



8-1995

## Effects of Polymers on Pressure Water Retention and Binder Migration of Aqueous Coatings

Arvind M. Singhal

Follow this and additional works at: [https://scholarworks.wmich.edu/masters\\_theses](https://scholarworks.wmich.edu/masters_theses)



Part of the Wood Science and Pulp, Paper Technology Commons

---

### Recommended Citation

Singhal, Arvind M., "Effects of Polymers on Pressure Water Retention and Binder Migration of Aqueous Coatings" (1995). *Master's Theses*. 4918.

[https://scholarworks.wmich.edu/masters\\_theses/4918](https://scholarworks.wmich.edu/masters_theses/4918)

This Masters Thesis-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Master's Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact [wmu-scholarworks@wmich.edu](mailto:wmu-scholarworks@wmich.edu).



**EFFECTS OF POLYMERS ON PRESSURE WATER RETENTION AND  
BINDER MIGRATION OF AQUEOUS COATINGS**

by

**Arvind M. Singhal**

**A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements for the  
Degree of Master of Science  
Department of Paper Science and Engineering**

**Western Michigan University  
Kalamazoo, Michigan  
August 1995**

## ACKNOWLEDGEMENTS

No person achieves his goal in vacuum. He is surrounded by an environment which affects his work in no uncertain terms. The inspiration comes from the people and the society he lives in.

The following are just a few people who contributed to the completion of this thesis. First, I extend my sincere appreciation to my thesis advisor Dr. Raymond Janes, Dr. Raja Aravamuthan and Professor James Kline for their guidance and support, and more importantly for "not giving up on me".

Finally, I want to thank my friend Shambhu Nath, who ran binder migration and Hercules Hi-shear viscosity tests for this thesis.

Arvind M. Singhal

## **EFFECTS OF POLYMERS ON PRESSURE WATER RETENTION AND BINDER MIGRATION OF AQUEOUS COATINGS**

**Arvind M. Singhal, M.S.**

**Western Michigan University, 1995**

The effects of the molecular properties (degree of polymerization and degree of substitution) of water soluble polymers (containing carboxyl and hydroxyl groups on cellulosic backbone) on water retention under pressure and subsequent binder migration of coating colors are documented. It is concluded that no single mechanism can explain either water retention or binder migration. The dominant mechanisms of water penetration under dynamic pressure pulse are different from the mechanisms of water absorption under static pressure.

It is proposed that the molecular properties affect the rate of consolidation of the coating layer and thus greatly affect the water penetration under a dynamic pressure pulse. The water absorption under constant pressure for several seconds was greatly affected by the amount of polymer, packing efficiency and to a lesser degree by molecular properties. Binder migration was primarily affected by the amount of polymer and to a lesser degree by molecular properties.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	ii
LIST OF TABLES.....	vi
LIST OF FIGURES .....	vii
INTRODUCTION .....	1
LITERATURE ANALYSIS.....	4
Water Retention .....	4
Instruments .....	8
Electrical.....	8
Mechanical.....	9
Optical.....	10
Ultrasound .....	12
Ultraviolet Absorption .....	12
Chemical and Others.....	12
Binder Migration .....	13
Mechanisms of Water Retention.....	15
Polymer Adsorption Onto the Pigment and/or Latex.....	15
Electroviscous Effects Due to Electric Double Layer.....	16
Summary of Literature Review .....	16

## Table of Contents-Continued

STATEMENT OF THE PROBLEM .....	18
Objectives.....	19
Rationale.....	19
EXPERIMENTAL DESIGN AND METHODS.....	21
General Approach.....	21
Materials.....	21
Instruments .....	23
Preparation of Coating Color.....	27
Experimental Plan.....	28
RESULTS AND DISCUSSION.....	30
Preliminary Experiments.....	30
Percent Water Penetration as Measured by Modified IGT .....	31
Static Water Absorption as Measured by Gravimetric Method....	38
Binder Migration .....	41
SUMMARY OF RESULTS.....	45
CONCLUSIONS .....	47
RECOMMENDATIONS FOR FUTURE WORK.....	48
APPENDICES	
A.    Derivation of Equations for Percent Penetration Calculations .....	49
B.    Coating Color Data .....	52

## Table of Contents-Continued

C.	Sample Calculations.....	56
D.	Preliminary Experiments.....	61
E.	Data for Percent Water Penetration Measurements by Modified IGT.....	66
F.	Data and Calculations of Water Absorption as Measured by Gravimetric Method.....	95
G.	Data and Calculations of Binder Migration as Measured by Ultra-Violet Method.....	98
H.	Typical Characteristics of Base Paper	102
REFERENCES .....		104

## LIST OF TABLES

1.	Polymeric Materials Selected.....	22
2.	Conditions Tested on Modified IGT and by Gravimetric Method	29
3.	Percent Water Penetration of Preliminary Experiments .....	30
4.	Percent Liquid Penetration Results on Modified IGT.....	32
5.	t-Test Values for Percent Water Penetration.....	35
6.	Static Liquid Absorption Results by Gravimetric Method .....	38
7.	Binder Migration .....	42
8.	Effect on Percent Water Penetration Under Dynamic Pressure Pulse.....	45
9.	Effect on Water Absorption by Static Pressure .....	46
10.	Effect on Binder Migration During Drying.....	46



## LIST OF FIGURES

1.	Instrument Used for Measuring Water Retention by Gravimetric Method .....	24
2.	Modified IGT Tester Used to Coat the Paper.....	24
3.	Placement of Hot Air Gun for Drying Samples.....	26
4.	Effect of DP of CMC on Percent Water Penetration .....	33
5.	Effect of DS of CMC on Percent Water Penetration at Medium DP.....	34
6.	Static Water Absorption Versus Percent Polymer .....	39
7.	Dynamic Pressure Percent Water Penetration by IGT Versus Percent Polymer.....	40
8.	Effect of DP on Static Water Absorption .....	40
9.	Effect of DP on Binder Migration.....	43
10.	Binder Migration Versus Percent Polymer.....	43

## INTRODUCTION

Over the past two decades considerable research effort has been directed to the development of pigmented coatings for paper to improve pick strength, opacity, brightness, smoothness and ink receptivity. Many water soluble polymers have been developed to impart the specific properties to the coating formulations.

Coating formulations (usually called coating color) are largely made of pigment (usually clay) and binder (such as latex). Water retention is the ability of coating color to hold water and thus prevent it from penetrating into the base sheet. Binder tends to migrate toward the upper surface upon drying. This is called binder migration.

Viscosity and water retention are among the most important factors affecting coating applications. Binder migration affects the coating strength and optical and printing properties of paper. Both water retention and binder migration can be modified and controlled by the addition of water soluble polymers. However, insufficient knowledge of mechanisms involved limits the ability to predict performance of these additives. This study is designed to increase the understanding of the relationship between polymer molecular properties and performance in water retention and binder migration of coatings.

Good coating holdout and runnability are important characteristics of coating colors for paper and paperboard. During formulation of coating colors, thickener and

rheology additives are added to promote productive coating application. Although these additives are added in small amounts (i.e. less than 1% based on total dry solids), they strongly affect water retention. Water retention is the ability of the coating color to avoid losing too much water to the base sheet after coating color application. This, therefore, affects runnability, rheology, coating holdout and coated paper properties.

Coating colors are two phase systems in which solid pigment particles are dispersed in water containing polymers (viz. latex particles) and soluble additives. When this mixture is applied onto the base paper, liquid phase starts to penetrate into the interstices between the fibers.

Two successive stages of material transport have been identified [1]: (1) surface irregularities of paper are filled with coating color without separation of its constituents and (2) after contact with paper fibers the coating color's continuous phase (i.e. water plus dissolved binders and additives) transfers from the color to the paper. There is some evidence that water penetrates faster than the binder molecules (dissolved starch) [2], although other experiments indicate that no separation of starch and water occurs until retrogradation has set in [3].

Essentially, two different mechanisms have been demonstrated to affect the transfer of liquids from coating color to base paper: (1) capillary penetration and (2) pressure penetration. Both of them are significant in coating transfer [1].

Binder (re)distribution is caused by (a) water retention (actually due to lack of water retention) in the coating application phase and (b) drying of coated paper

(due to migration of binder). Migration of binder within the coating layer affects the coating layer structure, porosity, ink holdout, gloss and smoothness. The finished coating layer becomes weak with excessive migration, whereas poor bonding between base sheet and coating layer results with insufficient migration. Drying rate and additive addition can be changed more conveniently than coating applicator and base sheet and may be used to control migration of the continuous phase. The most common additives which are used for modification of flow and water holding properties of coating color are sodium carboxymethylcellulose (CMC), alginates, polyacrylates, hydroxyethylcellulose (HEC), associative cellulose thickener (ACT) and synthetic associative thickener.

## LITERATURE ANALYSIS

Broadly, the available literature on liquid transfer of pigmented coating colors into base sheets of paper and paperboard can be subdivided into following major areas: (a) water retention, (b) instruments, (c) binder migration, and (d) mechanisms of water retention.

At the end of this chapter, a summary of literature is presented.

### Water Retention

Water is transported from coating color into the base sheet by two distinct mechanisms: (1) capillary penetration, this takes place in the distance between application of coating color and metering and between metering and/or levelling and the dryers; and (2) pressure penetration, this takes place during the application of coating color to the paper at applicator roll or by roll and blade pressure during metering and levelling. The absorption time for capillary penetration may vary from a few milliseconds to a few hundred milliseconds depending on the speed of the coater and the distance between application and metering / levelling device and between the latter and dryers. The absorption time in pressure migration is generally of the order of a few micro seconds and the pressure may be as high as  $6.7 \times 10^6$  Pa [1].

Hemstock and Swanson [3] found that water penetration decreased with

increasing viscosity of a sucrose solution. However, water penetration for clay suspensions at increasing solid contents was found to pass through a minimum. They attributed this behavior to the plugging efficiency of clay particles and hypothesized that plugging of pores was more important than viscosity in limiting migration.

Hagerman, Jahn and Somers [4] showed that the water retention of coating colors increased significantly when small amount of synthetic thickeners such as CMC, methylcellulose or sodium alginates were added. They indicated that the concentration of methylcellulose was more important than the molecular weight in increasing water retention.

They [4] also reported that the water retention decreased at higher percent solids, however, no explanation was attempted. A reduction in water retention was observed when the latex to casein ratio was increased.

Clark, Windle and Beazley [1] measured the rate of liquid transfer from coating color to paper under both capillary forces and high pressures (about 1000 psi). Extrapolation curves were used to predict the migration for short intervals (down to 0.01 second). They found that capillary migration was largely surface tension controlled and was strongly influenced by the state of sizing of the base sheet and the presence, type and amount of surfactant in latex-bound systems. Clark *et al* [1] observed more variation in the pressure penetration with the use of different natural polymeric binders (eight different starches and casein) than with the use of five different latices. They reasoned that this was because of less variation in viscosity of the different latices than the natural polymeric binders. Thus they

claimed that pressure migration was primarily controlled by the viscosity of liquid phase.

Clark *et al* [1] also observed that heavily sized base sheets absorbed more water during pressure penetration than low sized base sheets. However, the data obtained showed reverse trend in case of capillary migration. They argued that sizing stuck down the microfibrils on its fibers and thus gave more open structure and made it easier for liquid to be forced into it under pressure. Also, sizing made it more difficult to wet fibers and thus reduced capillary penetration.

Eklund and Salminen [5,6] studied capillary and pressure penetration of water. They found that capillary penetration of water into the hydrophobic base paper is highly dependent on temperature. Because of high dependence of vapor pressure on temperature, they hypothesized that water vapor increased the wetting of fibers ahead of water front which increased the water retention during capillary penetration [5]. In another study [6] they showed a linear correlation between water absorption and contact time at low external pressures and in the beginning of the absorption. At high external pressures the water absorption is linearly dependent on the square root of contact time.

Salminen [7] studied the effects of liquid and paper variables on water transport into the hydrophilic paper. He found less temperature dependence of capillary penetration of water into hydrophilic paper [7] than that of hydrophobic paper [5]. The author argued that the effect of temperature was only partially felt since it was reduced because of hydrophilic nature of paper. The effect of

temperature was further diminished in case of pressure penetration of water into the hydrophilic paper. The author argued that the external pressure increased the transport velocity and the influence of molecular and capillary pressure was diminished.

Salminen [7] also found that the slope of the penetration curves (Y axis liquid transfer, X axis square root of time) was proportional to the square root of inverted viscosity in case of pressure penetration of water into a hydrophilic base sheet. Thus, he hypothesized that during pressurized water transport, balance between external pressure and viscous drag was important and thus structural and viscous properties were of great importance.

Fujiwara, Fujisaki, Shimizu and Kano [8] found (on pilot plant) that water penetration into the base sheet after the applicator roll from 67% coatings at 1000 m/min was higher than that from 65% coatings at 500 m/min. They argued that if capillary penetration was dominant mechanism after blade tip, the results should have been opposite because higher coating solids will increase viscosity and thus reduce penetration. Moreover, at higher speed, the penetration time was lower and hence the penetration should have been reduced. They also found that the coating solids do not increase rapidly after the blade tip as would be expected if pressure penetration was the dominant mechanism. Therefore, they hypothesized that the compression of the base sheet under blade and the following recovery is the dominating mechanism of penetration.

Malik [9] studied the quantitative effect of CMC, HEC, PVA, PA and ALG



on the water retention and binder migration in the capillary region. He found that CMC and alginates behaved similarly despite vast difference in their viscosities. He also found that the addition of polyacrylates (PA) gave lowest water loss and argued that PA had relatively higher number of carboxyl groups than any other polymer he used, and hence the higher retention.

Young *et al* [10] obtained gloss decay data on the CLC coater. They concluded that water retention on a short dwell type coater depends not only on the coating color viscosity, but also the capability of the coating to form a high solids cake barrier at the coating-paper interface. They also concluded that the water retention was strongly influenced by interactions between the water soluble polymers and clay.

### Instruments

The techniques used to measure retention and migration can be classified into the following groups: (a) electrical, (b) mechanical, (c) optical, (d) ultrasound, (e) ultraviolet absorption and (f) chemical and others.

#### Electrical

All instruments under this category are based on the fact that the electric conductivity of the paper is changed as it absorbs water.

Stinchfield, Clift and Thomas [11] described the Warren tester. It measures capillary penetration of coatings into paper by measuring the time required to drop

in the current flowing through the paper from 1 mA to an arbitrarily chosen 0.5 mA value to measure the value of water transport to the paper.

Hagerman, Jahn and Sommers [4] also used Warren tester but placed coating color on the bottom of the weight rather than on paper. They argued that the modified instrument gave better reproducibility because of short penetration times encountered with coating color penetration.

However, all these have the limitation that there is no convenient method to relate the change in electric conductivity to the actual water penetration.

### Mechanical

Arnold [12] developed the Roll Inclined Plane Method to measure the viscosity of the coating slips. The apparatus was simple and able to measure the flow properties of coating colors under low pressures and shear rates. The experiment consisted of measuring the area of the oval shape made by a heavy roller (which could be chosen of different weights to change the pressure) when it was released from the top of an inclined plane (whose angle can be altered to vary the speed and thus to change the shear rate) on the drop of known volume of coating color. The author argued that the area of the oval was a function of the color viscosity.

Eklund and Salminen [5,6] developed an instrument to measure the water sorption during short times (0.001 to 20 seconds). The pressure was applied by the liquid head through an application slot against backing roll and the time was adjusted by changing the speed of backing roll. The amount of the water absorbed was

measured by movement of a small air bubble in a capillary tube. The temperature was varied by an electric heater. However, this instrument is usable only with water without pigments. The coating pigments would plug the capillary and application slot.

Sandas, Salminen and Eklund [13] developed a method based on pressure filtration which involved the gravimetric determination of aqueous phase penetrating through a filter into the paper. The contact time could be varied in the range of 40 to 600 seconds. This method was sensitive to the changes in coating color formulations and showed good reproducibility but required several seconds of contact.

