An Investigation into the Influence of Common Fillers on Color Reversion of BCTMP Pulp

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AN INVESTIGATION INTO THE INFLUENCE OF COMMON FILLERS ON
COLOR REVERSION OF BCTMP PULP

by

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Recent advances in the pulping and bleaching of high-yield pulps, particularly bleached thermomechanical pulp, have made these pulps suitable replacements for bleached kraft pulps. Unfortunately, these high-yield pulps are not appropriate for making high-grade papers because of their tendency to yellow. Extensive efforts have been made to reduce the yellowing, but none of the methods that have been investigated have been at once both practical and economical.

This study investigated the ability of common pigments used in the paper industry to reduce the extent of yellowing of an 80/20 blend of bleached chemithermomechanical and bleached softwood kraft pulp. The effectiveness of the various pigments at reducing photoyellowing differed considerably. Titanium dioxide (TiO_2) was found to be the most effective pigment in this study at reducing photoyellowing. Alumina trihydrate (ATH) was also found to be effective at reducing yellowing, though not as effective as TiO_2. ATH at a concentration of 16.1% was found to reduce the amount yellowing by up to 45%. In comparison, TiO_2 at 9.0% was able to reduce yellowing by up to 51%. Clay and ground calcium carbonate (GCC) were found to be non-significant at concentrations in the range of 1.2 to 5.9%.

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CHAPTER I

INTRODUCTION

High-yield pulps, particularly bleached chemithermomechanical pulp (CTMP), are principally used in the manufacture of magazines, newspapers, and catalogues. Recent advancements in the pulping and bleaching of mechanical pulps have led to the manufacturing of bleached chemithermomechanical and thermomechanical pulps with ISO brightness levels above 80%. Brightness at this level makes these pulps suitable in the manufacture of most high-grade printing papers. The use of these pulps for making these grades; unfortunately, has been limited due to their tendency to yellow. The yellowing, also known as brightness reversion, is predominantly due to the oxidation of lignin in the presence of light.

All mechanical and chemical pulps display some level of brightness reversion over time. High-yield pulps yellow much more readily then chemical pulps because of their high lignin content. Mechanical pulp that has been exposed to light for six to eight months can undergo a reduction in brightness up to 30 points as measured by TAPPI Standard method T452. Bleached Kraft pulp exposed to the same conditions displayed a reduction in brightness of only three points. Efforts to make high yield pulps as stable to light as bleached kraft pulps have met with little success. Those methods that have been employed to achieve light stability are too expensive to be applied commercially. Therefore, it is important to understand the factors that are

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involved in the photoxidation of lignin and to determine how other furnish components affect photoyellowing.

It is generally accepted that several reaction mechanisms are involved in the photoyellowing of high yield pulps. The phenoxy free radical is thought to particpate in at least five mechanisms that result in the production of o-quinonoid structures. O-quinonoid structures are responsible for the photoyellowing of high yield pulps. Possible phenoxy free radical pathways include the absorption of light by conjugated phenolic groups and abstraction of a phenolic hydrogen by oxygen-based free radicals. Other pathways are the abstraction of a hydrogen from a neighboring phenolic hydroxyl group by a photo-excited aromatic carbonyl, cleavage of non-phenolic phenacyl-α-O-aryl ethers, and abstraction of benzylic hydrogen by oxygen-containing free radicals.

Numerous approaches have been taken to inhibit photoyellowing. One approach has been the use of UV absorbers to prevent the initiation of the reactions. Another approach has been to treat the pulp with free radical-scavenging antioxidants. Chemical modification of lignin has also been used to inhibit the chromophore producing reactions. All of these methods have seen success at one level or another. None of the methods have been proven to be commercially viable.

Fillers already used in the paper industry may reduce photoyellowing of bleached CTMP. A study by Johnson (1) showed titanium dioxide and calcium carbonate improved the light stability of a 50:50 blend of CTMP and kraft pulp. He showed that paper filled with high concentrations of calcium carbonate helped

preserve brightness. Substitution of the calcium carbonate with titanium dioxide further improved brightness stability. It was also shown that brightness reversion was reduced when sheets were coated with titanium dioxide and clay. This preliminary study by Johnson demonstrates the need for further investigation into the effects of pigments on brightness reversion.

The main objective of this thesis is to quantify the effects of alumina trihydrate, ground calcium carbonate, titanium dioxide, and clay on the brightness reversion of commercial chemithermomechanical pulp.

CHAPTER II

LITERATURE REVIEW

Introduction

Great strides in the understanding of brightness reversion have been made in the last hundred years. One of the earliest recorded experiments involving brightness reversion was performed by Cross in 1897 as reported by Lewis and Fromuller (2). Although experiments involving brightness reversion began as early as 1897, extensive investigation did not occur until the 1940s and 50s. In 1961, Spinner (3) wrote a comprehensive literature review of this time period. Heitner and Scaiano reviewed knowledge on brightness reversion in their book "The Photochemistry of Lignocellulosic Materials" (4). Leary (5) also reviewed recent literature up to 1993. Both reviews contain significantly new material and an expanded view of the chemical mechanisms involved in photoyellowing.

Although a lot of research has been done in the last one hundred years in understanding photoyellowing, the picture is not completely clear. In the past, photoyellowing has been attributed to sizing, rosin, resins, metal ions, additives, glue, hemicelluloses, and lignin. It is now clear that lignin is the main contributing factor in brightness reversion.

Two main processes are used to classify brightness reversion. Brightness loss can be attributed to both thermal and photochemical oxidation. The discoloration due to thermal oxidation is caused by the auto-oxidation of lignin. Yellowing by photochemical oxidation is caused by the exposure of paper to daylight.

Definition and Measurement of Brightness Reversion

Brightness reversion can be defined as the reduction in reflectance in the blue region of the spectrum as defined by TAPPI Standard T 452 om-92. The majority of brightness loss is believed to be due to the reaction of phenoxy free radical groups present in lignin with oxygen to form chromphoric quinnone structures (6). Therefore, high-lignin containing pulps will yellow much more then chemical pulps under similar conditions.

Tongren performed one of the first quantitative investigations in brightness reversion in 1938 (7). He found that the ratio of light-absorption coefficient, K, to the light-scattering coefficient, S, increased linearly with the square root of exposure time. In 1945, Giertz (8) proposed the idea of post color number. He believed that the difference between the K/S ratio before and after aging was an accurate method in estimating the relative amount of discoloration of a sheet. This difference between the ratios multiplied by one hundred he defined as the Post Color Number or PC Number as shown by the following equation:

$$PC\ Number = 100[(K/S)_{after\ aging} - (K/S)_{before\ aging}]$$

Where the ratio K/S as defined by the Kubelka-Munk equation:

$$K/S = (1 - R_\infty)^2 / 2R_\infty$$

Where R_∞ is the brightness of an infinitely thick pad of paper.

Since its introduction, Post Color Number has been used extensively in brightness reversion studies. Post Color Number has been widely used in many experiments because the value is indicative of the relative amount of chromophores that are created during the aging process. Brightness difference is a poor indicator of brightness reversion because the relationship between brightness and chromophore concentration is not linear. As an example, fewer chromophores are needed to cause a brightness drop of two points for a sheet with an initial brightness of eighty than for a sheet with an initial brightness of seventy. Since Post Color Number is a relative measurement for the amount of created chromophores, it follows that the larger the Post Color Number the more extensive the discoloration.

<div align="center">Variables Affecting Brightness Reversion</div>

Wood Species

It has been shown that wood species can have a significant effect on the amount of brightness reversion. A study on the brightness reversion of eight Canadian wood species suggests that wood type has a significant effect on brightness after thermal aging (9). Table 1, "Effect of Species on the Thermal Reversion of Mechanical Pulp", displays the results of this study. As shown by the table, cedar

mechanical pulp was the most stable to thermally induced yellowing. Balsam fir, black spruce, and white spruce were equally stable, but less stable then cedar. Larch and jack pine had the lowest stability of all the softwoods. Of the hardwoods, birch and popular had comparable stability. Other studies show that species also have an effect on photochemical reversion as well (1,10).

Table 1

Effect of Species on the Thermal Reversion (100°C, 0% R.H.)
of Mechanical Pulp

Species	Thermal Reversion ($\Delta k_{457\,nm}$, m^2/kg)
	Softwood
Cedar	0.6 ± 1.0
Basalm fir	0.9 ± 0.3
Black Spruce	1.1 ± 0.1
White spruce	1.2 ± 0.1
Larch	2.0 ± 0.5
Jack pine	2.5 ± 0.6
	Hardwood
Birch	1.3 ± 0.8
Popular	1.2 ± 0.2

Pulping

The amount of brightness reversion due to the pulping process is dependent
upon the pulping conditions and method. As shown in Figure 1, stone groundwood
and thermomechanical pulp have the same degree of brightness reversion under
accelerated aging conditions (100 °C, 0% R.H., and 24 h) (11). Conversely, the
brightness loss of thermomechanical pulp is notably higher under ambient conditions
of 23 °C and 50% relative humidity.

