.62$  to  $0.65$ , and noted that these packing fractions increased to  $0.70$  to  $0.73$ , respectively, with electrolyte addition. Their void fractions of plastic pigment coatings ranged from  $0.27$  to  $0.38$ . It appears that the plastic pigment coatings consolidate to the packing volume fractions ranging from the loose random packing( $0.589$ ) (7) to the closest packing( $0.7409$ ) with the dense random packing( $0.639$ ) (7) as a most-likely average value, depending on both the colloidal properties of plastic pigments and coating conditions.

In order to estimate the average pore sizes of the model plastic pigment-latex binder coatings above the CPVC, two additional assumptions have been proposed:(1) Plastic pigment particles would maintain the dense random packing arrangement in a combined

phase of binder polymer and voids even after the consolidation and (2) The combined binder polymer and void phase domains subdivided by the plastic pigment particles(two per a plastic pigment particle) would have single voids rather than multiple voids. With these assumptions, we have calculated the number of pores per unit volume of coatings( $\text{cm}^3$ ) and the average equivalent spherical pore diameters of the plastic pigment( $0.45\mu\text{m}$ )-latex binder( $0.15\mu\text{m}$ ) coatings as a function of plastic pigment volume fractions based on the above-described three latex shrinkage models (Maximum, Minimum, and Average Latex Shrinkage Models), as follows:

The number of plastic pigment particles ( $0.45\mu\text{m}$ ) per unit volume of coatings ( $\text{cm}^3$ ):

$$N(\text{plastic pigment}) = \phi(\text{plastic pigment particles}) / [\pi \times (0.45 \times 10^{-4})^3 / 6]$$

$$\phi(\text{plastic pigment particles}) = [1 - \phi(\text{void})] \times X(\text{plastic pigment})$$

The number of pores:  $N(\text{pores}) = 2 \times N(\text{plastic pigment})$

$$N(\text{pores}) = 2 \times \phi(\text{plastic pigment particles}) / [\pi \times (0.45 \times 10^{-4})^3 / 6]$$

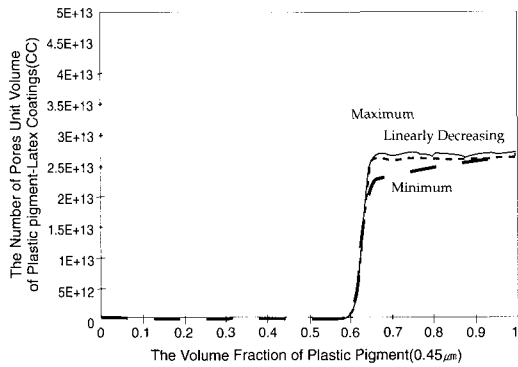
The average equivalent spherical pore diameter:

$$D(\text{e.s.p.d.}) = 0.45 \times \{[\phi(\text{void}) / N(\text{pores})] / (\pi / 6)\}^{1/3} \mu\text{m}$$

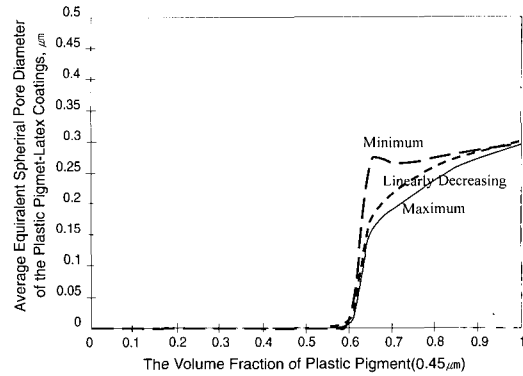
where  $\phi(\text{plastic pigment particles})$ ,  $\phi(\text{void})$ , and  $X(\text{plastic pigment})$  are the volume fraction of plastic pigment particles, the volume fraction of voids(coating porosity), and the volume fraction of plastic pigment in the plastic pigment-latex binder coatings, respectively.

