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A Study of the Effects of Pigment Size and Shape on Binder Migration

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A STUDY OF THE EFFECTS OF PIGMENT SIZE AND SHAPE ON BINDER MIGRATION

by

Hee Jong Yang

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Submitted to the
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A STUDY OF THE EFFECT OF PIGMENT SIZE AND SHAPE ON BINDER MIGRATION

Hee Jong Yang, M.S.
Western Michigan University, 1992

The effects of pigment size and shape on coating structure and binder migration has been investigated. Clays and ground calcium carbonates of different particle size distributions were used in coatings with 15 pph SB latex.

Coatings were applied to Mylar and a special Tyvek using a wire wound rod. The coatings were dried slowly under ambient conditions, and using hot air immediately or after having been allowed to reach immobilization through penetration into the Tyvek. The dried coatings were evaluated for water holding, relative pore size and migration using the UV technique to measure the increase in SB latex at the surface due to hot air drying.

Results showed that filler clay and calcium carbonate of large particle size resulted in a higher degree of binder migration. It was observed that rhombic shaped particles contributed to more migration than plate-shaped particles. Drying immediately after the application of coating allowed more binder to migrate to the surface than any other drying method.
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I would also like to express my appreciation to my wife, Seon Hae, my daughters, Yoon Jung, Hyun Jung, and my parents, for their love and support.

Hee Jong Yang
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CHAPTER I

INTRODUCTION

The redistribution of binder in the coating layer may cause paper quality problems. Uneven binder redistribution is a serious problem for printing quality. Therefore, many researchers have studied binder migration for the quality of coated paper. Actually, the binder can redistribute within the coating by penetration and evaporation.

Water holding or water loss rate is an important characteristic property of any coating color. Water holding capacity is believed to significantly affect binder redistribution in the coating layer upon application. Water, the continuous phase in the coating color, is lost either by penetration (may be by capillary penetration or by pressure penetration or by both) into the base stock or by evaporation during drying of the coating. The speed at which the continuous phase is lost plays a key role in binder redistribution and it depends on various factors including the substrate.

Coating color, which is dispersed pigments and binders in water with polymeric substances, is applied to the base sheet. During their application an applicator roll, when used, usually generates pressure, which is the important
driving force for water penetration. Another pressure is generated by the capillary absorption of the substrate. Therefore, water can penetrate into the base sheet, possibly taking the soluble binder (starch) or insoluble particle binder (latex) with it. Between the applicator roll and blade, the main penetration is capillary penetration. However, modern coaters commonly run at high speeds, so that penetration in between application and metering is negligible due to the short period. At the metering zone the blade pressure can lead to additional penetration of water. After the blade, the penetration is caused by capillary absorption of the base sheet. Both capillary and pressure penetration may contribute to binder redistribution.

During drying, evaporation makes the water move toward the free surface. This water movement may cause the soluble and particulate binders to move upwards to the surface of the coating layer. This movement is generally considered to take place before coating immobilization, and cause binder redistribution toward the surface which will be called "binder migration."

Until the immobilization point has been reached, pigment and binder particles can move freely in the aqueous dispersion. After the immobilization a bulky, deformable, three dimensional network is formed with binder particles trapped between pigment particles.
After the immobilization, binders have to migrate through the pigment matrix. Binder migration then will be affected by the coating structure, and the pigment size is one of the factors that determines the coating structure. Therefore, pigment size affects pore structure which is believed to be one of the important factors affecting binder migration.

During drying, the soluble binder can migrate through any pigment matrix, but insoluble binder migration is influenced by the pore size of the coating. Larger size pores should allow more binders to migrate through the pigment matrix. Smaller binders can migrate through the bigger pore size, so latex size compared to capillary size is another key factor for binder migration.

In this study, an effort is made to investigate the effects of pigment size and shape on the coating structure and how these structures can influence the binder migration. Also an effort is made to gain knowledge as to how the different drying methods will influence binder migration in these cases. Here, the coating structure is characterized by the pore size and pore volume. The pore size was determined by the following assumption. If the pore volume is the same, smaller pigment in the coating should make smaller pore size. Pore sizes of the coating were controlled by using four sizes of ground limestone and three kinds of clay. This assumption was confirmed by
measuring the pore size by using scanning electron microscope (SEM) photographs through image analysis.

The coating was allowed to dry by air to immobilization and then dried by hot air after immobilization, and another coating was dried by hot air immediately after application. This procedure attempted to determine the relative amount of migration before and after the immobilization, and the importance of particle size on migration with the different drying methods. UV analysis was used here to quantify the latex migration to the surface.

From the data collected during the study, an effort is made to establish the relationship between pigment sizes, pore size of coating, and binder migration.
CHAPTER II

REVIEW OF RELATED LITERATURE

Packing and Pore Structure

Coating color, which consists of pigments, binders, water, and other additives, is applied on the paper. Pigment size, pigment shape and distribution, binder type, binder level and the degree of dispersion are important factors affecting flow behavior, packing and pore structure and, therefore, affect coating properties. Flow behavior can be determined by the viscosity of the coating color. Viscosity is affected by the degree of mobility of pigment particles in the coating color. Because of this relationship, some feel viscosity can be used to predict coating structure such as porosity, light scattering, and gloss of finished paper. The coating porosity is usually evaluated by oil absorption, air permeability, mercury porosimetry, and scanning electron micrography. At a given viscosity, a higher concentration of coating color means a higher packing density, which will theoretically contribute to a lower pore volume in the dried coating. The size and distribution of pores can also influence the light scattering efficiency, and thereby the opacity and the brightness of the finished sheet (1).
Effect of Particle Size

In a pigment-water system, the viscosity of the slurry is primarily a function of the concentration of pigments and the viscosity of the continuous phase. The viscosity of the slurry increases with increasing pigment concentration. When adding the pigment into the slurry, the viscosity increases exponentially. The reason is that pigments in the slurry crash together due to no more space to move. If more pigment is added at this point, the pigment slurry attains more solid-like behavior (i.e., dilatancy). The solids level at which this occurs can be called the critical pigment volume concentration (CPVC).

Pigment size affects the CPVC value. In a well-dispersed clay-water system, as the size of particles decreases, the viscosity of coating color passes through a minimum value and then increases again due to the higher surface area of smaller pigment particles (2). The viscosity of the poorly dispersed pigment-water system cannot be predicted, even though the particle size is known. If particles agglomerate, their properties are not the same. At that time, their properties depend on the size of the agglomerates.

