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THERMOMECHANICAL PULP BLEACHING
OPTIMIZATION VIA DIMETHYLDIOXIRANE

by

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Thermomechanical Pulp Bleaching Optimization Via Dimethyldioxirane

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In recent years, the paper industry has received increased pressure from environmental groups to reduce both air-borne & water-borne discharges. During elemental-chlorine bleaching processes, absorbable organic halides are formed, some of which are considered harmful to aquatic life. To reduce absorbable organic halides, many mills are moving towards chlorine-free bleaching stages. A potential chlorine-free bleaching agent is dimethyldioxirane. Dimethyldioxirane is an intermediate produced in-situ from acetone and peroxymonosulfate. Due to the bond strain of the oxygen-oxygen bond in this cyclic peroxide, it behaves as a strong oxidizing agent.

The goal of this thesis was to determine the optimum levels for pH, dimethyldioxirane charge, and bleaching time for a thermomechanical pulp. It was determined that the optimum brightness of 40% could be reached at a pH of 8, charge level of 9%, and by bleaching for 30 minutes. This same brightness could be obtained by using two 2.5% (5%-split) dimethyldioxirane bleaching stages in-lieu of one 9% stage. When a 4% hydrogen peroxide stage is added to the optimized 5%-split run, a maximum brightness of 58.3% could be obtained.

A linear correlation between pulp yield and brightness was found until the pulp yield dropped below 82%. At this point, as the yield decreased, the brightness remained constant. There appeared to be no decrease in zero-span tensile index as the charge addition level was increased.

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I. INTRODUCTION

In recent years, the paper industry has received increased pressure from environmental groups to reduce both air-borne & water-borne discharges. During elemental-chlorine bleaching processes, AOX (absorbable organic halides) are formed, some of which are considered harmful to aquatic life (1). For this reason and reduced corrosiveness, many mills have converted or are being forced to convert to ECF (elemental chlorine-free) bleaching processes, while many other mills are considering TCF (total chlorine-free) bleaching processes. The ECF process consists of replacing all elemental chlorine with chlorine dioxide. This requires some capital investment. It also requires extended delignification, which is relatively expensive to incorporate into the process (2). Chlorine dioxide is considered less of an environmental threat, and yet due to a small formation of AOX, environmental groups are demanding the decreased use of ClO_2 (1). The proposed answer is the TCF process, which depends on the ability to increase the mills' delignification capacities (oxygen, or extended cooking), capital investment, and space availability (2).

Common oxygen bleaching stages include oxygen gas, ozone, and hydrogen peroxide (3). The use of enzymes, ozone, chelating agents, and hydrogen peroxide will produce TCF chemical pulps with brightness up to 90% ISO, while the strength properties and cleanliness of the pulps are unacceptable (2). Oxygen delignification can be used until 50% delignification is obtained. Once this limit is reached, the pulp strength decreases rapidly (4). Ozone is also a good bleaching agent, but due to its reactiveness with both the lignin fraction and the carbohydrate fraction, successive degradation of the pulp occurs (1). The limitations of these bleaching agents has increased the demand for a lignin-

selective TCF bleaching agent that has bleaching effects similar to ClO_2.

Dimethyldioxirane (DMD) appears to have many of the characteristics that have kept

chlorine dioxide-based stages superior to TCF-stages.

II. BACKGROUND

The first recorded reference to three-member cyclic peroxides was in 1899. The observation was made by Bayer and Villiger (5) during an experiment in which they converted menthone into its corresponding lactone. In 1974 it became known that commercial caroate could be decomposed by ketones in a pH range between 6-12. Commercially available caroate can be obtained from Dupont®, under the name Oxone®, as the potassium triple salt of Caro's acid (2 KHSO₅*K₂SO₄*KHSO₄) (1). Through the use of kinetics, stereochemical, and O-labeling studies, it was unconditionally determined that the oxygen transfer in the ketone-caroate system occurred by a dioxirane intermediate. In the case where acetone is used, the intermediate product would be dimethyldioxirane (DMD). See Figure 1 (5).

acetone   peroxymonosulfate   dimethyldioxirane
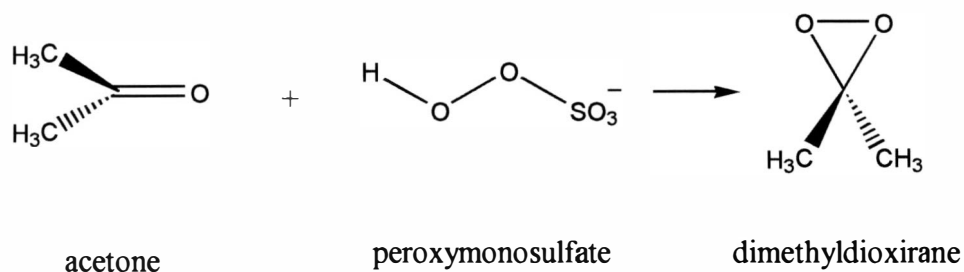
Figure 1. Formation of Dimethyldioxirane.

Dimethyldioxirane has been characterized as a mild oxidant that is capable of insertions and epoxidation (6). DMD is also referred to as an "AO," which represents the coined phrase "Activated Oxygen" (7).

Dioxiranes can be produced from a derivative of Caro's acid (Peroxymonosulfuric acid) in the form of bis(trimethylsisyl), Me₃SiOOSO₂OSiMe₃. The bis(trimethylsisyl) is

reacted with anhydrous CH_2Cl_2 (5). The simplest method of producing a low formula weight dialkyldioxirane is the in-situ formation of dimethyldioxirane from Oxone and acetone in an aqueous solution (8).

