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The Critical Pigment Volume Concentration Concept for Paper Coatings:
II. Latex-Bound Clay, Ground Calcium Carbonate, and Clay-Carbonate Pigment Coatings

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ABSTRACT

A previous study on the model coatings based on latex-bound plastic pigment coatings (1) has been extended to latex-bound No. 1 clay, ultra-fine ground calcium carbonate (UFGCC), and clay-carbonate pigment mixture coatings, which are being widely used in the paper industry. The latex binder used was a good film-forming, monodisperse S/B latex of 0.15㎛. No. 1 clay was representative of plate-like pigment particles, whereas UFGCC was of somewhat rounded rhombohedral pigment particles. Both of them had negatively skewed triangular particle size distributions having the mean particle sizes of 0.7㎛ and 0.6㎛, respectively. Their packing volumes were found to be 62.5% and 65.7%, respectively, while their critical pigment volume concentrations (CPVC's) were determined to be 52.7% and 50.5% (average of 45% caused by the incompatibility and 55.9% extrapolated) by coating porosity, respectively. Each pigment/latex coating system has shown its unique relationship between coating properties and pigment concentrations, especially above its CPVC. Notably, the clay/latex coating system has shown higher coating porosity than the UFGCC/latex system at high pigment concentrations above their respective CPVC's. It was also found that their coating porosity and gloss were inter-related to each other above the CPVC's, as predicted by the theory. More interestingly, the blends of these two pigments have shown unique rheological and coating properties which may explain why such pigment blends are widely used in the industry. These findings have suggested that the unique structure of clay coatings and the unique high-shear rheology of ground calcium carbonate coatings can be judiciously combined to achieve superior coatings. Importantly, the low-shear viscosity of the blends was indicative of their unique packing and coating structure, whereas their high-shear rheology was represented by a common mixing rule, i.e., a viscosity-averaging. Transmission and scanning electron and atomic force microscopes were used to probe the state of pigment / latex dispersions, coating surfaces, freeze-fractured coating cross-sections, and coating surface topography. These microscopic studies complemented the above observations. In addition, the ratio, **R**, of CPVC/ ϕ_p (Pigment Packing Volume) has been proposed as a measure of the binder efficiency for a given pigment or pigment mixtures or as a measure of binder-pigment interactions. Also, a mathematical model has been proposed to estimate the

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packing volumes of clay and ground calcium carbonate pigments with their respective particle size distributions. As well known in the particle packing, the narrower the particle size distributions, the lower the packing volumes and the greater the coating porosity, regardless of particle shapes.

INTRODUCTION

Since the critical pigment volume concentration concept for paper coatings was studied based on model coatings using plastic pigments and latex binders (1), this study has been extended to latex-bound clay, ground calcium carbonate, and clay-carbonate pigment mixture coatings. The experimental methods used in the previous study were used again for the present study. Coatings were made on polyester films as a function of pigment concentrations, the coating porosity was determined by a simple weight-thickness method, and the critical pigment volume concentrations (CPVC's) were determined graphically from the coating opacity, gloss, porosity vs. pigment concentration curves. Clay particles are plate-like particles so that they represent non-spherical particles whose packing is dependent on both the state of their dispersion and their orientations. Ground calcium carbonate particles are not perfectly spherical, but they are roughly symmetrical in all directions so that their packing is less dependent on their orientations, but significantly affected by the state of their dispersion. Additionally, the particle size distributions of both commercially available No. 1 clay and ultra-fine ground calcium carbonate (UFGCC) pigment particles used for the present study are broad so that their packing volumes are much larger than those of their narrow particle size counterparts (e.g., engineered pigments), that is, their coatings are more compact and less porous than those of their narrow particle size pigment counterparts. Furthermore, the blends of clay and ground calcium carbonate pigments are not only very important from their practical paper coating application's points of view, but also very interesting from their particle packing's points of view. For these reasons, their critical pigment volume concentrations have been studied and found to be somewhat different from those of the model coating systems studied previously (1). The viscosities of No. 1 clay, UFGCC, and the blends of No. 1 clay and UFGCC pigments at 75/25, 50/50, and 25/75 by weight, respectively, were also measured as a function of solids and shear rates to learn more about variations in their aggregate size and packing behaviors as a function of shear rates, and then predict their packing volumes at consolidation (2). The low-shear viscosities of the blends were correlated with their coating structure, especially coating porosity, with respect to those of No. 1 clay and UFGCC, while their high-shear viscosities decreased with increasing amount of UFGCC, thus resulting in an improved high-speed runnability. The state of pigment/latex dispersions, coating surfaces, freeze-fractured coating cross-sections, and coating surface topography were effectively investigated by the use of transmission and scanning electron and atomic force microscopes and the findings of these microscopic studies were in good agreement with their macroscopic properties such as rheological, optical and physical properties. Additionally, some attempts were made to define the binder efficiency for a given pigment or pigment mixtures by a ratio, **R**, of CPVC/ϕ_p (Pigment Packing Volume) and to estimate the packing volume fractions for clay and ground calcium carbonate pigments of known particle size distributions based on a mathematical model proposed by Lee (3).

THEORETICAL CONSIDERATIONS

The Critical Pigment Volume Concentration (CPVC)

The critical pigment volume concentration (CPVC) can be defined either as the transition point above or below which substantial differences in the appearance and behavior of a paint film will be encountered or as the point in a pigment-vehicle system at which just sufficient binder is present to completely fill the voids left between the pigment particles incorporated in the film after volatilization of all thinner (4, 5). In a previous study on the CPVC concept for paper coatings based on the model coatings (1), both definitions resulted in the nearly same points, that is, the CPVC's determined as the transition points by the measurements of coating opacity and gloss as a function of pigment concentrations were in very good agreement with the CPVC as the void-free point by the coating porosity vs. pigment concentration relationship (1), as shown in Figures 1 and 2. However, this good agreement may be somewhat unique to some coating systems such as the model coatings. As found in the present study on clay and ground calcium carbonate coatings, the transition and void-free points can be very different and sometimes very difficult to determine. In 1960, Weber (6) studied the effect of pigment binders (hydroxyethylated acid modified corn starch, corn white dextrin, and soy protein) on paper gloss, printed gloss, and oil absorption and defined their CPVC's as the transition points in paper gloss. The study showed that the transition and void-free points defining the CPVC's were either the same or different, depending on the type of the binders used. For this reason, there have been many attempts in paints to achieve mathematical methods to predict the void-free CPVC's. In 1972, Bierwagen (5) proposed a model which in mathematical form permitted the calculation of the CPVC of a paint from pigment properties. Using particle size distribution data corrected by oil absorption data, he calculated a random densest packing factor for the pigment plus adsorbed layer of resin based on an algorithm proposed by Lee (3) on particle packing. For paper coatings, it is expected that the CPVC's of paper pigment/latex coatings would be dependent on the random dense packing of pigment and latex particles, the pigment-latex interactions, the dispersion stability, latex/pigment particle size ratios, the film-forming properties of a latex or latex blends, the drying conditions, etc. No doubt that it is complex. However, the model coatings, such as plastic pigment and film-forming latex binder coatings, would be expected to be much simpler in understanding and analysis. If this is true, then we can analyze the data obtained in the previous study and get some insight into the relationship between

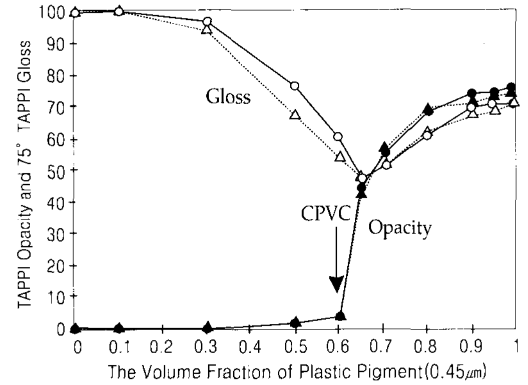


Fig. 1. The TAPPI opacity and 75° TAPPI gloss of plastic pigment(0.45㎛)/latex binder (0.15㎛) coatings on polyester films dried at room temperature(open and filled Δ) and 100℃ in a circulating oven for a minute(open and filled O), respectively, as a function of plastic pigment volume fractions(PVC's) (1).

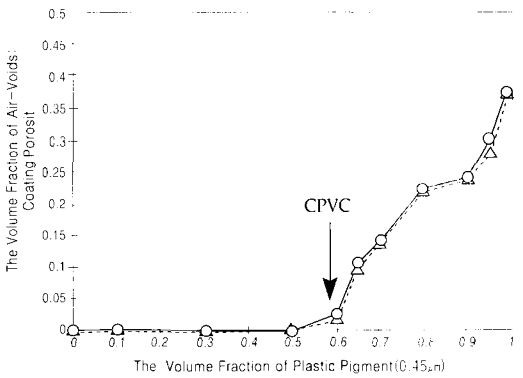


Fig. 2. The experimental porosity of the plastic pigment(0.45㎛)-latex binder(0.15㎛) model coatings on polyester films dried at room temperature(Δ) and 100℃ in a circulating oven for a minute(O), respectively, as a function of plastic pigment volume fractions(PVC's) (1).

the packing volume of the pigments and its CPVC.