Figure 1. Yellowing of Stone Groundwood (SGW), Thermomechanical Pulp (TMP),
and High Yield Sulfite (HYS) Under Ambient and Accelerated Aging Conditions.

The impregnation of chips with sodium sulfite before disc refining increases
the amount of brightness reversion. Figure 1 illustrates that high yield sulfite pulp at

80 % yield yellows to a much greater extent at both conditions. It has also been demonstrated that pulp produced from sulfonated CTMP chips yellow in the absence of light to a much greater extent then untreated thermomechanical pulp (12).

Bleaching

The method of bleaching can have a significant effect on the brightness reversion of high yield pulps. Bleaching with alkaline peroxide or sodium dithionite increases the amount of yellowing under ambient conditions (23°C, 50% R.H.) as shown in Figure 2 (13). Under these conditions, sodium dithionite bleached pulps yellow to a greater degree then alkaline peroxide bleached and unbleached pulp. It is known that sodium dithionite bleaching reduces colored quinones into colorless hydroquinones, while alkaline peroxide bleaching oxidizes colored quinnones into non-reactive structures (14). The hydroquinones produced during sodium dithionite bleaching are oxidized back into chromophoric quinnones causing the pulp to yellow to a greater extent (15). The same reasoning also explains the higher level of brightness reversion of unbleached high-yield sulfite pulp compared to the alkaline peroxide bleached HYS pulp. The tendency for dithionite and alkaline peroxide pulps to yellow more then unbleached pulp holds true to a greater or lesser extent for other aging conditions as well (16).

Metal Ion Type and Concentration

Metal ions enhance the effects of photoyellowing greatly. The formation of

colored bodies due to the presence of metal ions depends upon the pulping system

Figure 2. Yellowing of Peroxide- and Dithionite-bleached Stone Groundwood (SGW), Thermomechanical Pulp (TMP), and High-yield Sulfite (HYS) Under Accelerated Aging Conditions.

being used and the conditions under which it is pulped. Bleached mechanical pulps

are especially sensitive to the presence of metal ions (17). Some metal ions will

increase the absorption coefficient of the pulp by forming colored oxides or

complexes with lignin and resins (17). It has been reported that the formation of

colored inorganic salts by hydrolysis has a detrimental effect on brightness stability

(18). The presence of metal ions also increases the decomposition rate of phenolic

structures, further accelerating the formation of colored structures (17). Metal ions

affect color reversion to different degrees. Iron of both states of oxidation appears to

have the largest negative effect on brightness stability. Other metal cations such as

manganese, aluminum, and copper only have a minor effect on the brightness stability of pulp and paper (17).

pH

The pH of pulp and paper products can have a large impact on their brightness stability. In earlier work, Lewis (2) reported that photoyellowing of groundwood pulp was pH dependent when adjusted with acid and bases. Later Anddtbacka, Gratzl, and Holbom (19) used buffer solution to adjust pH and determined that pH had no effect on photoyellowing of pulp. Rapson and Polcin (20) made sheets from bleached sulfite pulps at pH levels ranging from 3 to 11. Initial sheet brightness was only slightly affected, but upon heating at 105°C for 18 hours a sharp rise in brightness loss was observed as pH increased above 6. Therefore, one can conclude that the role of pH in brightness reversion is dependent upon the type of pulp and experimental conditions.

Oxygen

It is generally accepted that oxygen plays a major role in the brightness reversion of paper. Leary (21) studied the photoyellowing characteristics of pulp in an oxygen-free atmosphere. After irradiating paper samples for 500 hours, the amount of yellowing was negligible. He concluded that oxygen is a necessary component of the yellowing reactions that were taking place. Another study showed that groundwood sheets discolored to less extent in the absence of oxygen, suggesting that oxygen is necessary for the majority of the yellowing (22). Therefore one can conclude that

atmospheric oxygen is needed to convert a majority of the colorless lignin compounds into chromophoric structures.

Moisture Content

The reported results on the effect of moisture on color reversion are inconclusive. Under elevated temperature, Corbi and Rapson showed that moisture can have a large effect on brightness reversion (23). Two samples of periodate oxidized cotton linters were heated, one at 105°C at 2% R.H. and the other at 100°C at 100% relative humidity. The brightness of the sample at 100°C and 100% R.H. dropped at a considerable rate while the other did not. Gellerstedt and his colleagues also concluded that it was possible to improve pulp brightness stability by avoiding high humidity at elevated temperature (24). Under ambient temperature, Van den Akker, Lewis, Jones, and Buchanan exposed pulp samples to relatively high and low humidity. They concluded that the effect of moisture was minimal. Gratzl and coworkers also concluded that moisture content did not affect the rate of yellowing (19).

Temperature

It is generally accepted that brightness reversion is temperature dependent. Accelerated aging of groudwood pulp has been done routinely at temperatures in the range of 80 to 120°C. Although the rate of brightness loss of thermal aged sheets is

not severe, considerable brightness loss is obtained in combination with UV irradiation.

Wavelength of Light

Many previous experiments (2) in brightness reversion employed the carbon-arc Fade-O-Meter as the UV light source. Nolan, Van den Akker, and Wink showed that two types of light induced reactions were occurring when groundwood was exposed to UV light (22). They reported that light in the range of 270 to 400 nm was shown to be responsible for the darkening of groundwood pulp. Light of wavelengths longer then 385 nm was shown to increase the brightness. Leary confirmed the findings of Nolan and coworkers by bleaching newsprint with light of wavelengths between 410 and 520 nm (21).

Mechanisms of Photoyellowing

Although lignin is known to be primarily responsible for the yellowing of high yield pulps, the chemical reactions governing light-induced brightness reversion are far from being perfectly understood. The discoloration of lignin containing pulps occurs by the photo-oxidation of lignin in the fiber wall. O-quinonoid structures believed to contribute to light-induced yellowing are formed by the reaction of phenoxy free radicals with peroxy radicals as shown by Figure 3. The peroxy free radicals that participate in the reaction shown in Figure 3 are formed through the auto-oxidation of lignin as shown by Figure 4. The phenoxy free radical, which is the

precursor of o-quinonoid structures, is known to evolve from at least five reaction

pathways as displayed in Figures 5 and 6. These five pathways are the following:

1. Direct absorption of light by phenolic chromophores (Figure 5, reaction 1).

2. Abstraction of a hydrogen atom from the phenolic hydroxyl group (Figure

5, reaction 2).

3. Abstraction of a phenolic hydrogen atom by a triplet excited state carbonyl

group (Figure 5, reaction 3).

4. Cleavage of the β-O-4 aryl ether bond of the singlet and triple excited

state of the phenacyl aryl ether group (Figure 6, reaction 1).

5. Abstraction of a benzylic hydrogen atom to form a ketyl free radical

followed by the facile cleavage of the β-O-4 aryl ether bond (Figure 6,

reaction 2).

Figure 3. Oxidation of a Phenoxy Radical to an O-quininoid Lignin Structure by
Peroxy Radicals.

Figure 4. Reaction Sequence for the Auto-oxidative Formation of Hydroxyl and Alkoxyl Radicals.

Figure 5. Formation of Phenoxy Radicals Through Direct and Indirect Light-induced Homolytic Cleavage of a Phenolic Hydroxyl Group.

Figure 6. Formation of Phenoxy Radicals Through Light-induced Homolytic Cleavage of the β-C-O Bond in the β-O-4 Ether Units.

Inhibition of Photoyellowing

Leary suggests possible methods of inhibiting light-induced yellowing during the three stages of the mechanism (5). The following shows the suggested methods of inhibition for the three stages of the mechanism:

1. The primary UV-absorbing chromophores could be eliminated or modified.

2. The ketyl and phenoxy radicals could be eliminated or prevented from forming. In addition, the elimination of oxygen radicals and singlet oxygen which tend to oxidize the phenoxy radicals.

3. The yellow chromophores that are created during the aging process could be bleached.

An illustration of the reaction pathways by Leary is shown by Figure 7. The initial step of light-induced yellowing is the absorption of light by chromophoric lignin structures producing various intermediate radicals. The intermediate radicals then react to form other radicals, specifically the phenoxy and ketyl radicals. Further reactions of these structures produce the yellow quinone and ketone products responsible for yellowing. A more descriptive illustration of the mechanistic pathways shown in Figure 7 is presented in Figure 8 (5).