TMP and Kraft Lignin Structures

The degree of delignification in the Kraft process depends on the ability to cleave the ether linkages. The carbon-carbon bonds are unaffected by both the pulping and bleaching processes. The number of phenylpropane repeat units are small in residual Kraft lignin. Some typical residual Kraft lignins can be seen in Figure 2 (9).
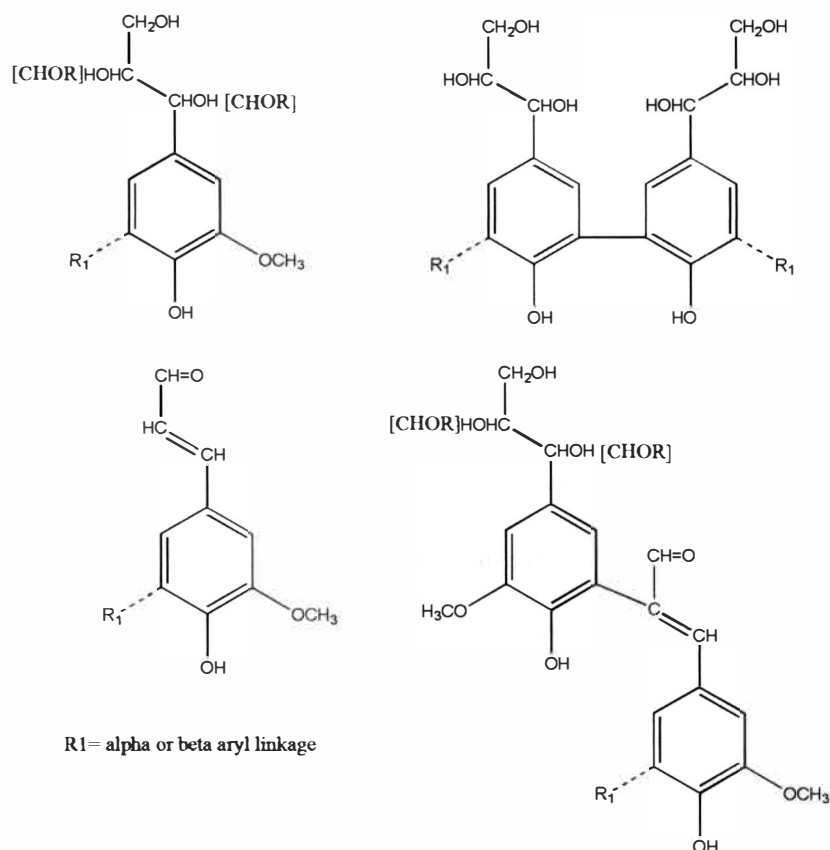
Figure 2. Common Kraft Residual Lignin Molecules.

The average yield loss for TMP is quite small, usually less than 5%. The lignin structure is for the most part unaffected. The TMP lignin structure is similar to that shown in Figure 3 (9).
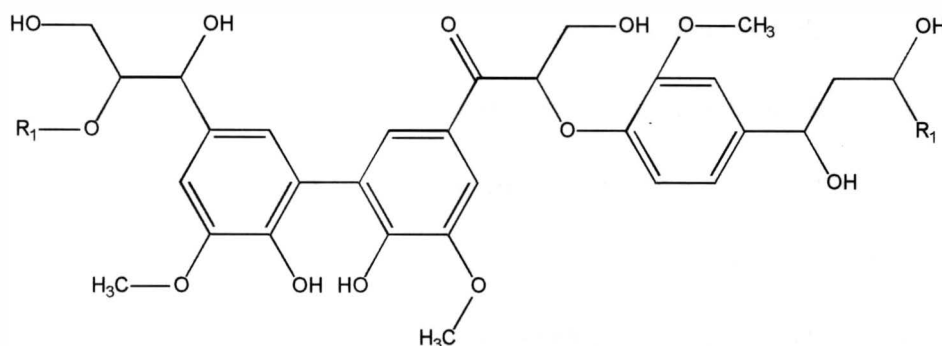
R₁= phenylpropane repeating units

Figure 3. Partial Lignin Structure.

Bleaching Concepts

A system was developed to designate the type of bleaching reaction that each bleaching agent acts through. The three types of bleaching chemicals are anionic, cationic, and radical. The cationic species are electrophilic; anionic species, are necleophilic; and the radical reactions can be either electrophilic or necleophilic depending on pH. The aromatic and oleofinic structures in lignin are attacked due to their electron-rich areas, whereas the carbohydrate fraction is deficient in dense electron regions and therefore is relatively unaffected by electrophilic attack (1). Nucleophiles will attack carbonyl and conjugated carbonyl structures and will help to remove or transform the chromophores of the pulp, and again the carbohydrate fraction is relatively unaffected (7).

DMD Reactivity

The Hemlett equation is used to relatively describe the electrophillicity of a substance. This equation is based on the LFER (Linear Free Energy Relationship). Under alkaline conditions, H_2O_2 has a p-value (degree of elctrophillicity from Hemlett equation) of +1.54. This implies that under the alkaline conditions, H_2O_2 is nucleophilic and will attack chromophoric groups rather than the lignin structure and carbohydrate fraction. When H_2O_2 is used under acidic conditions, the p-value is -1.13, and implies under this condition that H_2O_2 is electrophilic and could be used for delignification. Dimethyldioxirane has a p-value range from -1.54 to -.90 (7).

Dimethyldioxirane can be used for a wide range of transformations, some of which can be seen in Figure 4 (8).
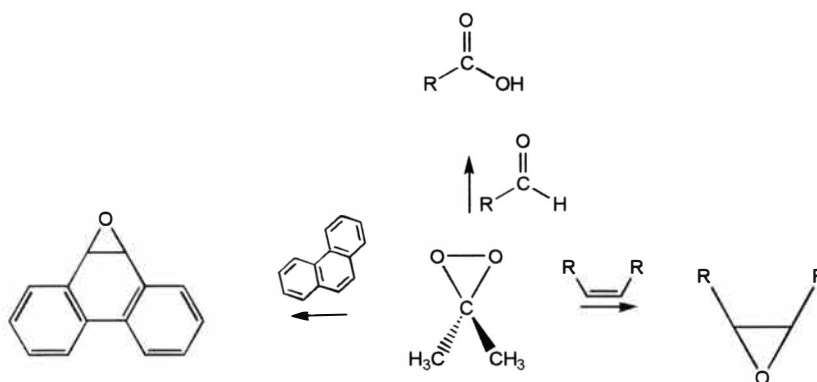
Figure 4. Sample Transformations via Dimethyldioxirane.

DMD generated in-situ from peroxymonosulfate (Caro's acid) and acetone converted cis-stilbene and trans-stilbene into their corresponding epoxides with a mean yield of 85% (8). This epoxide can then be converted to the corresponding diol by taking the pH to either

acidic or basic side. Once the epoxide is converted to the diol, it may be solubilized by caustic extraction. The caustic extraction will convert the diol into the sodium salt of the representative dioxide, which is soluble when the number of stilbene repeat units is small (10).

Yield

When oxygen delignification and DMD delignification are performed to equal levels, the yield from the DMD delignification is higher, as seen in Table 1 (11).

Table 1

Pulp Yields after DMD Treatment and Oxygen Delignification

Aspen Pulp	Kappa Number	Degree of Deliginification (%)	Yield (%) Unbleached Pulp
DMD-Treated	5.3	68	98.0
O$_2$-Delignified	5.4	67	92.7

pH Effects on Peroxymonosulfate

The decomposition of peroxymonosulfate is pseudo-first-order when the pH and HSO$_5^-$ concentration are constant (12). The half-life of dimethyldioxirane in acetone was 48 ± 1 hour at 25 degrees Celsius (8).