The Ratio of CPVC to Packing Volume as a Measure of Binder Efficiency or Pigment-Binder Interactions

In the previous study on the CPVC concept for paper coatings based on the model coatings (1), the CPVC of a plastic pigment (0.45㎛) / latex binder (0.15㎛) coating system was determined to be 60% by volume, while the packing volume of the plastic pigment coating on a polyester film was estimated to be 64% by volume. Thus, a ratio, **R**, of the CPVC to the packing volume, ϕ_p, is estimated as follows:

$$\mathbf{R} = \mathrm{CPVC} / \phi_p = 60/64 = 0.938$$

This ratio of the CPVC to the packing volume for various coatings may range from very low values to almost unity. In fact, the ratio may vary from very low values for flocculated coating systems to the maximum value of unity for the ideal binders. Thus, the ratio, **R**, can be used as a measure of the binding efficiency for latex binders as paper coating binders, that is, as the efficiency of latex binders increases, the ratio will increase, ultimately approaching the unity. For example, as the particle size ratio of latex binder to pigment decreases, the ratio will increase and may approach the unity. Schaller (7) and del Rio and Rudin (8) showed that the CPVC's of latex-based paints increased with decreasing latex particle size. As the latex binder particle size decreases with respect to the pigment particle size, the connectivitiy of latex particles will increase according to percolation theory so that the subsequent latex film formation can cause greater coating shrinkage. As shown by Schaller (7), as the film formation of latexes improves, the CPVC's of latex-based coatings increases. Also, if a latex binder can improve highly flocculated pigment dispersions, then the ratio may not only increase, but also exceed the unity. On the other hand, if a latex binder flocculates pigment particles, then the CPVC as well as the ratio will decrease significantly.

The Packing of Pigment Particles and Mathematical Models for the Packing of Pigment Particles of Different Sizes

Regarding the packing volumes of pigments, they can be experimentally measured as done in our previous and present studies even without any knowledge of their particle size distributions. On the other hand, the packing volumes of spherical particles such as plastic pigments can be calculated using Lee's algorithm (3), if their particle size distributions are known. The packing of spherical particles has been extensively studied both theoretically and experimentally, and a significant progress has been made in modeling the relationship

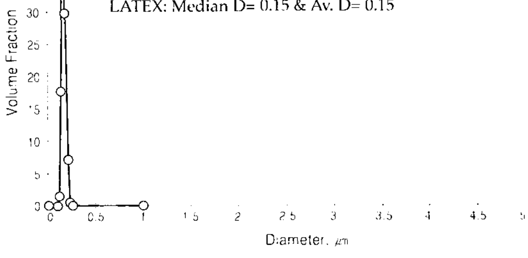


Fig. 3. The particle size distribution of an S/B latex used.

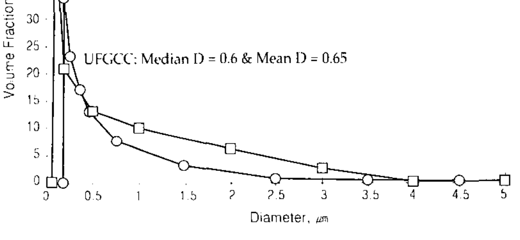


Fig. 4. The particle size distributions of No. 1 clay and ultra-fine ground calcium carbonate (UFGCC).

between packing volume fraction, which is equal to one minus porosity, and particle size distribution for spherical particles (9-17). Now, the question is how we can estimate the packing volumes of non-spherical particles like clay and ground calcium carbonate particles based on their particle size distributions. Although ground calcium carbonate particles are not perfectly spherical in shape, they may be treated as spherical particles with appropriate correction terms such as sphericity factor (the ratio of the surface areas between a sphere and a particle of the same volume) or equivalent spherical packing factor (the ratio of the packing volume fractions between the spherical and non-spherical particles of the same particle size distribution). Therefore, the packing volumes of ground calcium carbonate mixtures can be first calculated as the mixtures of spheres, and then their sphericity or equivalent spherical packing factors can be estimated by comparing the experimental and calculated packing volumes. On the other hand, since no attempt has been reported in the literature to develop mathematical models for non-spherical particles such as clay, the following approach is proposed to estimate the packing volumes of clay mixtures based on a mathematical model used by Lee (3):

1. Determine the packing volume fractions of the binary mixtures of clay particles having the same aspect ratio as a function of both particle size ratios and compositions, along with the packing volume fraction of uniform size clay particles having the same aspect ratio.
2. Since the packing volume fractions of the binary clay mixtures are not currently available in the literature, as an alternative to the absence of the information, they will be constructed as a function of particle size ratio, D_L/D_S (L and S stand for large and small particles.), and composition, X_L, by using the packing volumes of the binary mixtures of spheres on the assumption that the effect of particle size on packing would be similar to both spheres and non-spherical particles except for their respective packing volumes of uniform size particles. For instance, if the packing volume fraction of clay particles of uniform size and same aspect ratio is taken to be 0.57 (2), the maximum packing volume fraction and its composition for the infinite particle size ratio of large to small clay particle can be first calculated as follows:

$$\phi_{p,\ Max} = 0.57 + (1 - 0.57) \times 0.57 = 0.815$$
$$X_{L,\ Max} = 0.57 / [0.57 + (1 - 0.57) \times 0.57] = 0.699$$

3. Secondly, the maximum packing volume fractions of the binary clay mixtures can be constructed as a function of clay particle size ratio (D_L/D_S) by applying the correction factor (0.57/0.639=0.892) to those of the binary mixtures of spheres reported in Lee's paper (3) to be used until better data become available. Table 1 shows the calculated maximum packing volume fractions of the binary clay mixtures, along with those of the binary mixtures of spheres for reference.
4. Now, the packing volume fractions of clay mixtures of n-components (n-sizes) can be calculated by solving the following equations:

$$(\phi_p)_i = \sum^{j=n} \phi_{ij} \cdot X_j$$

Table 1. The calculated maximum packing volume fractions, $\phi_{Max}(D_i/D_j)$, of the binary clay mixtures of the same aspect ratio at the composition ($X_{L,\ Max}$) of 0.699 as a function of clay diameter ratios, based on the packing volume fraction of uniform clay particles of 0.57, along with those of the binary mixtures of spheres at the composition of 0.735 based on the random close packing volume fraction of uniform spheres of 0.639 (3): D. R. = Large / Small Diameter Ratio (D_L/D_S), S. P. = Spherical Particles, Clay = Clay Particles, and Inf. = Infinite Diameter Ratio.

D. R.	1	2	3	4	5	6	7	8	9	10	15	20	Inf.
S. P.	0.639	0.658	0.690	0.724	0.759	0.792	0.810	0.820	0.830	0.834	0.844	0.847	0.870
Clay	0.57	0.587	0.615	0.646	0.677	0.706	0.723	0.731	0.740	0.744	0.753	0.756	0.815

$j=1$

$$\sum_{j=1}^{j=n} X_j = 1.0$$

$$\phi_p = \mathrm{Min}\,[(\phi_p)_i]$$

where

$\phi_{ii} = 0.57$,

$\phi_{ij} = 0.57 + (\phi_{Max}(D_j/D_i) - 0.57) / 0.699$,

$\phi_{ji} = 0.57 + (\phi_{Max}(D_j/D_i) - 0.57) / 0.301$,

$D_j/D_i \geq 1$ or $j \geq i$ $(D_1 < D_2 < D_3 < \ldots..)$, and $\phi_{Max}(D_j/D_i)$ can be obtained from Table 1, X_j is the volume fraction of j-component available from the particle size distributions, and ϕ_p is the calculated packing volume fraction of the clay mixtures of n-components, which is the minimum value of $(\phi_p)_i$.

5. The packing volume fractions of the mixtures of spheres having various representative particle size distributions were previously calculated using the computer program (3) and found to be 0.691, 0.663, 0.687, and 0.662 for rectangular, triangular, negatively skewed triangular, and positively skewed triangular distributions, respectively, based on the random close packing fraction of 0.639. As already discussed, the mathematical model (3) for the packing volume of spherical particles will be used to calculate the packing volume of UFGCC, based on its particle size distribution later in the section of Results and Discussion.
6. Likewise, the packing volume fractions of clay mixtures can be calculated for rectangular, triangular, negatively skewed triangular, and positively skewed triangular distributions, respectively, by using the above equations and an Exel program with the random close packing fraction of 0.57 for uniform clay particles and the data for the binary clay mixtures given in Table 1. Their packing volume fractions have been calculated to be 0.616, 0.592, 0.613, and 0.591, respectively. Also, the packing volume of No. 1 clay will be later calculated by this method based on its particle size distribution, and then compared with its experimental value.