Figures 8 and 9 show the number of the pores per

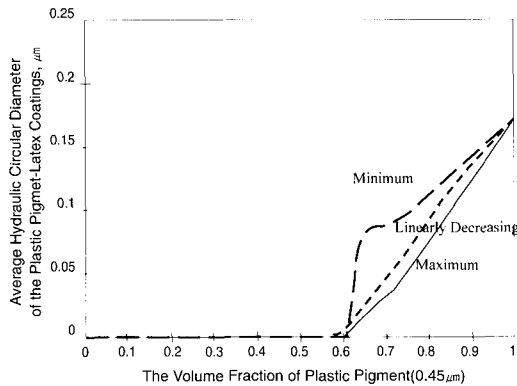




**Fig. 8.** The number of the pores per unit volume (cm<sup>3</sup>) of the plastic pigment-latex coatings as a function of plastic pigment volume fractions



**Fig. 9.** The average equivalent spherical pore diameters as a function of plastic pigment volume fractions



**Fig. 10.** The average hydraulic circular diameters calculated by the following equation:  $D_h = 2/3 [ \phi (void)/(1- \phi (void))] D$ , where  $D_h$  is the hydraulic circular diameter in  $\mu m$ ,  $\phi (void)$  is the void fraction (porosity), and  $D$  is the particle diameter in  $\mu m$

unit volume(cm<sup>3</sup>) of the coatings and the average equivalent spherical pore diameters, respectively. Figure 10 shows the average hydraulic circular diameters calculated by the following equation (3, 22):

$$D_h = 2/3 [ \phi (void)/(1- \phi (void))] D$$

where  $D_h$  is the hydraulic circular diameter in  $\mu m$ ,  $\phi (void)$  is the void fraction (porosity), and  $D$  is the particle diameter in  $\mu m$ .

## EXPERIMENTAL

The coating formulations were made with a plastic pigment of 0.45  $\mu m$  in diameter and a S/B latex binder of 0.15  $\mu m$  in diameter at different pigment volume concentrations (0 to 99%) at 45% volume solids, and then they were applied onto polyester films of uniform thickness by using a wire-wound rod (No. 30 Meyer Rod) and dried either at room temperature or at 100 °C in a circulating oven. The polyester film of uniform thickness was selected as an ideal substrate to study the immobilization and consolidation of model coatings in the absence of various uncertainties caused by paper substrates, such as coating penetration, dewatering, binder migration into the substrates, etc. The coat weights were in the range of 16 to 18 g/m<sup>2</sup>. Table

**Table 4.** The characteristics of plastic pigment and latex binder used in the present study

Latex Type	Composition	P.S., $\mu m$	MFFT, °C	Tg, °C	Polymer Density
Plastic Pigment	Carboxylated PS	0.45	>100	106	1.05
Latex Binder	Carboxylated S/B	0.15	7	7	1

4 shows the characteristics of the plastic pigment and latex binder used for the present study. All concentrations and ratios used in the present study were based on volume concentrations rather than on weight. Their opacity and gloss were measured as a function of the pigment volume fractions. A due caution was paid in measuring the gloss of transparent films and coatings on polyester films below the CPVC, because the light transmitted through the transparent films and coatings was specularly reflected at their interface with polyester films and increased the overall gloss by about 10-20 points. Therefore, in this study, latex films and coatings below the CPVC were made onto pre-coated opaque coatings on polyester films. Various methods, including the oil absorption method (2, 23), mercury intrusion porosimetry (3), and an electron microscopy method (6), were considered to measure the porosity of model coatings, but it was found that a simple method of determining coat weights and coating thickness on the polyester films was very reproducible and reliable, as previously reported by Groves, Pension, and Ruggles (23). This simple method was possible because commercially available polyester films are very uniform in thickness and weight. The weight was measured by an analytical balance and the coating thickness determined by a motorized micrometer. It has been found that three or more 1.5 x 1.5 inch squares of coated polyester films were sufficient to give reproducible porosity values.

The effect of plastic pigment particle size on the gloss, opacity and porosity of model coatings at 0.7 volume fraction of plastic pigments was also studied. The model coating formulations at 45% volume solids were applied onto commercial sheet offset coated papers using No. 16 Meyer Rod and dried in a circulating oven at 100°C for one minute. Both 20° and 75° TAPPI coating and ink gloss measurements were made on these model coatings as a function of both plastic pigment volume fractions and plastic pigment particle sizes, and their printability was evaluated on a flat bed Vandercook Proofing Press (24, 25, 26).