### Optical

All instruments under this category are based on measuring the reduced reflectance or increased transmittance of paper when it absorbs water from coatings.

Vincent [14] used an instrument to measure the transmittance of paper as the penetration of the fluid increased transmittivity of the light. Then he fitted the data in Lucas-Washburn equation for capillary flow, which made it possible to express the rate of penetration as a single numerical index. This experiment assumes that Lucas-Washburn equation holds good for the penetration of coating colors into the base sheet. However, Lucas and Washburn have assumed an oversimplified model, which does not hold good for the coating color penetration into the paper.

Napier [15] developed an instrument to measure the rate of change of reflectance with time as the liquid penetrates into the paper under capillary forces.

Author used the Kubelka - Munk equation to convert the reflectance measurements to the depth of penetration.

Lyne and Madsen [16] developed an instrument by modifying the IGT tester. They mounted a photocell inside the impression sector which was then connected to an oscilloscope. As the ink came into contact of the paper, the reflectance from the back side dropped and was continuously recorded on the oscilloscope. This method has the advantage that the pressure and speed of applicator roll can be changed to simulate the actual coating machine operation. Moreover, this method is dynamic and penetration can be measured in units of depth of penetration at short times (a few hundred micro-seconds) using Kubelka - Munk equation.

Clark, Windle and Beazley [1] used an instrument in which the pressure was applied through a piston and the reflectance was continuously monitored as a function of time on an attached oscilloscope. The pressure could be raised to 1000 psi and time could be adjusted down to 0.01 second. They also used Kubelka-Munk theory to convert their reflectance data to the depth of penetration.

Fifi and Arendt [17] used the same principle as of Lyne and Madsen [16], but did not mount the photocell inside the IGT tester. They used AC2 IGT tester with a coating blade attachment to simulate the blade coating process. The back-side reflectance readings were taken after removal of sample from the IGT tester. They showed experimentally that the measurements correlated very well with a pilot plant coater.

### Ultrasound

Taylor and Dill [18] developed an instrument based on the fact that the velocity of the sound decreases in the paper as the paper absorbs the water from the coating color. They calculated the ratio of sonic velocity in the paper before and after coating color was applied. This method is very simple, easy to clean up, takes less time and reproducible. They compared their data to that obtained by the electrical conductivity test as described by Stinchfield *et al.* [11] and found that the sonic velocity test had better reproducibility. Since there is no simple method to relate this ratio with the amount of water absorbed or depth of penetration, the results so obtained can not be used to analyze the penetration.

### Ultraviolet Absorption

Kline [19] and Malik [9] used ultra violet absorption technique developed by Fujiwara to measure the binder migration. They measured the surface concentration of styrene-butadiene and related it to the binder migration.

### Chemical and Other

Fujiwara, Fujisaki, Shimizu and Kano [8] and Malik [9] scrapped off the coatings at different time intervals and dried to measure the amount of water absorbed by the coatings.

Heiser and Cullen [20] used X - ray diffraction, electron beam probe and

nuclear magnetic resonance to measure latex distribution, but found them unsatisfactory because clay dominated the spectrum. They sectioned the coating layers and washed the sample with 57 % sulfuric acid to remove cellulose. Then, they washed the residue with hot concentrated nitric acid to remove latex. By weighing before and after washing with nitric acid the latex fraction could be calculated. Dappen [2] also scrapped off the coatings mechanically and by drying in an oven and igniting in furnace, he was able to calculate the latex concentration.

Lo [21] has summarized the available measurement techniques of water retention and binder migration. He has described the unglazed ceramic plate technique developed by Herbert. In this technique, the coating color is applied by draw down onto a porous ceramic plate. As the wet coating cake is drained by the ceramic plate, the gloss on the coating surface decreases. When the wet gloss is lost, the coating is removed to determine the immobilization solids.

### Binder Migration

Most of the work has centered towards evaluation of the effect of drying conditions on binder migration. Very little effort has been directed towards measuring the effect of water retention on binder migration. As a result of many studies the following conclusions are reached:

1. The drying conditions tend to redistribute the binder [2,20,22,23].
2. Direction of binder migration is primarily controlled by the rate of evaporation (i.e. rate of drying), being more towards the surface of coating at higher

rate of drying [19,20,22,23]. Hagen [22] suggested a model to explain the effect of evaporation rate on binder migration. According to him, the moving liquid and diffusion within the liquid tends to carry the binder molecules to the surface of the coating.

3. High solids tend to give low binder migration as evident in work of Heiser and Cullen [23]. High solids cause plugging and inhibit the binder migration.

There is good evidence that the water holding capability (or resistance to dewatering) of coatings affects binder migration. Coco and Shaw [24] argued that for minimum binder migration an ideal coating should have high solids, high vehicle viscosity, high water retention and high pigment-binder interactions. However, no quantitative data were supplied to establish the effect of water retention on the binder migration.

Malik [9] showed that a decreased water loss rate from coating color to the base sheet gave lower top surface latex concentration. He hypothesized that the polymers which reduced water loss, slowed down the rate of consolidation of structure which helped to increase the packing efficiency and therefore, reduced the migration of small latex particles.

Bushhouse [25] studied latex migration of clay/latex coatings applied on paper by a Keegan Coater. He found that a non-polymeric viscosity modifier (bentonite) had no effect on surface latex concentration, but polymeric viscosity modifiers (CMC, PVA and sodium alginate) significantly reduced the binder migration. Thus he concluded that the addition of polymeric additives will inhibit the binder

migration, but higher coating viscosity per se will not.

### Mechanisms of Water Retention

Water soluble polymers may interact with binder, pigment and/or water in the coating color. The following major mechanisms have been proposed (which may overlap also) for the rise in viscosity and/or water retention value due to addition of water soluble polymers: (a) polymer adsorption onto the pigment and / or latex, and electroviscous effects due to electric double layer.

#### Polymer Adsorption Onto the Pigment and / or Latex

Whalen-Shaw [26] concluded that the bridging of adsorbed CMC to other clay particles takes place via chain entanglement of non-adsorbed CMC due to hydrogen bonding or calcium ion cross linking. Under most conditions, CMC does not destabilize clay. Jarnstrom [27] found that adsorption of CMC and polyacrylic acid on kaolinite reached a plateau level with increased concentration. He showed that this plateau level was dependent on pH, electrolyte type, ionic strength and presence of counter ion which he explained in terms of electrical double layer effect. This plateau level was in excess of the concentration that was expected in case of monolayer adsorption flat on the surface. This suggested that the polymer was anchored at only a few points and thus the loops remained in the vicinity and increased the viscosity of the liquid phase.



### Electroviscous Effects Due to Electric Double Layer

Regions in the vicinity of surfaces in aqueous media are charged more often negatively than positively. This is because the cations are more hydrated than anions, and have greater tendency to reside in bulk solutions [9].

As a result of adsorption of anions, the overall negative charge of pigment or latex particles increases, which enhances electric double layer repulsion. The range of electric double layer will be increased by polymer adsorption. Ionization and high charge density will give polymers an extended configuration and, thus, it will increase the viscosity of the liquid phase.

### Summary of Literature Review

Studies have shown that water retention and viscosity of coating colors are altered by the addition of water soluble polymers [1,3-10]. Though the exact nature of the effect of water retention on binder migration is not very well documented, it is believed that water retention affects binder migration [24].

Most research workers concentrated their work towards the study of the effect of viscosity on water retention [3,5-7,9]. Very little has been reported about the effect of polymeric properties (viz. degree of substitution and degree of polymerization) on water retention as apart from viscosity.

Most instruments for measuring water retention under pressure take an indirect measurement. Warren tester [4,11] measures the change in conductivity of

paper. Arnold Roll Inclined Plane Method measures the area of the oval shape made by a heavy roller when it was released from the top of an inclined plane [12]. Vincent [14] used an instrument to measure transmittance of paper as the fluid penetration changed the transmittance. Taylor and Dill [18] measured the sound velocity as it increased because of water absorption.

Gravimetric method [13] measured the water retention directly in grams per square meter. However, the contact time was very large (40 to 600 seconds) and thus does not represent a dynamic pressure pulse such as experienced in blade coating.

Many research workers used optical methods to measure change in reflectance and then used Kubelka-Munk equations to calculate percent water penetration [15-17]. This technique was able to generate a pressure pulse by using IGT tester [16,17] for a few milliseconds.

Most studies on binder migration focused on effects of drying [2,19,20,22,23]. Relatively very few have documented the effect of water retention on binder migration [9,24]. Whereas, Coco and Shaw [24] argued that high vehicle viscosity is desirable to control binder migration, Bushhouse [25] found that non-polymeric viscosity modifier (bentonite) had no effect on surface latex concentration. Thus he argued that viscosity alone is not responsible to reduce binder migration.

## STATEMENT OF THE PROBLEM

The blade coating is the most common practice in coating applications. In this process, the substrate (paper) comes in contact with the blade for a few micro seconds and the pressure for that short period of time may reach as high as 6.7 MPa [1]. Most instruments for measuring water retention are not capable of creating the similar pressure and time conditions. By applying the coating on a modified IGT tester, the time can be reduced to a few milliseconds and pressure on blade can be varied by adjusting the counter weight. After applying black color coatings, the drop in back side reflectance can be used in Kubelka Munk equations to calculate the percent penetration [17].

Most research workers who reported the effect of polymeric properties on water retention did not keep the viscosity constant [3,5,9], hence, the effect of polymeric properties on water retention as apart from viscosity has not been well documented.

This study is intended to document the effects of polymeric properties (degree of substitution and degree of polymerization) on measuring water retention under dynamic pressure pulse and static pressure force. It is intended to document the binder migration after the dynamic pressure pulse water penetration.

### Objectives

1. Document the effect of CMC and HEC on water holding properties of coating colors under static and dynamically applied pressure.
2. Document the effect of degree of polymerization of HEC and degree of polymerization and degree of substitution of CMC on water retention.
3. Document the effect of these polymers on binder migration.

### Rationale

Water soluble polymers are used extensively to control the extent of water retention and binder migration of coating colors. However, extent and nature of these effects have not been studied systematically.

Different mechanisms have been postulated to explain how these polymers affect the water holding capability of coating colors; but no single mechanism can explain the entire process. This study will provide controlled data which can be useful in explanation of the possible mechanism(s). Moreover, since the viscosity of the colors is controlled by the molecular property such as degree of polymerization and degree of substitution, it will be very useful in understanding the effect of molecular properties of polymeric additives on water retention and subsequent binder migration.

Water retention and subsequent binder migration are affected by the addition of water soluble polymers because (a) they affect the viscosity of the dispersing phase

(i.e. binder plus water), and (b) they possibly form microstructures with the constituents of coating color (i.e. pigment and binder particles). Because each polymer has different chemical bonding nature, the adsorption of these polymers on pigment (clay particles) and binder (latex molecules) will be different. CMC and HEC both do not adsorb on latex [28]; however, they have definite but different affinities towards clay particles and paper fibers. HEC adsorbs on clay very strongly as compared to CMC. The affinity of HEC towards paper fibers has been found higher (adsorption 26%) than CMC (adsorption 15%) [28].

It is hypothesized that changes in molecular properties (degree of polymerization and degree of substitution) of water soluble polymers will produce different types of interactions among clay, binder, base sheet and water. The water retention and binder migration will be affected by the presence and nature of these interactions.

The proposed study will document the effect of degree of polymerization, degree of substitution of water soluble polymers (CMC and HEC) on water retention and subsequent binder migration during drying. The determination and evaluation of the adsorption and interactions of water soluble polymers with color constituents and base sheet is outside the scope of this study.

## EXPERIMENTAL DESIGN AND METHODS

### General Approach

Both sodium carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC) are cellulosic thickeners. They have affinity towards clay particles, latex and cellulosic fibers. This affinity can be changed by changing the degree of polymerization (DP) and/or the degree of substitution (DS) of these polymers. Because of solubility problems associated with HEC, a high value of DS [2.5] was selected for this study.

CMC over a wide range of degree of polymerization for a narrow range of degree of substitution of carboxyl group and vice-versa, and HEC over a wide range of degree of polymerization, were selected to document the effect of degree of polymerization and degree of substitution on the water retention of coating colors and subsequent latex migration.

The Brookfield viscosity was kept constant at  $1000 \pm 100$  cP at 100 rpm for each condition. This was achieved by mixing in different amounts of polymer, empirically.

### Materials

Seven CMCs, three HECs and one associate thickener (AT) were chosen for

the study. Table 1 lists the molecular properties of these polymers [29]. The selected AT (a,a-dimethyl-m-isopropenylbenzylisocyanate with dinonylphenoxy poly(ethyleneoxy)ethanol) had both hydrophilic as well as hydrophobic chains [30].

Table 1

Polymeric Materials Selected			
Polymer Selected		Molecular Weight	Degree of Substitution
	Type		
A	CMC	7,000	0.7
B	CMC	90,000	0.7
C	CMC	250,000	0.7
D	CMC	1,400,000	0.7
E	CMC	250,000	0.9
F	CMC	1,400,000	0.9
G	CMC	250,000	1.2
H	HEC	90,000	2.5
I	HEC	300,000	2.5
J	HEC	720,000	2.5
K	AT	Not Known	Not Applicable

U.S. clay No. 2 was used for all experiments. The experiments were conducted at two solids levels: 58.7% and 65.7%. Styrene-butadiene latex (11.89% on clay) was used for all experiments. Nigrosine "blue" dye was added (2.1% of clay) to make dark color coatings.

## Instruments

Water penetration under pressure was measured using two instruments. The static gravimetric method, developed by Sandas *et al* [13] gives the value of water retention directly. A schematic diagram of this instrument is given in Fig. 1. A filter and an absorbing paper were placed under the hollow cylinder. The coating color was poured into the cylinder and 1.0 bar pressure was regulated by the pressure regulator. After 50 seconds the pressure was released and the absorbing paper was detached from the filter and weighed. The gain of the weight of paper is the water absorbed which is divided by area of the opening in the cylinder to give water penetration in units of grams / sq. meter.

To simulate a typical blade coating operation, AC2 IGT printability tester was modified (Fig. 2). This design of inverted blade was taken from Fifi and Arendt [17] work and was manufactured at Western Michigan University. The blade was loaded with a weight to vary blade pressure. The IGT printability tester has a disc sector system which was operated at 1.5 meter / second speed. The paper was mounted on the sector and 10 Kgf pressure was applied by the applicator roll. The paper to be coated was cut into strips of 1.5 inches wide and 13 inches long. A plastic tape was put on the paper just before the applicator roll. A few drops of dark coating color was placed on this plastic tape with the help of a dropper. The plastic tape was used to avoid penetration of water before the experiment begins.



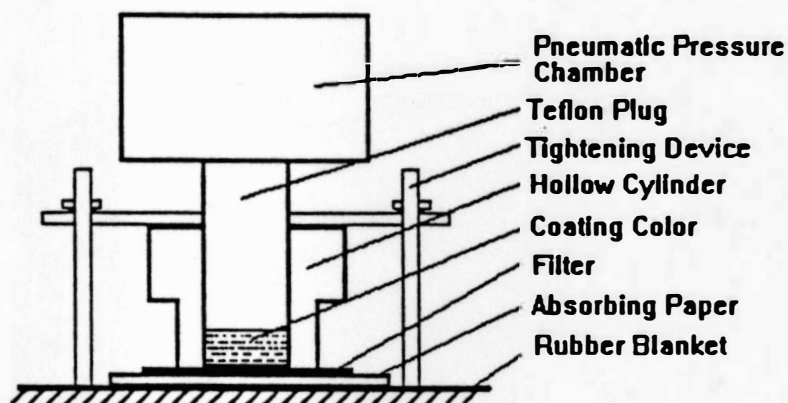


Figure 1. Instrument Used for Measuring Water Retention by Gravimetric Method.