There has been little agreement on the effects of pH on the decomposition of peroxymonosulfate. Francis et al. (1) showed that at a pH of 6, the majority of the peroxymonosulfuric acid is in the form of peroxymonosulfate, with a minute amount of SO$^{5=}$. At the 1993 Biennial Workshop on Emerging Pulping and Chlorine-Free Bleaching Technologies (13), it was reported that when the pH is increased above 6, Caro's acid

readily decomposes to the sulfate ion and oxygen. Francis et al. (1) showed that at a pH of 8 there are no apparent free radicals available for reaction. This can be explained by the reaction sequence proposed by Edwards et al. (1) in the form of equations 1, 2, and 3.

$$HSO_5^- + H_2O \leftrightarrow SO_5^= + H_3O^+ \qquad (1)$$

$$HSO_5^- + SO_5^= \rightarrow HSO_6^- + SO_4^- \qquad (2)$$

$$HSO_6^- + OH^- \rightarrow H_2O + SO_4^- + O_2 \qquad (3)$$

Allison et al. (4) showed that at low pH ranges, peroxymonosulfuric acid will hydrolyze to hydrogen peroxide and the sulfate ion. When the pH range is between 8 and 11, the decomposition yields peroxymonosulfate. Under stronger alkaline conditions, peroxymonosulfate will experience further decomposition to yield the sulfate ion and free radical oxygen.

The effects of buffers can be seen in the work done by Ball and Edwards. Between a pH range of 6 and 8, the rate constant takes the form of equation 4, and shows a tenfold relationship for each point increase in pH (1).

$$d[HSO_5^-]/dt = -k[HSO_5^-]^2/[H^+] \qquad (4)$$

The experimental value showed a six-fold increase in decomposition for each point increase in pH. The difference between the theoretical and experimental systems is that the theoretical system assumed a constant pH, via $NaHCO_3$ buffer solution. The buffer increased the ionic strength and therefore increased the rate of decomposition (1).

Free-Radical Effects

The effect of pH on viscosity was determined by acid washing a commercial softwood Kraft pulp that had a viscosity of 27.7cp. The pulp was reacted with 33mM

caroate solution at 60^0 C with a pulp consistency of 10%. The viscosity appears pH dependent as shown in Figure 5. This decrease in viscosity, which is proportional to pulp strength, is most-likely due to highly reactive free-radicals that are formed under acidic conditions (1).
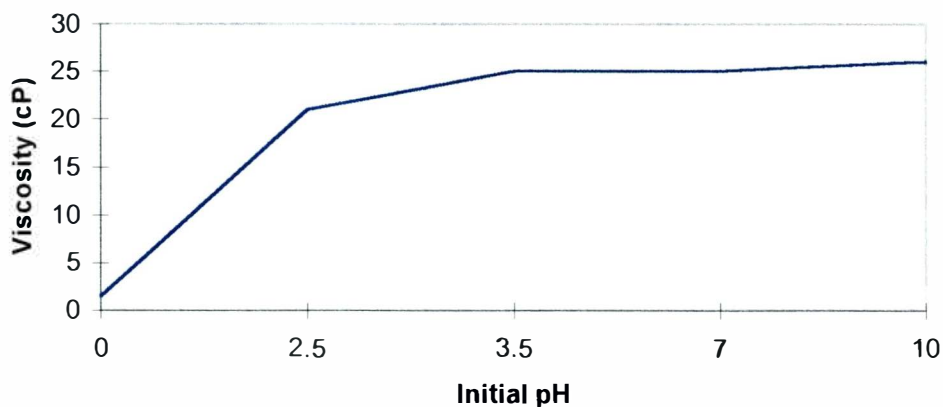
Figure 5. The Effects of Initial pH on Viscosity.

Since silver ions rapidly precipitate with the sulfate ion (k-3.0 x 10^9 $M^{-1}S^{-1}$) as well as with hydroxyl free-radicals, the addition of silver ions to the peroxymonosulfate solution under acidic conditions should trap the free-radicals and increase the viscosity of the pulp. This did occur as may be seen in Table 2 (1).

Table 2

The Use of Silver Ions to Trap Free-Radicals in an Oxygen-Delignified Pulp

Treatment	Kappa no.[b]	Viscosity (cP)[b]
None[a]	19.2	25.3
Ag$^+$	18.5	24.7
Caroate	14.8	6.7
Caroate + Ag$^+$	14.0	11.1

[a]An oxygen-delignified kraft pulp.
[b]After alkali extraction.

Chelating

Fenton's reaction is achieved when a chelating agent, such as EDTA or DTPA, is used to remove transition metals that could decompose peroxides and produce hydroxyl free-radicals that will degrade the cellulose and hemicellulose fractions (14). In an experiment by Allison, the pretreatment of EDTA (ethylene-diamene-tetracetic acid), showed a 52.8% decrease in chemical consumption of peroxymonosulfuric acid, and transition metals (Mn, Fe, and Cu) decreased by 45.05% with the addition of 1% EDTA (4). Table 3 shows the effects of an increased chelating agent on the removal of transition metals remaining in solution.

Table 3

The Effects of Chelating Agents on Metal Ion Removal

Treatment	Transition metals remaining (ppm)		
	Cu	Fe	Mn
None	35	98	13
0.5% DTPA on pulp	9	53	5
1.0% DTPA on pulp	7	53	4
3.2% DTPA on pulp	4	39	3
10% DTPA on pulp	1	10	3

From this table it can be seen that the largest decrease occurs at .5% DTPA addition on

dry pulp (14).

Charge

The results of a study by Lee et al. (7) presented in Table 4 shows that as the

charge of dimethyldioxirane (DMD) is increased from 0 to 5%, the kappa number

decreases 68.9% and viscosity decreases by 37.6%. In the case of DMD-E

(dimethyldioxirane-extraction) bleaching sequence with an dimethyldioxirane range from

0-5%, it can be seen that the kappa number decreases 84.8%, and the viscosity drops

45.7%.

Table 4

Kappa Number and Viscosity of the Activated Oxygen and AE-Treated Kraft Pulp

DMD Charge (%)	DMD			DMD-E		
	Kappa Number	Deg of Delig. (%)	Viscosity (mPa*s)	Kappa Number	Deg of Delig. (%)	Viscosity (mPa*s)
0.0	31.5	0.0	33.5	31.5	0.0	33.5
0.5	24.9	22.0	29.9	21.9	31.0	28.0
0.9	21.6	31.0	27.5	16.5	48.0	26.5
1.5	17.1	46.0	26.5	10.9	65.0	24.1
2.0	14.5	54.0	25.0	9.4	73.0	23.1
2.5	12.7	60.0	24.7	6.7	79.0	22.4
3.0	11.4	64.0	22.4	5.7	82.0	21.7
5.0	9.8	69.0	20.9	4.8	85.0	18.2

Solvent Mixture

Ketones can be considered as catalysts for peroxymonosulfate, since small quantities of ketone decompose large quantities of peroxymonosulfate. There is no loss of acetone in an acetone-Caro's acid mixture, which indicates that chemical consumption of acetone in the bleaching stage is negligible (12).