Watanabe et al. (2) showed the relationship between clay size and oil absorptivity. The particle size was decreased, the oil absorptivity of the coatings decreased
went through a minimum and then increased again. Around 2.5 \( \mu m \), the most compact density of the coating structure was shown. They also measured porosity by using electron microscope. The number of capillaries in the coatings increased, but decreased in diameter as the clay particle size decreased. The same trends were obtained by using mercury porosity. The packing efficiency of polydispersed particles is higher than that on monodispersed ones, and the CPVC is also higher. At a given concentration, the viscosity of a polydisperse system is lower than that of a monodisperse system \((3, 4)\) because the small pigments of a polydisperse system can get more chances to move in the space between large particles. The higher packing efficiency results in a lower pore volume in the coating structure. However, this relationship in not linear. Cook \((5)\) reported the relationship between void volume and percent of smaller pigment. The addition of smaller particles reduced the void volume when the smaller particles were smaller than the voids between the larger sizes. This data confirmed results by Dodd’s assumption \((6)\) who assumed that all spheres touch their neighbors. In the present study, different size pigments were used for making different pore structures.

**Effect of Particle Shape**

Particle shape affects coating structure due to
different packing patterns. Hagemeyer (7) reported the effect of particle shape on particle packing. He used the three kinds of pigment shapes, e.g., the plate, the needle, and the rhombohedral. He observed that the dry mixtures, water dispersions, and plastic models had different packing tendencies. In the dry mixture packing volume increases as the percent of plates increases, while the plastic model has decreased packing volume as the percentage of plates is increased. For the water dispersion, initially, packing volume decreases as either the needles of rhombohedral are added to the plate particles.

Alince (8) compared the viscosity of clay and calcium carbonate suspensions at 55% solids volume concentration. Particle shape also contributed to the fluid behavior. At a given concentration, the viscosity of sphere-like calcium carbonate is lower than that of plate-like clay. Furthermore, calcium carbonate slurry was shown to be Newtonian and clay slurry to be dilatant due to sphere shape allowing better packing. As a result, the viscosity of clay suspensions is considerably higher than that of calcium carbonate. The packing arrangement of calcium carbonate is better than that of clay. This is also reflected in the lower porosity of the dry coating.

Effect of Binder

Binder concentration affects the dried coating
structure. At low latex content, binder has been shown to expand the coating structure, and at high latex content, binder filled the voids of coating structure (9, 10 and 11). Burke (9) and Grafton (10) showed that a soluble binder (starch or polyvinyl alcohol) did not simply fill the voids present in a 100% clay film, but it caused an expansion of the clay matrix. Since the binder was added before film formation, it is perhaps better to regard the binder as preventing the clay particles from packing as closely upon drying as they would be in its absence. The increase in void volume was accompanied by an increase in void size. Above a certain level of binder addition, expansion stopped and pore size decreased (12). Lepoutre and Rezanowich (13) confirmed this phenomena. They measured the relationship between latex concentration in clay and the light scattering coefficient and porosity of coating color. Scattering was seen to increase quickly first, go through a maximum and then decrease.

Alince and Lepoutre (3) compared calcium carbonate and clay coating systems. Adding latex to the clay slurry caused it to pass through the maximum viscosity and then decrease, while adding latex to the calcium carbonate slurry increased the viscosity. In both cases the addition of latex improved the flow characteristics.

Alince (8) added latex to clay and calcium carbonate with a 0.2 volume fraction of pigment. The presence of
latex decreased the dilatant tendency in all the blends, and the binder-free system became less dilatant when calcium carbonate fraction was 0.2 and higher. The porosity of latex-containing coatings was lower than those of pure pigment only, and the light-scattering coefficient was increased with decreasing porosity.

The stiffness of the binder affects the dried coating structure. An increase in polymer stiffness was reported to reduce the collapse and provide a larger void fraction (13).

Effect of Substrate

The substrate is an important factor affecting the coating structure. Burke (9) investigated starch coatings applied on millipore filters and on foil. He observed that the absorbency of the substrate reduced the expansion of the coating structures.

Dalal and Kline (14) reported that the relative pore volume decreased when coating weight increased on black glass substrate, but with paper substrate relative pore volume increased up to a critical coat weight and then decreased.

Lepoutre (15) studied the influence of the absorbency of the substrate on the surface structure of clay-latex coatings. Clay coating color with various coating weights, at low (40%) and high (60%) solids, was applied to Mylar,
8 μm millipore filter, and wood containing publication basestock. The surface of a coating applied at 40% solids on a millipore filter showed a very disordered arrangement of the clay and almost an absence of latex and fine clay. These effects were reduced when coating weight increased and absorbency of the substrate decreased.

Whalen-Shaw (16) tested coating colors applied on Mylar film and on LWC paper. The thickness at the equal coat weight on Mylar was thinner than that of coating on LWC paper. Bessho and Ichikawa (17) confirmed that coatings applied on paper were much bulkier than those applied on polyester film.

The preceding discussion demonstrates the importance of pigment particle size and shape on the structure of the coating layer. It can be assumed from this discussion that a smaller pigment size contribute to smaller pore size in the coating layer. The data also shows that binder and substrate also can be important, but those factors will be held constant during this project.

Binder Migration During Drying

Binders migrate toward the surface of the coating layer during drying, so the drying process is an important factor affecting binder migration. The following factors affect binder migration: drying method, drying delay between application and drying, drying rate, and drying
Drying Methods

The driving force of drying is the temperature gradient. In addition, temperature profile of the web depends on the drying method. Therefore, drying methods affect binder migration. There are three kinds of drying methods; the convection dryer, the conduction dryer, and infrared dryer.

Convection drying is done by an air dryer. A system of ducts and nozzles uniformly discharges hot air that impinges directly on the web. Hot air temperatures of 150 to 205°C are common with impingement velocities of 1220 to 2135 m/min (4000 to 7000 fpm) (18). It is difficult to attain even temperature profiles of the web with hot air dryers. Hagen (19) reported that high drying rate with less binder migration was achieved as floater dryers applied heat to both sides simultaneously for more even temperature profiles. However, hot air drying favors binder migration, so hot air drying was used for inducing binder migration in this study.