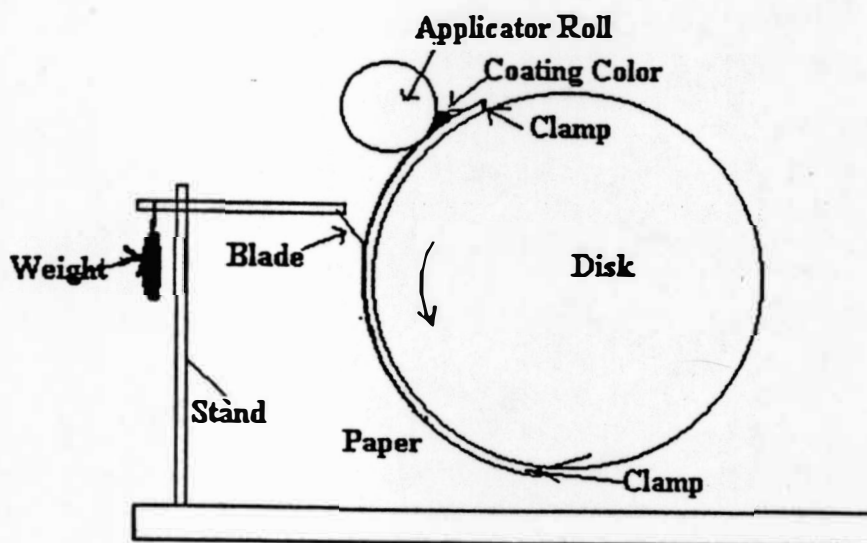


Figure 2. Modified IGT Tester Used to Coat the Paper.

The black coatings were prepared to measure water retention. The brightness of the back side of paper was measured before and after application of coating color. Kubelka Munk theory was applied to convert the data in to percent penetration. The following formulae were used to calculate percent penetration (the derivation of these equations is shown in Appendix A):

$$R_o = \frac{R_i - R_b}{[1 + R_i R_b - R_b \{(1/R_i) + R_i\}]} \quad (1)$$

$$SX = \frac{\ln[(R_o R_i - 1)\{R_i/(R_o - R_i)\}]}{\{(1/R_i) - R_i\}} \quad (2)$$

Where,  $R_o$  is the reflectance of paper sample with perfect black background,  $R_i$  is the reflectance of paper sample with dark background,  $R_b$  is the reflectance of dark background,  $R_i$  is the reflectance of paper sample pile so thick that further increase in thickness fails to increase reflectance,  $S$  is the scattering coefficient and  $X$  is the thickness of paper above dark background.

A dark backing pad was made by coating several sheets of paper. The brightness of the paper strips ( $R_i$ ) and dark backing ( $R_b$ ) were measured. The reflectance of the back-side of each paper strip (when backed by dark pad) was measured at six spots and averaged to obtain value of  $R_o$ . By using equation (1), it was possible to calculate the reflectance of paper sample with perfect black background. The value of  $SX_{initial}$  was calculated by equation (2).

The reflectance of the back-side of each paper strip after coating was measured at eight spots. The value of  $SX_{final}$  at each spot was calculated and then the

percent penetration at all eight spots of each paper strip was calculated by following equation:

$$\text{Percent Penetration} = \{1 - (SX_{\text{wet}}/SX_{\text{dry}})\} \times 100 \quad (3)$$

A hot air gun was clamped onto a vertical stand. The distance between the ground level and the air gun was kept 5 centimeters (Fig. 3).

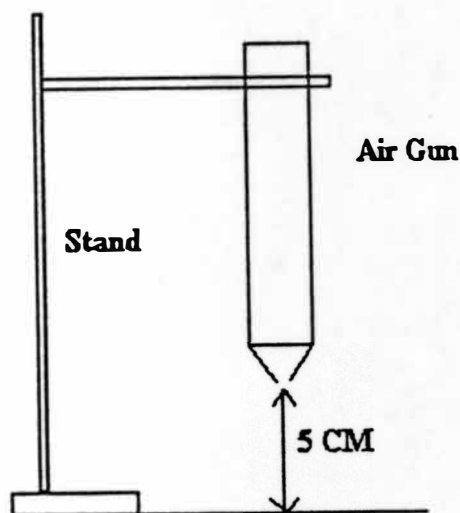


Figure 3. Placement of Hot Air Gun for Drying Samples.

Two coated strips were immediately dried (one at high heat setting; one at low heat setting) for studying binder migration during drying. The top surface latex concentration was measured and subsequent binder migration was calculated using the ultra violet reflectance scanning method as used by Kline [19]. In this instrument, monochromatic light is directed at the surface of coated paper and absorbance is

measured. The area of each illuminated surface is approximately 5 mm X 1.2 mm and a total of 63 readings were scanned for each strip. The conjugated double bonds of the styrene functionalities in the latex absorb UV at 260 nm. Absorbance at 235 and 285 nm is also measured to create a base line. The height above this base line of the absorbance at 260 nm is interpreted as a value which is proportional to the surface latex concentration. The data were fit into the straight line equation by measuring the ultraviolet absorption at 0, 4, 8, 12 and 16% latex concentration. The details are given in Appendix G.

### Preparation of Coating Color

Each type of CMC and HEC was dissolved in water by adding in incremental amounts to the vortex of agitated water. Each solution was visually inspected after preparation for the presence of any lumps. If any evidence of lumps was found, that solution was discarded and a fresh solution was made. Each solution was, then, stored in tightly capped bottles.

A master batch of coatings was prepared by following method. Two hundred grams of dye was dissolved in 4,000 grams of hot water. 9,512 grams of clay was added in incremental amounts to the water-dye solution and dispersed in a Cowles dissolver. After adding the clay, it was dispersed for an additional 30 minutes at high shear rate followed by 30 minutes dispersion at low shear rate. 2,012 grams of styrene butadiene latex emulsion (50% solids) was added and mixed at low shear rate for an additional half hour. It was stored in a plastic bottle with a sealed cap and

labeled as "Master Color Batch".

To make small batches from the above, 300 grams of "Master Color Batch" was taken and diluted to 310 grams for high solids (65.7%) and 350 grams for low solids (58.7%) by adding water and polymer solution. The mix of water and polymer solution was determined empirically, so that the Brookfield viscosity of the resultant color was  $1000 \pm 100$  cP at 100 rpm. Each of these batches was stored in a small plastic bottle with a air tight cap and properly labeled. Control color batches were made by adding water only (no polymer). All color data are given in Appendix B.

### Experimental Plan

Table 2 lists the conditions tested for percent penetration on the modified IGT and by gravimetric method. For water retention under dynamic pressure six strips were coated with dark coating color for each condition on modified IGT. Reflectance of each strip was measured at six spots before coating and at eight spots after coating. A sample calculation is shown in Appendix C.

All of the above conditions were tested for binder migration at low solids. At high solids, the polymer requirement was 0.03% to 0.13% (0.17% to 0.84% for low solids) to reach 1000 cP Brookfield viscosity. Since the amount of polymer requirement was low at high solids, it was suspected that the effect of polymer on binder migration may be overcome by natural variance in the test. Therefore, binder migration was tested at low solids only. All color data are given in Appendix B. For each condition, four strips were coated. Two were dried at low heat and two at

high heat. Each of the four strips was then tested for binder migration.

Table 2

Conditions Tested on Modified IGT  
and by Gravimetric Method

Additive	Polymer Group Type	Degree of Substitution	Degree of Polymerization	Low Solids	High Solids
Control	None	N/A	N/A	X	X
A	Carboxyl	Low	Very Low	X	X
B	Carboxyl	Low	Low	X	X
C	Carboxyl	Low	Medium	X	X
D	Carboxyl	Low	High	X	X
E	Carboxyl	Medium	Medium	X	X
F	Carboxyl	Medium	High	X	X
G	Carboxyl	High	Medium	X	X
H	Hydroxyl	Very High	Low	X	X
I	Hydroxyl	Very High	Medium	X	X
J	Hydroxyl	Very High	High	X	X
K	Hydrophobic & hydrophilic	Not Known	Not Known	X	X

## RESULTS AND DISCUSSION

### Preliminary Experiments

Preliminary experiments were run on the modified IGT to determine the effect of drying, polymer and blade on percent penetration. The comparison was made between the color with Polymer C (carboxyl group with low degree of substitution and medium degree of polymerization) and control (without any polymer). Table 3 records the percent penetration obtained with one standard deviation.

Table 3

Percent Water Penetration of Preliminary Experiments			
Blade	Control	With Additive	Immediate Drying
With Blade	30.14 $\pm$ 0.53%	32.92 $\pm$ 0.56%	Yes
Without Blade	27.73 $\pm$ 0.67%	30.28 $\pm$ 0.36%	Yes
With Blade	29.67 $\pm$ 0.57%	34.12 $\pm$ 0.62%	No
Without Blade	30.30 $\pm$ 0.52%		No

The t-test value for immediate drying and without immediate drying (with blade) was 0.60 for control color and 0.74 for color with polymer C. For 95% confidence interval, the t value should be 2.807 at 23 degrees of freedom (for 90% confidence interval, t value should be 2.500) [31]. Therefore, we conclude that either both the conditions have the same population mean or the sample sizes were

not sufficiently large to distinguish between them.

The t-test value for control and with polymer C was 5.30 when the color was applied with blade and it was air dried. This makes the confidence interval well above 99.9%. Therefore we conclude that the percent water penetration was significantly different for these two conditions.

By analyzing the percent water penetration data, we conclude the following:

1. Immediate drying after coating did not affect the percent penetration.

Therefore it was decided that the coated samples would be air dried before measuring the drop in back-side reflectance.

2. The method was able to distinguish very sharply between the no polymer and with polymer conditions. It was also able to distinguish the presence of blade, therefore establishing the validity of the experiments.

For complete details of preliminary experiments please refer to Appendix D.

#### Percent Water Penetration as Measured by Modified IGT

The average percent water penetration and standard deviation for the average of 48 measurements are summarized in Table 4 on the next page. All the detailed data can be found in appendices. It varied from 24.50% to 31.76% (standard deviation 2.28%) at low solids level, with the type of polymer. At high solids level, it varied from 25.30% to 30.4% (standard deviation 1.31%). Since the amount of polymer used at high solids was considerably less than that of at low solids level (0.03% to 0.13% at high solids level, 0.17 to 0.84% at low solid level), the effect



of polymer on water penetration was more evident at low solids level.

Table 4

Percent Liquid Penetration Results on Modified IGT					
Polymer	Low Solids		High Solids		Penetration
	Average %	Standard Deviation %	Average %	Standard Deviation %	Difference, (Low-High) %
Control	23.95	0.66	22.57	0.52	1.38
A	28.64	0.63	26.66	0.63	1.98
B	29.22	0.57	27.67	0.60	1.55
C	26.35	0.60	26.96	0.57	-0.65
D	31.76	0.44	27.89	0.57	3.87
E	25.86	0.72	26.01	0.68	-0.15
F	31.69	0.54	30.40	0.39	1.29
G	24.50	0.58	25.30	0.61	-0.80
H	28.02	0.60	27.17	0.63	0.85
I	28.15	0.75	27.63	0.58	0.52
J	30.17	0.66	27.90	0.58	2.27
K	28.56	0.68	26.53	0.57	2.03

The water penetration at low solids level was higher than at high solids level (average of 28.44% in comparison to 27.28%). All coating colors at low solids levels except those which had polymers of medium DP (molecular weight 250,000) and containing carboxyl groups (polymers C, E and G) gave higher penetration than

the colors at high solids levels. It is believed that the coating color with higher solids plugged the pores more extensively and thus inhibited the penetration of water. Since the water penetration was lower for low solids level for polymers of medium DP and carboxyl substituted groups, it is hypothesized that the water holding capability of these polymers was so strong as to overcome the lack of plugging efficiency in case of low solids coating.

Figs. 4 and 5 are the bar charts for the effect of DP and effect of DS of CMC, respectively, on water penetration. The effect of degree of substitution did not appear to be as dominant (DS range of 0.7 to 1.2) as degree of polymerization.

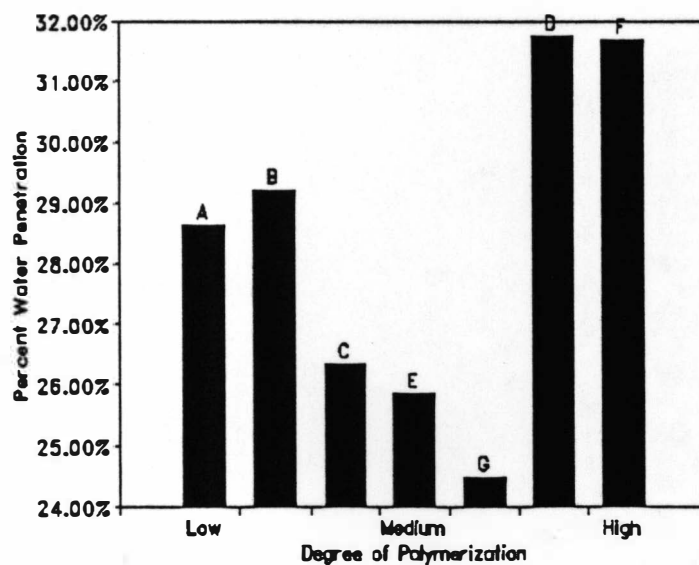


Figure 4. Effect of DP of CMC on Percent Water Penetration.

The student t test [31] was run among polymers (A through G) having carboxyl groups and polymers (H through J) having hydroxyl groups. Control was

compared to each polymer (A through K) and t-test value was calculated. These values are tabulated in Table 5. At 95% confidence interval, the significant t-value is 2.686 [31].

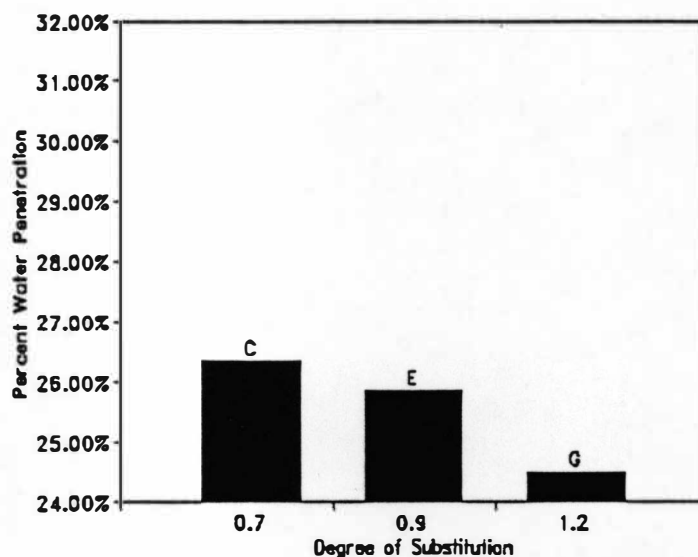


Figure 5. Effect of DS of CMC on Percent Water Penetration at Medium DP.

The t-values among the colors containing medium DP CMC for DS ranging from 0.7 to 1.2, varied from 0.52 to 2.22 (0.52 between C and E, 1.47 between E and G, 2.22 between C and G). The t-test value between D and F was 0.10 (both high DP CMC; DS 0.7 and 0.9 respectively). Therefore we conclude that the dynamic pressure percent penetration results for varying degree of substitution were statistically not significant.