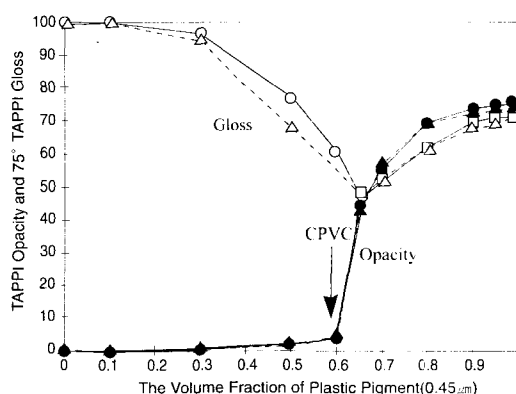
Since latex binders are required to deform and flow more with increasing pigment volume concentration, it has been speculated that the minimum film formation temperatures(MFFT's) of latexes may not be suffi-

cient to characterize their pigment binding capabilities. For this reason, it was proposed to determine the minimum crack-free temperatures(MCFT's) of pigmented latex coatings as a function of pigment volume concentration. The conventional "MFFT Apparatus" was used to determine the MCFT's by locating the temperatures where a crack starts on the metal plate with an equilibrated temperature gradient.

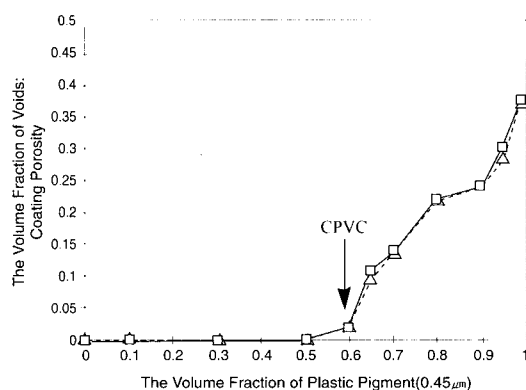
Transmission electron, scanning electron, and atomic force microscopes were used to examine the wet state of the dispersions of plastic pigment and latex binder particles, the surfaces of the model coatings, their internal structure, and their topography.

## RESULTS AND DISCUSSION

Figure 11 shows the TAPPI opacity and 75° TAPPI gloss of plastic pigment(0.45 $\mu$ m)-latex binder(0.15 $\mu$ m) coatings on polyester films dried at room temperature and in a circulating oven at 100°C for a minute, respectively, as a function of plastic pigment volume concentrations(PVC's). The TAPPI opacity values reported were corrected for the opacity of polyester films, but not for small coat weight differences. The



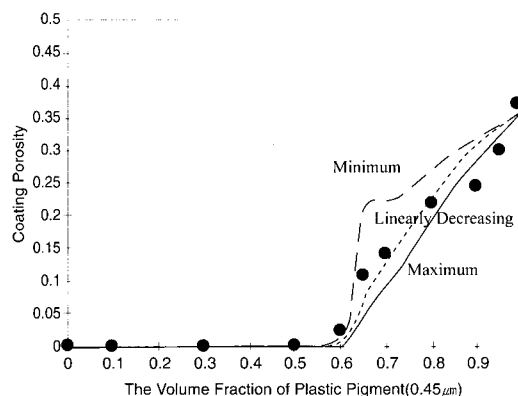
**Fig. 11. The TAPPI opacity and 75° TAPPI gloss of plastic pigment (0.45 $\mu$ m)/latex binder (0.15 $\mu$ m) coatings on polyester films dried at room temperature (open and filled  $\Delta$ ) and 100°C in a circulating oven for a minute (open and filled  $\circ$ ), respectively, as a function of plastic pigment volume fractions (PVC's)**



**Fig. 12.** The experimental porosity of the plastic pigment ( $0.45\ \mu\text{m}$ )-latex binder ( $0.15\ \mu\text{m}$ ) model coatings on polyester films dried at room temperature ( $\Delta$ ) and  $100^\circ\text{C}$  in a circulating oven for a minute ( $O$ ), respectively, as a function of plastic pigment volume fractions (PVC's)