Thomin et al. (20) tried to find the relationship between drying methods and binder migration. They compared hot-air drying at high air velocities and infrared heaters on an air knife coater. They concluded that papers dried with hot air almost invariably showed unfavorable binder
migration, whereas the use of infrared heaters yielded good results.

Drying Delay

Drying delay is the period of time between application and drying. Longer drying delay allows more water penetration into the substrate. Therefore, it is theorized to result in less binder migration.

Aschan (21) investigated the relationship between drying delay and binder migration with a soluble binder. By using starch, the K&N value was seen to raise suddenly with drying delay time. He interpreted that hot-air blowing before immobilization resulted in vigorous binder migration, while a much more open surface was formed by drying after the immobilization point. Therefore, immobilization solids was shown to be a critical point for binder migration. If drying starts long before immobilization, binders migrate toward the coating surface easily. If drying starts after immobilization, it is not as easy for binder to migrate toward the coating surface through the pigment-binder network. It results in a more open surface due to less binder and small pigment particles migrating toward the coating surface. The more open surface was claimed by Ashan (21) to result in a higher K&N value.

Engstrom and Norrdahl (22) confirmed that drainage before the dryer was a key factor determining the mottling.
They found a positive relationship between mottling and delayed time of drying. This was interpreted as due to non-uniform drainage, leaving some areas higher in solids than others. Therefore, a variability in the amount of migration led to mottle. If the drainage of water from the coating layer into the base sheet before the dryer was low, mottling was reduced.

**Drying Rate and Solids Level**

Drying rate affects the consolidation of the coating structure and water and binder migration. Dappen (23) reported that during rapid air-drying starch migrate to the surface of the coating, thus producing a non-uniform distribution, with less starch at the coating-fiber interface than at the top surface of the coating.

Heiser and Cullen (24) investigated the degree of binder migration with different drying rates and different solids levels. They tested the degree of latex binder migration by scraping off the coating with a razor blade and by using electron photomicrographs. In their experiments, they used samples which were prepared at different drying rates, solids levels and binder sizes. They concluded that at slow drying rates, the direction of migration seemed to be primarily toward the substrate, while at fast drying rates, the direction of migration was toward the coating surface as well as toward the substrate. They
also concluded that the degree of binder migration to the surface was proportional to the drying rate. Higher solids levels produced immobilization of the coating color with less time resulting in less binder concentration on the coating surface. Low solids level with a rapid drying rate allowed more binders to move toward coating surface, because of more space between the pigments and time before immobilization.

Visual comparisons (Figures 1 and 2) using electron photomicrographs confirmed the results obtained by quantitative analysis. The analyzed surface latex levels are 11, 18, 26, and 31% for Figures A, B, C, and D respectively (24). Small particle size latexes produced more surface binder concentration, because small particles can move more readily than large during water movement during drying.

Aschan (21) investigated the relationship between drying rate and binder migration of starch and casein. He reported that the effect of higher evaporation rate was an increase in binder migration at all coating weights of both starch and casein.

Krishanagopalan and Simard (25) investigated binder concentration by electron probe microanalyzer with osmium. They confirmed that the binder distribution gradients were generally steeper with fast drying than with slow drying. They also found that binder migration into the substrate was more in the case of unsized papers due to capillary
Figure 1. SEM Photomicrographs of Latex - Clay Coated Surfaces (Latex Particle Size is Large) (24).

A. High solids, slow drying rate
B. High solids, rapid drying rate
C. Low solids, slow drying rate
D. Low solids, rapid drying rate

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Figure 2. SEM Photomicrographs of Latex - Clay Coated Surfaces (Latex Particle Size is Small) (24).
forces. In the case of well-sized papers, binder migrated to the surface of the coating layer.

Engstrom and Persson (26) studied starch and latex binders. For a starch coating, the evaporation rate before the gel point was the main factor which influenced mottling, the higher the evaporation rate the more the mottling. After the gel point had been reached the evaporation rate could be high without any risk of mottling. To avoid mottling, the evaporation rate should be low while approaching the gel point. After the gel point the evaporation can be high. For a CMC/SB-latex coating, the evaporation rate usually had less influence on the mottling than in the case of starch coating. A high evaporation rate, adjusted by changing the temperature of the hot air, gave slightly more mottling than a low evaporation rate. Conversely, Engstrom and Norrdahl (22) reported that the higher the evaporation rate the less was the mottling. They explained that other studies (21, 24, 26) evaluated mottle with visual only stain tests, usually K&N, whereas he quantitatively evaluate K&N mottling and the mottling of full-scale offset prints.

**Drying Temperature**

Drying temperature can be used to adjust the drying rate, with high temperatures increasing drying rates. High drying temperatures reduce the surface tension and
viscosity of water, and also greatly increase vapor pressure. Rate of water removal increase with drying temperature affects binder migration.

Engstrom and Norrdahl (22) reported that the binder level of the coating surface was higher for oven-dried samples than room-dried. Engstrom and Persson (26) also found that with a CMC/SB-latex coating, increasing temperature of the hot air increased mottling. This was attributed to higher temperature causing an increase in the dewatering rate into the base paper. An uneven dewatering into the base sheet was believed to be an important factor causing mottling, so dewatering should be minimized to avoid mottling.

This discussion indicate the importance of drying rate and the delay between application and drying. Since Engstrom and Norrdahl’s study (26) indicates that more migration occurs by rapid hot air drying immediately after application, that method will be used in this study. This discussion also indicates that allowing the coating layer to reach immobilization before applying hot air drying may cause migration to be more sensitive to the pore structure in the coating.

Mechanism of Consolidation and Binder Migration

For easier understanding, the consolidation mechanism is separated; the first section focuses on pigment
behavior, and the second section focuses on binder movement during consolidation. However, in reality pigment consolidation and binder migration take place simultaneously.

**Mechanism for Consolidation of the Coating Structure** (27, 28)

After application of the wet coating color to the substrate, the water penetrates into the sheet due to the absorbency of the basesheet and evaporates at the coating surface. Lepoutre (27) proposed a mechanism for the consolidation of the coating structure. He (27) separated the consolidation process into three phases (Figure 3), Watanabe and Lepoutre (28) experimentally confirmed this proposed consolidation mechanism. They used the quick-freeze method for coating structure quenched during drying. The frozen coating structure was analyzed by electron microscope. They defined two critical concentrations. The gloss of wet coating color drops suddenly at the first critical concentration (FCC) and the opacity of coating color increases suddenly at the second critical concentration (SCC).