The t-test value for polymer A and B is 0.68. Therefore we argue that the

differences in dynamic pressure percent water penetration for low and very low DP (at 0.7 DS) were statistically not significant. However, since the t-test values varied from 2.63 to 6.48 for varying DP (2.63 between A and C, 3.47 between B and C, 3.53 between B and D, 4.06 between A and D, 6.48 between E and F), we conclude that the colors containing polymers of varying DP produced statistically different results. Therefore we argue that the effect of DP (molecular weight) on percent water penetration was more dominant than the effect of DS (for polymers containing carboxyl groups). These data show (Fig. 4) that the lowest percentage water

Table 5

## t-Test Values for Percent Water Penetration

Name	Polymers with Carboxyl Groups						
	A	B	C	D	E	F	G
Cont.	5.14	6.04	2.69	9.85	1.96	9.08	0.63
A		0.68	2.63	4.06	2.91	3.68	4.83
B			3.47	3.53	3.66	3.15	5.80
C				7.27	0.52	6.62	2.22
D					6.99	0.10	9.97
E						6.48	1.47
F							9.07
Name	Polymers with Hydroxyl Groups						
	H	I	J				
Cont.	4.56	4.20	6.66				
H		0.14	2.26				
I			2.02				

penetration (under dynamic pressure pulse) was achieved by using the polymers with medium DP (molecular weight 250,000), at  $1000 \pm 100$  cP Brookfield viscosity. The amount of polymer required to obtain this viscosity, varied largely depending on the DP and to a lesser extent on DS and type of substituting group (hydroxyl or carboxyl): the amount of polymer was 0.63% to 0.84% for low DP, 0.28% to 0.47% for medium DP and 0.17% to 0.22% for high DP.

Jarnstrom [27] found that the adsorption level of polymer on clay particles was in excess of the concentration that was expected in case of monolayer adsorption flat on the surface. He argued that this was because the polymer was anchored at only a few points and thus loops remained in the vicinity. The longer chain would make it possible to extend itself more into the liquid medium and thus making bigger loops. This would require less polymer to gain the viscosity. The bigger loops extending into the liquid medium would make it less likely to consolidate in very short times (few micro seconds), thus, keeping the coating structure open. This openness would make it more likely to absorb water. This would give higher water penetration, if water continued to penetrate into the base sheet, even after the pressure pulse was removed. This would be achieved only if the compression of the base sheet under the blade and the following recovery is the dominant mechanism. Fujiwara, Fujisaki, Shimizu and Kano [8] also support this hypothesis. At low molecular weight of polymer, the loops are much smaller and thus higher polymer concentration was required to obtain desired viscosity. This will also inhibit the consolidation of the coating layer and thus higher percent water penetration was

obtained. This may explain why the polymers of high and low DP resulted in higher water penetration than the polymers of medium DP.

At very high degree of substitution, the polymers would tend to remain in the liquid because of electric double layer effect (both clay and polymer substituted groups are anionic). This will make loops detached from the clay and not holding to solids. It is argued that this gave relatively more penetration time and thus polymer I of medium DP (DS 2.5, hydroxyl group, 300,000 molecular weight) resulted in higher water penetration (28.15%) than polymers C (26.35%), E (25.86%) and G (24.50%) of the medium DP (0.7 to 1.2 DS, carboxyl group, 250,000 molecular weights).

The water penetration results for HEC of all DPs were statistically not significantly different (t-values from 0.14 to 2.26).

The control color was found to be significantly different from most other colors containing polymers (t-values were varied from 0.63 to 9.08; being on the lower end for the polymers with medium DP and on higher end for polymers with high DP). The control color, to our surprise, resulted in the lowest percent water penetration. A possible mechanism for this is that the water penetrated into the base sheet was very fast in the beginning, thus creating a very packed coating layer (filter cake) adjacent to the base sheet. This prevented more water penetration in the later stage.

### Static Water Absorption as Measured by Gravimetric Method

Water absorption for high solids coating color (average of 89.6) was found lower than at low solids level (average of 111.4 for low solids). The data are presented in Table 6.

Table 6

Static Liquid Absorption Results by Gravimetric Method			
Polymer	Liquid Penetration Grams/meter <sup>2</sup> Low Solids	Liquid Penetration Grams/meter <sup>2</sup> High Solids	Liquid Penetration Grams/meter <sup>2</sup> Low - High Solids
Control	182.8	101.0	81.8
A	105.4	88.9	16.5
B	87.5	77.9	9.6
C	79.3	77.0	2.3
D	103.5	90.3	13.2
E	104.3	94.2	10.1
F	89.7	79.9	9.8
G	86.8	77.9	8.9
H	86.9	99.9	-13.0
I	147.0	105.5	43.5
J	149.0	95.0	54.0
K	114.5	87.5	27.0

This trend is similar to the one obtained for percent water penetration when

measured by IGT. It is believed that the plugging of pores inhibits the water absorption. Only color containing polymer H (hydroxyl group, low DP, 0.84%) gave lower absorption at lower solids level than at higher solids level.

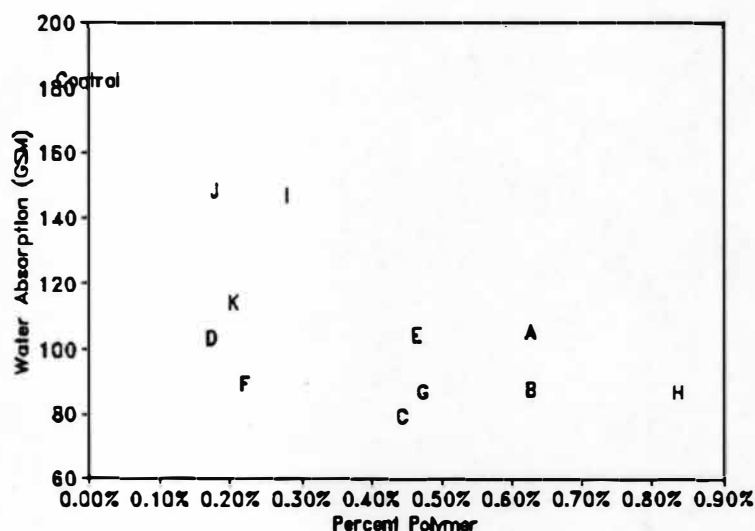


Figure 6. Static Water Absorption Versus Percent Polymer.

It should be noted that the amount of polymer H used was the highest (0.84% compared to 0.17% to 0.63% for all others). It appears that the amount of polymer was amongst the major factors affecting the water absorption. To test this hypotheses, the water absorption was plotted against the amount of polymer (Fig. 6). The data showed that the water absorption decreased as the amount of polymer increased (all the colors were made up to the same Brookfield viscosity). Such strong evidence of the effect of amount of polymer on percent water penetration, as measured by Modified IGT, was not found (Fig. 7).



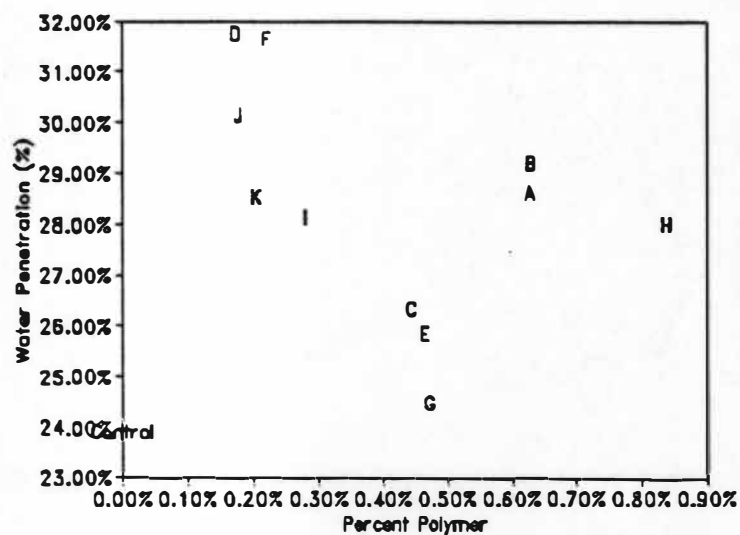


Figure 7. Dynamic Pressure Percent Water Penetration by IGT Versus Percent Polymer.

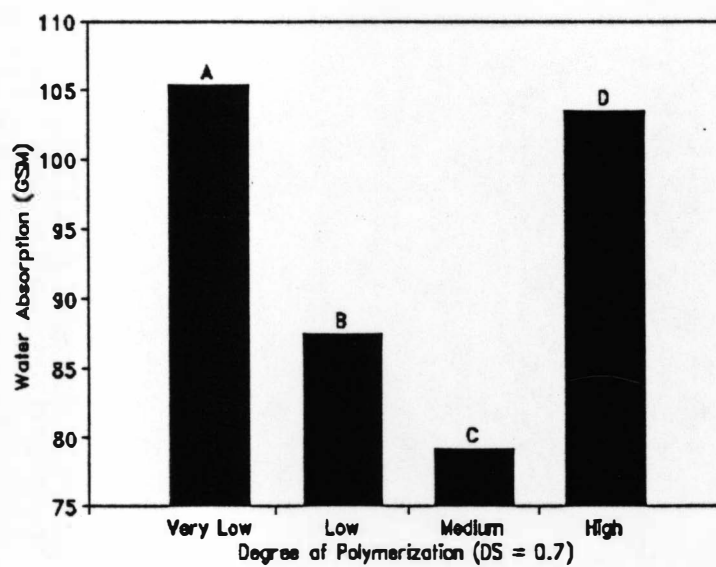


Figure 8. Effect of DP on Static Water Absorption.

Hence it is argued that concentration of polymer was not a dominant mechanism in case of dynamic pressure pulse, whereas it was a dominant mechanism in static pressure application.

Fig. 8 shows the bar chart of water absorption vs DP. It is evident that the water absorption was lowest at medium DP. It is similar to the trend obtained for percent water penetration as was measured by modified IGT (dynamic pressure pulse).

It is interesting to note that the polymer K (with hydrophilic and hydrophobic chains) did not produce statistically different results (for water absorption or penetration) either from CMC or HEC. It is also interesting to note that no generalization can be drawn for the effect of type of substituted group (between carboxyl and hydroxyl) on water retention.

### Binder Migration

Top surface latex concentration was found higher for coating colors with polymers of higher molecular weights (Table 7 and Fig. 9).

It has been hypothesized in the literature [19,20,22,23] that binder migration is primarily controlled by rate of evaporation. Hagen [22] suggested that the moving liquid during evaporation tends to carry binder molecules to the surface of coating. The presence of polymer capable of holding water molecules would offer more resistance to binder migration. This would tend to give higher binder migration for polymers which were added in low amounts. Since higher DP polymers were added

in smaller amounts, this may be a possible mechanism. This also suggests that the amount of polymer may play a dominant role in controlling binder migration. To test this hypothesis, binder migration was plotted against amount of polymer (Fig. 10). It shows a strong evidence that the binder migration was greatly affected by the amount of polymer.

Table 7

Polymer	Binder Migration	
	Binder Migration Low Drying Rate %	Binder Migration High Drying Rate %
Control	3.85	4.18
A	0.73	2.11
B	0.86	1.65
C	1.19	2.34
D	1.94	2.76
E	0.99	1.40
F	1.24	3.34
G	1.55	2.75
H	2.17	3.01
I	1.86	3.70
J	2.74	3.18
K	1.55	4.33

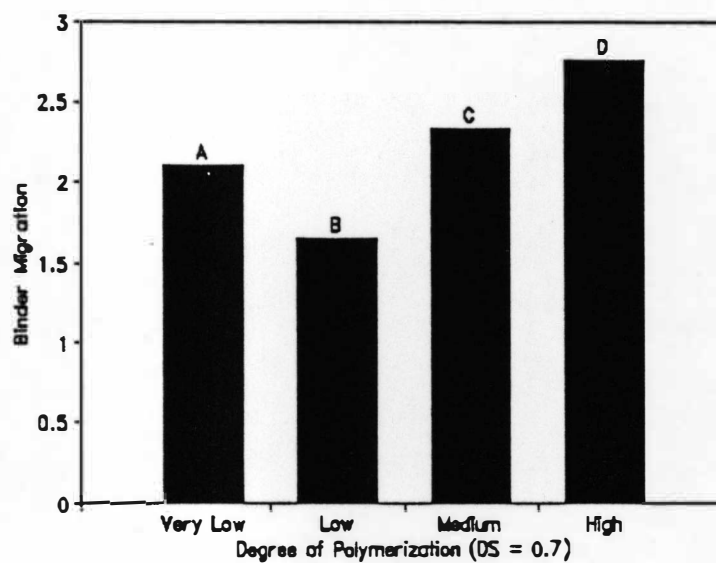


Figure 9. Effect of DP on Binder Migration.

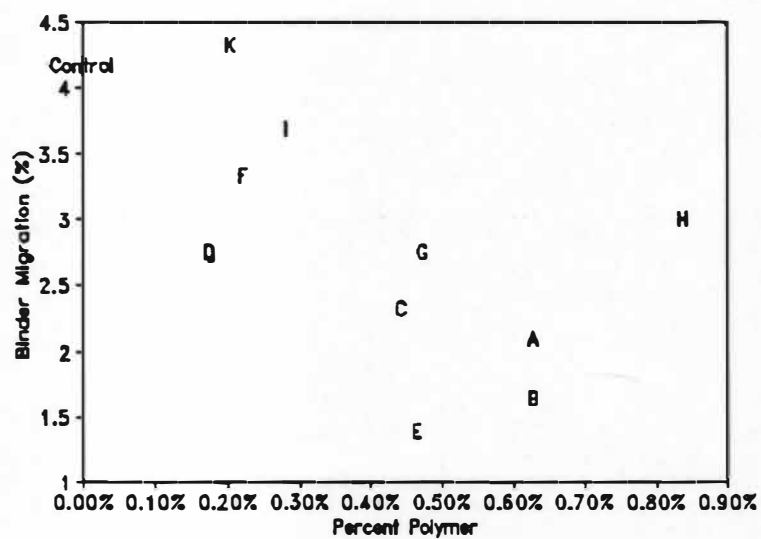


Figure 10. Binder Migration Versus Percent Polymer.

Binder migration was found much higher for polymers with hydroxyl groups at 2.5 degree of substitution (1.86 to 2.74) than those with carboxyl groups at 0.7 to 1.2 degree of substitution (0.73 to 1.94). It is argued that the higher DS polymer remained in between clay solids without anchoring due to electric double layer repulsion. Additionally, higher DS made the polymer more hydrophilic. Hence the polymer migrated with the liquid molecules and thus offered low resistance to binder molecules migration.

Polymer K (with hydrophilic and hydrophobic chains) was found effective (1.55) in controlling binder migration at low rate of drying; however, at higher rates of drying, this polymer was unable to hold binder molecules (4.33).

## SUMMARY OF RESULTS

Tables 8, 9 and 10 summarize the effect of degree of polymerization, degree of substitution, amount of polymer, solids level and type of substituted group, qualitatively, on percent water penetration under dynamic pressure pulse (coated on Modified IGT), water absorption under static pressure (gravimetric method) and binder migration (measured by top surface concentration).

Table 8

Effect on Percent Water Penetration Under Dynamic Pressure Pulse	
Variable	Effect
Degree of Polymerization	Minimum for medium DP. Higher values for both low and high DP. Very dominant effect.
Degree of Substitution	Not statistically significantly different for CMCs. Increased sharply for HEC in comparison to CMCs. Less dominant than DP.
Amount of Polymer	No measurable effect.
Solids Level	Lower for higher solids
Type of substituted group	No measurable effect.

Table 9

## Effect on Water Absorption by Static Pressure

Variable Name	Effect
Degree of Polymerization	Minimum for medium DP. Higher values for both low and high DP. Less dominant effect than amount of polymer.
Degree of Substitution	Low for DS from 0.7 to 1.2 (for carboxyl substituted groups). Very high for polymer of DS 2.5 (hydroxyl substituted group).
Amount of Polymer	Decreased with increasing amount of polymer. Very dominant effect.
Solids Level	Lower for higher solids.
Type of substituted group	No generalization can be drawn

Table 10

## Effect on Binder Migration During Drying

Variable Name	Effect
Degree of Polymerization	Increased as the DP increased (less polymer used at high DP).
Degree of Substitution	Low for DS from 0.7 to 1.2 (for carboxyl substituted groups). Very high for polymers of DS 2.5 (hydroxyl substituted group).
Amount of Polymer	Decreased with increasing amount of polymer. Very dominant effect.
Type of substituted group	Hydroxyl groups gave higher binder migration. The polymer having hydrophilic as well as hydrophobic chains was able to control migration at lower drying rate, but failed at higher drying rate.