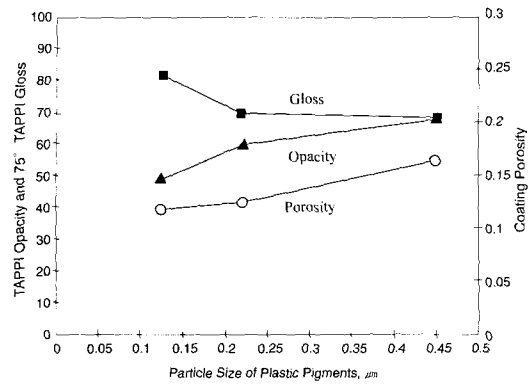
optical properties such as opacity and gloss change abruptly in a narrow range of the pigment volume concentrations at or near the CPVC, as shown in Figure 11. Although these narrow pigment volume concentrations corresponding to the so-called critical pigment volume concentrations (CPVC's) (1) can be determined from various structure-property-pigment concentration relationships, the CPVC determined by the opacity vs. PVC curve for the current model coating system best fits the definition of CPVC where no air-void is yet present in the coating, but air-voids start to appear slightly above that critical PVC. Since the plastic pigment and latex used in this study had nearly equal refractive indexes (1.55-1.59), the opacity of the current model coatings was very sensitive to the presence of air-voids. For this reason, the opacity even without the coat weight corrections was good enough to determine the CPVC's of model coatings very accurately. It would be interesting to point out that this study has again clearly shown that the coating gloss decreases with increasing pigment concentration up to the CPVC, as well known to paint specialists, then the gloss increases, as the pigment concentration further increases above the CPVC, as well known to paper coating specialists.

Figure 12 shows the experimental porosity data for



**Fig. 13.** The comparison between the experimental porosity data (dried at  $100^\circ\text{C}$  in a circulating oven for a minute (closed  $O$ )) and the theoretically calculated porosity values based on three proposed models shown in Figure 7

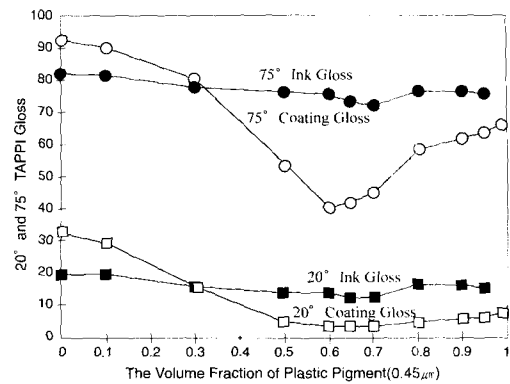
the plastic pigment ( $0.45\ \mu\text{m}$ )-latex binder ( $0.15\ \mu\text{m}$ ) model coatings on polyester films dried at room temperature and in a circulating oven at  $100^\circ\text{C}$  for a minute, respectively, as a function of plastic pigment volume fractions. The CPVC determined by the opacity vs. PVC curve coincides very well with the CPVC by the porosity vs. PVC curve. Both values are 0.6. In Figure 13, the experimental porosity data (coatings dried at  $100^\circ\text{C}$  only) are compared with the theoretically calculated porosity values based on the three proposed models shown in Figure 7. It appears that both the linearly decreasing and minimum latex shrinkage models fit the experimental porosity data better than the maximum shrinkage model, as shown in Figure 13. This finding suggests that latex binders can shrink to their maximum extent as long as they are able to maintain the continuous polymer phase in the coatings, but as soon as they become discontinuous, that is, at pigment volume concentrations above the CPVC, they would lose their maximum shrinking capability. Therefore, above the CPVC, latex binders may tend to shrink to intermediate values between the maximum and minimum latex shrinkage values. This finding is intuitively very reasonable because if latex binder particles can occlude all plastic pigment particles within themselves, then they can shrink globally



**Fig. 14.** The TAPPI opacity, 75° TAPPI gloss, and coating porosity of plastic pigment-latex ( $0.15\mu\text{m}$ ) model coatings at 0.7 volume fraction of plastic pigments on polyester films dried at  $100^\circ\text{C}$  for one minute as a function of plastic pigment particle size

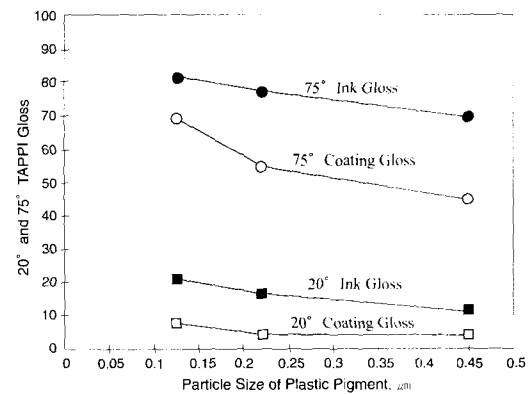
to their maximum shrinkage, however, if they are disconnected, then they can only shrink locally. The minimum latex shrinkage model is very close to "No Interference - Microdomain Concept" proposed by Lepoutre and Rezanowich (27) except that the minimum latex shrinkage model is only applied to the consolidation after the immobilization. In other words, the model does not influence the coating immobilization behavior. However, both approaches are very applicable to the coatings at very high pigment concentrations, that is, at very low latex binder concentrations.