Figure 7. Mechanistic Pathways of Light-induced Photoyellowing.

Figure 8. The Probable Paths of Chromophore Production and Lignin Degradation
in the Photo-yellowing or Photo-protection of Mechanical Pulps.

Significant progress has been made in determining the colored chromophores

and the pathways of their formation. Up until 1988, the main pathways believed to

contribute to photoyellowing only included the reactions illustrated in Figure 5. In

1990 the "phenacyl" pathway was identified by the observation that β-O-4 ether

lignin models containing carbonyl groups will photolyze to give ketones and phenoxy

free radicals (Figure 6, Reaction 1). In 1992 the major route of photo-degradation was

determined. Scaiano and co-workers (25) found that the model compound α-GAVH

will react with other radicals to form ketyl free radicals (Figure 6, Reaction 2).

Although much has been learned about these reaction pathways, more information is

needed about the oxidation step in which phenoxy free radicals are converted into quinones.

Chemical Modification of Lignin

There have been many methods used in the past to inhibit light-induced yellowing by modifying the functional groups that are associated with the reacting structures. Initial efforts to inhibit light-induced brightness reversion concentrated on modifying functional groups that were associated with the first three known reaction pathways (Figure 5). The functional group modifications to lignin that were attempted to reduce photoyellowing include hydrogenation of vinyl groups, etherification and esterification of the phenolic hydroxyl groups, reduction of aromatic carbonyl groups, and a combination of etherification of the hydroxyl group and reduction of the carbonyl group. It has been shown that the esterification or etherification of the phenolic hydroxyl groups in lignin significantly improves the stability of the pulp. Recent work has shown that esterification with acetic anhydride inhibits light-induced yellowing without detrimentally affecting pulp strength (26). The other methods of chemical modification have been successful in reducing the rate of yellowing. Although all of the methods have been proven to be useful to a certain extent, they only partially prevent yellowing. Also, chemical modifications that have been used are relatively expensive and can have adverse effects on pulp properties. Further studies are needed to find methods that can prevent most or all of the chemical reaction pathways.

UV Absorbers

UV absorbers are compounds that absorb UV light and dissipate it through non-yellowing mechanisms. UV absorbers have been used extensively to prevent light-induced degradation of a variety of materials. Nolan first reported the effect of UV absorbers on groundwood paper (27). He observed that sheets treated with Eastman Ultraviolet Sensitizer needed twice the amount of exposure as untreated sheets to reach the same level of discoloration. Hydroxybenzophenones have also been used extensively to prevent degradation of light sensitive materials. Hydroxybenzophenones absorb UV light and dissipate the energy as heat through tautomerizing as shown in Figure 9. Several studies have shown that UV absorbers can be very effective at decreasing light-induced yellowing (24, 28, 29). However, achievement of 93% stability requires more than a 4% charge UV absorber on the surface of the sheet, an amount too large and too expensive for commercial use.

Figure 9. Light-induced Tautomerization of 2-hydroxyzophenone.

Free Radical Scavengers

The most successful methods for inhibiting photoyellowing are those that scavenge free radicals. The success of scavengers can be attributed to their reaction with free radicals that participate in each of the five known reaction pathways. Ascorbates, thiols, and thioethers stabilize lignin in paper by quenching peroxyl and alkoxyl free radicals, structures known to convert phenoxy free radicals into o-quinonoid groups.

The use of ascorbic acid and sodium ascorbate to inhibit brightness reversion was first observed by Kringstad (28). When ascorbic acid is applied to a paper surface yellowing is inhibited for a finite time (1-2 h). Upon longer exposure to UV light, yellowing proceeds at the same rate as that for untreated paper (30). Ascorbic acid is believed to undergo air and photo-oxidation reducing its effectiveness at inhibition.

Thiols and thioethers have been shown to be extremely effective inhibitors of photoyellowing. Studies by Cole et al. (31, 32) found that thiols, thioethers, and their derivatives had a pronounced effect on lignin-containing papers. He found that sheets treated with thiols were brighter and more stable to yellowing. Similar studies confirm Coles's findings (29, 33).

Polymeric Inhibitors

Polyvinylpyrrolidone (PVP) has been used to improve the whiteness and gloss of paper coatings, decrease paper surface slippage, and improve dimensional stability of wood. PVP has also been shown to reduce the yellowing of pulp due to light

exposure (34). The monomer and lower molecular weight PVPs have been shown to be the most efficient. It has been proposed that the amide group in PVP strongly bonds to the phenolic hydroxyl structures, preventing its oxidation.

Polyethylene glycol has also been shown to inhibit photoyellowing. Its effectiveness increases as its degree of polymerization increases from 2 to 90 (35). The mechanism of inhibition of ethylene glycol is not well understood. It has been proposed that it inhibits yellowing by preventing air from reaching the paper fibers (36).

Pigments

It is believed that pigments may inhibit photoyellowing by blocking and/or absorbing the wavelengths of light that are responsible for brightness reversion. Pigments in the paper industry have been used to impart brightness, gloss, opacity, and smoothness to paper and paperboard. Also pigment is used to reduce the cost of production, since most pigments are less expensive than fiber. A study by Johnson (1) showed that some pigments may have a beneficial effect at reducing brightness reversion. Samples with a concentration of 25% calcium carbonate helped preserve brightness, but only slightly reduced the brightness reversion of the fiber. With a 1% substitution of calcium carbonate with titanium dioxide, modest improvements in brightness reversion were obtained. Clay coatings applied at 8 g/m^2 showed a 50% reduction in brightness reversion. Upon substitution of clay with titanium dioxide a

marked improvement in brightness reversion was observed at coat weights as low as

4 g/m^2.

CHAPTER III

STATEMENT OF THE PROBLEM

Over the years, high yield pulps have been used to make short-life paper products such as newspapers, magazines, and catalogues. In recent years the ISO brightness values of thermomechanical and chemithermomechanical pulp have increased to a level over 80%. At this brightness level, these pulps have become suitable for making higher valued papers such as book and writing paper. Paper made from CTMP and TMP however tend to yellow relatively quickly, making their use in these high-end grades limited. CTMP and TMP would be ideal pulps to use for these types of grades if it were not for their yellowing. These pulps possess high opacity, bulk, and compressibility, which give them excellent printing characteristics. These pulps are also less expensive then those pulps that are currently used to make high-value grades. Therefore, it is desired to produce high-yield pulps with greater resistance to brightness reversion.

A number of methods have been attempted to reduce the brightness reversion of high-yield pulps. One approach has been to chemically alter the functional groups in lignin that are responsible for photoyellowing. Chemical modification of the phenolic hydroxyl group by alkylation or acylation, the reduction of aromatic carbonyl groups, and the hydrogenation of vinylic double bonds have proven to considerably improve brightness stability. These chemical modifications

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only partially reduce light-induced yellowing because they do not prevent the homolytic cleavage of the guaiacylglycerol-β–O-4-guaiacyl ether. Other methods have included blocking near-UV light with UV-absorbing compounds or quenching of peroxy and alkoxy radicals with a hydrogen-donating compound such as sodium borohydride. All of these methods are effective to a certain extent; but they are either too expensive or impractical for commercial production.

The objective of this thesis is to determine the effect of various pigments already used in the paper industry on the light-induced brightness reversion of a 80/20 blend of bleached aspen chemithermomechanical pulp and bleached softwood kraft pulp. This work will focus on increasing the knowledge and understanding of the following areas:

1. The impact of titanium dioxide, ground calcium carbonate, alumina trihydrate, and clay on light-induced brightness reversion of paper made with the aforementioned pulp blend.

2. The effect of the loading level of various pigments on brightness reversion after exposure to UV light.

CHAPTER IV

EXPERIMENTAL APPROACH

Design

This work evaluated the effect various pigments have on the brightness reversion of bleached chemithermomechanical pulp by accelerated aging with light. The experimental work was performed in one stage. The fiber source selected was a 80/20 blend of bleached aspen chemithermomechanical pulp and bleached softwood kraft. The various pigments used were titanium dioxide, aluminum trihydrate, clay, and ground calcium carbonate. A general linear model was used as shown in Table 2. A control experiment without any added filler was also conducted for comparison.

Table 2

General Linear Models Procedure (Class Level Information)

Class	Levels	Values
Pigment Type	4	ATH, TiO_2, Clay, GCC
Pigment Concentration (%)	5	0, 5, 10, 15, 20
Paper Side	2	Felt, Wire
Exposure Time	4	4, 8, 16, 24 hours

As shown in Table 2, the samples were irradiated for 4, 8, 16, and 24 hours using the SunTest CPS+ Fade-O-Meter. The sample's temperature was maintained at 35 °C during the aging process and at 72 °F during their storage and testing. All samples were stored in an opaque plastic bag to avoid exposure to light. The absorption coefficient, K, and scattering coefficient, S, were measured before and after the accelerated aging. The light-induced brightness reversion was evaluated by calculating the Post Color (PC) Number of each sample. Each sample was aged on both the felt and wire side at four different exposure times. Two replicates of each sample were measured amounting to a total of 408 measurements. Table 3 shows the breakdown of the samples.