## CONCLUSIONS

The molecular properties (specially degree of polymerization) were found to be a key characteristic in controlling water penetration under a dynamic pressure pulse. Medium degree of polymerization (molecular weights in the neighborhood of 250,000 to 300,000) resulted in lowest water penetration. It is proposed that several competing mechanisms play an important role in determining the water retention. The dominant mechanisms in determining the water absorption under static pressure appeared different from the mechanisms for water penetration under dynamic pressure pulse. The data supported that the water penetration under dynamic pressure pulse was greatly affected by degree of polymerization, to a lesser degree by degree of substitution and was independent of amount of polymer. It is hypothesized that the polymeric properties affected the plugging efficiency and rate of consolidation of coating layers. This changed the available penetration times and thus affected the water penetration.

The water absorption under static pressure was greatly affected by the amount of polymer and to a lesser degree by molecular properties.

Top surface latex concentration (a measure of binder migration) was strongly affected by polymer percent on solids, degree of polymerization and type of substituted group. It was higher for hydroxyl groups than carboxyl groups.



## RECOMMENDATIONS FOR FUTURE WORK

The present study focused on documenting the effect of polymeric properties of water soluble polymers on water retention under dynamic pressure pulse. To eliminate the effect of viscosity, the Brookfield viscosity was kept constant by adding the polymers in different amounts.

Future work is needed to determine the effect by keeping both (amount of polymer and Brookfield viscosity) constant. The viscosity can be controlled by the addition of bentonite, a non-polymeric substance.

The determination and evaluation of microstructures created by polymers onto the clay particles will give better insight into the understanding of mechanisms.

## **Appendix A**

### **Derivation of Equations for Percent Penetration Calculations**

Steele (31) published the substance of derivations of Kubelka-Munk Equations. He simplified the Kubelka-Munk Equation to:

$$\frac{(R_s - 1/R_i)(R_s - R_i)}{(R_s - 1/R_i)(R_i - R_i)} = \exp[SX(1/R_i - R_i)]$$

Where,  $R_i$  is the reflectance of paper sample with dark background,  $R_s$  is the reflectance of dark background,  $R_i$  is the reflectance of paper sample pile so thick that further increase in thickness fails to increase reflectance,  $S$  is the scattering coefficient and  $X$  is the thickness of paper above dark background. This equation can be rewritten for the reflectance of paper sample ( $R_o$ ) with perfect black background. In this case, the value of  $R_s$  will be zero. Hence:

$$\frac{(R_o - 1/R_i)(0 - R_i)}{(0 - 1/R_i)(R_o - R_i)} = \exp[SX(1/R_i - R_i)]$$

Solving the above equation and simplifying:

$$R_o\{(1 - R_i^2) + R_i R_s(1 - R_i^2) - (R_s/R_i)(1 - R_i^2)\} = (1 - R_i^2)(R_i - R_o)$$

$(1 - R_i^2)$  from the above equation is cancelled out, thus:

$$R_o = \frac{(R_i - R_o)}{\{1 + R_i R_s - (R_s/R_i)(1 + R_i^2)\}}$$

or,

$$R_o = \frac{(R_i - R_o)}{[1 + R_i R_s - R_s\{(1/R_i) + R_i\}]} \quad (1)$$

Steele (31) also simplified the Kubelka-Munk Equation to:

$$R_o = \frac{\exp[SX\{(1/R_o) - R_i\} - 1]}{(1/R_o) * \exp[SX\{(1/R_o) - R_i\}] - R_i}$$

Let,

$$A = \exp[SX\{(1/R_o) - R_i\}]$$

Then  $R_o$  can be rewritten as-

$$R_o = \frac{(A-1)}{(A/R_i) - R_i}$$

Simplifying the above equation and solving for A, gives:

$$A = (R_o R_i - 1) \{R_i / (R_o - R_i)\}$$

Substituting the value of A and taking logarithm of both sides yields-

$$SX = \frac{\ln[(R_o R_i - 1) \{R_i / (R_o - R_i)\}]}{\{(1/R_o) - R_i\}} \quad (2)$$

Equations (1) and (2) were used for calculation of percent penetration in paper as illustrated in Appendix C.

**Appendix B**  
**Coating Color Data**

## Amount of Materials in Master Color Batch Preparation

Material	Dry Weight (Grams)	Total Weight (Grams)
Dye (Nigrosine Blue)	200	200
Water	0	4000
Clay (U.S. # 2)	9430	9512
Latex (Styrene-Butadiene)	986	2012
<b>TOTAL</b>	<b>10616</b>	<b>15724</b>

## Properties of Coating Colors of Low Solids

Type	Polymer (%)	Brookfield Viscosity (cP)	Hercules Viscosity (cP)	Coat Weight (GSM)
Control	0.00	480	14	10.5
A	0.63	980	27	8.4
B	0.63	1080	27	9.6
C	0.44	1000	26	9.1
D	0.17	1000	24	9.7
E	0.47	1010	27	9.3
F	0.22	980	29	9.7
G	0.47	960	26	8.9
H	0.84	960	34	8.0
I	0.28	1020	22	8.5
J	0.18	1000	22	7.8
K	0.21	970	21	9.3

## Properties of Coating Colors of High Solids

Type	Polymer (%)	Brookfield Viscosity (cP)	Hercules Viscosity (cP)	Coat Weight (GSM)
Control	0.00	850	35	11.9
A	0.10	1020	64	11.0
B	0.12	1080	67	10.7
C	0.07	960	59	10.3
D	0.03	940	58	11.7
E	0.08	990	65	11.6
F	0.04	920	65	13.4
G	0.09	1000	60	10.6
H	0.13	1080	68	10.8
I	0.12	1030	68	12.1
J	0.03	920	58	9.7
K	0.08	970	105	12.7

## Master Color Batch Solids Determination

Foil (Grams)	Foil + Color (Grams)	Foil + Oven Dry Color (Grams)	Solids (Percent)
1.5770	5.8177	4.4621	68.03%
1.6009	5.3535	4.1553	68.07%
1.5922	5.8144	4.4646	68.03%
1.5658	5.1090	3.9764	68.03%

**Master Color Batch Data**

Ash	76.64% $\pm 0.27\%$
Clay Moisture	99.14% $\pm 0.03\%$
Clay Ash	85.75% $\pm 0.04\%$
Latex Solids	49.02% $\pm 0.01\%$
Percent Latex on Clay	11.89%



**Appendix C**  
**Sample Calculations**

### Sample Calculations for Modified IGT

The Brightness of Paper,  $R_i$  = 86.89%

The reflectance of the dark backing,  $R_b$  = 21.64%

For strip number 221, the following reflectances were measured when backed by dark backing of reflectance  $R_b$

Before Coating, % ( $R_d$ )	After Coating, % ( $R_c$ )
82.20	78.00
81.92	79.43
81.88	79.95
81.60	80.03
81.91	79.22
82.09	78.86
	79.48
	80.56

Average Reflectance before Coating (when backed by dark backing)  $R_d$  = 81.93%

Reflectance if the strip would be backed by perfect black body (before coating)  $R_{\infty}$  can be calculated by using equation (1) on page 50.

$$\begin{aligned}
 R_{\alpha} &= \frac{R_d - R_b}{[1 + R_d R_b - R_b \{(1/R_d) + R_i\}]} & \text{.....(a)} \\
 &= \frac{(0.8193-0.2164)}{\{1+0.8193*0.2164-0.2164*(1/0.8689+0.8689)\}} \\
 &= 0.8146 \text{ or } 81.46\%
 \end{aligned}$$

The product of scattering coefficient and the grams per square meter of paper underneath the dark backing can be calculated by equation (2) on page 54.

$$\begin{aligned}
 SX_i &= \frac{\ln[(R_{\alpha} R_i - 1)\{R_i/(R_{\alpha} - R_i)\}]}{\{(1/R_i) - R_i\}} & \text{.....(b)} \\
 &= \frac{\ln[(0.8146*0.8689-1)\{0.8689/(0.8146-0.8689)\}]}{(1/0.8689-0.8689)} \\
 &= 5.4667
 \end{aligned}$$

Similarly  $SX_r$  was calculated for each of the eight values of reflectances. By dividing the  $SX_r$  by  $SX_i$  scattering coefficient of paper (S) was cancelled out, yielding the ratio of penetration depth after coating to the depth (total) before coating. The percent penetrated basis weight of paper was calculated by subtracting this ratio from 1 and then multiplying by 100. The value of  $SX_r$  at 78.00% reflectance was calculated 3.7917. Hence Percent Water Penetration for this case was

$$\begin{aligned}
 \text{Penetration} &= 1 - SX_r / SX_i \\
 &= 1 - 3.7917/5.4667 \\
 &= 0.3064 \text{ or } 30.64\%
 \end{aligned}$$

Percent water penetration at all eight spots was calculated.

### Sample Calculations for Gravimetric Method

The weight of the absorbing paper for control color at low solids = 1.3812 grams

The weight of the absorbing paper after the test at above condition = 1.5274 grams

Water absorbed for this condition = 0.1462 grams

Water absorbed in grams per square meter (area of cell = 8 cm<sup>2</sup>) =  $0.1462 \times 1250$   
 = 182.8 grams per square meter

### Sample Calculations for Binder Migration

Five paper strips were coated with the coating color at 0, 4, 8, 12 and 16% latex and the ultra-violet intensity was measured. A straight line was fitted by regression. Following are the data:

Latex Concentration	UV
0	12322
4	13481
8	15308
12	16634
16	18568

The best fit of straight line gives following equation (R squared = 0.994)

$$UV = 12133.6 + 391.125 * \text{Latex concentration}$$

Latex concentration was calculated by above equation for a known UV Reading. Since originally 12% latex was used, binder migration was calculated by:

$$\text{Binder Migration} = \text{Latex Concentration} - 12$$

For the strip coated with control color and dried at high rate of drying, the UV reading of two experiments was 18703 and 18219. The average these UV reading is 18461. Hence

$$18461 = 12133.6 + 391.125 * \text{Latex concentration}$$

or latex concentration = 16.18%. The binder migration, therefore, would be

$$16.18 - 12.00 = 4.18\%$$

The standard deviations for each condition were calculated utilizing the range method (32). The standard deviation for the average of "N" number of tests was calculated by dividing the standard deviation by square root of number of tests (32).

**Appendix D**  
**Preliminary Experiments**

### Preliminary Experiments Set # 1

Two batches of color coating were made (i) "Control" (without addition of any additive) and (ii) "additive addition" (a polymer of medium viscosity with carboxyl groups at 0.7 degree of substitution was added). The objective of this study was to determine if the technique of measurement was capable of discriminating between (i) with additive and without additive conditions and (ii) with blade and without blade conditions. The objective was also to determine if the immediate drying of coated strips will be necessary. Following conditions were tested:

Blade	Control	With Additive	Immediate Drying
With Blade	X	X	Yes
Without Blade	X	X	Yes
With Blade	X	X	No
Without Blade	X		No

For each set of experiment, six strips of paper were coated with the color. Four measurements of reflectance before coating were taken and four measurements of reflectance were taken after the coating. Calculation procedure is explained in Appendix B.

The following results were obtained:

Blade	Control	With Additive	Immediate Drying
With Blade	30.14 $\pm$ 0.53%	32.92 $\pm$ 0.56%	Yes
Without Blade	27.73 $\pm$ 0.67%	30.28 $\pm$ 0.36%	Yes
With Blade	29.67 $\pm$ 0.57%	34.12 $\pm$ 0.62%	No
Without Blade	30.30 $\pm$ 0.52%		No

The experiment was repeated for the first condition (control with blade and immediate drying) to check for repeatability. The percent penetration was found 30.77 $\pm$ 0.63%. The following conclusions were drawn based on these data:

1. There was no significant effect of immediate drying on percent water penetration after blade coating. The t-test value for immediate drying and without immediate drying (with blade) was 0.60 for control color and 0.74 for color containing additive.

2. When the blade was not attached (i.e. the coating was applied by applicator roll only), the immediate drying stopped further liquid penetration. The t-test value for immediate drying and without immediate drying (without blade) was 3.03.

3. The percent water penetration was significantly more when the coating was applied by the blade than when it was applied by applicator roll alone. However, if the sheet was not dried immediately in case of coating application with applicator roll only (without blade), the coating color continued to penetrate until it reached to the depth closer to what was achieved with blade. The t-test value with blade and without blade in (when the sheet was immediately dried) was 2.81 for control color



and 3.94 for color containing additive. The t-test value with blade and without blade in (when the sheet was air dried) was 0.82.

4. The percent water penetration readings were significantly different for control color from the color containing additive. The t-test value with control and color containing additive (with blade) was 3.59 when the sheet was immediately dried and 5.30 when the sheet was air dried.

5. The percent water penetration values were found statistically repeatable. The t-test value for repeatability test was 0.76.

#### Preliminary Experiments Set # 2:

This set of experiments was to find out if the reflectance of the backside of the strips after coating should be measured immediately (while the color was still wet) or it can be measured after some time. Data are given in the table on next page.

Set 1 shows the brightness of backside within 7 seconds after coating, set 2 shows the brightness after one day and set 3 shows brightness data after two days. The average  $\pm$  one standard deviation of reflectance of backside after coating of above sets is as follows:

Set 1:  $68.91 \pm 0.30$

Set 2:  $68.84 \pm 0.27$

Set 3:  $68.96 \pm 0.26$

The t-test value for immediate and one day = 0.69

The t-test value for immediate and two days = 0.57

Hence it was concluded that the sheets can be air dried and kept for a couple of days before measuring the backside reflectance.