Alkali Extraction

Alkaline extraction was performed by Francis et al. (1) at 2% NaOH on pulp at 12% consistency and 80^0 C during his experimental DMD bleaching trials on kraft pulps. These parameters will be implemented during the extraction stages of this experiment.

Analysis of Literature

To date, no reported research work deals with the concept of bleaching thermomechanical pulp with dimethyldioxirane. Because of this, all the information

available with DMD is based on the kraft pulping process. The following analysis will then be applied to a thermochemical pulp, as if it were similar to a kraft pulp.

TMP & Kraft Lignin Structure

The DMD bleaching stage followed by caustic extraction will remove a large percentage of the residual lignin in kraft bleaching stages. When looking at organic molecules such as alcohols, as the molecule size increases its solubility decreases. It is thought that this relationship may hold true for residual lignin molecules. Since the size of the kraft residual lignin structure is much smaller than that of the TMP lignin structure, it is believed that the lignin fraction removed for the TMP pulp will be smaller.

Effect of pH

At a pH of 5, Caro's acid appears to take the form of HSO_5^- (13). Francis et al. (1) showed that at a pH of 7, optimum DMD bleaching conditions can be achieved. Allison (4) reported that at a pH between 8 and 11, HSO_5^-, is the predominant species. A separate phase of the experiment will determine the starting range for pH.

Free-Radical Effects

The effect of pH as a driver for free-radicals should not pose a problem between a pH range of 5-9, as was shown in Figure I. In order to reduce the possibility of severe degradation of the fibers due to free-radical effects, the pH range used in the preliminary phase of this experiment will be between 4-10.

Chelation Effects on Metal Ions

It is necessary to control free-radicals during the bleaching stage so that viscosity and pulp strength are not affected. Free-radicals that are formed from transition metals can be removed with chelating agents. The greatest reductions in transition metals occurred at 0.5% DTPA in the experiment by Francis et al.. (1).

Charge Levels

Table IV showed that the level of delignification with respect to DMD charge started to drop off at the 3.0% charge addition level. Based on this maximum, the experiment will be conducted on charge levels of 1.0, 3.0, and 5.0% DMD charge.

Solvent Mixture Effects

The importance of the solvent mixture is only to provide sufficient ketone for the HSO_5^- to produce the DMD intermediate. The acetone/peroxymonosulfate ratio of 1.5/1.0 mole proposed by Francis et al. (1) will be implemented in this experiment.

III. PROBLEM STATEMENT

This thesis was conducted in order to determine the optimum conditions to maximize brightness, without severe degradation to the pulp strength, for single-stage DMD bleaching of TMP pulp.

OBJECTIVES

I.   The first objective is to determine the pH range to be used during the experiment.

II. The next objective will be to do the actual bleaching experiment and determine the hypochlorite number, brightness, and zero-span tensile-index.

III. The last objective will be to determine the DMD run that provides optimum brightness.

IV. EXPERIMENTAL DESIGN

This experiment was composed of two phases. The purpose of the first phase was to determine the pH range that should be used in the second phase of the experiment. Phase II experiments are used to determine the optimum variable levels for dimethyldioxirane in the bleaching of thermomechanical pulp.

Phase I

During the first phase of the experiment, only the pH was varied. To determine the pH range, all other variable levels were held constant. These levels were determined from review of the previous works. The variables held constant included temperature, charge level, chelate addition level, consistency, and time. Chelate addition and consistency were held constant throughout this experiment. Bleaching variables used in this phase are shown in Table 5.

Table 5

Phase I Bleaching Conditions

Bleaching Variable	Median Level
Reaction Time (min)	30
Charge Level (% AO)	3
Temperature (C)	70
Consistency (%)	5.5
Chelate Charge (%)	3

The pH levels chosen for phase I were 4,6,8, and 10. These levels span the range in which free-radical formation is minimum. The two pH levels that provide the brightest pulp will be used as the upper and lower pH boundary limit with their mean as the median

level. For example, if 6 and 8 provide the optimum brightness, then the phase II pH levels will be 6, 7, and 8.

Phase II

In an optimization experiment, factorial designs provide many advantages. The first is that the factorial design is more efficient than manipulating a single variable at a time. The factorial design also removes the possibility of false conclusions that may arise in the presence of interactions between variables. Factorial designs do not limit the number of variables that can be manipulated or the number of variable levels. For these reasons, this part of the experiment was set up in a 3^3 factorial design. A 3^3 design is one in which three variables are manipulated each at three levels. This design is graphically shown in Table 6.

Table 6

Phase II Experimental Design

			pH							
		L			M			H		
					Time					
DMD-Charge	L	M	H	L	M	H	L	M	H	
L										
M										
H										

Since time is a limiting factor in this experiment, it was not feasible to perform multiple runs of each bleaching sequence. In order to estimate the error variability, the optimized bleaching run will be reproduced in triplicate. The bleaching variables and their representative levels can be seen in Table 7. These bleaching variable ranges were determined from the literature.

Table 7

Phase II Bleaching Variable Ranges

	Lower Range	Median Range	Upper Range
pH	to be determined	to be determined	to be determined
Charge Level (% AO)	1	3	5
Reaction Time (min)	10	20	30
Temperature (C)	70	70	70
Chelation (%)	3	3	3

Experimental Materials

Industrial-grade thermomechanical pulp was obtained from ABTCO, Inc. in Alpena, Michigan. Oxone®, acetone, EDTA, sodium acetate, acetic acid, potassium phosphate, sodium bicarbonate, reagent grade sodium hydroxide, and reagent grade hydrochloric acid were obtained from Fischer Scientific. (Ziploc® bags were purchased at Meijer®.)

Chemical Makeup

The preparation of a .10 Formal solution of EDTA was achieved by placing 1.6600 grams of EDTA into a 100 ml volumetric flask and diluting with distilled water to the 100 ml mark. A 1.0 Formal solution of NaOH was prepared by placing 39.9972 grams of sodium hydroxide into a 100 ml volumetric flask and diluting to the mark. The preparation of the .10 Formal solution of NaOH was prepared by placing 3.9997 grams of sodium hydroxide into a 100 ml volumetric flask and diluting to the mark.