Figure 14 shows the effect of plastic pigment particle size on the coating opacity, gloss and porosity of plastic pigment-latex ( $0.15\mu\text{m}$ ) model coatings containing the volume fraction of plastic pigment at 0.7 on polyester films dried at  $100^\circ\text{C}$ . As can be seen from Figure 14, the opacity and porosity of model coatings increase with increasing plastic pigment particle size, but their gloss decreases. Although the increase in coating opacity and the decrease in coating gloss with increasing plastic pigment particle size were somewhat expected, the decrease in coating porosity with decreasing plastic pigment particle size was surprising. This finding suggests that the smaller particle size plastic pigment particles consolidate to the tighter coatings under the same conditions.

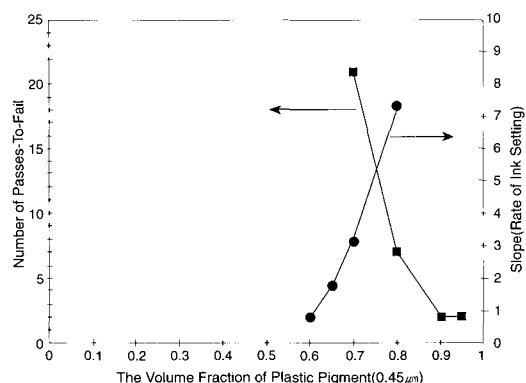


**Fig. 15.** The 20° and 75° TAPPI gloss of the uncalendered model coatings on a commercial sheet offset coated paper and quick-set cyan ink films printed onto the same model coatings as a function of plastic pigment volume fractions (PVC's)

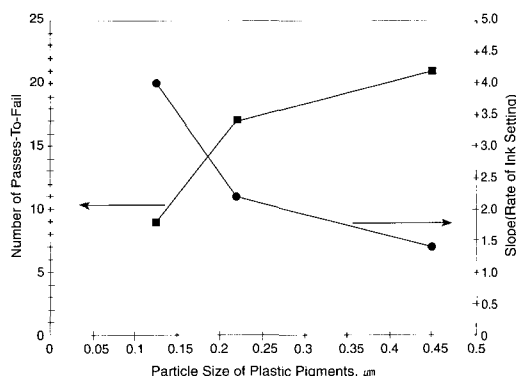
Figure 15 shows the 20° and 75° TAPPI gloss of the uncalendered model coatings applied onto commercial sheet offset coated papers dried at  $100^\circ\text{C}$  and the quick-set cyan ink films printed onto the same model coatings. It is interesting to note that the 20° and 75° ink gloss values of the model coatings on a commercial sheet offset paper are affected by both their coating gloss and porosity, as shown in Figure



**Fig. 16.** The effect of plastic pigment particle size on the 20° and 75° TAPPI gloss of plastic pigment-latex ( $0.15\mu\text{m}$ ) model coatings at 0.7 volume fraction of plastic pigments on a commercial sheet offset coated paper and quick-set cyan ink films printed onto the same model coatings



**Fig. 17.** Number of passes-to-fail and slope (rate of ink setting) of the model coatings on a commercial sheet offset coated paper as a function of plastic pigment volume fractions (PVC's)



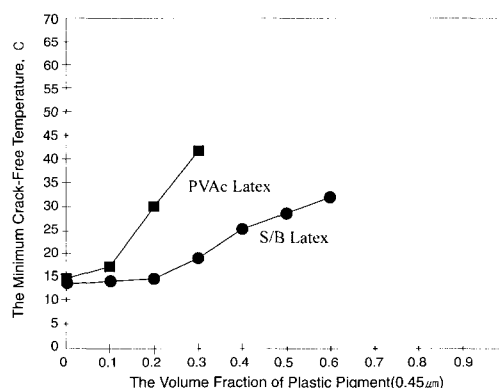
**Fig. 18.** Number of passes-to-fail and slope (rate of ink setting) of the model coatings at 0.7 volume fraction of plastic pigments on a commercial sheet offset coated paper as a function of plastic pigment particle size