Strip Number	Set 1 (%)	Set 2 (%)	Set 3 (%)
89	68.79	68.96	69.26
89	68.41	68.84	68.56
89	68.64	68.53	69.37
89	69.41	69.38	69.14
90	69.33	69.28	69.22
90	68.72	68.84	68.22
90	69.16	68.62	68.82
90	68.98	68.78	68.81
91	69.09	68.84	69.16
91	68.66	68.95	69.26
91	69.10	69.07	69.03
91	68.51	68.42	68.76
92	69.30	68.43	68.88
92	68.65	68.71	68.54
92	68.82	68.93	68.63
92	68.94	68.81	69.06

## **Appendix E**

### **Data for Percent Water Penetration Measurements by Modified IGT**

## Reflectance Data

Strip No.	R <sub>s</sub>	R <sub>w</sub>	Strip No.	R <sub>s</sub>	R <sub>w</sub>
Control Low Solids No Heat			Polymer A Low Solids No Heat		
221	82.20%	78.00%	311	81.24%	76.24%
221	81.92%	79.43%	311	81.56%	77.63%
221	81.88%	79.95%	311	81.41%	77.39%
221	81.60%	80.03%	311	81.30%	77.30%
221	81.91%	79.22%	311	82.18%	76.33%
221	82.09%	78.86%	311	81.18%	76.25%
221		79.48%	311		76.53%
221		80.56%	311		75.56%
222	81.44%	78.15%	312	81.60%	77.87%
222	81.50%	78.76%	312	81.62%	78.28%
222	82.31%	78.91%	312	82.04%	78.58%
222	81.91%	79.00%	312	81.90%	77.58%
222	81.92%	79.10%	312	81.67%	78.22%
222	81.58%	79.65%	312	82.51%	78.64%
222		79.14%	312		80.05%
222		78.15%	312		78.63%
223	81.42%	77.08%	313	81.32%	79.33%
223	81.45%	78.89%	313	81.91%	77.66%
223	81.76%	79.71%	313	81.92%	78.34%
223	81.59%	78.42%	313	82.04%	77.85%
223	81.05%	78.29%	313	81.46%	77.86%
223	81.45%	78.62%	313	81.03%	78.30%

Strip No.	$R_i$	$R_o$	Strip No.	$R_i$	$R_o$
223		78.58%	313		78.80%
223		78.44%	313		78.65%
224	81.11%	77.57%	314	81.36%	74.87%
224	81.40%	77.60%	314	80.98%	76.80%
224	81.14%	77.52%	314	80.96%	77.41%
224	81.42%	77.09%	314	81.47%	77.39%
224	81.27%	77.21%	314	81.32%	76.48%
224	80.99%	79.50%	314	80.08%	76.70%
224		77.70%	314		76.94%
224		77.59%	314		77.39%
225	82.20%	78.50%	315	81.49%	77.53%
225	82.03%	79.47%	315	82.06%	77.23%
225	82.11%	78.84%	315	81.24%	76.77%
225	81.79%	79.68%	315	81.28%	78.54%
225	82.30%	79.79%	315	81.80%	78.47%
225	81.53%	78.82%	315	81.94%	76.10%
225		79.59%	315		77.10%
225		79.35%	315		78.47%
226	82.87%	80.15%	316	81.53%	77.81%
226	82.19%	79.87%	316	81.84%	79.30%
226	81.74%	79.26%	316	81.27%	79.88%
226	81.89%	78.43%	316	82.02%	78.88%
226	81.95%	79.19%	316	81.35%	78.97%
226	81.98%	79.46%	316	81.58%	77.78%
226		78.57%	316		78.77%
226		78.89%	316		78.77%

Strip No.	$R_i$	$R_o$	Strip No.	$R_i$	$R_o$
Control High Solids No Heat			Polymer A High Solids No Heat		
227	82.41%	79.75%	317	80.40%	76.04%
227	82.14%	79.02%	317	80.41%	76.74%
227	82.07%	79.77%	317	80.55%	77.18%
227	81.69%	79.91%	317	79.86%	76.53%
227	81.99%	78.24%	317	79.71%	76.10%
227	81.54%	79.34%	317	81.05%	75.57%
227		79.24%	317		77.87%
227		78.29%	317		77.50%
228	81.66%	77.60%	318	80.50%	76.80%
228	80.89%	78.16%	318	81.10%	76.72%
228	80.93%	77.46%	318	81.19%	77.23%
228	81.38%	78.24%	318	80.61%	76.62%
228	81.66%	79.12%	318	80.51%	76.33%
228	81.35%	79.10%	318	81.20%	75.27%
228		77.79%	318		77.56%
228		78.94%	318		75.06%
229	81.38%	78.09%	319	80.94%	78.10%
229	81.15%	78.00%	319	81.70%	78.88%
229	80.89%	78.40%	319	80.98%	77.75%
229	81.40%	77.18%	319	80.59%	76.72%
229	81.21%	78.73%	319	81.41%	78.44%
229	81.21%	77.85%	319	80.84%	78.48%
229		78.41%	319		78.82%

Strip No.	$R_d$	$R_o$	Strip No.	$R_d$	$R_o$
229		77.51 %	319		75.93 %
230	81.77 %	79.17 %	320	81.46 %	77.94 %
230	81.55 %	78.95 %	320	82.02 %	78.55 %
230	81.38 %	78.68 %	320	80.77 %	78.93 %
230	81.60 %	79.11 %	320	82.17 %	78.17 %
230	82.04 %	79.18 %	320	81.37 %	78.21 %
230	81.67 %	79.05 %	320	81.41 %	78.01 %
230		78.92 %	320		78.61 %
230		78.67 %	320		78.44 %
231	81.40 %	78.69 %	321	80.69 %	77.49 %
231	81.69 %	79.54 %	321	81.42 %	78.34 %
231	81.88 %	79.59 %	321	82.16 %	77.07 %
231	81.91 %	78.13 %	321	81.79 %	79.19 %
231	82.12 %	79.25 %	321	81.73 %	79.42 %
231	81.91 %	79.65 %	321	81.97 %	78.40 %
231		80.06 %	321		79.36 %
231		79.57 %	321		78.62 %
232	81.22 %	79.14 %	322	81.75 %	77.73 %
232	81.18 %	78.75 %	322	81.46 %	78.40 %
232	81.18 %	78.71 %	322	81.80 %	76.08 %
232	81.25 %	80.32 %	322	81.15 %	78.03 %
232	81.70 %	78.90 %	322	81.67 %	77.88 %
232	81.42 %	79.47 %	322	80.71 %	76.84 %
232		78.69 %	322		78.19 %
232		78.29 %	322		78.11 %

Strip No.	R <sub>s</sub>	R <sub>o</sub>	Strip No.	R <sub>s</sub>	R <sub>o</sub>
Polymer Low Solids No Heat			Polymer J Low Solids No Heat		
233	81.33%	78.80%	323	80.91%	76.17%
233	81.53%	79.21%	323	81.52%	77.84%
233	81.59%	78.04%	323	81.60%	77.22%
233	81.27%	79.10%	323	81.65%	76.42%
233	81.31%	78.14%	323	81.03%	75.22%
233	81.24%	77.80%	323	80.45%	76.07%
233		78.88%	323		77.89%
233		79.26%	323		77.39%
234	80.73%	75.95%	324	81.36%	76.27%
234	81.05%	78.20%	324	81.20%	77.57%
234	81.03%	76.29%	324	81.75%	75.57%
234	80.59%	78.15%	324	81.67%	76.91%
234	81.41%	77.50%	324	81.10%	78.09%
234	81.30%	77.27%	324	81.09%	76.56%
234		77.62%	324		76.29%
234		78.31%	324		76.75%
235	81.39%	81.15%	325	81.94%	77.20%
235	81.89%	78.38%	325	82.57%	76.36%
235	81.73%	80.53%	325	81.17%	76.27%
235	81.44%	78.54%	325	82.02%	77.83%
235	81.47%	77.89%	325	81.22%	76.87%
235	82.08%	78.04%	325	81.35%	76.73%
235		78.70%	325		77.40%



Strip No.	R <sub>s</sub>	R <sub>e</sub>	Strip No.	R <sub>s</sub>	R <sub>e</sub>
235		78.06%	325		76.95%
236	81.98%	78.82%	326	81.46%	76.39%
236	81.69%	78.80%	326	81.80%	78.22%
236	81.66%	78.67%	326	81.73%	77.83%
236	81.82%	78.43%	326	81.93%	77.91%
236	81.40%	78.18%	326	81.74%	77.63%
236	81.59%	77.13%	326	81.64%	76.89%
236		78.17%	326		77.77%
236		78.92%	326		78.54%
237	81.16%	79.61%	327	81.69%	77.89%
237	81.71%	78.71%	327	81.50%	76.27%
237	81.77%	78.65%	327	80.97%	77.38%
237	81.18%	78.67%	327	80.85%	76.76%
237	81.84%	79.34%	327	80.41%	79.04%
237	81.81%	79.16%	327	80.90%	77.53%
237		79.05%	327		78.66%
237		79.02%	327		77.82%
238	81.68%	76.83%	328	80.99%	77.56%
238	80.99%	77.95%	328	80.65%	77.19%
238	81.13%	78.59%	328	81.18%	79.59%
238	81.39%	78.11%	328	81.83%	77.47%
238	81.22%	77.60%	328	81.02%	76.94%
238	81.53%	78.29%	328	81.24%	77.12%
238		78.82%	328		78.13%
238		78.38%	328		77.68%

Strip No.	$R_d$	$R_w$	Strip No.	$R_d$	$R_w$
Polymer High Solids No Heat			Polymer J High Solids No Heat		
239	81.55%	76.62%	329	81.64%	77.89%
239	80.99%	78.53%	329	81.73%	77.40%
239	81.07%	77.40%	329	81.81%	77.01%
239	81.36%	78.86%	329	81.29%	77.73%
239	81.75%	79.17%	329	81.64%	78.24%
239	81.99%	78.33%	329	81.62%	78.07%
239		78.69%	329		79.56%
239		79.09%	329		79.17%
240	81.91%	79.58%	330	82.45%	79.09%
240	82.34%	79.06%	330	82.34%	80.53%
240	82.25%	80.30%	330	82.23%	79.73%
240	81.67%	80.37%	330	82.09%	79.32%
240	81.67%	79.44%	330	82.12%	78.82%
240	82.32%	79.58%	330	81.81%	78.64%
240		78.72%	330		79.19%
240		79.36%	330		78.56%
241	82.07%	78.39%	331	81.35%	76.90%
241	81.75%	77.34%	331	81.44%	78.90%
241	81.43%	78.26%	331	81.41%	77.43%
241	81.57%	77.62%	331	81.62%	76.75%
241	81.97%	78.43%	331	81.86%	77.26%
241	82.17%	79.30%	331	81.12%	77.84%
241		78.14%	331		78.05%

241		78.74%	331		77.04%
242	81.64%	79.20%	332	81.27%	77.68%
242	81.61%	78.92%	332	80.81%	77.30%
242	81.85%	79.04%	332	80.35%	77.64%
242	81.87%	78.77%	332	81.36%	76.47%
242	81.58%	79.37%	332	80.72%	77.28%
242	82.22%	79.30%	332	81.13%	77.07%
242		78.87%	332		77.12%
242		80.10%	332		77.64%
243	81.07%	76.09%	333	81.01%	76.67%
243	81.36%	77.67%	333	80.89%	77.47%
243	81.27%	77.84%	333	81.37%	76.21%
243	81.23%	77.40%	333	81.10%	77.51%
243	81.36%	76.74%	333	81.44%	77.89%
243	81.26%	78.06%	333	81.04%	77.17%
243		78.57%	333		76.58%
243		78.77%	333		76.49%
244	80.34%	75.86%	334	81.31%	78.40%
244	80.76%	77.56%	334	81.29%	77.64%
244	79.80%	76.34%	334	82.13%	78.87%
244	80.96%	77.14%	334	81.92%	78.43%
244	81.11%	75.58%	334	82.19%	77.88%
244	80.91%	77.09%	334	80.95%	77.42%
244	79.58%	76.81%	334		76.71%
244		77.22%	334		78.28%
245	82.43%	78.14%	335	82.16%	79.00%
245	81.54%	79.52%	335	82.48%	78.13%

245	82.38%	79.35%	335	82.17%	77.81%
245	82.08%	78.95%	335	81.85%	79.44%
245	81.82%	79.44%	335	82.40%	78.79%
245	82.19%	80.08%	335	82.12%	78.56%
245		80.04%	335		78.71%
245		80.15%	335		78.86%
246	81.94%	78.97%	336	81.66%	78.01%
246	82.35%	79.29%	336	81.09%	79.74%
246	82.28%	78.28%	336	81.78%	77.66%
246	81.66%	77.80%	336	81.95%	78.71%
246	81.72%	77.99%	336	82.21%	78.06%
246	82.35%	78.05%	336	82.01%	78.79%
246		78.70%	336		78.03%
246		79.75%	336		78.70%
247	81.60%	79.07%	337	80.56%	76.36%
247	82.05%	77.20%	337	80.93%	77.02%
247	81.81%	78.57%	337	80.71%	78.81%
247	81.49%	78.97%	337	80.66%	75.87%
247	82.09%	78.44%	337	80.60%	77.26%
247	81.72%	78.55%	337	80.30%	76.36%
247		78.41%	337		75.66%
247		78.42%	337		76.28%
248	81.00%	79.58%	338	81.26%	75.38%
248	81.55%	78.21%	338	81.33%	76.18%
248	81.81%	77.74%	338	81.04%	76.25%
248	81.74%	78.82%	338	80.69%	75.87%
248	81.30%	78.82%	338	80.61%	78.76%

248	80.99%	77.50%	338	80.27%	76.65%
248		78.47%	338		77.09%
248		79.10%	338		76.45%
249	81.61%	77.19%	339	82.13%	77.70%
249	81.59%	76.44%	339	81.05%	76.52%
249	81.60%	76.97%	339	81.42%	79.03%
249	81.82%	79.04%	339	81.80%	77.75%
249	81.71%	79.08%	339	81.91%	78.39%
249	81.91%	78.70%	339	81.54%	80.13%
249		78.91%	339		79.05%
249		79.63%	339		77.67%
250	81.53%	78.82%	340	81.17%	76.68%
250	82.23%	77.32%	340	81.29%	77.20%
250	82.10%	79.03%	340	81.48%	77.29%
250	81.94%	79.27%	340	80.95%	77.09%
250	82.03%	77.98%	340	81.43%	76.95%
250	82.13%	79.20%	340	80.72%	76.68%
250		78.91%	340		77.85%
250		78.28%	340		77.87%
251	81.19%	79.26%	341	81.70%	78.90%
251	81.97%	78.34%	341	81.54%	79.98%
251	81.48%	77.00%	341	81.94%	78.07%
251	81.37%	77.13%	341	81.98%	80.06%
251	81.22%	77.57%	341	82.26%	79.20%
251	81.18%	78.18%	341	81.97%	79.33%
251		77.06%	341		79.94%
251		77.63%	341		79.02%

252	81.27%	76.16%	342	81.46%	76.62%
252	81.05%	77.86%	342	81.25%	78.25%
252	81.14%	78.57%	342	81.25%	77.52%
252	81.59%	78.75%	342	80.94%	77.43%
252	81.35%	77.24%	342	80.62%	77.35%
252	80.75%	76.98%	342	80.98%	77.06%
252		78.65%	342		77.23%
252		79.64%	342		77.76%
253	81.86%	78.80%	343	80.62%	75.79%
253	81.52%	77.39%	343	80.70%	76.23%
253	81.13%	78.33%	343	79.99%	75.20%
253	80.98%	78.19%	343	80.88%	75.93%
253	81.37%	78.24%	343	80.73%	75.98%
253	81.63%	79.48%	343	80.71%	76.43%
253		78.57%	343		75.93%
253		78.44%	343		75.96%
254	81.64%	78.19%	344	81.83%	77.66%
254	81.97%	79.26%	344	81.67%	78.57%
254	81.52%	78.45%	344	81.36%	78.36%
254	81.86%	79.11%	344	81.29%	75.29%
254	81.81%	78.41%	344	80.75%	77.84%
254	81.69%	78.18%	344	81.15%	78.31%
254		77.98%	344		77.49%
254		79.35%	344		77.90%
255	82.24%	76.32%	345	82.12%	79.09%
255	82.17%	78.85%	345	81.93%	78.48%
255	82.12%	77.70%	345	81.59%	76.65%

255	81.63%	77.79%	345	81.78%	78.26%
255	81.41%	78.17%	345	81.97%	78.97%
255	82.14%	79.30%	345	81.58%	78.58%
255		78.06%	345		79.36%
255		79.02%	345		79.48%
256	82.62%	79.67%	346	82.29%	78.29%
256	81.82%	78.87%	346	82.03%	77.69%
256	81.92%	79.45%	346	81.82%	77.69%
256	82.20%	79.13%	346	81.52%	78.98%
256	82.04%	80.03%	346	81.58%	78.43%
256	81.46%	78.94%	346	81.89%	78.29%
256		79.21%	346		77.71%
256		78.10%	346		78.15%
257	80.82%	75.84%	347	80.49%	77.45%
257	80.93%	76.17%	347	81.49%	77.53%
257	80.91%	75.41%	347	81.29%	76.90%
257	80.91%	74.45%	347	80.62%	77.62%
257	80.49%	75.65%	347	81.11%	76.88%
257	80.78%	74.00%	347	81.29%	78.74%
257		75.43%	347		77.81%
257		75.60%	347		76.85%
258	81.91%	79.04%	348	81.73%	76.55%
258	81.76%	80.42%	348	80.80%	75.67%
258	82.31%	79.49%	348	80.90%	76.12%
258	81.63%	79.70%	348	81.21%	75.95%
258	82.23%	79.03%	348	81.21%	75.44%
258	81.72%	78.95%	348	80.95%	75.81%