Pigment Blending

As for the pigment blending in paper coatings, Hagemeyer published three pioneering papers on the effect of pigment combination and solids concentration on particle packing and coated paper characteristics (18) in 1960, the effect of particle shape and chemical composition on the packing characteristics of pigment combinations (19) in 1964, and the influence of chemical composition on the packing of pigment particles (20) in 1964. It would be interesting to note that he found that the blends of clay particles (plates) and calcium carbonate particles (rhoms) had gone through the maximum sediment volume that is equivalent to the lowest packing volume, as found also in the present study on the blends of No. 1 clay and UFGCC.

EXPERIMENTAL

No.1 clay and UFGCC pigments were dispersed adding 0.2 part additional sodium polyacrylate at 71.43% and 74.65% solids, respectively. Table 2 shows their characteristics (21, 22), along with those of an S/B latex used. Their particle size distributions (21, 22) are shown in Figures 1 and 2. These pigment dispersions were blended with an S/B latex to prepare the coating formulations at 60% solids having the pigment / latex ratios of 0/100 to 99/1 by

Table 2. The characteristics of an S/B latex binder, No. 1 clay, and ultra-fine ground calcium carbonate (UFGCC).

	Density, g/cm³	Particle Shape	Median Diameter,μm	Mean Diameter,μm
S/B Latex	1.03	Spherical	0.15	0.15
No. 1 Clay	2.6	Plate-like	0.7 (19)	0.75
UFGCC	2.7	Rounded Rhombohedral	0.6 (20)	0.65 (20)

weight, respectively. They were applied onto both polyester films and commercial sheet offset papers using No. 30 and No. 16 Meyer Rods, respectively. Also, No. 1 clay and UFGCC pigments were blended to prepare a series of pigment blends having the No. 1 clay/UFGCC ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 by weight at 60%, 65%, and 70% solids, respectively, for the rheology studies, and they were mixed with an S/B latex to prepare the coating formulations at 60% solids containing the 85/15 and 99/1 pigment / latex weight ratios, respectively. These coating formulations were also applied onto polyester films and commercial sheet offset papers using No. 30 and No.16 Meyer Rods, respectively. All coatings were dried in an oven at 100℃. Opacity, brightness, and 20° & 75° TAPPI gloss were measured on all coatings on polyester films and commercial sheet offset papers. Also, the porosity of their coatings on polyester films was determined by a weight-thickness method (1). The present paper will only report the data on the coatings made on polyester films, but the experimental results on the coatings applied onto commercial sheet offset papers and their printability will be reported in the subsequent papers.

In order to study the state of pigment/latex dispersions, a cryo-transmission electron microscopy method was carried out: A small drop of the dispersions was applied to an aluminium specimen stub and plunged into liquid propane at - 180℃, the frozen samples were microtomed, and then about 90 nm-thick cross-sections were examined by a transmission electron microscope. For the examination of coating surfaces and freeze-fractured coating cross-sections, a scanning electron microscope was used. For the topographical visualization and roughness measurement of coating surfaces, an atomic force microscope was effectively utilized.

RESULTS AND DISCUSSION

The optical properties (opacity, brightness, and gloss) of both No. 1 clay and UFGCC/(S/B) latex binder coatings on polyester films are plotted against the pigment concentration by weight for easier reference in Figures 5 and 8, and then against the calculated pigment volume concentration in Figures 6 and 9. The porosity of these coatings is shown as a function of both pigment weight and volume concentrations in Figures 7 and 10. The critical pigment weight and volume concentrations (CPWC's and CPVC's) for both No. 1 clay and ultra-fine ground calcium carbonate (UFGCC) pigment/(S/B) latex binder coatings were graphically determined from the coating opacity, brightness, gloss, and porosity vs. pigment concentration curves, respectively, as shown in Figures 5-10. These critical values are given in Table 3. The CPVC values

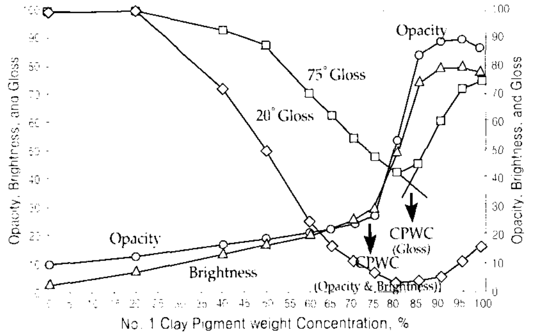


Fig. 5. The optical properties of No. 1 clay / (S/B) Latex coatings vs. pigment weight concentration.

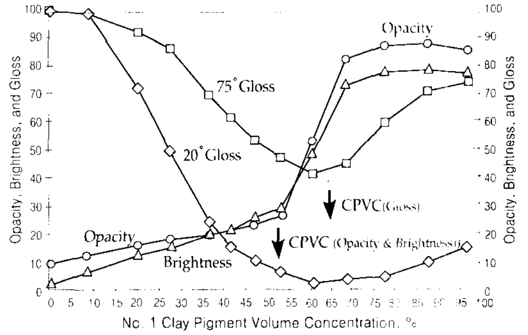


Fig. 6. The optical properties of No. 1 clay / (S/B) Latex coatings vs. pigment volume concentration.

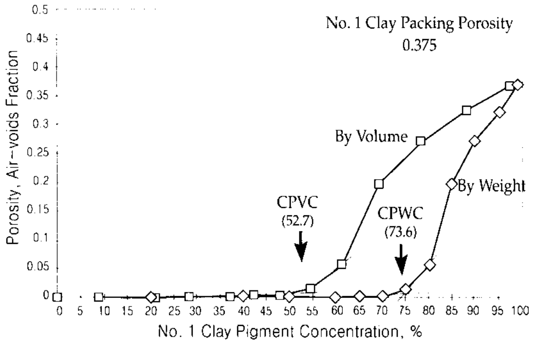


Fig. 7. The porosity of No. 1 clay / (S/B) Latex coatings vs. pigment volume and weight concentrations.

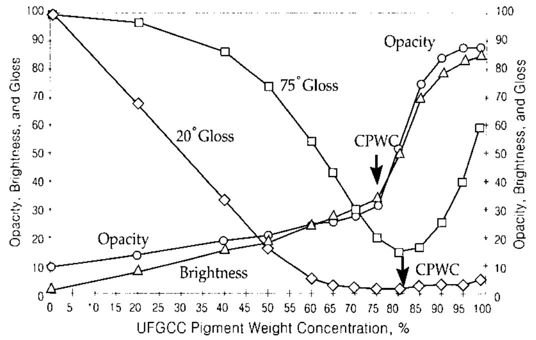


Fig. 8. The optical properties of UFGCC / (S/B) Latex coatings vs. pigment weight concentration.

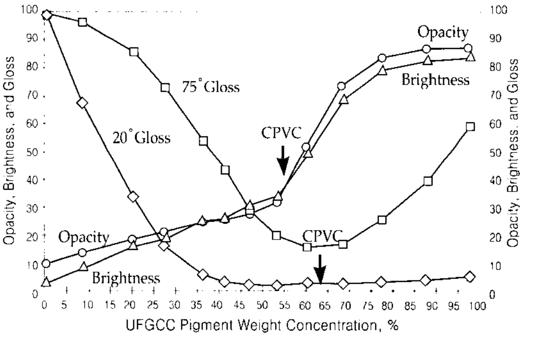


Fig. 9. The optical properties of UFGCC / (S/B) latex coatings vs. pigment weight concentration.