15: the higher the coating gloss, the higher the ink gloss, but the higher the coating porosity, the lower the ink gloss. This finding indicates that the ink gloss is affected by both the penetration and leveling of ink. Figure 16 shows the effect of plastic pigment particle size on the 20° and 75° ink gloss of the uncalendered model coatings on a commercial sheet offset paper. Figure 16 again clearly shows that the ink gloss is a function of both coating gloss and porosity, as observed in Figure 15: the higher coating gloss and the lower coating porosity, the higher ink gloss.

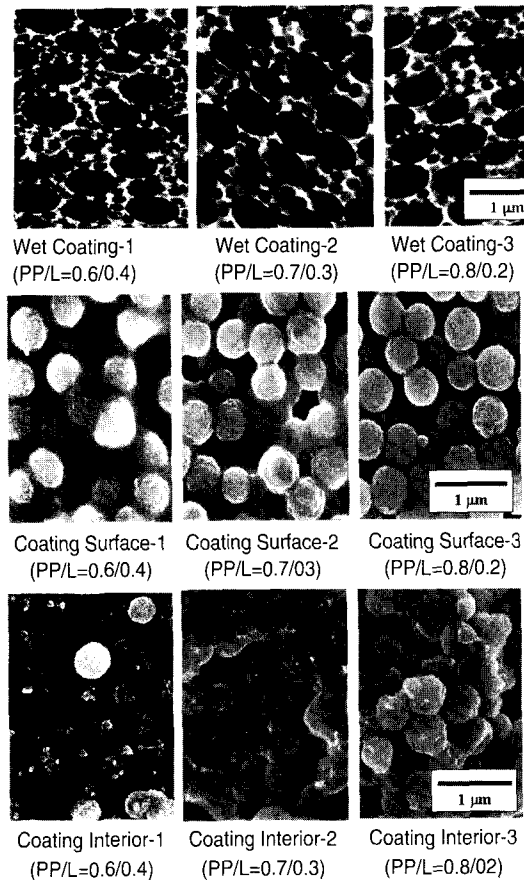
The printability of the model coatings on a commercial sheet offset coated paper was evaluated on a flat bed Vandercook Proofing Press (24, 25, 26) in terms of the number of passes-to-fail and the rate of ink setting as a function of both plastic pigment volume fractions and plastic pigment particle sizes. Figures 17 and 18 show the number of passes-to-fail and slope(rate of ink setting) as a function of plastic pigment volume fractions and plastic pigment particle sizes, respectively. We can see that the number of passes-to-fail decreases and the rate of ink setting increases with increasing plastic pigment volume concentration above the CPVC, as shown in Figure 17. However, it is interesting to note that the number of passes-to-fail increases and the rate of ink setting decreases with increasing plastic pigment particle size,

as shown in Figure 18. These findings suggest that the printability of model coatings is affected by both their coating porosity and pore sizes: for the model coatings made with the same binder level, the smaller the pore size, the quicker the ink setting and the less the number of passes-to-fail.

Figure 19 shows the minimum crack-free temperatures(MCFT's) of plastic pigment-latex binder coat-



**Fig. 19.** The minimum crack-free temperatures (MCFT's) of plastic pigment (0.45µm)-latex binder coatings as a function of plastic pigment volume fractions for two common paper coating latexes: S/B and PVAc latexes

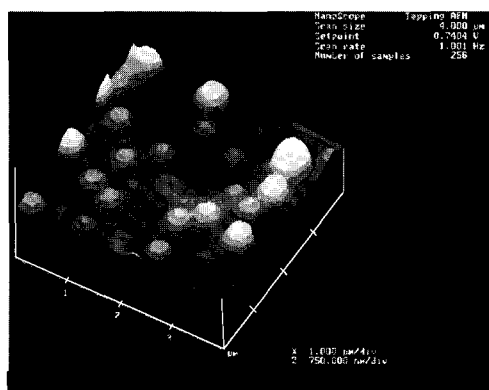


**Fig. 20. TEM's showing the wet state of plastic pigment-latex dispersions (Wet Coating-1 (PP/L=0.6/0.4), 2 (0.7/0.3), and 3 (0.8/0.2)), SEM's showing the surfaces of the plastic pigment-latex coatings (Coating Surface-1, 2, and 3), and SEM's showing their fractured coating structures (Coating Interior-1, 2, and 3)**