**Pigment-Soluble Binder Systems** (27)

Phase I (To FCC): If the pigment suspension is dispersed well, the pigments, having similar charges, are oriented randomly. Under the applicator roll or blade, the
pressure creates a shear force which may reorient the pigments, and water is forced to penetrate into the sheet. During drying water evaporates bringing soluble binder such as starch or the insoluble binder such as latex outward to the coating surface with it. This results in the pigment particles getting closer to each other. At some point, the repulsion of the pigment particles due to the electric double layer is overcome and pigments come together. The pigment particles then start to touch each other due to agglomeration. The coating color at this point is a large floc, however, the structure is still deformable. This formation of a coating pigment structure creates the loss of gloss referred to as the First Critical Concentration (FCC).
Phase II (Between FCC and SCC): Water is still penetrating into the substrate and evaporating from the surface. However the closeness of the pigment particles allows the surface tension of the receding water film to became a factor. Surface tension acts as a compressive force, which compacts the particle structure. This compacting force rearranges particles until immobilization. Shrinkage of the structure occurs during this phase.

Phase III (After SCC): During this period evaporation continues, so water in the capillaries of the coating structure is removed and is replaced by air. At this point the opacity of coating color increases because the refractive index of air (1.0) is lower than that of water (1.33). At the same point, formation of the coating structure is believed to be completed. The coating structure will probably not be changed markedly after this point, except very little further collapse of the capillaries, caused by water and the binder shrinkage.

In the present study, drying was started before or after the FCC, because this point is believed to be important for binder migration. Hot air blowing before the FCC allows binder to migrate rapidly toward the coating surface. Hot air blowing after the FCC has been proposed to cause less binder to migrate. It was one of the objective of this present study to check this hypothesis.
Binder concentration affects coating structure. At low latex concentration, binder has a tendency to expand coating structure, but pigments still control the consolidation of the coating color. At high latex concentration, binder fills the voids of the coating structure and latex controls the consolidation of coating color.

**Low Latex Content**

Adding latex to the pigment slurry affects the properties of the coating color. Electrolytes in the latex system could affect the stability of the pigment dispersion by compressing the electrical double layer of pigments resulting in decreased mobility of the pigments.

Phase I: Pigments and latex can move freely in the coating color. Water penetrates to substrate, and latex migrates towards the coating surface, taking the binder with it. At some point, free motion of coating color stops, when the three-dimensional network forms. Latex can then be trapped between the pigment particles. The first meniscus forms at the FCC, and the gloss drops immediately after this point if the latex particles are hard enough to resist the compressive force arising from the water surface tension (28). Soft latex can deform to delay formation of menisci and to raise the FCC.
Phase II: The increasing capillary forces due to continued water evaporation allow the wet coating to shrink. Coalescence of latex particles begins after the FCC. Some latex particles plug the interstices of pigments. As more dewatering occurs, some latex particles are squeezed by pigments, and local stresses are not transmitted throughout the whole structure. At the second critical concentration (SCC), overall latex coalescence in completed. Void structure does not change after the SCC. The FCC and the SCC depend on latex stiffness and latex content, and particle size (28).

Phase III: During this period, the capillaries continue to empty until drying is completed, and water in the capillaries of the coating color is replaced with air.

**High Latex Content**

Increasing the latex addition causes latex particles to surround the pigment particles. At the FCC, the coating structure is more disordered and bulky. Surrounding the particles results in a pigment matrix that is separated by voids filled with latex particles. Therefore, latex-clay capillaries are more prevalent than clay-clay capillaries. As latex coalescence occurs, the local stresses can be transmitted throughout the whole structure. Consequently, the thickness of coating color continuously decreases. Latex coalescence provides a compacting force, and latex
provides a little mobility to the pigment particles. Coalescence and mobility can be controlled by the mechanical properties of latex.

Mechanism of Binder Migration During Drying (29)

Evaporation and penetration cause binder redistribution toward the coating surface and into the base sheet. A soluble binder such as starch moves easily with water, while insoluble binders such as latex may also move through the pigment matrix by the viscous drag of the water. The movement of the binder is counteracted by frictional drag of the pigment particles which makes the binder move slower than water. Hagen (29) explained this phenomena in more detail as shown in Figure 4. The movement of a particulate binder is created by the viscous drag of the water on the

Figure 4. Particulate Binder Behavior Schematic (29).
particles, as long as there is a relative velocity between particles. Thus, the velocity of particulate binders is slower than that of the water. Binder particle groups or agglomerates resist migration in the coating color, but individual binder particles can migrate through the pigment matrix. Collisions between an individual particulate binder and pigment particles create a frictional drag. This friction drag against the pigment particles interrupts the binder movement through the pigment matrix. As a consequence, latex particulates move more slowly than water (30). Immobilized particulate binders can not move any more since they are be trapped by the pigments.

During drying, the top surface of the coating layer may be considered to be a porous skin. Water can evaporate through this coating matrix, but particulate binder can not move through the pore structure. Therefore, particulate binder accumulates at the coating surface, and binder accumulation results in increasing binder concentration at the surface. On the other hand, soluble binder can move through the coating surface like a porous skin, so that this layer does not affect binder migration. During drying, soluble binder has a tendency to restore uniformity by molecular diffusion. If the evaporation rate is higher than the diffusion rate, binder concentration at the surface will be increased. Conversely, if the evaporation rate is lower than the diffusion rate, binder concentration will be uniform through the whole coating structure (30).
CHAPTER III

APPROACH AND OBJECTIVES

Pigment size can control the pore structure of coatings such as pore volume and pore size. If the pore volume remains constant and the pigment particle size is reduced, the pore size must be smaller. Therefore, although the actual pore size can not be measured directly, the relative pore size can be estimated by altering pigment and pigment size distribution.

By applying coating to a porous "paper like" Tyvek substrate, the coating can be dried with hot air immediately after coating color is applied or after the FCC has been reached. By measuring the solids level at the FCC, the voids volume at the FCC can be determined as shown in appendix A. By reducing the pigment size, the relative pore size can be reduced and the effect on migration observed.

The specific objectives are as follows:

1. To investigate the relationship between the size of pigments and pore volume and size during the consolidation of the coating colors.