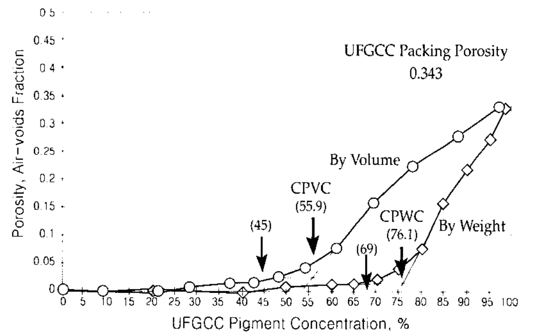


Fig. 10. The porosity of UFGCC / (S/B) latex coatings vs. pigment volume and weight concentrations.

determined by the opacity, brightness, and porosity curves are in good agreement. As expected, the coating opacity and porosity showed the same trends against the pigment concentration. On the other hand, it was somewhat surprising to observe that the coating brightness showed the same trend as those of the opacity and porosity. As shown in Figures 7 and 10, the porosity curves were extrapolated to the 100% pigment axis and then, the porosity values of binder-free pigment coatings were determined. These values are given in Table 4, along with the packing volumes of the binder-free No. 1 clay and UFGCC coatings, respectively, which are equal to 100 x (1 - porosity)%. These experimentally determined packing volumes of No. 1 clay and UFGCC, 62.5% and 65.7%, respectively, are compared below with the values calculated based on their respective particle size distributions by using the mathematical model discussed and proposed in the section of Theoretical Considerations:

The Packing Volume Fraction of No. 1 Clay: Using the particle size distribution of No.1 clay shown in Figure 2 and the maximum packing volume fractions of binary clay mixtures given in Table 2, the proposed model estimated the packing volume fraction of No. 1 clay to be 0.686, that is, 68.6% by volume. This value is about 10% larger than the experimental value, that is, 100 x [(68.6% - 62.5%)/62.5%] = 9.8%. Considering that the maximum packing volume fractions of binary clay mixtures used for the calculation were estimated from those of binary spherical particles, it is

Table 3. The critical pigment weight and volume concentrations of No. 1 clay and UFGCC / (S/B) Latex coatings determined graphically from their opacity, brightness, porosity, and gloss vs. pigment weight and volume concentrations, respectively: Subscripts (1) and (2) are the first and second sets of CPWC and CPVC values.

	Critical Pigment Weight Concentration (CPWC), %			
Coating System	Opacity vs. PWC	Brightness vs. PWC	Gloss vs. PWC	Porosity vs. PWC
No. 1 Clay / Latex	75	75	82.6	73.6
UFGCC / Latex	74.2	73.3	82.5	69(1) & 76.1(2) 72.6 (Av.)
	Critical Pigment Volume Concentration (CPVC), %			
	Opacity vs. PVC	Brightness vs. PVC	Gloss vs. PVC	Porosity vs. PVC
No. 1 Clay / Latex	54.3	54.3	65	52.7
UFGCC / Latex	52.5	51.4	63.6	45(1) & 55.9(2) 50.5 (Av.)

Table 4. The packing volumes of No. 1 clay and UFGCC determined from the porosity vs. pigment weight and volume concentrations.

Pigment Type	Packing Porosity, %	Packing Volume, %
No. 1 Clay	37.5	62.5
UFGCC	34.3	65.7

expected that the more accurate input for the binary clay mixtures would improve the result from the model.

The Packing Volume Fraction of UFGCC: Using the particle size distribution of UFGCC shown in Figure 2 and the maximum packing volume fractions of binary spherical particles given in Table 2, the proposed model yielded its packing volume fraction to be 0.697, that is, 69.7% by volume. The comparison between the experimental and calculated values suggests that its equivalent spherical packing factor is (65.7%/69.7%) = 0.943 or its sphericity factor is $(65.7\%/69.7\%)^{2/3} = (0.943)^{2/3} = 0.962$. It appears that the model for the mixtures of spherical particles is reasonable for the packing volume of ground calcium carbonate pigment mixtures, that is, the model may be able to predict the packing volumes of ground calcium carbonate particle mixtures within an error of less than 10%.

As shown in Figures 5-6 and 8-9, the minimum coating gloss occurred at concentrations well above their CPWC's and CPVC's determined by the coating opacity, brightness, and porosity, unlike the model coating system which showed the minimum coating gloss almost at the same CPVC's (1). This behavior suggests that the maximum coating shrinkage in latex-bound inorganic pigment coating systems such as clay and ground calcium carbonate pigment coatings occurs well above the CPWC's and CPVC's defined by opacity, brightness, and porosity.

The structure of No. 1 clay/(S/B) latex binder coatings shows that over relatively high pigment concentrations (85-95% by weight and 75-90% by volume) which we are most interested in for the actual paper coating applications, the opacity and brightness as well as the coating porosity are somewhat flatter with respect to the latex binder level, that is, variations in the properties of latex-bound clay paper coatings, particularly porosity, opacity and brightness, are less sensitive to the latex binder level than their counterpart ground calcium carbonate coatings are. This interesting behavior is believed to be due to the packing characteristics of non-spherical, highly anisotropic particles: a kind of structured pigment behaviors. These differences can be seen in Figures 5-11.

For the No. 1 clay/(S/B) latex coating system, its CPVC as the void-free point can be easily determined from the coating porosity vs. pigment concentration relationship, as shown in Figure 7. Its CPVC and CPWC values are 52.7% by volume and 73.6% by weight. Using the packing volume of the latex-free No. 1 clay coating, 62.5% by volume, the ratio, **R**, of CPVC/ϕ_p for the No. 1 clay coating system can be calculated to be 52.7/62.5 = 0.843. For the UFGCC/(S/B) latex coating system, it was very difficult to determine its void-free CPVC and CPWC values from the coating porosity curves, as shown in Figure 10. Two sets of the CPVC and CPWC values were determined. The first set of 45% by volume and 69% by weight was determined as the void-free points, while the second set of 55.9% by volume and 76.1 by weight was obtained as the transition points in porosity. This unusual situation is suspected to be due to a slight incompatibility (poor dispersion) between UFGCC and latex binder particles near and at the CPVC. Since no adjustment, such as pH, was made to the coating formulations, those formulations near the CPVC might have been too low in pH due to the lower pH of the latex used (pH 8 compared to the pH 9 of carbonate). This reduction in pH might have caused the instability of carbonate particles. The first set is considered to be too low so that the second set should be taken to be the more-likely void-free points, but their average values, 50.5% by volume and 72.6% by weight, would reflect the more representative CPVC and CPWC values for the UFGCC/(S/B) latex system presently studied. If 55.9% is taken to be the CPVC of the UFGCC/(S/B) latex coating system, the ratio, **R**, can be calculated to be 55.9/65.7 = 0.851 and a very small difference in the **R** values (0.843 for No. 1 clay and 0.851 for UFGCC) between No. 1 clay and UFGCC pigments can be found, suggesting that the efficiency of the S/B latex binder used in the present study with respect to No. 1 clay and UFGCC pigments appears to be very similar. This result would have been expected, if both pigments had been equally compatible with the latex binder used for the study. However, compared to the model coatings (**R** = 0.938) studied previously (1), all these values are much lower, clearly indicating that the synthetic pigments have much higher binder efficiency than natural inorganic pigments. On the other hand,, if the average value of 50.5% is taken to be its CPVC, then the ratio, **R**, becomes (50.5/65.7) = 0.769, suggesting that our UFGCC/(S/B) latex coating system had some incompatibility problems so that its **R** value was much lower than expected, particularly at concentrations near its CPVC.

Figure 11 shows the direct comparison in coating porosity between No. 1 clay and UFGCC/(S/B) latex binder coatings as a function of pigment concentration. In terms of coating porosity, the clay system is lower than the calcium carbonate up to about 80% pigment by weight (65% by volume), then becomes higher all the way to 100% pigment, that is, to the zero latex binder. Since the clay packing volume is smaller than the calcium carbonate packing volume, it is expected that in the absence of any unforeseen interactions or instability, the porosity of No. 1 clay/(S/B) latex coatings would be higher than that of UFGCC/(S/B) latex coatings above their respective CPVC's. For this reason, it is suspected that there might have been some dispersion problems between UFGCC and latex particles at concentrations from its critical pigment concentration (CPC) to about 85% by weight and 67.7% by volume, as discussed before.

The structure of UFGCC/latex binder coatings shows that the opacity and porosity of the latex-bound calcium carbonate coatings are smaller than those of the latex-bound clay coatings at the same

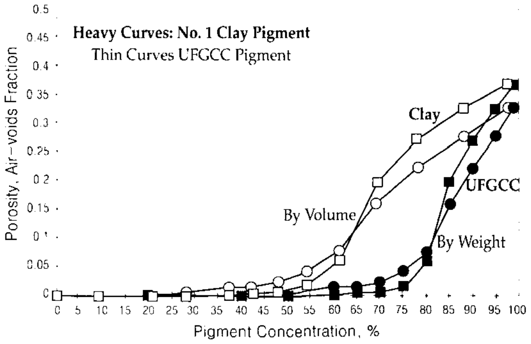


Fig. 11. The porosity of No. 1 clay and UFGCC / (S/B) latex coatings vs. pigment volume and weight concentrations, respectively.