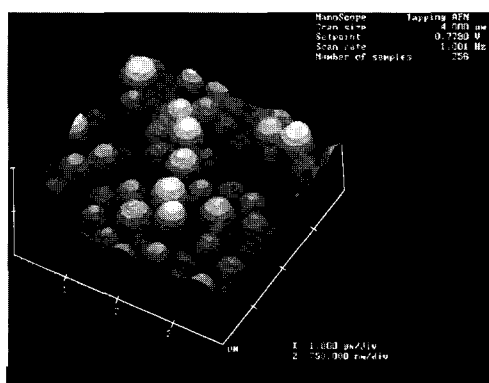
ings as a function of plastic pigment volume concentration for two common paper coating latexes: S/B and PVAc latexes. It is not surprising that the MCFT's of S/B and PVAc latexes increase with increasing pigment volume concentration, as shown in Figure 19, because they have to deform to a greater extent when pigmented than for their neat film formation. What is more interesting is that although both latexes have the same MFFT's, one latex (PVAc latex) requires higher MCFT's than the other latex (S/B latex). This finding suggests that the minimum film formation temperatures (MFFT's) of latexes alone may not be sufficient

to predict their thermal behaviors as coating binders during drying, depending on the pigment volume concentration. For this reason, the minimum crack-free temperatures (MCFT's) of latexes may be more useful for coating applications so that they are recommended to be used in addition to their MFFT's. This subject will be more discussed in terms of the effect of drying temperatures on paper coating structure and the role of latex binders in the consolidation and structure development of paper coatings in the future.

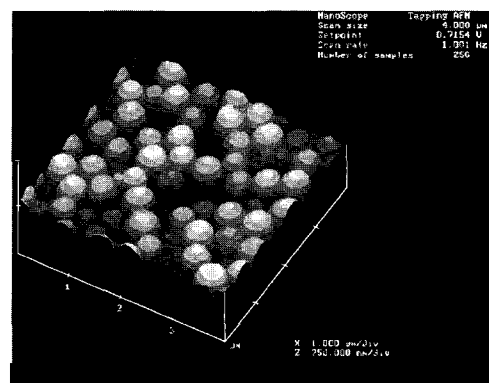
Figure 20 shows the transmission electron micrographs (TEM's) of the microtomed cross-sections ( $\sim 0.1 \mu\text{m}$ ) of the dispersions of plastic pigment ( $0.45 \mu\text{m}$ ) and latex ( $0.15 \mu\text{m}$ ) particles having the volume fractions of plastic pigment, 0.6, 0.7, and 0.8, respectively, at 45% volume solids rapidly frozen in the liquid propane ( $-180^\circ\text{C}$ ), the scanning electron micrographs (SEM's) of their dried model coating surfaces, and the SEM's of their freeze-fractured coating surfaces. The TEM's of the cross-sections of rapidly-frozen dispersions are an excellent way of looking at the state of wet dispersions, because by quickly freezing the dispersions we can preserve the actual state of dispersions. Wet Coating-1, 2, and 3 indicate that the model coating particles are uniformly dispersed and that no coagulation or flocculation is present in the dispersions. Please note that the cross-sections of plastic pigment particles appeared as ellipsoidal because they were elongated during microtoming. The SEM's of the model coating surfaces (Coating Surface-1, 2, and 3) provide information on coating surface porosity and make-up (the distribution of plastic pigment particles and the placement of latex polymer films on the coating surface). The SEM's of the freeze-fractured coating surfaces (Coating Interior-1, 2, and 3) show the internal coating porosity very clearly. No porosity is seen in the SEM of Coating Interior-1 at the volume fraction of plastic pigment of 0.6 corresponding to the CPVC. All these findings appear to be very similar to the immobilization and consolidation models depicted in Figure 1. Figure 21 shows the atomic force micrographs (AFM's) of the surfaces of the model coatings which are the same as the Coating Surface-1, 2, and 3 of Figure 20. These AFM's exhibit more clearly coating surface structure and composition. The topography



AFM-1 (PP/L=0.6/0.4)



AFM-2 (PP/L=0.7/0.3)



AFM-3 (PP/L=0.8/0.2)

**Fig. 21. Atomic Force Micrographs showing the surface of plastic pigment-latex coatings: AFM-1 (PP/L=0.6/0.4), AFM-2 (PP/L=0.7/0.3), and AFM-3 (PP/L=0.8/0.2)**

of the model coatings shown in Figure 21 agrees very well with their coating gloss and their SEM's as well.