2. To investigate the relationship between the size of pigments and binder migration during drying.
3. To investigate the relationship between drying delay and binder migration (before and after the FCC).

4. To measure the latex concentration at the top surface of coating layer with Tyvek and Mylar for determining the degree of binder migration.

5. From the above data, attempt to determine the correlation between pigment size, pore size of the coating and binder migration.
CHAPTER IV

EXPERIMENTAL DESIGN

Coating Preparation

Model coating colors consisting of either ground limestone or clay pigments and SB latex without any other additives were used for this study. The pigments were dispersed in distilled water under high shear for 30 minutes. The pigment slurries were prepared at 70% solids by weight. The following pigments and binder were used:

Pigments

1. Fine carbonate with a mean particle diameter of .65 $\mu$m (Hydrocarb 90, OMYA).
2. Medium carbonate no. 1 with a mean particle diameter of 1.00 $\mu$m (C1, OMYA).
3. Medium carbonate no. 2 with a mean particle diameter of 1.40 $\mu$m (Hydrocarb 60, OMYA).
4. Filler carbonate with a mean particle diameter of 3.00 $\mu$m (C3, OMYA).
5. No. 2 clay: Hydrasperse, Huber.
6. Delaminated clay: Alphaplate, ECCA.
7. Filler clay: Klondyke (KWW), Englehard.
**Latex**

Styrene Butadiene

Particle Size: 1200 Å

Tg: 20°C

Acid Modification: Medium

Latex and water were added slowly under medium shear for five minutes. All coating colors were applied at 55% solids (by weight) and 15 pph latex concentration at pH 8.

**Application of Coatings**

Coatings were applied on the Tyvek with a wire wound rod. The paper was coated with seven different coating colors, and each process was repeated six times for investigating reproducibility. The Tyvek used had strips of pressure sensitive adhesive (PSA) applied to its back side. These strips of PSA have been observed to accelerate the penetration of water from the coating into the substrate. The coating was watched after application and the time required for the gloss to drop suddenly was observed at the first critical concentration (28). The coatings at the FCC were scraped off the sheet and the solids level measured.

The coated sheets were dried before and after the FCC with a hot air gun dryer. During drying, the sheets were moved around for even drying. After drying the pore volume was calculated by using the percent solids level at the FCC. A sample calculation is given in Appendix A.
size was estimated by using SEM microphotographs analyzed by an image analyzer.

The coating weight was also measured manually. The coated paper was punched, and then the punched area was weighed. The circle area of the base sheets was punched and weighed. The difference between the two circles for was the coating weight.

Measurement of Water Loss Rate

The coating color was scraped at FCC by a razor blade, and the time to reach the FCC was also measured. After oven drying, coat weight was determined by cutting a strip of coated paper of known area and basepaper weight.

Water loss rate is water to penetrate into the substrate and the water loss rate in grams per unit area per unit time was calculated by the following formula:

\[
\text{Water loss rate} = \frac{\text{Coat weight} \times [(1/a) - (1/b)]}{\text{Time}}
\]

Where 
\( a = \) initial solid fraction \\
\( b = \) solid fraction at FCC \\
\( \text{Time} = \) Time to reach to FCC

Measurement of Pore Size

Scanning Electron Microscope

Hieser and Baker (31) examined the coating surface with a stereoscopic electron microscope. This was one of
the first experiments which attempted to estimate the actual pore structure of the coating surface. The results with respect to pore structure qualitative rather than quantitative technique for determining binder presence. In the present study photomicrographs were made to show the surface structure at 5000 x magnification.

Image Analysis

In this study an Omnicon 3600 Image Analysis system was used for the determination of pore size of coating surface. SEM microphotographs of coating surfaces were used to obtain mean pore size and pore distributions. The image analyzer uses a high-quality microscope to view the sample and transmits the image to an image processor with a high-resolution camera. The image is displayed on the monitor. Coating surface pores in the SEM microphotographs appear as dark spots and can be selected by intensity difference. The image can be improved or made more sensitive by adjusting its shading or enhancement. When the desired image is shown on to the screen, the measure button is pressed and the image analyzer measures the area and size of the black spots and calculates the total count and pore distributions. Calibration should be done by using the "measure and select factor" options under the calibration menu of the image analyzer software.
Measurement of Binder Migration

UV Analysis

In this experiment UV analysis was used for measurement of binder migration. This technique was developed by Fujiwara and Kline (32) for determining the amount of styrene butadiene (SB) latex on the surface of coatings. SB-latex is composed of styrene and butadiene, and it has a double bond. Conjugated double bonds absorb in the UV range. Therefore, the proper wavelength can detect SB-latex on the sheet surface. Reflected absorption of UV was used for obtaining the surface amount of SB-latex. In order to eliminate other effects, multiple wavelengths in the UV region were used. The UV instrument was equipped with a scanning X-Y stage, 90° light source and a 45° detector. The samples were put on the X-Y stage, and scanned. A single scanned area was 5 mm x 1.0 mm, and 63 areas in the machine direction were scanned. Therefore, a 5*63 mm² area was measured as a single sample for this study.

The amount of reflected ultraviolet measured by the detector determined the amount of styrene butadiene (SB) latex on the surface of the coating. Known latex concentration values, i.e., 10, 15, 20 parts per hundred in carbonate and clay, respectively, were used to calibrate the instrument.
CHAPTER V

RESULTS AND DISCUSSION

Coatings were prepared in the laboratory having different pigments to study the effect of pigment type and particle size on binder migration under variable drying conditions. Four different types each of carbonate and three different types each of clay were used and mixed in all-synthetic binder formulations. The coatings were prepared at 55% solids level. The carbonates were ground limestones of four different grades having average particle size diameters of 0.65, 1.00, 1.4, and 3.0 microns, respectively. The clays were No. 2, delaminated and filler grade. The synthetic binder, a styrene butadiene (1200 Å average particle size, 20 °C Tg, and medium acid modification) was added at a level of 15 parts per 100 parts of pigments. The coatings were applied on an absorptive substrate, i.e., Tyvek, and a non-absorptive Mylar film.

The wet coating films were dried by three drying methods: air drying, hot air drying at FCC, and immediate drying with a hot air gun. Air drying starts to dry the sample at ambient conditions, FCC drying is to start drying the sample with the hot air gun at the first critical concentration, and immediate drying acts to dry immediately
after the coating color has been applied.