258		78.42%	348		75.92%
258		77.26%	348		78.41%
259	81.14%	77.67%	349	81.49%	76.90%
259	81.37%	79.38%	349	81.02%	77.30%
259	81.57%	78.68%	349	81.09%	77.03%
259	81.75%	78.85%	349	80.97%	78.25%
259	81.31%	76.12%	349	81.35%	77.11%
259	81.29%	77.83%	349	82.05%	76.98%
259		78.05%	349		77.08%
259		78.20%	349		76.74%
260	81.46%	77.93%	350	82.20%	76.89%
260	80.75%	76.95%	350	81.25%	76.33%
260	80.70%	76.82%	350	81.32%	77.74%
260	80.50%	76.98%	350	81.50%	77.72%
260	80.69%	77.07%	350	81.23%	77.49%
260	80.98%	77.26%	350	81.20%	77.31%
260		76.93%	350		78.34%
260		77.45%	350		78.18%
261	81.02%	78.38%	351	81.70%	79.33%
261	80.66%	79.34%	351	82.03%	77.60%
261	81.23%	78.44%	351	81.55%	78.23%
261	81.21%	78.66%	351	81.36%	78.78%
261	81.46%	77.91%	351	81.42%	78.78%
261	81.81%	76.59%	351	81.66%	78.09%
261		77.03%	351		78.39%
261		78.22%	351		78.91%
262	80.30%	76.91%	352	80.88%	76.21%



262	80.62%	75.81%	352	81.07%	75.73%
262	80.62%	76.72%	352	80.42%	76.10%
262	79.75%	75.29%	352	80.32%	75.73%
262	80.15%	76.15%	352	80.46%	75.81%
262	80.56%	76.38%	352	80.53%	76.12%
262		77.68%	352		77.13%
262		75.95%	352		77.30%
263	81.56%	78.92%	353	80.17%	77.28%
263	82.04%	79.53%	353	80.73%	77.22%
263	82.12%	78.25%	353	79.88%	77.30%
263	81.08%	80.41%	353	80.33%	75.73%
263	81.39%	80.31%	353	80.05%	75.23%
263	82.20%	79.18%	353	80.23%	76.16%
263		78.51%	353		75.15%
263		78.06%	353		75.81%
264	80.75%	78.18%	354	81.22%	77.95%
264	81.27%	78.26%	354	81.84%	77.64%
264	81.30%	78.70%	354	82.06%	78.49%
264	81.62%	79.46%	354	81.15%	77.89%
264	81.04%	78.83%	354	80.84%	76.14%
264	81.41%	78.20%	354	81.68%	77.39%
264		79.40%	354		76.71%
264		79.25%	354		75.23%
265	80.96%	77.80%	355	82.41%	76.85%
265	80.74%	78.05%	355	82.17%	78.34%
265	81.16%	77.99%	355	81.32%	79.26%
265	80.99%	78.00%	355	81.30%	77.83%

265	80.55%	76.68%	355	81.79%	79.39%
265	81.67%	77.87%	355	82.37%	78.87%
265		78.19%	355		77.50%
265		78.10%	355		77.51%
266	81.40%	78.16%	356	81.40%	78.30%
266	81.25%	77.79%	356	81.30%	79.21%
266	81.20%	77.50%	356	81.60%	77.84%
266	81.47%	78.04%	356	81.32%	77.91%
266	81.56%	77.33%	356	81.99%	78.54%
266	81.49%	77.74%	356	80.78%	78.60%
266		77.64%	356		77.94%
266		78.28%	356		77.88%
267	81.96%	77.96%	357	81.05%	77.31%
267	81.01%	78.37%	357	80.81%	77.22%
267	80.81%	77.97%	357	80.25%	77.85%
267	81.24%	78.44%	357	80.70%	77.10%
267	82.26%	77.40%	357	81.04%	78.25%
267	80.98%	77.06%	357	80.76%	77.46%
267		77.36%	357		77.65%
267		76.99%	357		76.27%
268	81.48%	78.92%	358	80.82%	76.29%
268	81.81%	78.94%	358	80.55%	75.44%
268	80.87%	78.93%	358	81.29%	75.58%
268	81.81%	78.44%	358	80.98%	76.50%
268	82.30%	77.53%	358	80.34%	76.88%
268	81.30%	78.14%	358	79.90%	77.17%
268		78.93%	358		76.24%

268		79.29%	358		76.21%
269	82.27%	79.46%	359	80.76%	77.63%
269	81.68%	78.05%	359	81.08%	77.47%
269	81.97%	78.67%	359	81.09%	77.67%
269	81.66%	79.07%	359	80.99%	77.01%
269	81.73%	78.68%	359	81.45%	77.72%
269	81.38%	79.27%	359	81.18%	77.23%
269		79.15%	359		78.75%
269		77.97%	359		78.25%
270	80.12%	77.16%	360	81.61%	78.92%
270	81.34%	75.73%	360	81.70%	78.47%
270	81.03%	77.54%	360	81.47%	77.06%
270	80.77%	77.10%	360	82.29%	77.94%
270	80.60%	78.46%	360	81.80%	78.22%
270	80.85%	77.75%	360	82.10%	78.26%
270		78.50%	360		77.75%
270		77.79%	360		77.88%
271	81.00%	77.04%	361	81.19%	77.98%
271	81.46%	75.77%	361	81.24%	77.55%
271	80.95%	76.29%	361	81.79%	77.75%
271	81.67%	76.81%	361	81.66%	78.68%
271	80.41%	76.84%	361	81.63%	79.09%
271	81.10%	78.05%	361	81.38%	77.44%
271		77.55%	361		77.34%
271		78.40%	361		77.98%
272	81.79%	77.00%	362	81.48%	76.85%
272	81.70%	77.15%	362	81.28%	77.30%

272	81.54%	77.79%	362	81.14%	78.16%
272	81.27%	76.92%	362	81.02%	78.60%
272	81.06%	77.45%	362	80.84%	76.82%
272	81.71%	77.57%	362	80.12%	77.35%
272		77.80%	362		78.07%
272		78.82%	362		78.37%
273	81.88%	78.66%	363	81.17%	77.17%
273	81.73%	77.43%	363	81.96%	79.70%
273	81.55%	78.18%	363	81.76%	78.44%
273	81.90%	78.29%	363	81.69%	77.32%
273	81.93%	77.94%	363	80.50%	77.68%
273	81.75%	79.25%	363	80.60%	76.77%
273		78.48%	363		78.28%
273		78.67%	363		77.23%
274	81.98%	79.34%	364	82.26%	76.34%
274	81.39%	79.18%	364	81.77%	77.89%
274	82.13%	78.66%	364	81.18%	78.51%
274	82.13%	79.46%	364	81.35%	77.13%
274	82.24%	79.95%	364	81.60%	77.89%
274	82.50%	79.36%	364	81.57%	76.82%
274		79.39%	364		78.25%
274		80.12%	364		78.95%
275	80.52%	77.18%	365	82.03%	79.01%
275	80.44%	75.96%	365	82.26%	77.84%
275	81.21%	77.78%	365	82.11%	78.10%
275	80.81%	77.14%	365	81.93%	77.80%
275	81.20%	77.05%	365	82.00%	76.95%

275	80.71%	77.37%	365	81.98%	78.12%
275		78.08%	365		78.08%
275		76.95%	365		77.56%
276	82.01%	79.78%	366	81.12%	77.37%
276	81.42%	78.55%	366	81.22%	76.36%
276	82.11%	77.97%	366	80.91%	76.32%
276	81.73%	77.89%	366	81.01%	77.57%
276	81.72%	79.16%	366	81.43%	77.21%
276	81.66%	78.84%	366	81.73%	77.61%
276		78.88%	366		77.60%
276		77.50%	366		77.74%
277	80.79%	77.20%	367	82.59%	77.70%
277	81.04%	76.49%	367	82.66%	78.57%
277	81.39%	77.83%	367	82.02%	78.36%
277	81.90%	78.53%	367	81.96%	78.03%
277	81.12%	76.04%	367	82.13%	80.90%
277	81.48%	78.68%	367	81.93%	80.78%
277		78.27%	367		78.72%
277		78.70%	367		78.77%
278	82.18%	79.01%	368	82.40%	78.45%
278	82.19%	79.42%	368	82.06%	79.46%
278	82.34%	79.20%	368	82.52%	79.70%
278	82.40%	78.39%	368	81.46%	79.37%
278	82.21%	78.00%	368	82.36%	80.38%
278	82.05%	77.87%	368	81.58%	79.33%
278		78.41%	368		78.70%
278		78.91%	368		78.04%

279	81.49%	78.89%	369	81.89%	78.85%
279	81.94%	79.01%	369	81.19%	78.46%
279	81.28%	78.28%	369	82.41%	78.12%
279	81.57%	78.25%	369	82.04%	77.74%
279	81.78%	77.78%	369	81.27%	78.83%
279	82.13%	78.57%	369	81.81%	77.88%
279		79.18%	369		77.01%
279		79.03%	369		77.19%
280	80.42%	76.54%	370	81.41%	77.13%
280	80.38%	77.51%	370	81.86%	77.56%
280	80.66%	76.67%	370	81.69%	75.94%
280	80.98%	76.51%	370	81.39%	77.84%
280	80.86%	77.45%	370	82.05%	78.72%
280	80.85%	77.26%	370	81.49%	78.44%
280		75.82%	370		77.71%
280		76.26%	370		78.10%
281	80.87%	77.18%	371	81.39%	78.11%
281	81.31%	77.28%	371	81.62%	79.17%
281	81.29%	77.21%	371	81.81%	78.73%
281	81.30%	78.05%	371	81.15%	78.04%
281	81.79%	77.90%	371	82.11%	80.05%
281	81.54%	76.45%	371	81.72%	78.39%
281		76.79%	371		78.28%
281		78.49%	371		78.30%
282	81.26%	79.48%	372	82.84%	79.18%
282	82.22%	80.26%	372	82.07%	77.38%
282	81.38%	80.57%	372	81.25%	78.38%

282	81.89%	80.36%	372	81.50%	78.62%
282	81.03%	78.97%	372	81.24%	77.45%
282	81.22%	80.90%	372	81.87%	80.40%
282		80.70%	372		77.69%
282		78.98%	372		79.77%
283	82.16%	78.46%	373	82.83%	79.20%
283	82.29%	78.97%	373	82.81%	79.52%
283	82.00%	79.08%	373	82.18%	78.73%
283	81.98%	79.53%	373	82.16%	78.89%
283	81.54%	79.37%	373	82.91%	79.67%
283	81.85%	78.50%	373	82.31%	79.84%
283		79.10%	373		80.06%
283		79.46%	373		79.71%
284	81.80%	76.57%	374	82.23%	78.99%
284	81.03%	77.33%	374	82.21%	79.13%
284	81.39%	76.23%	374	81.90%	79.54%
284	81.18%	77.34%	374	82.13%	78.75%
284	81.41%	77.78%	374	82.14%	79.48%
284	81.36%	77.29%	374	82.43%	78.77%
284		77.50%	374		79.15%
284		77.25%	374		79.12%
285	81.19%	78.71%	375	82.09%	77.13%
285	81.69%	78.51%	375	80.79%	77.45%
285	81.46%	76.57%	375	81.88%	77.43%
285	82.01%	77.93%	375	81.06%	76.32%
285	81.73%	77.23%	375	80.46%	78.72%
285	82.34%	77.03%	375	81.10%	78.68%

285		76.65%	375		76.98%
285		76.88%	375		78.31%
286	81.56%	76.65%	376	81.92%	77.01%
286	81.74%	78.16%	376	81.50%	78.23%
286	81.38%	78.03%	376	81.45%	77.94%
286	81.80%	77.17%	376	81.69%	77.81%
286	82.16%	76.92%	376	81.44%	77.23%
286	81.66%	78.16%	376	81.88%	78.09%
286		78.57%	376		77.93%
286		78.56%	376		78.01%
287	82.11%	78.12%	377	82.22%	77.93%
287	82.04%	78.76%	377	81.32%	77.47%
287	82.42%	78.42%	377	82.51%	76.97%
287	82.87%	78.48%	377	81.91%	77.98%
287	81.78%	77.69%	377	82.06%	78.18%
287	81.82%	78.29%	377	82.17%	79.67%
287		78.74%	377		79.48%
287		78.16%	377		79.19%
288	81.85%	78.28%	378	81.77%	76.90%
288	82.11%	78.92%	378	81.51%	76.49%
288	82.20%	78.26%	378	81.75%	77.76%
288	81.74%	78.77%	378	81.59%	78.14%
288	81.34%	79.61%	378	81.26%	78.10%
288	81.95%	78.21%	378	82.17%	79.14%
288		79.28%	378		79.24%
288		78.43%	378		76.71%
289	81.73%	77.66%	379	81.85%	79.45%



289	81.77%	78.27%	379	82.17%	79.88%
289	81.79%	78.08%	379	81.99%	78.62%
289	81.56%	76.56%	379	81.86%	77.80%
289	81.94%	77.28%	379	82.08%	78.40%
289	81.36%	77.33%	379	82.49%	78.36%
289		77.07%	379		79.09%
289		77.71%	379		78.50%
290	81.27%	76.64%	380	81.42%	77.12%
290	81.76%	77.42%	380	80.80%	78.46%
290	81.27%	77.61%	380	81.16%	77.62%
290	80.85%	77.61%	380	81.73%	77.55%
290	81.82%	76.86%	380	82.05%	77.41%
290	81.53%	75.58%	380	82.34%	78.84%
290		76.12%	380		77.20%
290		76.01%	380		77.82%
291	81.96%	78.18%	381	82.39%	78.15%
291	81.20%	77.42%	381	82.22%	78.62%
291	81.56%	76.78%	381	81.95%	77.46%
291	82.87%	76.88%	381	81.60%	77.68%
291	82.46%	76.24%	381	82.01%	78.21%
291	82.28%	77.43%	381	81.99%	79.08%
291		79.46%	381		78.12%
291		77.69%	381		78.65%
292	81.78%	77.60%	382	81.08%	76.60%
292	81.27%	77.37%	382	80.61%	76.44%
292	82.02%	76.61%	382	81.50%	75.75%
292	82.12%	77.17%	382	81.97%	75.72%

292	81.31%	77.05%	382	82.03%	78.47%
292	81.66%	76.83%	382	81.43%	75.78%
292		76.63%	382		76.23%
292		77.90%	382		77.66%
293	82.25%	77.95%	383	82.15%	78.25%
293	82.34%	79.02%	383	82.38%	78.81%
293	81.44%	79.53%	383	82.38%	77.40%
293	82.59%	77.47%	383	82.64%	78.45%
293	81.99%	77.69%	383	82.04%	79.17%
293	81.57%	78.50%	383	81.94%	78.87%
293		79.17%	383		78.83%
293		78.35%	383		78.98%
294	81.70%	78.38%	384	81.34%	77.64%
294	81.80%	78.46%	384	81.92%	77.51%
294	81.31%	78.91%	384	81.83%	77.95%
294	81.21%	77.78%	384	82.13%	77.99%
294	81.64%	78.05%	384	81.51%	78.50%
294	81.47%	78.29%	384	82.04%	77.26%
294		77.37%	384		76.87%
294		77.18%	384		77.15%
295	81.60%	78.38%	385	80.89%	76.38%
295	81.30%	77.62%	385	80.95%	76.65%
295	81.32%	77.22%	385	81.09%	75.16%
295	82.08%	78.74%	385	80.33%	76.97%
295	82.01%	77.99%	385	81.82%	76.52%
295	81.48%	78.14%	385	81.85%	76.72%
295		79.02%	385		76.18%