Table 3

Sample Breakdown

Filled Samples		Control Samples	
4 Pigment Types x 4 Pigment Concentrations		1 Control	
Total: 16 Samples	+	1 sample	= 17

Total Number of Measurements = 17 Samples * 4 Exposure Times * 2 Sides * 3 Measurements per Exposure Time = 408

CHAPTER V

METHODOLOGY

The focus of this experiment was to determine the effect of pigment type and level on the light-induced brightness reversion of BCTMP. The fiber furnish used for this study was bleached aspen CTMP and BSWK. The experiment was initially designed to use BCTMP as the only pulp source, but BSWK was also used because of a limited supply of BCTMP. The pigments used for this study were ground calcium carbonate, titanium dioxide, alumina trihydrate, and clay. The paper for this experiment was made on the paper pilot machine located at Western Michigan University. Other equipment used for this experiment were the SunTest CPS+, made from Atlas Material Testing Solutions, and the Technidyne Brightimeter S-5 manufactured by Technidyne Corporation. The storage and testing of the samples were done in the controlled temperature and humidity lab located at Western Michigan University.

Pulp and Pigment Preparation

Bleached Aspen CTMP and BSWK were the selected pulps used throughout the experiment. Tembec Inc. supplied the mechanical pulp necessary for the paper pilot trial and the bleached softwood kraft pulp was donated by Western Michigan

University's Paper and Printing Department. The physical and optical properties of the mechanical pulp, as measured by the manufacturer, are shown in Table 4. Several manufacturers donated the pigments used for the paper machine trial. Millennium Inc. donated the titanium dioxide; Omya donated the ground calcium carbonate, and Alcoa donated the alumina trihydrate. The clay used in the experiment was from Huber, and was available for use in the paper pilot plant. The product names along with the corresponding brightness and refractive index for each pigment, as specified by the manufacturers, are located in Table 5.

Table 4

Analytical Data of Bleached Aspen Chemithermomechanical Pulp

Canadian Standard Freeness (ml)	257
ISO Brightness	85.5
Sommerville Shive Content (%)	0.003
Tensile (Nm/g)	53.8
Tear (mNm^2/g)	5.4
Burst (KN/g)	2.7
Bulk (cm^3/g)	1.6
Average Fiber Length (mm)	0.79
Fines (% <0.410 mm)	14.1
Opacity (%)	77.8

The day before the paper machine trial the pigments and pulp were prepared. Approximately ½ ton of BCTMP and the BSWK were repulped at a ratio of 80 to 20 respectively. Each of the pigments was slurried with a high-shear mixer at the

maximum recommended percent solids for 30 minutes in order to ensure appropriate pigment dispersion.

Table 5

Product Name, Brightness, and Refractive Index of Pigments

Product Name	Brightness	Refractive Index
Hydral 710 (ATH)	<99	1.57
Tiona AT-1	94-97	2.55
Hydrocarb 60 (GCC)	95-97	1.56
Hydrasperse (clay)	86-88	1.57

Paper Machine Trial

The production conditions for the paper machine trial were set as shown in Table 6. The pigment and stock flow rates were the main control variables. The basis weight of the sheet was held constant ($\pm$ 3 g/m^2) during the trial by adjusting the pigment and stock flow rates. A cationic retention aid, Nalco 625, was applied at 2 lbs/ton (the highest recommended level) to ensure pigment retention. The pH of the headbox and whitewater were not controlled.

The BSWK stock was refined before being mixed with the BCTMP to obtain approximate Canadian Standard Freeness of 300 ml. Refining the pulp was necessary to obtain enough wet web strength on the machine.

Table 6

Production Conditions

Production Rate:	Approximately 160 lbs/hr
Machine Speed:	Approximately 82 fpm at reel
Basis Weight:	Controlled to 70 ± 2 g/m^2
pH:	Uncontrolled
Pigment Flow Rate:	Varied as necessary
Calendering:	One nip at 35 psi

The trial was set up as shown in Table 7. The control was the first sample to be made. The first sample was gathered approximately 30 minutes after the trial began. The length of each run after the control sample was restricted to 15 minutes because of the limited pulp supply. A sample from the reel, headbox, and couch pit, was obtained for each condition after stabilization was achieved. After runs 5, 9, and 13, the white water was drained and the machine was purged for twenty minutes of any remaining pigment in the system.

After the paper machine trial, the papers samples were cut down to 8 ½" x 11" sheets. To avoid any discoloration, the sheets were then placed into a cardboard box, which was then put into two opaque plastic bags. The samples were then put inside a cabinet located in a controlled temperature and humidity room ($50\% \pm$ RH and 73.4 ± 1.8 °F) until further testing could be performed. The corresponding white water and headbox samples were stored in a refrigerated environment.

Table 7

Run Conditions

Run #	Clay (lbs/ton)	TiO2 (lbs/ton)	GCC (lbs/ton)	ATH (lbs/ton)
1	-	-	-	-
2	100	-	-	-
3	200	-	-	-
4	300	-	-	-
5	400	-	-	-
Purge	Drain white water, then purge machine of pigments for 20 minutes			
6	-	100	-	-
7	-	200	-	-
8	-	300	-	-
9	-	400	-	-
Purge	Drain white water, then purge machine of pigments for 20 minutes			
10	-	-	100	-
11	-	-	200	-
12	-	-	300	-
13	-	-	400	-
Purge	Drain white water, then purge machine of pigments for 20 minutes			
14	-	-	-	100
15	-	-	-	200
16	-	-	-	300
17	-	-	-	400

Headbox and White Water Samples

Several tests were performed on the headbox and white water samples to

obtain a better understanding of the trial conditions. The pH and total alkalinity of the

headbox and white water samples were determined according to TAPPI standard T-

620 cm-83. Single-pass retention was determined according TAPPI standard T-269 cm-92.

Physical Testing

For the purpose of understanding the physical characteristics of the paper samples a number of physical tests were performed. Table 8 presents a list of tests along with the corresponding TAPPI standard used.

Table 8

Physical Tests of Experimental Samples

Test	TAPPI Standard
1. Tensile Strength	T 494 om-88
2. Grammage	T 410 om-93
3. Identification of Wire Side	T 455 om-93
4. Ash of Paper at 900°C	T 413 om-93

Determination of Filler Level

From the data obtained from ashing the paper at 900°C (T 413 om-93), an estimate of the filler level of the paper samples was determined. The ash of the control sample and paper made during the purging of the headbox were found to be minimal. Therefore, an assumption was made that each filled sample contained only one type of filler. The following equation shows how the filler level was calculated:

Percent filler of sample = (S − C)/(100 − L)

Where S is the percent ash of the particular sample, C is the percent ash of the control sample, and L is the loss upon ignition of the type of filler within the sample. Table 9 shows the loss upon ignition of each type of filler as supplied by the manufacturers.

Table 9

Percent Loss Upon Ignition of Fillers at 900 °C

Pigment	Percent loss upon ignition
Hydral 710 (ATH)	34.6
Tiona AT-1	00.0*
Hydrocarb 60 (GCC)	42.6
Hydrasperse (clay)	13.5

*Loss upon ignition of titanium dioxide is minimal.

Accelerated Aging With Light

Accelerated color reversion of the samples was achieved by irradiation with a Fade-O-Meter equipped with a xenon arc lamp. The Fade-O-Meter model used in this experiment was the SunTest CPS+ made by Atlas Material Testing Solutions. All the samples were irradiated using D filter of the instrument. The D filter was chosen because it best simulated the spectrum of sunlight.

The samples were aged at 35 °C with a light intensity of 500 kw/m^2 for periods of 4, 8, 16, and 24 hours. Brightness was measured before and after exposure by using TAPPI method T 452 om-92.

The color reversion was determined by calculating Post Color (PC) Number.

PC Number $= 100[(K/S)_{\text{after aging}} - (K/S)_{\text{before aging}}]$,

$K/S = (1-R_\infty)^2/2R_\infty$

where,

K is the absorption coefficient, m^2/kg

S is the scattering coefficient, m^2/kg

R_∞ is the brightness of the sample at infinite thickness according to TAPPI method T-452 om-92.

Data Analysis

The initial general linear model, as shown in Table 2, was revised because the targeted pigment concentrations were not obtained during the paper machine trial. The revised general linear model is presented in Table 10.