Parameters measured were the water loss rate and pore volume based on estimation of the first critical concentration (FCC). The relative pore size was estimated from SEM photomicrographs by using an image analyzer. Latex concentration at the surface was measured by using the ultraviolet technique (32).

Data for Water Loss Rate

The two types of pigments used, carbonate and clay, had inherently different particle size and shape distributions and different degrees of pigment-latex interactions, depending on the topochemistry of the particles. Because of these differences, the solids levels at the FCC were variable.

As shown in Table 1, overall, carbonates coatings had 102% greater water loss rate values than clay-based coatings. The characteristic time to reach the FCC was 30% shorter for carbonates than clays. Gane et al. (33) mentioned that close packing of blocky pigment particles, such as fine carbonates, creates a network of fine capillaries, which tends to slow capillary dewatering of colors into absorbent basepapers. In contrast, the closely packed plate-like clay particles introduce an added tortuosity which tends to resist the passage of fluid. As a result, the period of time to reach FCC was longer for clay than
Table 1
Water Loss Rate at FCC

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Time (S)</th>
<th>Solids level (%)</th>
<th>Coat WT. (g/m²)</th>
<th>Water Loss Rate (g/m² min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine</td>
<td>3.7</td>
<td>70.0</td>
<td>23.1</td>
<td>146 ± 39</td>
</tr>
<tr>
<td>Med.1</td>
<td>2.1</td>
<td>68.6</td>
<td>14.2</td>
<td>146 ± 16</td>
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<tr>
<td>Med.2</td>
<td>2.5</td>
<td>71.0</td>
<td>21.8</td>
<td>214 ± 22</td>
</tr>
<tr>
<td>Filler</td>
<td>6.4</td>
<td>68.7</td>
<td>18.5</td>
<td>63 ± 15</td>
</tr>
<tr>
<td>Average</td>
<td>3.7</td>
<td>69.6</td>
<td>19.4</td>
<td>145 ± 23</td>
</tr>
<tr>
<td>#2 Clay</td>
<td>7.8</td>
<td>68.2</td>
<td>14.8</td>
<td>40 ± 6</td>
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<tr>
<td>DLM Clay</td>
<td>4.0</td>
<td>68.1</td>
<td>13.0</td>
<td>68 ± 11</td>
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<tr>
<td>Filler Clay</td>
<td>2.7</td>
<td>67.3</td>
<td>13.9</td>
<td>102 ± 20</td>
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<tr>
<td>Average</td>
<td>4.8</td>
<td>67.9</td>
<td>13.9</td>
<td>70 ± 12</td>
</tr>
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</table>

Water loss rate = Coat weight [(1/a) - (1/b)]/ Time

Where,  
- a = initial solids fraction = .55
- b = solid fraction at FCC
- Time : time to reach to FCC
- Coat weight : coat weight at FCC

carbonate based coatings.

The data obtained in this study indicated that carbonates may have created continuous and regular capillaries, which facilitated fast dewatering into the absorbent Tyvek basepaper.

In this study, it was expected that smaller pigment particles would create fine capillaries which would slow capillary dewatering of the coating into the absorbent basepaper. The results in Table 1 illustrate that fine pigment particles contributed to a slower water loss rate.
Plate-like clay particles compared to spherical-like carbonates also led to a slower water loss rate. The water loss rate data for clay based coatings followed the above trend, but the carbonate data did not. For the carbonate coatings, coat weights also showed variation from 14.2 g/m² to 23.1 g/m², but coat weight of clay coating showed a roughly constant value. Coat weight is another factor influencing the water loss rate. In this study, the carbonate system had two factors affecting the water loss rate, i.e., coat weight and particle size & shape, so that the effect of each factor on the water loss rate could not be isolated.

Malik (34) reported a significant correlation between water loss rate and binder migration. Water loss is the amount of water absorbed into the substrate, but it could also be correlated to the degree of water migration. The theory is that, if the water is able to move freely into the substrate, it could also move freely to the surface. When the water moves in either direction, it is possible that the latex also moves with it.

According to the present study, there was a correlation between water loss rate and binder migration. Table 1 shows that water loss rate increased with increasing pigment particle size for clay coating. As shown in Figure 5, latex concentration at the surface increased with larger clay pigment particles. Therefore, the water loss rate and
Bar refers to latex concentration, and line refers to water loss rate.

Figure 5. Latex Concentration and Water Loss Rate of Clay.

binder migration had a positive correlation. However, the carbonate results did not show this trend as shown in Table 1 and Figure 6. It can be conjectured that coat weight influenced these results.

Data for Pore Volume

The pore volumes were calculated by using the percent solids level at the FCC. A more detailed description of
the calculation method is found in appendix A. The calculated pore volumes of the carbonate and clays coatings are shown in Table 2. In this experiment, the pore volume of the clay coatings was found to be 1% higher than that of carbonate coating.

In this experiment, it was assumed that if the pore volume remained constant and the pigment particle size was
Table 2
Pore Volume at FCC

<table>
<thead>
<tr>
<th>Pigment</th>
<th>Solids level (%)</th>
<th>Specific Gravity</th>
<th>Pore Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine</td>
<td>70.0</td>
<td>2.7</td>
<td>54.0 ± 1.0</td>
</tr>
<tr>
<td>Med.1</td>
<td>68.6</td>
<td>2.7</td>
<td>55.0 ± 1.5</td>
</tr>
<tr>
<td>Med.2</td>
<td>71.0</td>
<td>2.7</td>
<td>52.0 ± 2.1</td>
</tr>
<tr>
<td>Filler</td>
<td>68.7</td>
<td>2.7</td>
<td>55.0 ± 2.5</td>
</tr>
<tr>
<td>Average</td>
<td>69.6</td>
<td>2.7</td>
<td>54.0 ± 1.8</td>
</tr>
</tbody>
</table>

| #2 Clay  | 68.2             | 2.6              | 55.0 ± 0.4      |
| DLM Clay | 68.1             | 2.6              | 55.0 ± 0.9      |
| Filler   | 67.3             | 2.6              | 56.0 ± 0.9      |
| Average  | 66.8             | 2.6              | 55.0 ± 0.7      |

Solids level: solids level at FCC
Specific Gravity: specific gravity of pigment
Pore Volume: pore volume at FCC

reduced, the resulting pore size must be smaller. The pore volume data in Table 2 shows that the pore volumes of all carbonate coatings were similar. Therefore, the assumption based on constant pore volume indicates that the pore size in the carbonate coatings should increase with pigment particle size. The void volume of the clay coatings were also constant. Having constant void volume, implies that as the clay particle size increased pore size also increases.