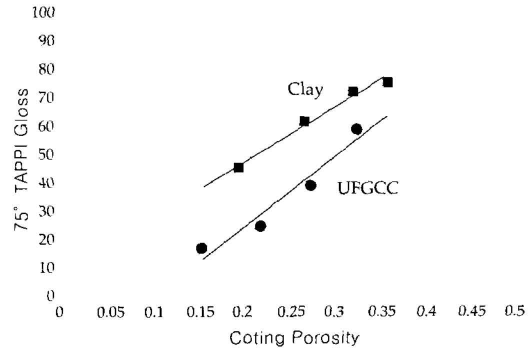


Fig. 12. The porosity of No. 1 clay and UFGCC / (S/B) latex coatings vs. coating porosity, respectively

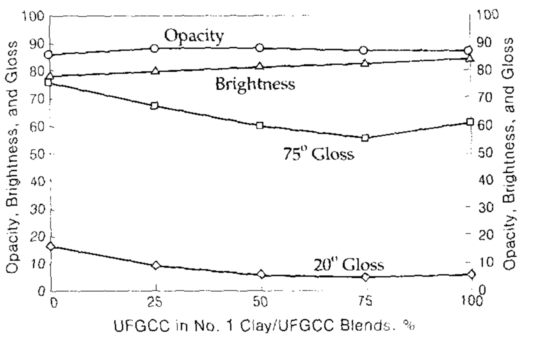


Fig. 13. The optical properties of No. 1 clay-UFGCC blend / (S/B) latex coatings at 99/1 vs. pigment blend ratio.

latex binder levels, as can be seen in Figures 5, 8, and 11. However, the brightness of the latex-bound calcium carbonate coatings is higher, that is, although their opacity is lower because of the lower porosity, the brightness is still higher because of their higher pigment brightness, as shown in Figures 5 and 8.

Figure 12 shows the coating gloss vs. porosity relationships for No. 1 clay and UFGCC/(S/B) latex coatings, respectively, over the pigment-to-binder ratios of 85/15 to 99/1 by weight. It will be interesting to note that there is a good correlation between coating porosity and gloss: the higher the coating porosity, the higher the coating gloss and vice versa. This correlation can be understood by the fact that both coating porosity and gloss are affected by coating shrinkage (23-27). Importantly, this relationship can be useful in estimating uncalendered coating porosity, which is very difficult and time-consuming to measure, from uncalendered coating gloss, which is very easy to measure.

Figure 13 shows the opacity, brightness, and gloss of No. 1 clay-UFGCC blend/(S/B) latex coatings at 99/1 by weight as a function of the pigment blend ratio. The mixtures of No. 1 clay and UFGCC pigments formulated with an S/B latex binder at 1% by weight, respectively, show that their coating opacity increases with increasing amount of UFGCC pigment particles in the blend, resulting in the maximum between 25 and 50 parts of calcium carbonate, but their coating gloss decreases and

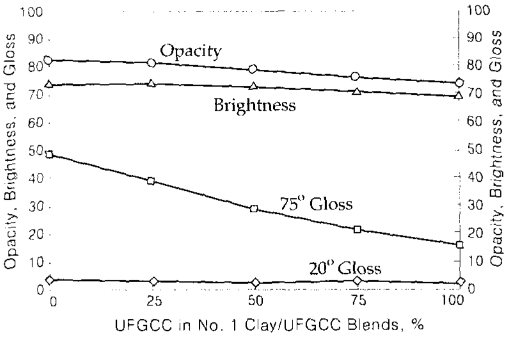


Fig. 14. The optical properties of No. 1 clay-UFGCC blend / (S/B) latex coatings at 85/15 vs. pigment blend ratio

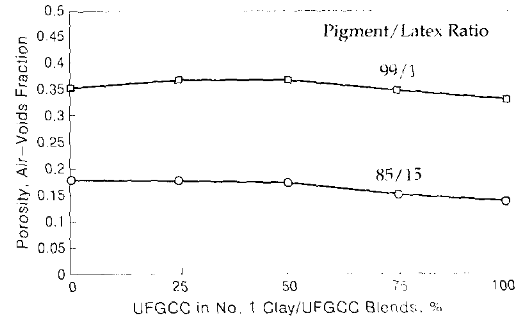


Fig. 15. The porosity of No. 1 clay-UFGCC blend / (S/B) latex coatings at 99/1 and 85/15, respectively, vs. pigment blend

becomes the minimum at 75 parts of calcium carbonate, as shown in Figure 13. Interestingly, the brightness increases with increasing calcium carbonate all the way up to all UFGCC coating, as shown in Figure 13. Figure 14 shows the opacity, brightness, and gloss of No. 1 clay-UFGCC blend/(S/B) latex coatings at 85/15 by weight as a function of the pigment blend ratio. As can be seen from Figure 14, all their optical properties (opacity, brightness, and gloss) decrease with increasing amount of UFGCC. The mixtures of No. 1 clay and UFGCC pigments formulated with an S/B latex binder at 15% by weight, respectively, have shown very different coating properties compared with the mixtures formulated with the latex binder at only 1% shown in Figure 13. Figure15 shows the porosity of the pigment blend coatings containing 1% and 15% of the latex binder, respectively, against the blend ratio. As shown in Figure 15, the porosity of No. 1 clay-UFGCC blend/(S/B) latex coatings at 85/15 decreases with increasing amount of UFGCC, unlike that of the same pigment blend coatings at a lower latex binder level (1%) shown in Figure 13, suggesting that the structural strength of the pigment blends is somewhat weaker than that of clay particles alone so that the structure of the pigment blends collapses during consolidation at higher latex binder levels. This explains why the optical properties of the latex-bound pigment blends are different at different latex binder levels, as shown in Figures 13 and 14.

The low-shear Brookfield viscosities of the pigment blends at 70% and 65% solids are plotted against the blend ratio and RPM with No. 3 Spindle in Figures 16 and 17. Figure 18 shows the low-shear Brookfield and relative viscosities, which are the same because the medium viscosity is equal to 1 cp, as a function of pigment volume fractions and blend ratios. The low-shear viscosities of the pigment mixtures with increasing amount of ground calcium carbonate are almost constant up to 50/50, then decrease. These viscosity behaviors show similar trends as those of the porosity and opacity of the pigment blend coatings, especially for the pigment blend / latex coatings at 99/1 by weight, as shown in Figures 13 and 15. The mixture viscosity was much higher than their average values of clay and UFGCC slurries alone over the blend ratios up to about 25/75, suggesting that the addition of ground calcium carbonate particles to clay particles actually induces larger aggregates and bulkier structure rather than breaking down the clay aggregates (2). In other words, clay and ground calcium carbonate particles interfered with each other's packing and created bulkier packing together, as shown by Hagemeyer (18-20). Particularly, Figure 18 suggests that larger clay-calcium carbonate aggregates are formed over a wide range of solids concentrations between the blend ratios of about 75/25 and 50/50. This is a very interesting packing phenomenon which has many implications in designing paper coating formulations

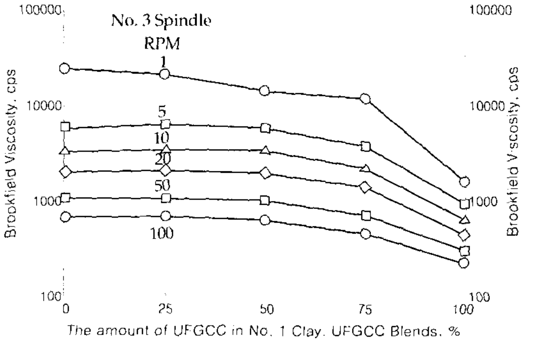


Fig. 16. The viscosity of No. 1 clay-UFGCC blends at 70% solids vs. pigment blend ratio and shear rates.

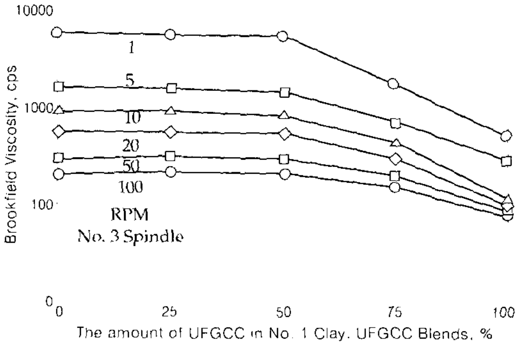


Fig. 17. The viscosity of No. 1 clay-UFGCC blends at 65% solids vs. pigment blend ratio and shear rates.

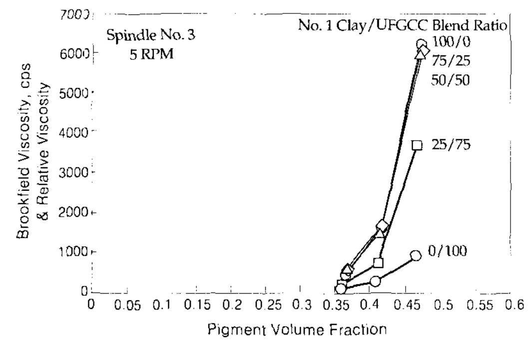


Fig. 18. The viscosity and relative viscosity of No. 1 clay-UFGCC blends at a shear rate of ~1 sec^{-1} vs. pigment blend ratio and volume fraction.

containing both clay and ground calcium carbonate pigments or blending different pigments having different particle shapes. Clay and ground calcium carbonate particles are interactive and non-cooperative in terms of the packing efficiency, leading to bulkier structure formation, whereas different size particles of the same shape tend to be cooperative in packing and increase the packing efficiency (3, 7-17, 28-30).