Measurements of Total Alkalinity, pH, and First-Pass retention were made to aid in determining the cause of poor filler retention for ground calcium carbonate and clay. The results of these tests are shown in Table 11.

As shown in Table 11, the relationship between pH, total alkalinity, and first-pass retention is unclear. Testing for Zeta potential may have given some insight into

the retention of the fillers. Unfortunately, the equipment necessary for testing Zeta potential was unavailable. It is known that the Zeta potential of titanium dioxide under basic conditions is negative, and becomes more negative with increasing pH. The Zeta potential of calcium carbonate under basic conditions is positive and increases with the amount of calcium ion that is present in the system. With the presence of a multivalent cationic retention aid (at the highest recommended level), the Zeta potential of the system running calcium carbonate could have been excessively positive. This also could have occurred during the retention of the clay pigments, explaining the poor retention. It is clear that it is difficult to predict the magnitude and sign of the surface charge that filler particles will adopt when incorporated in a papermaking systems.

Table 10

Revised General Linear Models Procedure (Class Level Information)

Class	Levels	Values	
Pigment Type	5	ATH, TiO$_2$, Clay, GCC	
Pigment Concentration (%)	17	2.10, 3.65, 7.29, 16.14	unique to ATH
		2.51, 4.76, 9.02, 19.64	unique to TiO$_2$
		1.22, 2.43, 3.61, 5.88	unique to Clay
		1.91, 2.32, 2.58, 4.47	unique to GCC
		0.00	Control
Paper Side	2	Felt, Wire	
Exposure Time	4	4, 8, 16, 24 hours	

Table 11

First-Pass Retention, pH, and Total Alkalinity
of Paper Machine Trial

| Sample | Filler Conc. (%) | PH | | Total Alkalinity (ppm CaCO3) | | |
		Head Box	White Water	Headbox	White Water	First-pass Retention (%)
Control	Na	7.45	8.03	365	331	85.7
Clay	1.22	7.44	7.96	339	377	83.1
	2.43	7.68	7.75	336	345	76.7
	3.61	7.60	8.22	337	339	69.3
	5.88	7.52	8.18	338	351	65.4
TiO2	2.51	7.52	7.97	334	329	86.2
	4.76	7.53	7.51	335	302	82.0
	9.02	7.54	7.80	331	310	82.0
	19.64	7.56	7.90	331	308	77.2
GCC	1.91	7.72	7.87	761	745	83.8
	2.32	7.59	7.80	1128	1014	80.0
	2.58	7.79	7.83	1688	1672	71.6
	4.47	7.75	8.10	2418	5190	47.7
ATH	2.1	7.87	8.06	432	426	85.8
	3.65	8.03	8.05	410	335	85.8
	7.29	8.06	8.05	363	201	78.9
	16.14	8.04	8.40	371	351	73.2

The statistical software SAS (version 6.12) was used to analyze the data. The first analysis that was performed was the general linear model (GLM) regression. The GLM was used to determine the significance of the main effects and interactions. SAS was also used to perform several Duncan Multiple Range tests to determine if the differences between means within a given effect were significant. For example, Duncans test was used to determine if the ATH samples were significantly different

from the control. The Duncan's multiple range test was also used to determine if a statistical significance existed between filler levels within a given filler type. All of the tests were performed at a confidence level of 95%. For the GLM analysis, the effects and interaction were determined to be significant if the corresponding p-values were < 0.05, which is the same as 95% confidence.

Excel 97 was used to perform a simple regression analysis for each pigment type and concentration. The regression analyses were performed to examine the effect that each pigment type had on the rate of yellowing.

CHAPTER VI

RESULTS AND DISCUSSION

This study examined the effects of various pigments on the light-induced brightness reversion of paper made with an 80/20 blend of BCTMP and SWK pulps. The preparation of the pulps and the making of the samples have been outlined in the previous chapter. There were a total of 136 unique experimental conditions, with each condition repeated twice. The filled paper samples were exposed to light under accelerated conditions for 4, 8, 16, and 24 hours. The extent of brightness reversion was determined by measuring the brightness of the samples before and after the aging process. The brightness measurements were used to calculate Post Color number, which is the response of this brightness reversion study.

The statistical program, SAS, was used to analyze the data. A general linear model with four variables was selected for the analysis. The levels of pigment concentrations used for the GLM were determined by ash analysis. The result of the ash analysis is shown in Table 10. The model had 20 degrees of freedom from a corrected total of 135. A portion of the SAS output is shown in Table 12.

The SAS output of the general linear model has an extensive amount of information with respect to the significance of the main effects and interactions. The R^2 value shown in Table 12 represent the amount of variability in the response that is

accounted for by the independent variables. Therefore, pigment type and concentration, paper side, and exposure time account for 93.9% of the variability of Post Color Number. The P values shown in some of the following tables indicate the level of significance for the independent variable or model. The lower the P value the higher the level of significance. For this analysis, a P value less than or equal to 0.05 means that the variable or model is significant at a confidence of 95%.

Table 12

General Linear Model

Source	DF	Sum of Squares	Mean Squares	F Value	Pr > F (P value)
Model	20	460.1457	23.0073	87.95	0.0001
Error	115	30.0827	0.2616		
Corrected Total	135	490.2284			

$R^2 = 0.9386$

The SAS output indicated the significance of the main effects and interactions. Three of the four main effects were found to be significant. Of those that were significant, exposure time was found to be the most significant followed by the filler type and lastly by the filler level. The P and F values for the main effects are displayed in Table 13. Three of the two-way interactions were found significant. The two way interactions that were found significant were type*exposure, type*side, and

level*exposure. The P values for the other two-way interactions terms ranged from 0.3900 to 0.8950.

Table 13

Main Effect Variables and Significance for Post Color No.

Source	DF	F Value	Pr > F
Pigment Type	4	68.09	0.0001
Pigment Concentration	12	12.15	0.0001
Paper Side	1	0.01	0.9423
Exposure Time	3	446.96	0.0001

Another test that was performed by SAS was the Duncan's Multiple Range test. The Duncan's test was used to determine if the different pigments within the main effect of pigment type were significantly different from the control. Duncan's test was also used to determine the significance of each concentration. At the filler levels that were obtained during the paper machine trial, only titanium dioxide and alumina trihydrate were found to be significantly different from the control. Titanium dioxide was found to be significant at all concentrations and ATH was found to be significant at the two highest concentrations. The Duncan tests were performed at a 95% confidence level. The results of these tests are displayed in Table 14. The variables that have means that are not significantly different are grouped together.

Table 14

Determination of Pigment Significance by
Duncan's Multiple Range Test

$\alpha = 0.05$			DF = 115		MSE = 0.2616
Duncan Grouping		Mean	N	Type	Signigicant Levels
	A	4.6576	32	Clay	None
	A				
B	A	4.5701	8	Control	------
B					
B		4.2847	32	GCC	None
	C	3.6717	32	ATH	7.29, 16.14
	D	2.7418	32	TiO_2	2.51, 4.76, 9.02, 19.64

Means with the same letter are not significantly different

Effect of Exposure Time on Photoyellowing

Although it is understood that paper made from high yield pulps yellow when exposed to light, it is important to understand the relationship between the extent of exposure and photoyellowing. In this model exposure time was indicated as being the most significant effect of the model. The effect that exposure time had on PC number varied greatly with changing filler types and concentrations. The influence of exposure time was greatly reduced with the samples that contained titanium dioxide. A graphical representation of the relationship between PC Number and exposure time is shown in Figure 10. From the trendline equations, the rate of yellowing of the

control sample was reduced to less then 1/3 of its original value by the introduction of fillers into the paper.

Figure 10. Relationship Between PC Number and Exposure Time.

Effect of Paper Side on Photoyellowing

There was some initial concern that the concentration of pigment would not be uniform throughout the z-direction of the paper. On most production fourdrinier machines pigment added at the wet end of the paper machine tends to fall through the wire side, causing a higher concentration of pigment on the felt side. This did not turn out to be the case for this experiment. Since photoyellowing is largely a surface phenomenon, both sides of the paper samples were irradiated. Table 13 shows that the

side of the paper was not significant. A graphical representation of the PC Number

for all of the samples is shown Figure 11.

Figure 11. Comparison of Side on Post Color Number.

Effect of Pigment Type and Concentration on Photoyellowing

Clay Filled Sheets Exposed to Light

Clay, as indicated by Duncan's multiple range test, was determined to be non-

significant at the obtained experimental level. When the PC Numbers of the clay

filled sheets are compared to the control, it is shown that clay had little or no effect on

reducing the brightness reversion. Table 15 displays this comparison. The PC

Numbers of some of the clay filled samples were actually higher then the control. The

reason for this is not understood; but it could be due to experimental error. Figure 12

shows a graphical representation of the data in Table 15.