Data for Relative Pore Size

Photomicrographs of carbonate and clay samples were
taken with the Scanning Electron Microscope (SEM). The actual pore size could not be measured by this technique, but the relative pore size was determined by using an image analyzer. The procedure is described in the following paragraph.

The analysis was based on the fact that the pores in the coating layer looked like black spots on the SEM photomicrograph. An image analyzer can measure the black spot size. However, all pores were not of the same intensity. When the image analyzer was used, the density of black color characteristic of a pore had to be determined by the user. An attempt was made to keep the cut-off intensity constant so that a relative pore size could be calculated. The absolute value for pore size could not be measured since the exact pore size of both pigments could not be determined and used for calibration.

For the carbonate-latex system, as shown in Figure 7, it can be seen that the relative pore size increased as the pigment particle size increased. Similar results were obtained for the clay-latex system, as shown in Figure 8. The data do support the hypothesis that the pore size increased with increasing particle size at roughly constant pore volume. This may be due to the lower number of particles of large size occupying the same volume resulting in decreased number of pores of bigger size. Visual comparisons, as shown in Figure 9 and 10, using SEM
photomicrographs confirmed the result obtained by image analysis. Clay photomicrographs showed a more clear difference than carbonate photomicrographs. Larger particles also showed a lower pore uniformity.

Pore size is theorized to be important for binder migration. During drying, water moves with latex toward the coating surface. This results in pigment particles getting closer to each other. At some point, assumed to be
Figure 8. Relative Pore Size of Clays.

After the FCC is reached, the repulsion of pigment due to the electric double layer is overcome, and pigments form a structure. After the FCC is reached, the capillary structure of the coating starts to form and binder must migrate through these capillaries. Pore size becomes a critical factor for binder migration after the FCC, because binder migration should require larger capillaries than the latex particle size. Therefore, this study used four different pigment
A) No. 2 Clay, Air Drying

B) Delaminate Clay, Air Drying

C) Filler Clay, Air Drying

Figure 9. SEM Photomicrographs of Latex-Clay Coated Surfaces on Tyvek.
particle sizes of carbonates and three different pigment particle sizes of clays for controlling the pore size. In this study, the results showed that it is possible to control the pore size by using different pigment particle sizes as inferred from the Figures 7, 8, 9 and 10.

Statistically, air drying and immediate drying gave the same pore size for all-sized particles except for the largest carbonate and filler clay particles. Drying at the
FCC gave pore sizes significantly larger than with the other two drying methods. From the SEM photographs, the carbonate pores are smaller than with all clays. The largest carbonate had a few comparatively large pores. All other carbonates had qualitatively smaller and more uniform pores. The clay-based coating photographs show more larger pores than carbonate coatings, particularly, the filler clay had relatively large pores and a wide pore size distribution. This was also shown with the FCC drying data.

As expected, the pore size and binder migration gave a significant correlation as shown in Figures 11 and 12. The larger pigment size gave the larger pore size and also resulted in more binder migration.

Effect of Substrate on Binder Migration

Figures 13, 14, 15, and 16 show the effects of drying method and the type of substrate on the surface latex concentration for different carbonates (Figures 13 and 14) and clays (Figures 15 and 16). Tyvek paper is a porous or absorbent base paper having a well defined pore size distribution with pressure sensitive adhesive (PSA) strips on the back which accelerates the penetration of water or liquid phase from the coating into the substrate by changing the contact angle. Mylar is a non-absorbent, impervious polyester film substrate.

Air drying showed no significant differences in latex
Bar refers to relative pore size, and line refers to latex concentration.

Figure 11. Relative Pore Size and Latex Concentration of Calcium Carbonates.

concentration at the surface between different carbonates or clays. Actually, there was little difference between the two pigments. In contrast, immediate drying showed substantial difference in latex concentration between pigments and particle sizes. For carbonates, surface latex concentration was much higher, i.e., by more than 100% with
immediate hot air than air drying. Concentration of latex also increased almost linearly with particle size. For clays, results were mixed. Delaminated and filler clays had higher surface latex concentrations with immediate than with air drying. However, concentration of latex at the surface was higher for carbonates than clays above and beyond differences in relative pore size. Water, and
consequently latex particles took a longer time to penetrate through the pigment matrix in the case of clay than carbonates. This is in agreement of the water retention difference between the two systems as presented by Gane et al. (33).

Presumably, immediate drying shows the response of the coating matrix to pressure penetration during application of coating by a rod. Although water retention is
Figure 14. Latex Concentration of Calcium Carbonates on Mylar.

comparatively low for carbonates, i.e., water penetration is high, latex concentration at the surface was high with drying immediately after coating application.

Differences in surface latex concentration were smaller with the porous Tyvek paper and non porous Mylar. Here, coatings at air drying did not show substantial variation with pigment particle size. Immediate drying with Tyvek and Mylar showed the same trend which is greater
latex concentration with increasing particle size for both pigments and both substrates, but surface binder concentration with clay coating on Tyvek showed higher than on Mylar.

In conclusion, pore size and its distribution in the coating matrix was important only under forced drying. Under these conditions, capillary structure and size appear to play a dominant role for manifesting penetration of the
continuous coating phase through the pigment matrix. However, latex concentration at the coated film surface was influenced by more than the size and distribution of pores. It seems that there was a time delay for latex particles in penetrating the matrix. At this time, there is no good explanation for this phenomenon. Latex concentration at the surface was higher for an absorbent than a non-absorbent substrate.
Effect of Particle Size on Binder Migration

Data for Carbonate/Latex Coatings

The experimental data shown in Figures 13 and 14 are interpreted to show that there was no difference in the degree of binder migration when coating was air dried. When the coatings were dried with hot air, the latex concentration at the surface increased for all pigment types and particle sizes, showing a tendency for rapid drying to contribute to increased binder migration. As the pigment particle size increased, the degree of migration also increased. These data indicate that forced hot air drying induced binder migration due to vigorous evaporation and larger particles in the coating allowed a greater amount of binder migration due to larger pores in the coating layer.