Buffering Agents and Makeup

The first step in dimethyldioxirane bleaching is to prepare the buffer solution. The buffer solutions consisted of three types. The first was an acetic acid buffer solution used to achieve a pH of $4.0 \pm .3$. The second buffer system was potassium phosphate and was used to achieve buffer levels of $6.0 \pm .3$ and $8.0 \pm .3$. The last buffering system used, sodium bicarbonate, provided a final pH of $10.0 \pm .3$.

In the production of the buffer solution, a 500 ml Erlenmeyer flask was filled with 100 ml of water. The second step involved adding a 3% chelate, EDTA, charge (based on oven dried fiber) to the flask. The third step involved adding the appropriate mass of buffer for adequate pH control. Next, acetone was added to the flask. The amount of acetone added corresponded with the required 1.5/1.0 molar ratio of acetone to HSO_5^-. Concentrated sodium hydroxide or hydrochloric acid were then added to the buffer solution until the necessary pH was reached. The necessary volume of distilled water was then added to the flask to achieve a consistency of 5.5% when the buffer solution, oxone, and pulp were placed in the Ziploc® bag.

Bleaching Methodology

The single-stage dimethyldioxirane bleaching-stage consisted of the following steps. To begin with 50 grams (oven dry basis) of thermomechanical pulp were placed into a Ziploc® bag. At this point, the Ziploc® bag was placed into another Ziploc® bag to protect against the possibility of leakage. The buffer solution containing the acetone, dilution water, and EDTA was then poured slowly into the Ziploc® bag. The bag was kneaded for one minute and then placed into the water bath for five minutes to allow the

system to equilibrate to 70^0 C. The peroxymonosulfate charge was then added to the bag in dry form. Immediately after adding the peroxymonosulfate, the bag was sealed and kneaded for one minute. The bag was then placed in the water bath at 70^0 C. Every five minutes, the bag was kneaded, and the pH was measured. If the pH needed adjusting, 1.0 Formal NaOH and 1.0 Formal CH_3COOH were used accordingly.

After the desired reaction time, the pulp was washed thrice with 500 ml aliquots of distilled water. The pulp was then pressed in a clean pillow case until a consistency of 12% was achieved, after which the pulp was placed in a Ziploc® bag, and 12.5 ml of 1.0 formal NaOH was added. The bag was immediately placed in the water bath at 80^0 C for one hour. The pulp was then washed thrice with 500 ml aliquots of water.

The pulp sample was then diluted to approximately one percent consistency and a 300 ml sample was taken and formed into a pulp pad. The pad was then dried at 105 degrees Celsius for 24 hours, after which it was placed in an anhydrous $CaCl_2$ desiccater for 30 minutes. The pad was then weighed and yield was determined. The one percent stock suspension was pressed in a clean cotton pillow case until a 3.0% consistency was reached. Samples were taken for brightness pad formation immediately after washing the bleached stock, then the remaining stock was placed in a Ziploc® bag and stored at 4^0 C until pulp testing was performed.

Pulp Testing

Immediately after each bleaching run, samples were taken and brightness pads were formed according to TAPPI Standards (T452 om-92). After all of the pulp bleaching sequences were completed, ten samples at a time were removed from

refrigeration and allowed to adjust to room temperature. The samples were each tested for hypochlorite number (T253 om-92). Handsheets from each pulp sample were then made according to TAPPI Standards (T205 om-88). The samples were then tested for zero-span tensile index (T220 om-88).

V. RESULTS AND DISCUSSION

This chapter is broken down into two sections. The first section deals with the analysis of the data from the first phase, and the second section deals with the analysis of the data from the second phase of the experiment.

Phase I

Before the 4,6,8, and 10 pH runs could be performed, it was necessary to determine the molar ratio of buffer to dimethyldioxirane. A logarithmic experimental sequence was utilized, in order to minimize the number of runs needed in determining the optimum buffer charge. For the sodium acetate buffer, four runs were conducted at 0.001, 0.010, 0.100, and 1.000 moles of sodium acetate to .044 moles of dimethyldioxirane. After five minutes of bleaching time had elapsed, each run was analyzed for pH. Runs 1,2, and 3 dropped from the required pH of 4.0x to 1.8x. This can be seen in Table 8.

Table 8

Phase I Initial Sodium Acetate Buffering Results

Run Number	Buffer/DMD Ratio (mole/mole)	pH Initial (#)	pH after 5 min. (#)	DMD (moles)	NaOAc (moles)
1	0.022	4.0X	1.8X	0.044	0.001
2	0.22	4.0X	1.8X	0.044	0.010
3	2.2	4.0X	1.8X	0.044	0.100
4	23.	4.0X	3.9X	0.044	1.000
5	12.	4.0X	3.9X	0.044	0.550
6	7.3	4.0X	3.8X	0.044	0.325
7	4.8	4.0X	3.5X	0.044	0.213
8	4.8	5.0X	4.0X	0.044	0.213

These data show that the optimum sodium acetate buffer usage must fall within the 0.100 and 1.000 molar sodium acetone charge. The most logical step was to perform successive averages until the decrease in buffer level could not sustain a pH of 4.0 ± .3. At a molar sodium acetate charge of .213 moles per run, the pH showed a decrease of .5x pH units. Since the majority of the pH change does occur in the first five minutes, it was thought that by starting at the higher end of the pH range and dropping down to the mean variable range within the first five minutes of the bleaching sequence would be less detrimental to the bleaching process than to allow the pH to drop to the lower limit within the first five minutes and remain there for the remainder of the bleaching sequence. Run 8 shows that when the pH is started at a pH of 5.0x with a sodium acetate loading of .213 moles per run, the pH stabilized at 4.0x. For the next 55 minutes the runs were watched and did not drop below the lower boundary value of 3.70. Table 9 shows that to reach the pH level after five minutes, the initial pH must be approximately 1 pH unit higher.

The same buffer optimization technique was utilized to determine the optimum buffer loading for potassium phosphate and sodium bicarbonate. The summary of the optimum levels are shown in Table 9 below.

Table 9

Summary of Buffer Loading Data

Run Number	Buffer Type	Buffer/DMD Ratio (mole/mole)	pH Initial (#)	pH after 5 min. (#)	DMD (moles)	Buffer (moles)
8	Sodium Acetate	4.84	5.0X	4.0X + .3	0.044	0.213
11	Potassium Phosphate	4.54	7.0X	6.0X + .3	0.044	0.200
15	Potassium Phosphate	4.54	9.0X	8.0X +.3	0.044	0.200
22	Sodium Bicarbonate	8.52	11.0X	10.0X +.3	0.044	0.375

The sodium acetate and potassium phosphate buffers showed a buffer/dimethyldioxirane ratio of approximately 4.5, while the sodium bicarbonate buffer/dimethyldioxirane ratio was approximately 8.5. This is important when considering any possible interactions that may occur between the dimethyldioxirane and the buffer in solution.