Table 15

Comparison of PC Numbers of Clay With the
Control at Different Exposure Times

Sample	Level	PC Number			
		4 hrs.	8 hrs.	16 hrs	24 hrs
Clay	1.22%	2.62	3.37	5.96	8.18
	2.43%	2.55	3.49	5.54	7.68
	3.61%	2.33	3.26	4.69	7.35
	5.88%	2.00	3.27	5.41	6.83
Control	na	2.44	3.39	5.11	7.34

Figure 12. Comparison of PC Numbers of Clay With Control.

GCC Filled Sheets Exposed to Light

Ground calcium carbonate was also determined to be non-significant as tested by Duncan's multiple range test. Although GCC was indicated as being non-significant, a comparison of the control with the GCC filled sheets show a modest reduction in PC number at some levels (Table 16). As shown by the data, all the PC numbers at 4, 8, and 24 hours of exposure were lower then the controls. From the samples after the sixteen hours of exposure time, it could be argued that GCC may be significant at higher filler levels. Figure 13 shows the trend of lower PC number for the GCC when compared with the control.

Table 16

Comparison of PC Numbers of GCC With the
Control at Different Exposure Times

Sample	Level	PC Number			
		4 hrs.	8 hrs.	16 hrs	24 hrs
GCC	1.91%	2.23	3.28	5.34	6.41
	2.32%	2.28	3.19	5.49	6.81
	2.58%	2.20	3.21	5.14	6.69
	4.47%	2.02	2.76	5.07	6.46
Control	Na	2.44	3.39	5.11	7.34

Figure 13. Comparison of PC Numbers of GCC With Control.

ATH Filled Sheets Exposed to Light

Alumina trihydrate had a substantial effect at reducing the rate of light-induced brightness reversion. At the highest concentration of 16.14%, ATH consistently reduced the extent of brightness reversion by over 35% at all of the exposure times (Table 17). At 7.29% concentration, the reduction in brightness ranged from 13.59% to 23.71%. The trend of reduced brightness reversion is shown in Figure 14.

Table 17

Comparison of PC Numbers of ATH With the
Control at Different Exposure Times

		PC Number			
Sample	Level	4 hrs.	8 hrs.	16 hrs	24 hrs
ATH	2.10%	2.12	3.31	5.21	6.43
	3.65%	2.04	3.17	4.78	6.45
	7.29%	1.76	2.79	4.42	5.60
	16.14%	1.36	2.00	3.31	4.00
Control	na	2.44	3.39	5.11	7.34

Figure 14. Comparison of PC Numbers of ATH With Control.

TiO₂ Filled Sheets Exposed to Light

Of all the pigments, titanium dioxide had the greatest impact on light-induced brightness. Table 18 and Figure 15 show the influence of titanium dioxide on reversion. The effect of the length of exposure is also presented in the table and figure.

Table 18

Comparison of PC Numbers of Titanium Dioxide With the
Control at Different Exposure Times

Sample	Level	PC Number			
		4 hrs.	8 hrs.	16 hrs	24 hrs
TiO₂	2.51%	1.48	2.69	4.63	6.50
	4.76%	1.60	2.26	3.93	4.92
	9.02%	1.19	1.84	2.89	3.60
	19.64%	0.69	1.11	1.94	2.60
Control	na	2.44	3.39	5.11	7.34

Titanium dioxide at all concentrations was effective at reducing light-induced brightness reversion. At the lowest concentration of 2.51% there was a decrease in PC number to 4.63, and 6.50 from the control values of 5.11 and 7.43, for sixteen and twenty-four hours, respectively. At the highest concentration of 19.64%, the decrease was even more substantial to 1.94 and 2.60 for sixteen and twenty-four hours. The reduction of PC number for the other exposure times and concentrations followed the same trend. For all of the data, the percent reduction in PC number ranged from 9.44% to 72.19%.

Figure 15. Comparison of PC Numbers of Titanium Dioxide With Control.

Grouped Comparison of Pigments

The previous discussion pertaining to the effect of the individual pigments is summarized in Figures 16-24 and Table 19. Figures 16-19 compares the PC Numbers of all the filled samples at varying concentrations against the control sample at the exposure times of 4, 8, 16, and 24 hours. Figure 20 compares the PC Numbers of the filled samples at similar concentration against the control. Figures 21-24 show the percent reduction in PC number of the pigments found to be significant by Duncan's multiple range test (ATH and TiO_2) at 4, 8, 16, and 24 hours of exposure. On the following page is an example of how percent reduction of PC number was calculated.

Example: Effect of Titanium Dioxide at 4.76% for four hours of exposure

Post Color Number of control   = 2.44

Post Color Number of sample   = 1.60

Percent Reduction due to TiO_2 = [(2.44-1.60)/2.44]*100
                                                         = 34.42

Figure 16. Comparison of PC Numbers for Different Pigments at Various Concentrations (4 Hours).

Figure 17. Comparison of PC Numbers for Different Pigments at Various Concentrations (8 Hours).

Figure 18. Comparison of PC Numbers for Different Pigments at Various Concentrations (16 Hours).

Figure 19. Comparison of PC Numbers for Different Pigments at Various Concentrations (24 Hours).

Figure 20. PC Numbers of Various Pigments and Control at Similar Concentrations.

Figure 21. Percent Reduction in PC Number After 4 Hours of Exposure for Significant Pigment Types.

Figure 22. Percent Reduction in PC Number After 8 Hours of Exposure for Significant Pigment Types.

Figure 23. Percent Reduction in PC Number After 16 Hours of Exposure for Significant Pigment Types.

Figure 24. Percent Reduction in PC Number After 24 Hours of Exposure for Significant Pigment Types.

In order to determine the effect each loading level for each filler type had on the rate of brightness reversion, a simple regression analysis was performed. A regression equation was obtained for each data set that corresponded to the specified filler type and concentration. The regression equations are of the form:

$$y = mx + b$$

where y is post color number, m is the slope (rate), x is the exposure time, and b is the intercept. For each regression analysis the intercept was set to zero, since at t_0 PC Number is equal to zero. Table 19 shows the results of the analysis.

Table 19

Rate Comparison of PC Numbers

Sample	Filler Concentration in the Sheet	Rate of Yellowing (PC No./hr exposure)	R^2
Control	na	0.323	0.774
ATH	2.1	0.299	0.777
	3.65	0.29	0.835
	7.29	0.257	0.827
	16.14	0.187	0.779
Clay	1.22	0.361	0.899
	2.43	0.341	0.855
	3.61	0.314	0.867
	5.88	0.312	0.859
GCC	1.91	0.301	0.744
	2.32	0.313	0.824
	2.58	0.303	0.826
	4.47	0.292	0.886
TiO2	2.51	0.282	0.969
	4.76	0.225	0.845
	9.02	0.167	0.782
	19.64	0.115	0.925

From these figures and table, the following conclusions can be made:

Titanium dioxide had the greatest effect on reducing light-induced brightness reversion. The figures show that titanium dioxide had a much greater effect on brightness reversion then any of the other pigments used in this study. At the modest levels of 2.10 and 3.65%, TiO_2 substantially reduced the PC Number by 12.3 and 31.0%, respectively at twenty-four hours of exposure. The ability of TiO_2 to absorb the UV rays that initiate photoyellowing makes it very effective.

Alumina trihydrate was the second most significant pigment at reducing photoyellowing. ATH had a substantial effect on reducing the PC Numbers at the highest two concentration levels. A reduction in brightness reversion up to 45% was achieved at a concentration of 16.14%.

Clay had little effect on reducing light-induced brightness reversion at the experimental concentrations. At some levels the clay-filled sample had higher PC numbers then the control.

Ground calcium carbonate was effective at reducing brightness reversion at most of the exposure times. It is difficult to determine the extent of its effectiveness due to the low experimental concentrations that were obtained during the paper machine trial and inconsistencies in the data. At higher concentrations, GCC may be as effective as ATH (refer to Figure 17).

Tensile Strength

Whenever pigments are substituted for fiber in paper, an accompanying loss in strength occurs. This is especially important at the high filler levels of this experiment. The greater color stability achieved by increasing the filler level needs to be weighed against the loss in strength. For this study, the loss of strength caused by filler loading was determined by measuring the tensile strength of the samples. Table 20 shows the tensile strength and indexed tensile of the samples and the percent loss in tensile strength due to the filler content. A dramatic drop in tensile strength is seen at concentration higher then 4% for all of the fillers.