After the coating had reached the FCC, capillary formation was initiated. The formation of capillaries can be affected by many factors, such as pigment size, shape, distribution, and drying method. Upon drying, it is theorized that the binder can migrate only through certain capillary sizes. If the capillary size is larger than the binder size, the binder can migrate during drying. If the capillary size is too small, the binder can not migrate through the capillaries. After drying these capillaries became pores. Although more migration was seen with the coating dried immediately, considerable migration was also shown

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with the coatings not dried until after the FCC had been reached.

Overall Comparison

Coating structure is theorized to be influenced by the pigment size of the coating color (2). The larger pigment particles have been shown to lead to a larger pore size in the coating layer. Therefore, a larger pore size allows more binder to migrate through the pigment matrix. In this experiment, it has been shown that binder concentration at the surface increased as pigment particle size increased for both carbonate and clay based coatings.

Effect of Particle Shape on Binder Migration

A comparison of sphere-like carbonate and plate-like clay, as shown in Figures 13, 17 and Figures 15, 18 respectively, with immediate hot air drying, indicated that there was generally a higher level of latex at the surface with carbonate. In other words, the more sphere-like carbonate allowed more binder migration than the plate-like clay. When the coatings were air dried, the surface latex concentration did not show any evidence of different degrees of migration between carbonate and clay pigments.

Latex binder migration requires pores in the pigment matrix to allow the particles to move. Pore volume is not the critical point for binder migration, but pore size is
Figure 17. SEM Photomicrographs of Latex-Carbonate Coated Surfaces on Tyvek.

more important. Binder movement requires capillaries larger than the binder particle size, and continuous capillaries would be preferred. One of the most important factors for binder migration is theorized to be the size of the smallest continuous capillaries. In the case of clay-latex system, capillaries are more likely to be discontinuous due to the plate-like shape. As mentioned earlier,
Figure 18. SEM Photomicrographs of Latex-Clay Coated Surfaces on Tyvek With Immediate Drying.

A) No. 2 Clay, Immediate Drying

B) Delaminate Clay, Immediate Drying

C) Filler Clay, Immediate Drying

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platy particles introduce an added tortuosity, so that binder migration in the clay-latex system should be more difficult than in the carbonate-latex systems.

Effect of Drying Methods on Binder Migration

Immediate drying of carbonate coatings on Tyvek showed the highest binder concentration at the surface, as illustrated in Figures 13. Aschan (21) proposed that hot-air blowing on the coating before the immobilization solids (FCC) is reached results in vigorous binder migration. Comparing ambient air to FCC and immediate hot air drying in the carbonate-latex system (Figure 13) showed that hot air drying after the FCC can lead to more binder migration than ambient air drying. The clay-latex system (Figure 15) showed the same trend. Immediate hot air drying gave the highest binder concentration at the surface. Ambient air drying was associated with the lowest binder concentration. Drying at FCC showed an intermediate level of migration. As shown in Figures 19 and 20, visual comparison of SEM photomicrographs support the above quantitative data.

Watanabe and Lepoutre (28) proposed a consolidation mechanism for pigment-binder systems. Their proposed consolidation mechanism can explain that immediate hot air drying, which starts to dry before FCC, induces higher binder migration. Before the FCC, pigment and binder particles can move freely in the aqueous dispersion. After
Figure 19. SEM Photomicrographs of Latex-Carbonate Coated Surfaces on Tyvek.

A) Filler Carbonate, Air Drying

B) Filler Carbonate, Drying at FCC

C) Filler Carbonate, Immediate Drying

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Figure 20. SEM Photomicrographs of Latex-Clay Coated Surfaces on Tyvek Comparing Air Drying to Immediate Drying.
the FCC, they theorized that the free motion ceases and a bulky and deformable three-dimensional network forms with binder particles trapped in between pigments particles.

The data shown in this thesis fail to support this claim. On the contrary, the data presented indicate almost as much migration by hot air drying after the FCC as before the FCC.
CHAPTER VI

CONCLUSIONS

This experiment investigated the effects of pigment sizes and shapes on water loss and binder migration through the pigment matrix in a coating layer. Based on the experimental results, the conclusions are as follows:

1. Pigment size affected coating structure only under forced drying.
   (a) The larger pigment size contributed to a larger pore size and wider size distribution in the coating layer.
   (b) The larger pigment particle size contributed to an increase in binder migration for forced hot air drying methods.

2. The calcium carbonate coatings showed a faster rate of water loss into the porous substrate than clay based coatings.

3. Calcium carbonate induced more binder migration than clay due to coating structure.

4. Forced hot air drying contributed to binder migration.

5. Binder migration can be influenced by pore size as this is affected by pigment sizes and shapes. Therefore, pigment size is one of the factors influencing binder migration.
REFERENCES


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Appendix A

Calculation of Pore Volume
Calculation of Pore Volume

Let $x$ be the solids level fraction at FCC
- $a$ be the specific gravity of water: 1.00
- $b$ be the specific gravity of pigment: Carbonate = 2.7
  Clay = 2.6

Volume of water = \( \frac{(1 - x)}{a} \)

Total volume of coating at FCC
= \( \frac{(1 - x)}{a} + \frac{x}{b} \)

Pore volume = \( \frac{(1-x)/a}{(1-x)/a + x/b} \)
Appendix B

Pore Size Measurements
OMNICON 3600 MEASUREMENT REPORT

Calibration: 1x 1.3622E-02 μm²/μμ
SAMPLE NAME: #2 CLAY, AIR DRYING ON TYVEK

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<th>Equiv Diam.</th>
<th>Percent Area</th>
<th>Field Area</th>
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<tbody>
<tr>
<td>4.0310</td>
<td>49.542</td>
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</tbody>
</table>

Statistics:
- count: 454
- min: 0.13170
- max: 1.1705
- mean: 0.32401
- std Dev: 0.18447

DISTRIBUTION ANALYSIS on Equiv Diam.

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<th>END</th>
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<th>START</th>
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ONNICON 3600 MEASUREMENT REPORT

Calibration: 1x 1.3622E-02 μm²/μm
SAMPLE NAME: #2 CLAY, AIR DRYING ON TYVEK

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Offset: 0.13170
Size: 0.03203
Range: 1.1827
Under: 0
Over: 0
Cal.: μm

Frequency Histogram - 0 #2 CLAY

Bins

End Of Measurement.

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