After bleaching runs 1-22 and washing thrice with 500 ml of water, caustic was added to the pulps for the extraction stage. It was noted that bubbling occurred in the 4 pH runs. One possible cause for this could be an acid-base reaction occurring between the sodium hydroxide and the sodium acetate buffer. If this was in fact occurring, it would imply that the pulp washing method chosen for this experiment was insufficient. It was then decided upon to use a Britt dynamic drainage jar. The jar was used at low torque and high angular velocity conditions. This provided optimum contact between the fibers and water. The initial filtrate from the Britt jar was a dark brown. The pulp was continually washed with distilled water until the filtrate from the Britt jar was clear. It was feared that

the yield loss in the Britt jar may be substantial, so run 15 was repeated (run 23). The yield decrease in the washing step amounted to a 9% loss as shown in Table 10.

Table 10

The Effect of Washing with the Britt Jar

Run Number	Buffer Type	Washing in Britt Jar	Yield (%)
15	Potassium Phosphate	No	83.02
23	Potassium Phosphate	Yes	91.91
	Std. Dev.		.93

Run 23 was repeated twice more (run 23b, rub 23c) in order to calculate the standard deviation for the washed yield. In order to remove such washing losses from the bleaching loss calculations, all the pulp used for the experiment was washed prior to bleaching.

Runs 25-28 were then used to determine the optimum bleaching pH range. Table 11 below shows the effect of pH on brightness. The two brightness values are defined by the type of bleaching stage they underwent. DMD-E is dimethyldioxirane stage followed by an extraction stage, and the DMD-E-P is a dimethyldioxirane stage followed by extraction and finally a hydrogen peroxide stage.

Table 11

Brightness Summary for Phase I

Run	pH	Brightness	
(#)	(#)	DMD-E	DMD-E-P
24	Reference	23.1	37.1
25	4	26.1	39.5
26	6	28.4	42.7
27	8	29.5	46.8
28	10	26.2	39.0
Std. Dev.		0.47	0.69

From Table 11, it was determined that the pH range to be used in phase II of the experiment will be 6,7 and 8. The extraction stage darkened the pulp as would be expected via alkali darkening. In order to determine the maximum obtainable brightness from a two-stage chlorine-free sequence, hydrogen peroxide was chosen. The hydrogen peroxide levels used in this experiment are shown in Table 12.

Table 12

Hydrogen Peroxide Variable Levels

Variable	Addition Level
Hydrogen Peroxide Charge (%)	4.0
Sodium Hydroxide Charge (%)	4.0
Sodium Silicate (%)	3.0
Edta (%)	0.5
Time (min)	90
Temperature (C)	60

Before proceeding to phase II of the experiment, the effect of lignin degradation was determined for runs 24-28. This is shown in Table 13. The P designation after the run number indicates that the pulp has undergone the DMD-E-P bleaching sequence.

Table 13

Lignin Degradation Analysis of Phase I

Run (#)	pH in DMD-stage (#)	Hypochlorite Number (#)
25-P	4	12.8
26-P	6	13.4
27-P	8	12.9
28-P	10	13.4
24-P	4% H2O2 only	13.6
	Std. Dev.	1.0

Hypochlorite number provides a relative comparison of lignin content between pulps. Table 13 shows that there is no noticeable trend between the various pH levels. This graph also provides information as to the degradation effects of dimethyldioxirane at 3% charge compared to H_2O_2 at 4%. It is seen from the data for hypochlorite number is statistically equivalent for DMD at 3% and H_2O_2 at 4%.

Phase II

In order to determine if the DMD charge range proposed from past literature was correct, the first nine runs of the 3^3 factorial were completed. This was done at a constant bleaching time. The data obtained for the first nine runs is shown in Table 14.

Table 14

Phase II Preliminary Brightness Data

Run (#)	Charge (%)	pH (#)	Brightness DMD-E (%)
29	1	6	27.2
38	1	7	27.2
35	1	8	30.8
30	3	6	31.2
39	3	7	31.4
36	3	8	33.9
31	5	6	34.0
37	5	7	34.6
34	5	8	36.2
	Std. Dev.		0.47

Table 14 provided enough data to conclude that a pH of 8 is the optimum pH level; also, at all pH levels, the brightness also increases with increased charge. At this point, the plan of attack for this experiment was changed. Since a pH of $8.0 \pm .3$ provided optimum brightness regardless of the charge, the pH for the remainder of the experiment was set at 8.0.

The remaining variables needed for optimization of the single-stage DMD bleaching stage were time and charge. In order to determine the optimum levels for time, thirty-seven runs were completed. Table 15 below contains the brightness data for the charge and time.

Table 15

Summary of Data for Time and Charge Optimization

Run Number	Time (min)	DMD-Charge (%)	Brightness After DMD stage	Run Number	Time (min)	DMD-Charge (%)	Brightness After DMD stage
41	5	3	33.1	60	50	7	37.0
42	10	3	33.3	61	5	9	36.7
43	20	3	33.4	62	10	9	38.3
44	30	3	34.7	63	20	9	39.1
45	40	3	34.5	64	30	9	39.7
46	50	3	34.7	65	40	9	39.9
47	60	3	34.7	66	50	9	39.9
48	5	5	34.4	67	5	11	38.4
49	10	5	34.6	68	10	11	38.7
50	20	5	34.6	69	20	11	38.6
51	30	5	35.5	70	30	11	40.0
52	40	5	35.7	71	40	11	39.5
53	50	5	35.7	72	50	11	40.0
54	60	5	35.8	73	5	13	39.6
55	5	7	35.6	74	10	13	39.7
56	10	7	35.4	75	20	13	39.9
57	20	7	36.4	76	30	13	39.0
58	30	7	36.3	77	40	13	39.9
59	40	7	36.8	78	50	13	39.7
				Std. Dev.			0.47

The highlighted squares in the brightness column designate the maximum brightness obtainable for each charge addition level. For every charge addition level except for 13%, the maximum obtainable brightness occurs at 30 minutes. These maximums were determined by using successive maximum slope approximations. This method is demonstrated in Appendix A. When examining the maximum obtainable brightness at 30 minutes, slope approximations show that 9% charge provides maximum brightness.

Due to the oxidation potential of dimethyldioxirane, it was believed that secondary reactions must be occurring, thereby reducing the effectiveness of the bleaching agent. In this way the oxidation would take place more in the liquid phase instead on the solid substrate. This hypothesis was tested by performing four runs. The runs were 3%, 3%-split, 5%, and 5%-split. In the split runs, each run contained half of its DMD charge for 30 minutes. Then it was washed and bleached for another 30 minutes with the second half

of its charge. This was also done in three stages instead of two. After the final bleaching stage, the pulp was extracted in the same fashion as the other pulps. Table 16 below shows the results of the charge splitting.