Figure 19 shows the Hercules Hi-Shear rheograms of the No. 1 clay-ground calcium carbonate pigment blends at 70% solids as a function of pigment blend ratio. Interestingly, the high-shear viscosities of these pigment blends decrease with increasing amount of the ground calcium carbonate, as shown in Figure 19 and reported in a product brochure on ground calcium carbonates (22). This is a well-known fact that the paper coating industry is extensively taking advantage of. This phenomenon can be explained by the fact that under high shear rates, the aggregates of pigment particles would be broken down and become fully deflocculated so that their rheological properties will be mainly affected by their individual particle shapes and relative concentrations, that is, as the amount of plate-like clay particles in the blends decreases, the viscosity of the fully deflocculated blends will decrease and their high-shear rheology will become less dilatant.

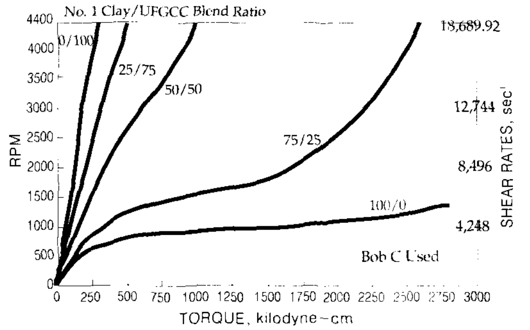
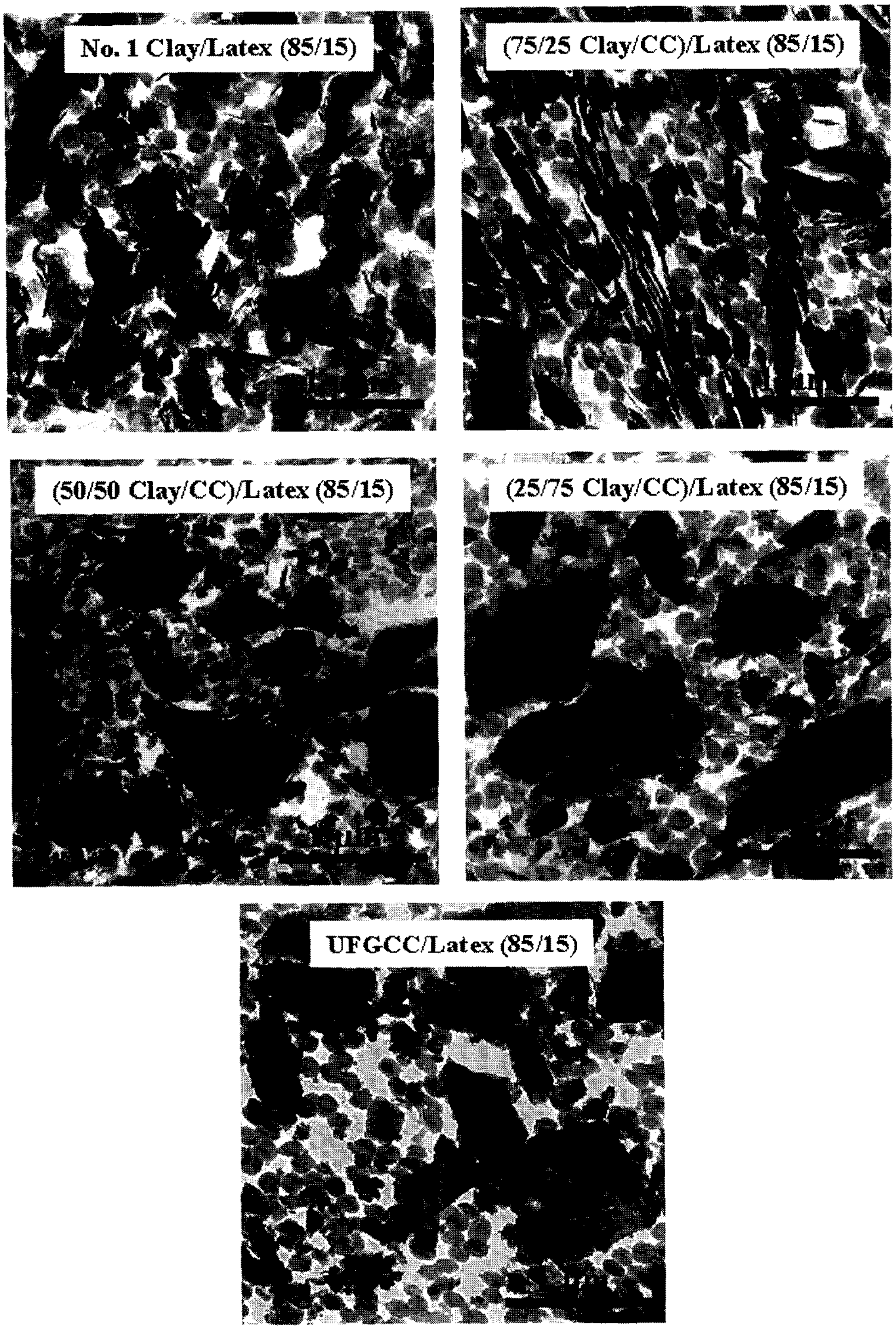
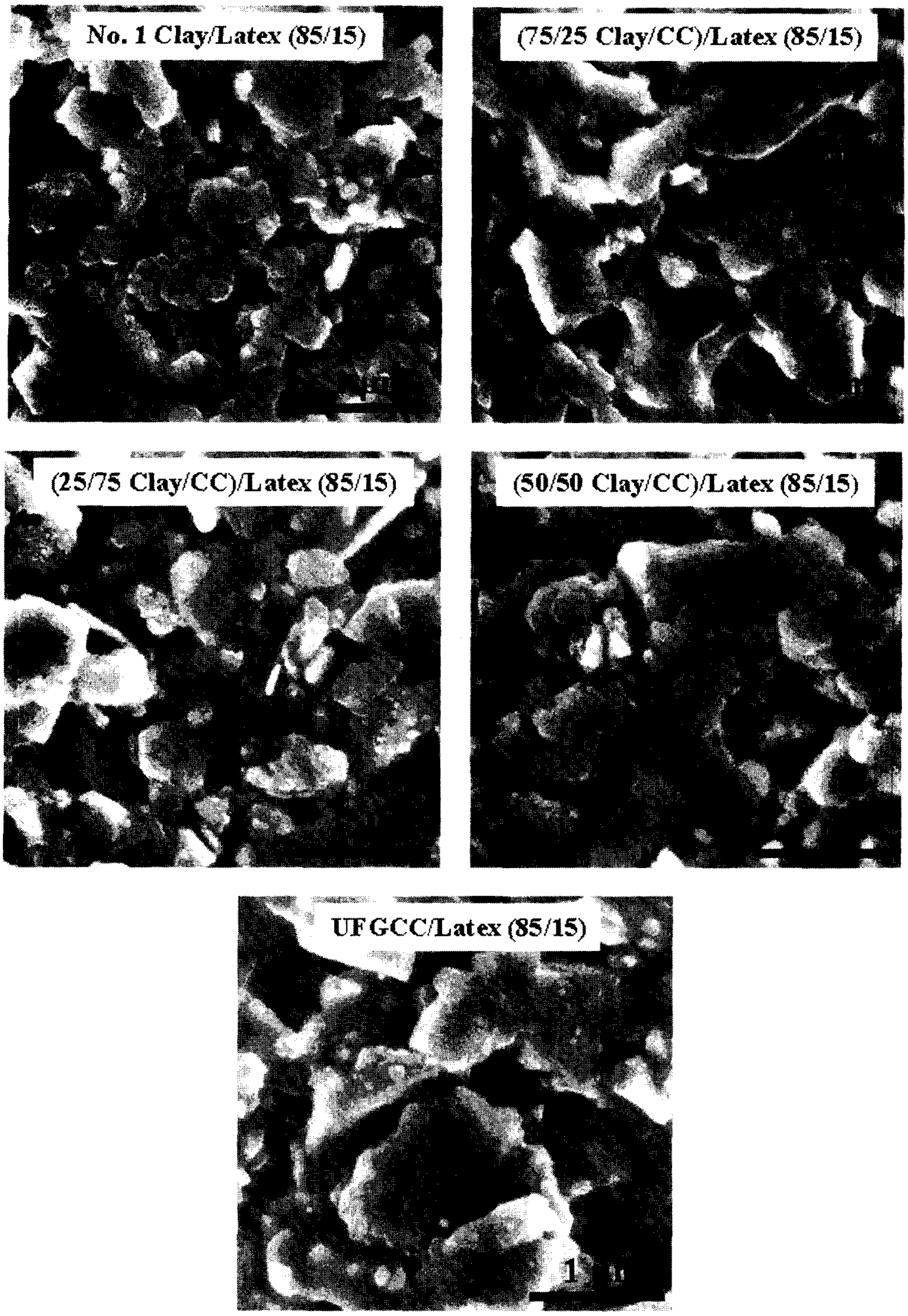


Fig. 19. The Hercules Hi-Shear rheograms of No. 1 clay-UFGCC blends at 70% solids vs. pigment blend ratio.