The theoretical considerations used in this study to

calculate the number of pores per unit volume of model coatings (Figure 8), the average equivalent spherical pore diameters of the model coatings (Figure 9), and the average hydraulic circular diameters of the model coatings (Figure 10) should be further critically reviewed and experimentally tested in the future. If the structure of model coatings can be theoretically characterized and better understood, then we can attempt to theoretically characterize the more complex systems such as latex-bound clay and calcium carbonate coatings in the future.

## SUMMARY AND CONCLUSIONS

Part of the Theoretical Considerations:

1. The immobilized volume of model coatings has been predicted by the dense random packing fraction of the binary spheres of different particle sizes, and then the total immobilized volumes per unit volume of coating solids have been calculated.
2. The maximum latex shrinkage has been calculated from the CPVC's on the assumption that only latex binders would be responsible for the total coating volume shrinkage at the CPVC's, since plastic pigment particles are not capable of shrinking.
3. Three latex shrinkage models, Maximum, Minimum, and Linearly Decreasing Latex Shrinkage, have been proposed to calculate the porosity of the model coatings above the CPVC's, then the total air-void volumes have been calculated by combining the total immobilized coating volumes with three proposed shrinkage models.
4. The number of plastic pigment particles per unit volume of coatings have been calculated from three theoretically calculated porosity values as a function of plastic pigment volume fractions, and then the number of pores has been calculated by multiplying the number of plastic pigment particles by 2, based on the assumption that the number of pores per sphere in the dense random packing is 2.
5. The average equivalent spherical pore diameters have been calculated from the number of pores and porosity values. This information will be useful for

the future study on the light-scattering of the model coatings.

6. The average hydraulic circular diameters of model coatings have been also calculated. This information will be useful for studying the flow properties such as capillary penetration through the model coatings.

### Experimental Part:

1. It has been found that the CPVC's of model coatings on polyester films can be easily determined by the coating opacity vs. PVC curves very accurately.
2. It has been discovered that the coat weight and thickness of coatings on polyester films can be easily determined by using a cutter, an analytical balance, and a micrometer.
3. The CPVC's can be determined either by the opacity vs. PVC curves or by the coating porosity vs. PVC curves. In the present study, the CPVC was found to be 0.6.
4. The optical properties of the model coatings such as opacity and gloss are strongly dependent on their critical pigment volume concentrations (CPVC's): the opacity of the model coatings suddenly takes off at the CPVC's, while the coating gloss becomes the minimum near the CPVC's, below which the gloss increases with increasing latex binder level and above which it increases with decreasing latex binder level.
5. The minimum and maximum latex shrinkage values have been estimated to be 0.566 and 1.173, respectively.
6. The comparison between the experimental and theoretical porosity values has shown that the intermediate value between the maximum and minimum latex shrinkage best fits the experimental porosity data, suggesting that the latex binder shrinkage is global below and up to the CPVC, but becomes local below the CPVC.
7. It has been found that the ink gloss of the uncalendered model coatings applied onto commercial sheet offset coated papers is affected by both the coating gloss and porosity: the higher the coating gloss, the higher the ink gloss, but the higher the coating porosity, the lower the ink gloss.
8. The printability of model coatings has shown to be strongly affected by both the volume concentration and particle size of plastic pigments: the number of passes-to-fail decreases and the rate of ink setting increases with increasing plastic pigment volume concentration above the CPVC, while the number of passes-to-fail increases and the rate of ink setting decreases with increasing plastic pigment particle size.
9. The minimum crack-free temperatures(MCFT's) of latex binders as a function of plastic pigment volume concentrations have been considered to be very useful for understanding the role of latex binders in the consolidation and structure development of paper coatings so that it has been proposed to determine the MCFT's in addition to the MFFT's for coating applications.
10. The wet state of model coating dispersions and their consolidated coating structure(surface structure, internal structure, and surface topography) examined by both electron and atomic force microscopes have reinforced our proposed immobilization and consolidation models shown in Figure 1.

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