Table 16

Charging Splitting Effects .

Run (#)	pH (#)	Charge (%)	Time of Cook (min)	Brightness (#)
44	8	3.0	30	34.7
79	8	1.5 - 1.5	30 - 30	36.2
81	8	1.0 - 1.0 - 1.0	30 - 30 - 30	36.2
51	8	5.0	30	35.5
80	8	2.5 - 2.5	30 - 30	39.7
82	8	1.7 - 1.7 - 1.7	30 - 30 - 30	39.9
		Std. Dev.		0.47

Table 15 does show an increase in obtainable brightness when charge-splitting is introduced. It was also found that a two-split was as good as a three-split.

When looking at the data for single-stage optimization and split optimization, the 3% and 5% charge split can be equated to a single-stage charge level. Another parameter that is important in bleaching is the yield obtained. Table 17 shows the summary of obtainable brightness and its effect on yield.

Table 17

Obtainable Brightness and the Effect on Yield

Run (#)	Charge (%)	Yield (%)	Brightness (#)
83	3.0	92.4	34.7
84	5.0	90.6	35.7
89	1.5 - 1.5	89.7	36.2
85	7.0	88.7	37.0
86	9.0	81.6	39.9
90	2.5 - 2.5	80.7	39.7
87	11.0	80.3	40.0
88	13.0	79.8	39.7
Std. Dev.		0.93	0.47

Table 17 shows that the 5% split produces a brightness approximately equal to the

9% charge, and the 3% split produces a brightness comparable to the 5% charge. When

examining the data in Table 17, it appears that there is a relationship between the yield and

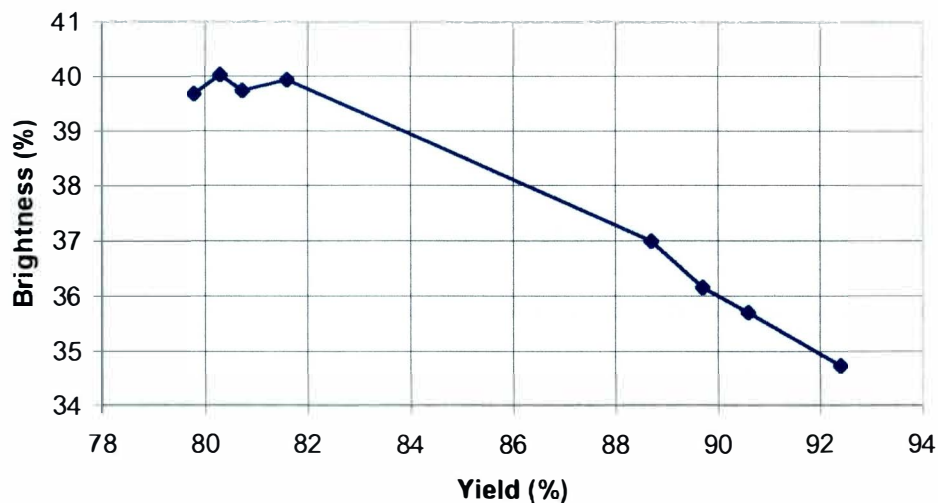brightness obtained. Figure 6 below shows this trend.

Figure 6. The Effect of Pulp Yield on Obtainable Brightness.

Figure 6 shows a linear correlation between the brightness obtained and the pulp yield down to 82% yield. When the yield drops below 82%, there is no longer an improvement in brightness.

Due to the economic feasibility of the 5% charge split run in comparison to a single 9% charge run, the 5% split run is considered to provide optimum DMD bleaching potential. The next step in this thesis was to determine the effects of H_2O_2 on the 5% split charge run. In order to determine if the lower yield of the 5% split-run had an impact on the potential brightness increase produced by hydrogen peroxide, the 5% split-run was compared to the 5% charge run. This is shown in Table 18 below.

Table 18

The Maximum Obtainable Brightness and Effects of Yield

Run (#)	Charge (%)	Brightness (DMD)	Max Brightness (DMD-E-P)	Brightness Increase (%)	Yield (%)
31	5	33.6	52.3	18.7	90.6
93	2.5 - 2.5	38.8	58.3	19.5	80.7
Std. Dev		0.47	0.69	0.83	0.97

From Table 18, it is apparent that the brightness increase associated with the hydrogen peroxide stage for the 5% and 5% split run is statistically not a function of yield. The maximum obtainable brightness for a DMD-DMD-E-P bleaching stage is 58.3 when using chemical charge addition levels of 2.5%-2.5%-2.0%-4.0%.

Table 19

The Effect of Charge on Lignin Content after Bleaching for 60 Minutes

Run #	Time (min)	Charge (%)	Yield (%)	Hypochlorite #
Reference	...	...	...	19.8
83	60	3	92.4	15.5
84	60	5	90.6	14.6
89	60	3-split	89.7	14.3
85	60	7	88.7	13.7
86	60	9	81.6	12.9
90	60	5-split	80.7	12.3
87	60	11	80.3	11.5
88	60	13	79.8	10.7
Std. Dev.			0.97	1.0

The decrease in the hypochlorite numbers in Table 19 decrease with the decreasing yield. The bleaching time for these runs was 60 minutes in order to determine the maximum yield loss that may occur during the bleaching process. More important than the data in Table 19 is the fact that as bleaching time increases after the maximum brightness is reached, the hypochlorite number decreases. This is shown in Table 20.

Table 20

The Effect of Bleaching Time on Lignin Content at a Constant Brightness

Run #	Time (min)	Charge (%)	Hypochlorite #	Brightness (%)
79	30	3-split	15.2	34.7
89	60	3-split	14.3	34.7
80	30	5-split	14.1	35.5
90	60	5-split	12.3	35.7
Std. Dev.			1.0	0.47

This would imply that after the maximum brightness is obtained, the additional effects of the dimethyldioxirane no longer change the optical structure of the lignin but

instead solubilized the lignin. It has already been noted that the majority of the brightness

occurs in the first five minutes of the bleaching stage. Split stages for 5 minutes may

produce brightness slightly below the maximum obtainable, but with larger lignin content

and yield.