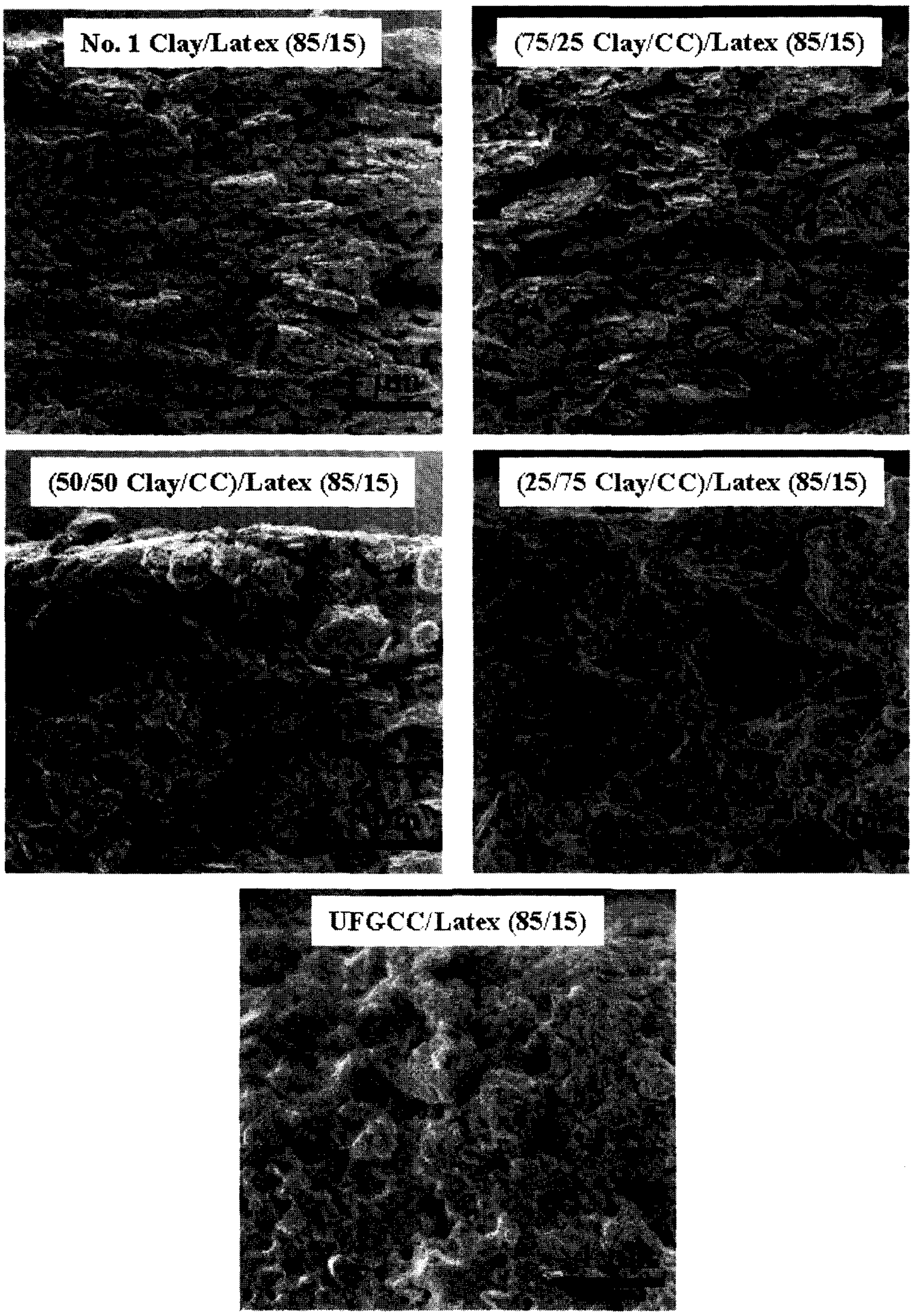
Micrograph 1 shows the transmission electron micrographs (TEM's) of the cryo-fixed and ultra-microtomed cross-sections (about 90 nm- thick) of No. 1 clay, 75/25 clay/CC, 50/50 clay/CC, 25/75 clay/CC, and UFGCC/(S/B) latex dispersions at a pigment-to-binder ratio of 85/15 by weight, respectively. These micrographs clearly show the state of pigment/latex dispersions and the distribution of pigment and latex particles. As the amount of calcium carbonate pigment (UFGCC) increased, the state of dispersions and the distribution of pigment and latex particles became less uniform. This finding is consistent with the speculation that UFGCC and latex particles were somewhat incompatible. Micrograph 2 shows the scanning electron micrographs (SEM's) of the surfaces of No. 1 clay, 75/25 clay/CC, 50/50 clay/CC, 25/75 clay/CC, and UFGCC/(S/B) latex coatings at a pigment-to-binder ratio of 85/15 by weight, respectively. These SEM images suggest that as the amount of calcium carbonate pigment (UFGCC) increased, the coating surfaces became less porous and rougher. This finding agrees well with their coating porosity and gloss data shown in Figures 14 and 15. Micrograph 3 shows the scanning electron micrographs (SEM's) of the freeze-fractured cross-sections of No. 1 clay, 75/25 clay/CC, 50/50 clay/CC, 25/75 clay/CC, and UFGCC/(S/B) latex coatings at a pigment-to-binder ratio of 85/15 by weight, respectively. These images show clearly that clay particles in the all-clay/latex coating was uniformly aligned and oriented across its cross-



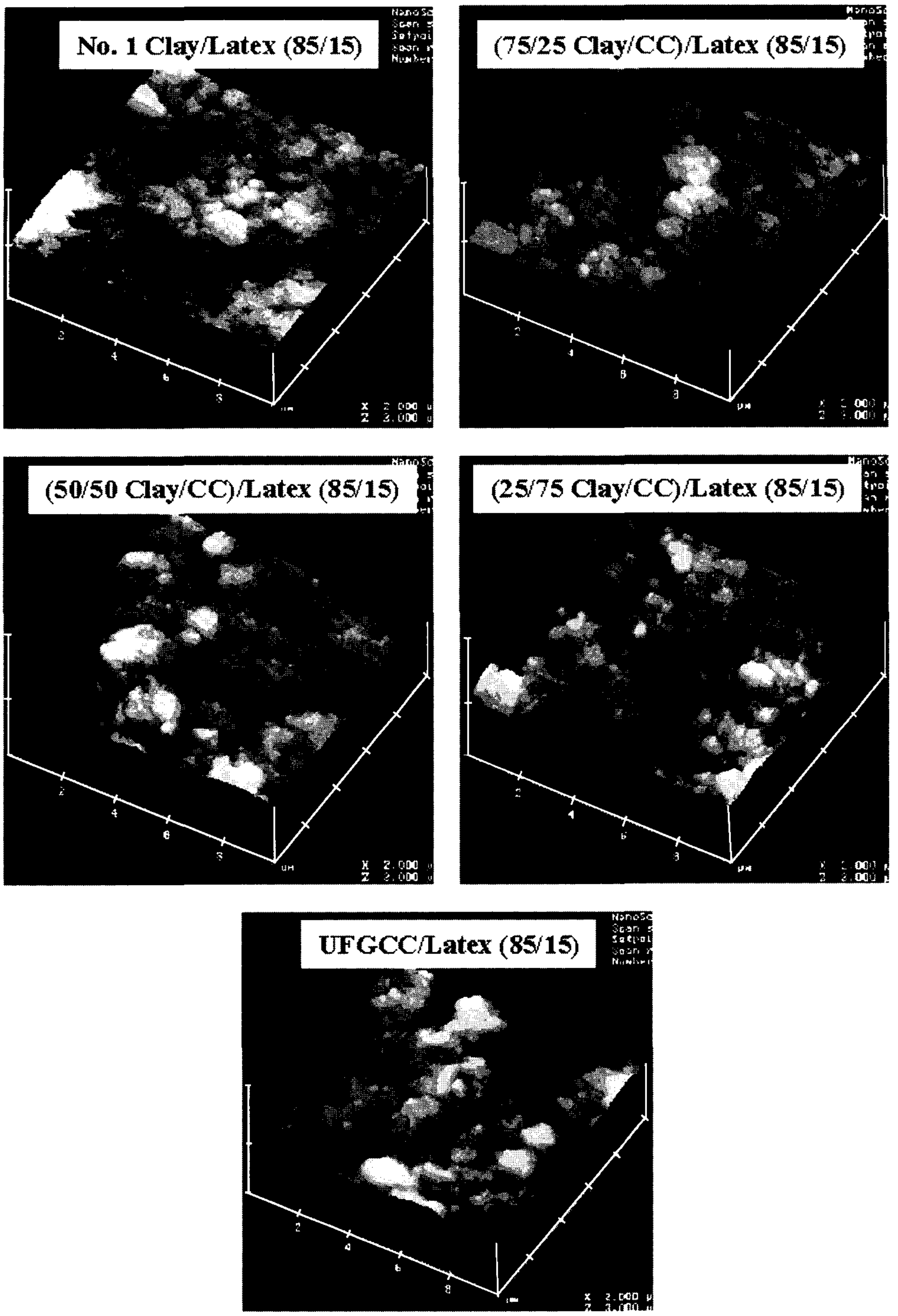
Micrograph 1. Transmission electron micrographs of the cryo-fixed and microtomed cross-sections (about 90 nm- thick) of No. 1 clay, 75/25 clay/CC, 50/50 clay/CC, 25/75 clay/CC, and UFGCC / (S/B) latex dispersions at a pigment-to-binder ratio of 85/15 by weight, respectively.