Table 20

Tensile Strength and Percent Reduction
in Tensile Strength Due to Loading

Sample	Filler Concentration in Sheet (%)	Tensile (kN/m)		Tensile Index (Nm/g)		% Reduction	
		MD	CD	MD	CD	MD	CD
Control	Na	4.293	2.597	65.0	39.3	na	na
	1.22	4.351	2.331	66.1	35.4	-1.75	8.52
	2.43	4.205	2.289	66.7	36.3	-2.60	6.29
	3.61	3.785	2.116	59.6	33.3	8.36	14.05
Clay	5.88	3.584	2.174	56.1	34.0	13.67	12.15
	2.51	4.447	2.300	67.3	34.8	-3.51	10.18
	4.76	3.743	1.976	55.6	29.4	14.44	24.22
	9.02	3.806	1.985	56.6	29.5	12.90	23.79
TiO2	19.64	3.105	1.520	45.7	22.4	29.74	42.26
	1.91	4.176	2.322	65.8	36.6	-1.19	5.57
	2.32	4.216	2.242	66.2	35.2	-1.82	9.14
	2.58	4.288	2.028	66.7	31.6	-2.67	18.50
GCC	4.47	4.036	2.177	62.3	33.6	4.18	13.26
	2.1	4.314	2.335	65.0	35.2	-0.05	9.15
	3.65	4.317	2.116	64.4	31.6	0.90	18.51
	7.29	3.651	1.864	53.5	27.3	17.64	29.44
ATH	16.14	2.891	1.552	42.1	22.6	35.29	41.71

CHAPTER VII

CONCLUSIONS

From the results of this thesis work the following conclusions can be drawn:

1. The extent or rate of yellowing of paper made with fillers and an 80:20 blend of BCTMP and BSWK is significantly affected by pigment type, pigment concentration, and exposure time.

2. Titanium dioxide at varying concentration had the greatest impact at reducing light-induced brightness reversion. Titanium dioxide at equal concentrations with the other pigments used in this study is superior in reducing the extent of brightness reversion.

3. Alumina trihydrate also significantly reduced brightness reversion for a wide range of concentrations and exposure times.

4. Clay had little effect on brightness reversion at the experimental concentration obtained during the paper machine trial. In some instances, clay had a negative impact on brightness reversion.

5. Ground calcium carbonate at concentrations in the range of 1.91 to 4.47% did not significantly affect brightness reversion.

6. Filler retention varied greatly between filler types in the paper making system. The retention of TiO_2 and ATH was markedly better at all of the loading levels than GCC and clay.

CHAPTER VIII

RECOMMENDATIONS FOR FURTHER STUDY

The following areas are recommended for future work on this study:

1. Cross effect of different pigments at various concentrations when two or more pigments are present together within the sheet.

2. Accelerated aging with heat and combination of light and heat.

3. Accelerated aging at exposure times longer then those already investigated in this study.

4. Pigments applied to the surface of the sheet by a size press or by some form of coating application.

5. Aging of the samples at controlled ambient conditions for extended periods of time.

6. The effects of pigments on other high-yield pulps.

7. The effect of pigment dipersion within the sheet.

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APPENDICES

Appendix A

Average Data for Brightness and PC Number

Table 21

Brightness Data (%) and PC Number – Felt Side at Four Hours of Exposure

Filler Type	Concentration (%)	Initial Brightness	Final Brightness	PC Number
		Felt Side		
Control	na	77.48	61.79	2.38
Clay	2.10	77.59	61.05	2.56
	3.65	77.85	61.44	2.58
	7.29	77.96	62.72	2.39
	16.14	79.78	63.99	2.42
TiO_2	1.22	79.12	66.38	1.70
	2.43	80.33	67.85	1.57
	3.61	78.47	71.45	1.14
	5.88	84.07	77.16	0.55
GCC	1.91	77.79	61.53	2.28
	2.32	78.68	61.93	2.43
	2.58	77.85	62.11	2.39
	4.47	78.62	64.16	2.10
ATH	2.51	78.72	62.51	2.06
	4.76	79.37	63.33	2.12
	9.02	81.16	67.06	1.78
	19.64	84.17	70.77	1.28

Table 22

Brightness Data (%) and PC Number – Wire Side at Four Hours of Exposure

		Wire Side		
Filler Type	Concentration (%)	Initial Brightness	Final Brightness	PC Number
Control	na	77.10	61.67	2.50
Clay	2.10	77.39	60.43	2.67
	3.65	77.64	61.02	2.53
	7.29	77.96	62.66	2.27
	16.14	80.06	64.67	1.58
TiO$_2$	1.22	78.86	65.06	1.26
	2.43	80.32	67.60	1.63
	3.61	81.61	70.82	1.24
	5.88	84.06	75.62	0.81
GCC	1.91	77.59	61.35	2.18
	2.32	78.36	63.00	2.12
	2.58	77.83	64.58	2.01
	4.47	78.32	63.86	1.94
ATH	2.51	78.13	62.28	2.17
	4.76	79.21	62.89	1.97
	9.02	80.91	68.08	1.74
	19.64	83.46	71.36	1.43

Table 23

Brightness Data (%) and PC Number – Felt Side at Eight Hours of Exposure

Felt Side				
Filler Type	Concentration (%)	Initial Brightness	Final Brightness	PC Number
Control	na	77.65	54.83	3.35
Clay	2.10	77.03	54.25	3.50
	3.65	77.52	55.20	3.48
	7.29	77.13	55.91	3.18
	16.14	80.30	58.39	3.26
TiO_2	1.22	78.96	58.51	2.59
	2.43	80.76	61.27	2.18
	3.61	82.05	64.73	1.80
	5.88	84.17	71.57	1.02
GCC	1.91	77.87	56.56	3.09
	2.32	77.85	56.72	3.12
	2.58	78.07	56.94	2.96
	4.47	78.46	57.32	3.04
ATH	2.51	78.81	54.92	3.41
	4.76	79.72	56.85	3.10
	9.02	81.51	58.93	2.68
	19.64	84.05	64.25	1.99

Table 24

Brightness Data (%) and PC Number – Wire Side at Eight Hours of Exposure

		Wire Side		
Filler Type	Concentration (%)	Initial Brightness	Final Brightness	PC Number
Control	na	76.55	54.35	3.42
Clay	2.10	76.31	54.33	3.24
	3.65	77.84	50.58	3.49
	7.29	77.77	56.20	3.35
	16.14	79.76	57.56	3.27
TiO$_2$	1.22	79.03	58.44	2.80
	2.43	81.16	61.40	2.35
	3.61	81.60	63.97	1.88
	5.88	83.83	70.95	1.20
GCC	1.91	77.35	54.38	3.47
	2.32	77.96	55.35	3.26
	2.58	78.05	54.71	3.45
	4.47	78.55	61.35	2.48
ATH	2.51	78.36	56.17	3.20
	4.76	79.62	56.14	3.23
	9.02	81.09	57.77	2.89
	19.64	84.03	64.31	2.00

Table 25

Brightness Data (%) and PC Number – Felt Side at Sixteen Hours of Exposure

		Felt Side		
Filler Type	Concentration (%)	Initial Brightness	Final Brightness	PC Number
Control	na	78.05	48.06	5.29
Clay	2.10	77.86	46.13	5.99
	3.65	78.49	47.39	5.57
	7.29	77.57	51.71	4.64
	16.14	79.71	48.69	5.56
TiO_2	1.22	79.33	50.24	4.63
	2.43	80.62	52.93	4.07
	3.61	81.60	58.50	2.80
	5.88	84.19	66.10	1.79
GCC	1.91	77.78	47.19	5.35
	2.32	77.75	46.79	5.52
	2.58	78.68	49.24	5.14
	4.47	79.28	48.75	5.03
ATH	2.51	78.68	47.64	5.22
	4.76	80.22	48.99	4.99
	9.02	81.72	50.60	4.38
	19.64	83.93	55.44	3.36

Table 26

Brightness Data (%) and PC Number - Wire Side at Sixteen Hours of Exposure

		Wire Side		
Filler Type	Concentration (%)	Initial Brightness	Final Brightness	PC Number
Control	na	77.30	49.79	4.93
Clay	2.10	77.53	45.63	5.94
	3.65	78.16	47.98	5.52
	7.29	78.05	50.97	4.75
	16.14	80.00	50.35	5.26
TiO$_2$	1.22	79.01	50.30	4.63
	2.43	80.34	53.59	3.78
	3.61	81.64	57.06	2.99
	5.88	83.68	63.56	2.10
GCC	1.91	77.79	46.88	5.32
	2.32	77.89	46.68	5.46
	2.58	78.68	49.24	5.14
	4.47	79.59	49.44	5.10
ATH	2.51	78.37	47.10	5.21
	4.76	79.99	51.62	4.57
	9.02	81.50	51.24	4.45
	19.64	83.53	56.38	3.27