The last parameter that was looked at in this experiment was zero-span tensile

index. The effect of charge addition on zero-span tensile index is presented in Figure 7
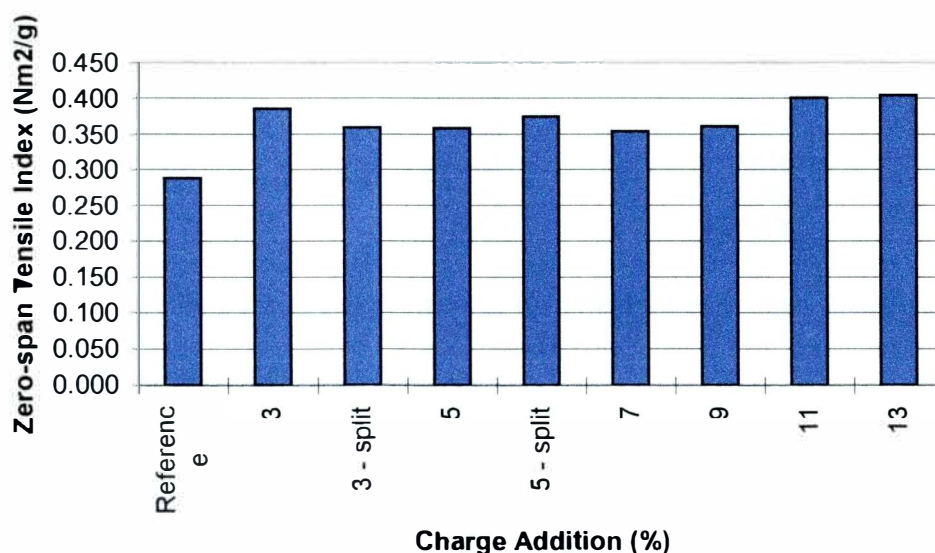
below.

Figure 7. The Effect of Charge Addition on Zero-span Tensile Index.

From this graph it can be seen that there is no obvious decrease in fiber strength

with increasing chemical addition. One problem that exists in this data is that the

reference pulp has the lowest strength. This can occur only if the zero-span tensile

instrument is taking into effect the bonding strength of the fibers. The bonding strength is

higher for the bleached pulps due to the removal of lignin which can hinder bonding.

Another problem that could cause the reference pulp to be lower than the bleached runs

could be gross error. In order to determine if error could be the cause, the standard

deviations were calculated for the zero-span tensile results for each charge level. Fifteen

tests were performed for each of the charge levels. This is presented in Table 21.

Table 21

Summary of Error for Zero-span Tensile

Charge (%)	Zero-span Tensile Index (N/m2)	Std. Dev. (#)
Reference	0.288	0.017
3	0.385	0.034
3 - split	0.359	0.024
5	0.358	0.037
5 - split	0.374	0.027
7	0.353	0.010
9	0.361	0.016
11	0.400	0.016
13	0.4037	0.0099

With the calculated standard deviations, the reference zero-span tensile indexes are

statistically different from the 3% addition level.

VI. CONCLUSIONS

- In phase I of this experiment, it was determined that the optimum pH range for DMD bleaching of high yield pulps is between 6 and 8.

- Upon further experimentation, the optimum pH to maximize the brightness was found to be 8.

- Washing the pulp in the Britt-jar produced a decrease in yield of approximately 9%. Because of this, all of the pulp was washed before the bleaching experiments were started.

- Maximum brightness was obtained with an DMD charge of 9%. This same brightness could be obtained with two 2.5% DMD charges. This brightness was approximately 40. The addition of a H_2O_2 stage to the 5% split stage produced a maximum brightness of 58.3.

- The optimum bleaching time for the 9% stage or the 5% split stage was 30 minutes.

- A linear correlation between yield and brightness was found until the yield dropped below 82%. Below an 82% yield the brightness remained constant.

- As yield decreased, the hypochlorite number decreased, and the zero-span tensile index remained relatively constant.

FUTURE WORK

- Since data was shown in Table 19 that showed that the lignin content decreased with increasing bleaching time, the bleaching time that produced the optimum brightness may not be the best bleaching bleaching time in terms of brightness obtained with respect to lignin loss. Therefore, the effect of increasing brightness with bleaching time while optimizing yield would provide more insight into the maximum achievable brightness without severe lignin loss.

- In this experiment DMD was used only as the first stage of the experiment. It is unknown whether the efficiency of the bleaching sequence would decrease by using DMD later in sequence. Since DMD efficiency is controlled partially by the amount of secondary reactions it undergoes, it may be theorized that as the available lignin concentration decreases, the relative amount of secondary reactions will increase. This thereby decreases the overall efficiency of the bleaching sequence.

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Appendices

Appendix A

Sample Calculations

Calculation of required charge of dimethyldioxirane:

(.03 chemical) * 50 gr OD fiber * $\frac{\text{mole O}}{16\ gr}$ * $\frac{614.9\ gr\ Oxone}{2\ mole\ O}$ = 57.6 gr Oxone

Calculation of required charge of acetone:

(50 gr OD fiber) * (0.03 Oxone) * $\frac{\text{mole O}}{16\ gr}$ * 1.5 mole ratio * $\frac{58.1\ gr\ acetone}{mole}$ = 6.88 gr

Calculation of required charge of buffer:

$\frac{\text{(exp. determined charge of buffer /moles)}}{(.03\ charge\ of\ Oxone)}$ * (charge of oxone / percent) * (molecular weight of buffer)

$\frac{(.200\ moles\ KH_2PO_4)}{(.03\ Oxone\ charge)}$ * (.03 oxone charge) * $\frac{136\ gr}{mole}$ = 27.2 gr KH_2PO_4

Calculation of required Extraction Charge:

(50 gr OD fiber) * (.02 NaOH charge) * $\frac{100\ ml\ soln}{4\ gr\ NaoH}$ = 25 ml of NaOH solution

Calculation of required peroxide charge:

(50 gr OD fiber) * (.04 H_2O_2 charge) * $\frac{100\ ml\ soln}{3\ gr\ H2O2}$ = 66.7 ml soln

Calculation for pulp yield:

$\frac{\text{(mass after DMD-E stage)}}{50\ gr\ OD\ fiber}$ * 100 = yield

$\frac{(40\ gr\ of\ OD\ fiber)}{50\ gr\ OD\ fiber}$ * 100 = 80.0% yield

Calculation for zero-span tensile index:

(tensile /psi) * (7564.0 conversion to / N/m2) * (strip width / m2) / (basis weight / g/m2) =

(17 psi) * (7564.0 N/(m2*psi)) * (.000225 m2) / (60 g/m2) = .482 Nm2/g zero-span tensile index

Calculation of the optimum bleaching time:

Time (min)	Brightness (%)	Change in Brightness (#)	Difference in the Change in Brightness
0	23		
5	33	10	8
10	35	2	1
20	36	1	0.86
30	36.14	0.14	0.02
40	36.26	0.12	-0.01
50	36.39	0.13	...

It can be seen in the data above that at 30 minutes, the difference in the change in brightness becomes constant. Therefore when the brightness reaches 36.14, the optimum time of 30 minutes has been determined. The standard deviation between the change in brightness from 30 minutes to 50 minutes is .01. This helps to assure that this method does produce the optimum bleaching time.