Micrograph 2. Scanning electron micrographs of the surfaces of No. 1 clay, 75/25 clay/CC, 50/50 clay/CC, 25/75 clay/CC, and UFGCC / (S/B) latex coatings at a pigment-to-binder ratio of 85/15 by weight, respectively.



Micrograph 3. Scanning electron micrographs of the freeze-fractured cross-sections of No. 1 clay, 75/25 clay/CC, 50/50 clay/CC, 25/75 clay/CC, and UFGCC / (S/B) latex coatings at a pigment-to-binder ratio of 85/15 by weight, respectively.



Micrograph 4. **Atomic force micrographs of the surfaces of No. 1 clay, 75/25 clay/CC, 50/50 clay/CC, 25/75 clay/CC, and UFGCC / (S/B) latex coatings at a pigment-to-binder ratio of 85/15 by weight, respectively.**

section, while calcium carbonate particles in the clay/CC mixture coatings disturbed the orientation and packing of clay particles. Also, the freeze-fractured cross-section of the UFGCC/latex coating shows a significant agglomeration of small size calcium carbonate particles. Finally, Micrograph 4 shows the atomic force micrographs (AFM's) of the surfaces of No. 1 clay, 75/25 clay/CC, 50/50 clay/CC, 25/75 clay/CC, and UFGCC/(S/B) latex coatings at a pigment-to-binder ratio of 85/15 by weight, respectively. These images provide an excellent visualization of coating surface topography. They show visually that the roughness of coating surfaces increased with increasing amount of calcium carbonate. Furthermore, atomic force microscope can measure the surface roughness directly, as demonstrated by Haunschild et al. (31). In fact, the measured surface roughness of coatings by AFM was in good agreement with their gloss shown in Figure 14.

SUMMARY AND CONCLUSIONS

The optical properties and porosity of No. 1 clay and ultra-fine ground calcium carbonate (UFGCC)/(S/B) latex binder coatings on polyester films were measured over a wide range of pigment concentrations (pigment concentration ladder) from 0 to 99/1 by weight, and then their critical pigment volume concentrations (CPVC's) and latex-free pigment packing volumes were graphically determined from their property profiles as a function of pigment concentrations. Also, the rheological and coating properties of No. 1 clay-UFGCC pigment mixture/(S/B) latex binder coatings were studied. It was once again found in the present study that the clay-ground calcium carbonate mixture coatings exhibit combinations of unique rheological (e.g., high-shear rheology) and coating properties (e.g., coating structure and brightness).

The ratio, **R**, of CPVC/ ϕ_p (Pigment Packing Volume) was proposed as a measure of the binder efficiency for a pigment or pigment mixtures as well as a measure of binder-pigment interactions. It was found that the **R** values of No. 1 clay and UFGCC/(S/B) latex coatings were smaller than those of the model coatings. Also, the **R** value of No. 1 clay coatings was greater than that of UFGCC coatings, suggesting that S/B latex and UFGCC particles had some incompatibility problems, particularly at pigment concentrations at or near the CPVC.

It was found that the higher the coating porosity, the higher the coating gloss and vice versa over the pigment-to-binder ratios of 85/15 to 99/1 by weight, thus suggesting that coating porosity can be estimated qualitatively from coating gloss.

Mathematical models were proposed to estimate the packing volume fractions of non-spherical particles such as clay and ground calcium carbonate particles of known particle size distributions. The present approach was based on the assumption that any mathematical models developed for spherical particle mixtures could be used, provided that the packing of binary mixtures of any non-spherical particles under study would be used. For clay mixtures, the packing of binary clay mixtures was constructed from that of binary spherical particles by multiplying a factor of (0.57/0.639) = 0.892 to the maximum packing volume fractions of binary spherical particles as a first approximation. For ground calcium carbonate mixtures, the model for spherical particles was used and the correction factors were considered for their non-sphericity. This study has clearly shown the importance of pigment particle size distributions for coating properties, such as rheology, structure, optical properties, etc., through particle packing.

Transmission and scanning electron and atomic force microscopes were found to be very useful for probing the state of pigment/latex dispersions as well as coating surface, internal structure, and surface topography.

The present study has again amply demonstrated the value of investigating the properties of any coating systems over a wide range of pigment concentrations beyond the narrow range of interests for paper coatings. In fact, CPVC's, pigment packing

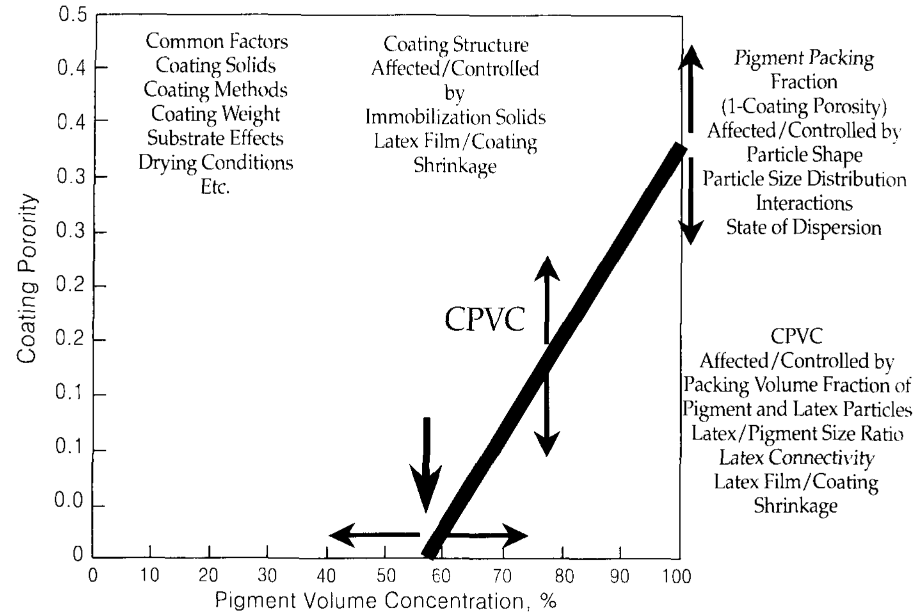


Fig. 20. The coating porosity vs. pigment volume concentration relationship showing the factors affecting and controlling "pigment packing" equal to one minus coating porosity, "CPVC", and "coating structure" between the CPVC and the binder-free pigment coating.

volumes, **R** ratios, relationships between coating structure/property and pigment concentration, etc. can provide us, paper coating specialists, with very valuable information not only on the understanding of our existing coating systems, but also on our future design of superior coating formulations.

Figure 20 summarizes the factors affecting and controlling the packing volume fraction of pigments equal to one minus coating porosity, the CPVC of latex-bound pigment coatings, and the coating structure vs. PVC relationship between the CPVC and the binder-free pigment coating, along with the common factors which are coating solids, coating methods, coating weight, substrates effects, drying conditions, etc. The packing volume fraction of pigment particles is known to be affected and controlled by the shape and particle size distribution of pigment particles, particle interactions, the state of dispersions, etc., whereas the CPVC is affected and can be controlled by the packing volume fraction of pigment and latex coating formulations at the immobilization, which is dependent on pigment particle shape, the combined particle size distribution of pigment and latex particles, pigment-latex interactions, etc., latex particle sizes relative to pigment particle sizes affecting latex connectivity, latex film and coating shrinkage, etc. Then, the relationship between coating structure and PVC above the CPVC is affected and controlled not only by both the CPVC and the packing volume fraction of pigment particles, but also by the immobilization solids, latex and coating shrinkage due to latex film formation, etc.

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