295		78.35%	385		75.71%
296	82.31%	79.49%	386	81.78%	78.49%
296	81.89%	78.97%	386	81.78%	77.95%
296	81.56%	78.09%	386	82.46%	77.59%
296	82.20%	77.51%	386	82.42%	77.88%
296	81.89%	78.27%	386	81.42%	78.46%
296	81.88%	78.78%	386	82.12%	76.43%
296		77.67%	386		78.53%
296		78.46%	386		78.32%
395	81.24%	78.25%	387	81.88%	77.85%
395	82.69%	77.30%	387	81.44%	78.66%
395	81.48%	78.06%	387	81.39%	76.71%
395	81.85%	78.06%	387	81.23%	77.26%
395	81.48%	78.54%	387	81.03%	77.05%
395	81.43%	79.23%	387	82.33%	76.63%
395		77.80%	387		77.86%
395		78.06%	387		77.55%
298	81.99%	78.74%	388	82.27%	76.60%
298	82.80%	77.93%	388	82.29%	77.27%
298	82.22%	79.75%	388	81.94%	78.33%
298	81.95%	78.54%	388	82.16%	78.78%
298	81.94%	78.48%	388	82.60%	78.05%
298	82.00%	78.70%	388	82.11%	77.14%
298		78.84%	388		79.25%
298		78.16%	388		77.74%
299	81.40%	77.94%	389	81.62%	78.88%
299	81.69%	77.69%	389	81.80%	78.42%

299	81.91%	78.20%	389	81.87%	79.06%
299	81.67%	77.68%	389	81.96%	78.82%
299	81.81%	77.52%	389	81.88%	78.65%
299	81.78%	79.16%	389	81.72%	79.64%
299		78.42%	389		79.44%
299		78.22%	389		78.31%
300	81.18%	76.82%	390	82.06%	76.97%
300	81.91%	76.91%	390	81.98%	77.04%
300	81.78%	76.45%	390	81.64%	77.49%
300	81.18%	77.32%	390	82.50%	77.92%
300	81.94%	79.28%	390	81.56%	78.53%
300	81.60%	78.09%	390	81.87%	78.45%
300		77.71%	390		77.44%
300		77.16%	390		77.57%
301	81.84%	77.37%	391	81.48%	77.55%
301	82.24%	77.95%	391	81.46%	78.02%
301	82.54%	77.49%	391	81.70%	76.98%
301	82.05%	78.60%	391	82.02%	76.92%
301	81.56%	78.16%	391	82.15%	77.45%
301	82.16%	77.35%	391	81.55%	76.84%
301		77.34%	391		77.61%
301		77.64%	391		76.30%
302	82.34%	76.87%	392	81.77%	77.68%
302	81.82%	76.94%	392	81.95%	78.60%
302	81.51%	78.11%	392	82.40%	78.68%
302	82.17%	78.65%	392	82.01%	78.28%
302	82.06%	78.77%	392	80.98%	77.27%

302	81.84%	77.67%	392	82.12%	78.43%
302		79.34%	392		78.63%
302		78.44%	392		78.69%
303	81.33%	76.94%	393	81.44%	75.44%
303	81.47%	79.25%	393	81.97%	76.84%
303	81.51%	77.91%	393	81.26%	75.75%
303	81.37%	78.41%	393	81.26%	76.73%
303	81.41%	78.08%	393	81.43%	77.06%
303	81.48%	78.77%	393	81.85%	76.45%
303		79.36%	393		75.85%
303		78.18%	393		75.77%
304	81.38%	77.65%	394	81.04%	78.27%
304	81.50%	77.80%	394	81.15%	77.61%
304	81.76%	77.89%	394	81.12%	77.71%
304	81.50%	77.93%	394	81.63%	76.90%
304	81.62%	77.77%	394	81.05%	77.65%
304	81.64%	77.07%	394	81.39%	78.31%
304		77.95%	394		78.02%
304		78.09%	394		78.95%
305	81.99%	79.38%			
305	81.28%	79.46%			
305	82.04%	78.88%			
305	81.91%	79.30%			
305	81.50%	78.73%			
305	81.79%	78.47%			
305		78.66%			
305		78.48%			

306	81.51%	78.60%			
306	82.04%	78.75%			
306	82.42%	78.51%			
306	81.87%	78.16%			
306	81.94%	75.64%			
306	81.86%	76.80%			
306		79.22%			
306		78.57%			
307	81.96%	76.98%			
307	82.15%	78.41%			
307	82.00%	78.42%			
307	81.48%	78.23%			
307	82.15%	77.94%			
307	82.29%	78.73%			
307		78.11%			
307		77.22%			
308	81.73%	78.24%			
308	81.91%	79.16%			
308	81.39%	79.68%			
308	81.87%	80.17%			
308	81.54%	79.56%			
308	81.62%	78.89%			
308		78.32%			
308		79.81%			
309	81.47%	78.52%			
309	81.71%	78.24%			
309	81.40%	78.32%			

309	81.38%	77.42%			
309	81.08%	78.25%			
309	81.40%	78.12%			
309		76.31%			
309		78.19%			
310	81.62%	78.31%			
310	82.15%	77.80%			
310	82.03%	79.03%			
310	81.16%	78.33%			
310	81.43%	77.70%			
310	81.94%	77.47%			
310		77.05%			
310		77.47%			

## **Appendix F**

### **Data and Calculations of Water Absorption as Measured by Gravimetric Method**



**Data and Calculations of Water Absorption as Measured by  
Gravimetric Method for Low Solids**

<b>Color Name</b>	<b>Pad Weight (Grams)</b>	<b>Pad+ Water (Grams)</b>	<b>Water Weight (Grams)</b>	<b>Water Absorbed (GSM)</b>
Control	1.3812	1.5274	0.1462	182.8
A	1.0712	1.1555	0.0843	105.4
B	1.3422	1.4122	0.0700	87.5
C	1.3592	1.4226	0.0634	79.3
D	1.3627	1.4455	0.0828	103.5
E	1.3291	1.4125	0.0834	104.3
F	1.3687	1.4405	0.0718	89.7
G	1.2867	1.3561	0.0694	86.8
H	1.1081	1.1776	0.0695	86.9
I	1.2539	1.3715	0.1176	147.0
J	1.0871	1.2063	0.1192	149.0
K	1.3809	1.4725	0.0916	114.5

**Data and Calculations of Water Absorption as Measured by  
Gravimetric Method for High Solids**

<b>Color Name</b>	<b>Pad Weight (Grams)</b>	<b>Pad+ Water (Grams)</b>	<b>Water Weight (Grams)</b>	<b>Water Absorbed (GSM)</b>
Control	1.3698	1.4506	0.0808	101.0
A	1.0985	1.1696	0.0711	88.9
B	1.3192	1.3815	0.0623	77.9
C	1.1649	1.2265	0.0616	77.0
D	1.3664	1.4386	0.0722	90.3
E	1.3176	1.3930	0.0754	94.2
F	1.1553	1.2192	0.0639	79.9
G	1.1931	1.2554	0.0623	77.9
H	1.1078	1.1877	0.0799	99.9
I	1.2090	1.2934	0.0844	105.5
J	1.1640	1.2400	0.0760	95.0
K	1.3734	1.4434	0.0700	87.5

## **Appendix G**

### **Data and Calculations of Binder Migration as Measured by Ultra-Violet Method**

**Data and Calculations of Binder Migration as Measured by  
Ultra-Violet Method at Low Drying Rate**

<b>Color Name</b>	<b>Test 1</b>	<b>Test 2</b>	<b>Average</b>	<b>Top Surface Conc.</b>	<b>Latex Migration</b>
<b>Control</b>	18285	18384	18335	15.85	3.85
<b>A</b>	17168	17058	17113	12.73	0.73
<b>B</b>	17020	17306	17163	12.86	0.86
<b>C</b>	17223	17359	17291	13.19	1.19
<b>D</b>	17679	17492	17586	13.94	1.94
<b>E</b>	17233	17195	17214	12.99	0.99
<b>F</b>	17228	17399	17314	13.24	1.24
<b>G</b>	17159	17708	17434	13.55	1.55
<b>H</b>	17862	17492	17677	14.17	2.17
<b>I</b>	17343	17766	17555	13.86	1.86
<b>J</b>	17976	17820	17898	14.74	2.74
<b>K</b>	17331	17539	17435	13.55	1.55

**Data and Calculations of Binder Migration as Measured by  
Ultra-Violet Method at High Drying Rate**

<b>Color Name</b>	<b>Test 1</b>	<b>Test 2</b>	<b>Average</b>	<b>Top Surface Conc.</b>	<b>Latex Migration</b>
<b>Control</b>	18703	18219	18461	16.18	4.18
<b>A</b>	17548	17755	17652	14.11	2.11
<b>B</b>	17645	17303	17474	13.65	1.65
<b>C</b>	18091	17392	17742	14.34	2.34
<b>D</b>	17996	17819	17908	14.76	2.76
<b>E</b>	17324	17427	17376	13.40	1.40
<b>F</b>	18351	17917	18134	15.34	3.34
<b>G</b>	17865	17944	17905	14.75	2.75
<b>H</b>	18124	17887	18006	15.01	3.01
<b>I</b>	18225	18322	18274	15.70	3.70
<b>J</b>	18270	17492	18070	15.18	3.18
<b>K</b>	18257	18784	18521	16.33	4.33

The top surface latex concentration was calculated by fitting a straight line equation with the known latex concentration vs ultraviolet absorption data. Following data were obtained:

Actual Latex Concentration	Ultraviolet Absorption
0	12322
4	13481
8	15308
12	16634
16	18568

Linear regression yielded the following equation:

$$\text{Ultraviolet Absorption} = 12133.6 + 391.125 * \text{Top Surface Latex Concentration}$$

The value of R squared was 0.994 and the coefficient of standard error was 17.9.

**Appendix H**  
**Typical Characteristics of Base Paper**

Brightness	86.89% $\pm$ 0.46%
Parker Printsurf smoothness by model PPS 78 @ 10 Kg/cm <sup>2</sup> wire side	5.69 $\pm$ 0.15
Parker Printsurf smoothness by model PPS 78 @ 10 Kg/cm <sup>2</sup> felt side	5.41 $\pm$ 0.19
Compressibility as measured by Parker Printsurf smoothness	1.20
Opacity	82.16% $\pm$ 0.82%



## REFERENCES

1. Clark N.O., Windle W. and Beazley K.M., "Liquid Migration in Blade Coating", Tappi J. 52(11) : 2191-2202 (1969)
2. Dappen J. Wayne, "Distribution of Starch in Clay Coatings", Tappi J. 34(7) : 324-335 (1951)
3. Hemstock, G.A. and Swanson, J.W., "A Study of the Penetration of Coating Colors Components by means of the Roll-Inclined Plane Technique", Tappi J. 40(10) : 833-838 (1957)
4. Hagerman R.L., Jahn R.G. and Somers W.H., "A Study of the Water Retention of Latex-Bound Pigmented Coating Colors", Tappi J., 42(9) : 746-751 (1959)
5. Eklund, D.E. and Salminen P.J., "Water Transport in the blade coating process", Tappi J., 69 (9) : 117 (1986)
6. Eklund D. E. and Salminen P.J., "Water sorption in paper during short times", Appita, 40(5): 340 (1987)
7. Salminen P.J., "Water Transport in Base Paper - Effects of some Liquid and Paper Variables", Proceedings of 1988 Coating Conference, pp. 209-215, Tappi Press, Atlanta, GA 30348
8. Fujiwara H., Fujisaki N., Shimizu I. and Kano I., "Effect of water penetration on offset mottling", Proceedings of 1989 Coating Conference, pp. 121-128, Tappi Press, Atlanta, GA 30348
9. Malik, J., M.S. thesis at Western Michigan University 1992
10. Young, T.S., Pivonka, D.E., Weyer, L.G., Ching, B., "A Study of Coating Water Loss and Immobilization Under Dynamic Conditions", Proceedings of 1993 Coating Conference, Tappi Press, Atlanta, GA, pp. 223-231.
11. Stinchfield, J.C., Clift, R.A. and Thomas J.J., "The 'Water Retention Test' in Evaluating Coating Color", Tappi J., 41(2) : 77-79 (1958)
12. Arnold, K.A., "Flow Properties of Coating Clays at High Rates of Shear", Technical Association Papers, 26(1) 224-230.

13. Sandas, S.E., Salminen, P.J. and Eklund D.E., "Measuring the water retention of coating colors", Tappi J., 72(12) : 203-210 (1989)
14. Vincent, H.L., "The Photoelectric Determination of the Permeability of Paper to Fluids", Technical Association Papers, 3(1):187-191 (1940)
15. Napier, J.D., "Liquid Penetration into Paper", Paper Technology, 5(3) : 275-280 (1964)
16. Lyne, L.M. and Madsen, V., "An Apparatus for the Measurement of Liquid Penetration into Porous Webs at a Press Nip", Pulp and Paper Magazine of Canada Dec. T523-T528 (1964)
17. Fifi, P.A. and Arendt F.P., "Coating Penetration: Laboratory Evaluation and Effect on Print Quality", Tappi J., 53(10) : 1954-1959 (1970)
18. Taylor, D.L. and Dill, D.R., "Water Retention of Coating Colors : A Study of the Sonic Velocity Method and the Effect of Color Composition on Water Retention", Tappi J., 50(11):536-541(1967)
19. Kline, J.E., "The measurement of binder migration with ultra-violet analysis", Proceedings of 1990 Coating Conference, Tappi Press, Atlanta GA, pp.201.
20. Heiser, E.J., Cullen, D.W., "The Effects of Drying Rates on Adhesive Redistribution", Paper Trade Journal, 148(20) : 44-45 (1964)
21. Lo, D.K., "Detection and Measurement", Chapter 6, Binder Migration, Tappi Press, Atlanta, Ga
22. Hagen, Kenneth G., "A fundamental assessment of the effect of the drying on the coating quality", Tappi J., 69(1) :93-96 (1986)
23. Heiser, E.J. and Cullen, D.W., "Effects of Drying Rates on Adhesive Redistribution and Coated Paper properties", Tappi J., 48 (8) : 80A-85A (1965)
24. Coco, C.E., Whalen-Shaw, M., "Pigment-Binder Interaction in Air Knife Coatings", TAPPI Notes, Air Knife Coating Seminar, May 18-19, 1989, pp. 47-61.
25. Bushhouse, S.G., "The Effect of Coating Viscosity on Surface Latex Migration", Proceedings of 1991 Coating Conference, Tappi Press, Atlanta, GA, pp. 221-231

26. Whalen-Shaw, M., "A Model for the Colloidal and Rheological Characteristics of Clay, Latex CMC Formulations", Proceedings of 1990 Coating Conference, Tappi Press, Atlanta, GA, pp. 371-385.
27. Jarnstrom, L., "The adsorption of dispersing and thickening polymers and its effect on the rheology of coating colors", Proceedings of 1987 Coating Conference, May 17-21, Tappi Press, Atlanta, GA, pp. 123-132.
28. Young, T.S. and Fu, E., "Rheological Behavior of LWC Coatings containing Associate Cellulose Thickeners", Proceedings of 1991 Coating Conference, Montreal, Quebec, May 19-22, pp. 61-70, Tappi Press, Atlanta, GA 30348
29. Personal Communication with Rick Patterson, Hercules Inc., Oct. 1994.
30. Technical Data Sheet UCAR.
31. Moore, D.S. and McCabe, G.P., "Introduction to the Practice of Statistics", Second edition, 1993, Ch. 1-7.
32. Steele, F.A., "The Optical Characteristics of Paper", Paper Trade Journal, March 21, 1935, Technical Association Section 37-42.
33. Wheeler, D. J. and Lyday, R. W., "Evaluating the Measurement Process", Second Edition, 1989 Ch. 1-4.