Table 27

Brightness Data (%) and PC Number - Felt Side at Twenty-four Hours of Exposure

		Felt Side		
Filler Type	Concentration (%)	Initial Brightness	Final Brightness	PC Number
Control	na	77.25	41.26	8.46
Clay	2.10	77.09	40.20	7.90
	3.65	77.05	40.44	7.60
	7.29	77.90	41.45	7.58
	16.14	78.98	43.76	7.05
TiO_2	1.22	79.31	43.97	6.49
	2.43	80.29	48.58	4.97
	3.61	81.72	53.73	3.67
	5.88	83.63	59.85	2.53
GCC	1.91	77.78	44.11	6.41
	2.32	77.78	42.73	6.78
	2.58	77.80	42.93	6.73
	4.47	78.47	44.02	6.46
ATH	2.51	79.12	43.99	6.69
	4.76	79.45	45.36	6.56
	9.02	81.42	47.26	5.59
	19.64	84.26	53.34	4.04

Table 28

Brightness Data (%) and PC Number - Wire Side at Twenty-four Hours of Exposure

Filler Type	Concentration (%)	Initial Brightness	Final Brightness	PC Number
		Wire Side		
Control	na	76.79	43.79	6.22
Clay	2.10	76.68	39.66	8.45
	3.65	77.11	40.33	7.75
	7.29	77.63	41.52	7.12
	16.14	80.14	45.95	6.61
TiO$_2$	1.22	79.01	43.59	6.51
	2.43	79.97	49.62	4.87
	3.61	81.67	54.24	3.54
	5.88	83.58	58.84	2.68
GCC	1.91	77.85	43.48	6.41
	2.32	77.87	42.60	6.83
	2.58	77.85	43.99	6.65
	4.47	78.30	44.19	6.47
ATH	2.51	79.01	45.17	6.18
	4.76	79.22	44.55	6.34
	9.02	81.57	47.08	5.61
	19.64	84.10	54.09	3.96

Appendix B

Tensile Strength Data

Table 29

Tensile Strength of Samples (Lb$_{force}$/inch)

		Tensile MD			Tensile CD		
Filler Type	Concentration (%)	1	2	3	1	2	3
Control	na	24.27	23.96	25.37	14.78	14.27	15.47
Clay	2.10	24.31	25.72	24.56	12.83	13.69	13.44
	3.65	24.01	24.6	23.48	13.59	12.50	13.16
	7.29	20.97	22.19	21.72	12.42	11.84	12.00
	16.14	19.49	21.23	20.73	12.27	12.15	12.85
TiO$_2$	1.22	26.12	25.63	24.48	13.42	13.54	12.45
	2.43	21.02	22.12	21.04	11.47	11.16	11.24
	3.61	22.97	20.84	21.44	11.41	11.36	11.25
	5.88	16.95	17.85	18.43	8.54	8.54	8.98
GCC	1.91	23.11	22.87	23.2	12.59	11.84	12.90
	2.32	26.54	26.89	27.84	12.04	13.23	13.16
	2.58	27.43	28.26	27.88	13.72	13.13	12.96
	4.47	24.23	24.94	25.84	11.64	11.24	11.89
ATH	2.51	26.48	25.7	25.88	13.35	13.13	13.53
	4.76	25.47	25.35	23.18	11.81	12.08	12.38
	9.02	21.49	19.77	21.31	11.01	10.32	10.62
	19.64	16.33	16.45	16.78	8.74	9.37	8.50

Appendix C

First-Pass Retention

Table 30

First-Pass Retention

Sample	Conc. (%)	Headbox			White Water			FPR (%)
		Weight. of Filter	Weight of Filter with Pulp	Weight of Fiber	Weight of Filter	Weight of Filter with Pulp	Weight of Fiber	
Control	na	1.502	2.048	0.546	1.507	1.585	0.078	85.7
Clay	2.10	1.52	2.051	0.531	1.491	1.581	0.09	83.1
	3.65	1.643	2.26	0.617	1.533	1.677	0.144	76.7
	7.29	1.669	2.304	0.635	1.653	1.848	0.195	69.3
	16.14	1.546	2.301	0.755	1.49	1.751	0.261	65.4
TiO_2	1.22	1.662	2.198	0.536	1.705	1.779	0.074	86.2
	2.43	1.513	2.118	0.605	1.677	1.786	0.109	82.0
	3.61	1.5	2.122	0.622	1.506	1.618	0.112	82.0
	5.88	1.52	2.187	0.667	1.667	1.819	0.152	77.2
GCC	1.91	1.518	2.118	0.6	1.516	1.613	0.097	83.8
	2.32	1.528	2.138	0.61	1.506	1.628	0.122	80.0
	2.58	1.513	2.161	0.648	1.531	1.715	0.184	71.6
	4.47	1.526	2.084	0.558	1.489	1.781	0.292	47.7
ATH	2.51	1.537	2.162	0.625	1.525	1.614	0.089	85.8
	4.76	1.644	2.333	0.689	1.533	1.631	0.098	85.8
	9.02	1.483	2.137	0.654	1.677	1.815	0.138	78.9
	19.64	1.541	2.284	0.743	1.558	1.757	0.199	73.2

All Weights are in grams

Appendix D

Total Alkalinity and pH

Table 31

Total Alkalinity and pH

Sample	Filler Concentration (%)	pH		Milliliters of H_5O_4 to titrate to pH of 4	
		Head Box	White Water	Headbox	White Water
Control	na	7.45	8.03	37.1	33.6
Clay	1.22	7.44	7.96	34.4	38.2
	2.43	7.68	7.75	34.1	35.0
	3.61	7.60	8.22	34.2	34.4
	5.88	7.52	8.18	34.3	35.6
TiO_2	2.51	7.52	7.97	33.9	33.4
	4.76	7.53	7.51	34.0	30.6
	9.02	7.54	7.80	33.6	31.4
	19.64	7.56	7.90	33.6	31.2
GCC	1.91	7.72	7.87	77.2	75.6
	2.32	7.59	7.80	114.4	102.8
	2.58	7.79	7.83	171.2	169.6
	4.47	7.75	8.10	245.2	526.4
ATH	2.1	7.87	8.06	43.8	43.2
	3.65	8.03	8.05	41.6	34.0
	7.29	8.06	8.05	36.8	20.4
	16.14	8.04	8.40	37.6	35.6

Normality of H_2SO_4 was 0.197 N

Appendix E

Grammage and Ash Data

Table 32

Grammage and Ash (900 °C) Data

Sample	Percent Ash			Basis weight (lbs/3000 ft^2) average of 3
	1	2	3	
Control	0.63	0.54	0.56	41.13
Clay	1.09	1.09	1	40.35
	2.11	2.08	2.15	38.68
	3.09	3.21	3.1	38.98
	5.07	5.15	5.12	39.18
TiO$_2$	2.51	2.49	2.55	40.54
	4.8	4.68	4.8	41.29
	9.02	8.9	9.14	41.24
	19.37	19.89	19.65	41.70
GCC	1.08	1.1	1.11	38.94
	1.31	1.35	1.33	39.07
	1.46	1.5	1.48	39.41
	2.6	2.53	2.57	39.75
ATH	1.37	1.36	1.39	40.69
	2.42	2.39	2.35	41.11
	4.7	4.83	4.77	41.83
	10.41	10.55	10.68	42.16

Appendix F

General Linear Model Analysis Tables
and Duncans Multiple Range Tests

Table 33

General Linear Model Analysis

Source	DF	SS	Mean Square	F-Value	P-value
Model	87	486.471	5.592	71.43	0.0001
Error	48	3.758	0.078		
Corrected-Total	135	490.228			

Source	DF	SS	Mean Square	F-Value	P-Value
Type	4	71.244	17.811	227.52	0.0001
Level	12	38.139	3.178	40.60	0.0001
Side	1	0.001	0.001	0.02	0.8950
Exposure	3	350.761	116.920	1493.53	0.0001
Type*Level	0	0.000	.	.	.
Type*Side	4	1.371	0.343	4.38	0.0043
Type*Exposure	12	12.287	1.024	13.08	0.0001
Level*Side	12	1.023	0.085	1.09	0.3900
Level*Exposure	36	11.564	0.321	4.10	0.0001

Table 34

Duncans Multiple Range Tests for Filler
Type and Concentrations

α= 0.05		DF = 115		MSE = 0.2616
Duncan Grouping		Mean	N	Type	Signigicant Levels
---	---	---	---	---	---
	A	4.6576	32	Clay	None
	A				
B	A	4.5701	8	Control	------
B					
B		4.2847	32	GCC	None
	C	3.6717	32	ATH	7.29, 16.14
	D	2.7418	32	TiO$_2$	2.51, 4.76, 9.02, 19.64

Means with the same letter are not significantly different

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