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OPTIMIZATION OF A KRAFT PULP DIOXIRANE BLEACHING STAGE

by

Eric A. Thompson

A Thesis submitted  
in partial fulfillment of  
the course requirements for the  
Degree of Bachelor of Science in Engineering  
Department of Paper and Printing  
Science and Engineering

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Western Michigan University  
Kalamazoo, Michigan  
April, 1995

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## OPTIMIZATION OF A KRAFT PULP DIOXIRANE BLEACHING STAGE

Eric A. Thompson

Western Michigan University, 1995

This research characterized and optimized the bleaching potential of dimethyldioxirane (DMD) on an oxygen-delignified hardwood kraft pulp. The DMD was produced in-situ using a caroate ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ ) and acetone under controlled conditions. The studied variables included chemical concentration, consistency, temperature, reaction time, and chelation. Statistically designed experiments with response surface methodology were used to help locate the optimum conditions with respect to pulp brightness and strength. These conditions were located at 2.8% AO (activated-oxygen charge), 5.5% consistency, and 55°C.

It was found that over 95% of the total brightness increase and about 70% of the total viscosity decrease occurs during the first 5 minutes of reaction time. The bleaching response quickly diminishes beyond this initial time. Bleaching efficiency was improved using a separate chelation stage prior to the DMD stage. Step-wise chemical addition during bleaching improved brightness, but increased viscosity loss.

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Eric A. Thompson

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## INTRODUCTION

The U.S. paper industry is currently under pressure to eliminate chlorine-containing compounds from its bleaching operations (1,2). Chlorine compounds have been historically employed as bleaching agents because they can bleach wood pulps to high brightness without greatly sacrificing pulp strength. The use of oxidative chlorine compounds, however, creates chlorinated organic compounds called dioxins (1,2,3). These dioxins are held to be environmentally hazardous, and are under close scrutiny by the U.S. Environmental Protection Agency (EPA). EPA legislation continually places stricter limitations on bleach-plant effluent emissions, which include dioxins (1). These restrictions provide an impetus for the industry to find alternative ways to bleach without relying on chlorine compounds. Market pressure to employ environmentally-friendly practices is also a stimulus to eliminate chlorine compounds.

Industry response to these environmental pressures has been directed towards two primary technologies: ECF and TCF bleaching (1). Elemental chlorine free (ECF) bleaching eliminates the use of elemental chlorine ( $\text{Cl}_2$ ) from operations. This technology relies on chlorine dioxide ( $\text{ClO}_2$ ), and is found to significantly reduce dioxin emissions. This method is a proven means to produce quality pulp and is in wide practice.

An approach which is gaining interest is totally chlorine free (TCF) bleaching, which eliminates all forms of chlorine in bleaching (1). This method is gaining notice because it avoids possible future limitations on any form of chlorine use, and it is more compatible with the low effluent close-cycle mill concept. The effluent from this process can be recycled in a kraft recovery system (1,4,5). The effluent from chlorine bleaching is too corrosive to be effectively recycled.

Current TCF technology, however, has drawbacks. Besides higher costs, it is more difficult to produce high quality market pulp with this method (1,6,7). TCF bleaching relies heavily on the use of oxygen and ozone ( $O_3$ ). These compounds are not selective lignin-removing agents and attack cellulose if large amounts of these oxidants are consumed during bleaching. Therefore, they can only remove about 50% of the required lignin before pulp strength is severely degraded. Other TCF agents, such as hydrogen peroxide ( $H_2O_2$ ), do not remove lignin well and are limited to post-delignification brightening stages. Currently, attention is being focused on finding new TCF reagents to help overcome these drawbacks (1,6). Potential candidates include organic peroxides.

Organic peroxides, or dioxiranes, show promise as new TCF bleaching agents. Initial research shows that dioxiranes react with lignin structures in a way similar to chlorine-containing compounds (2,6,8). That is, they appear to be good delignifying and brightening agents while preserving pulp strength.

## LITERATURE SURVEY

### Historical Background of Dioxiranes

Dioxiranes are oxidative organic cyclic peroxides. The general structure of these compounds is shown in Figure 1. Dioxiranes were first postulated in 1899 by Bayer and Villiger (9), but were not confirmed until 1972. Although dioxiranes can be produced by various methods, the most efficient method is to produce them in-situ using a buffered solution of peracid and ketone (6,9).

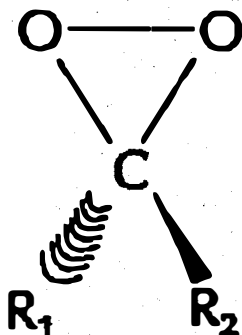
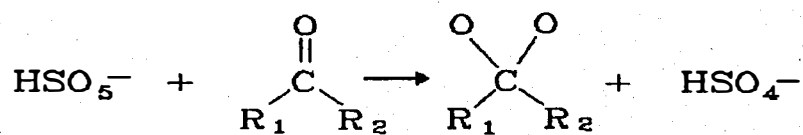


Figure 1: Structure of Dioxiranes (6)

Montgomery (10) was the first to recognize that ketones catalyze certain oxidative monoperoxysulphuric acid reactions with organic substrates. He also noticed that commercial triple-salt caroate (e.g. OXONE:  $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$ ) evolves oxygen gas in the presence of ketones (e.g. acetone). This suggested the in-situ formation of dioxirane intermediates (9,10). The

simplified dioxirane-formation reaction is shown in Equation I.



Equation I: Simplified Dioxirane Formation Mechanism (6)

As shown in Equation I, the monopersulfate ion ( $\text{HSO}_5^-$ ) oxidizes the ketone into a dioxirane. When the dioxirane oxidizes a substrate, it loses an oxygen and reverts back to the ketone (see Equation II). Therefore, the ketone acts as a catalyst (9). In the special case where acetone ( $\text{R} = \text{CH}_3$ ) is the catalyzing ketone, the dioxirane intermediate is dimethyldioxirane or DMD. In 1985, Murray and Jeyaraman (11) were the first to isolate DMD from an acetone-caroate solution by distillation at reduced pressures. Isolation allowed this pale yellow compound to be studied and characterized with spectral methods.

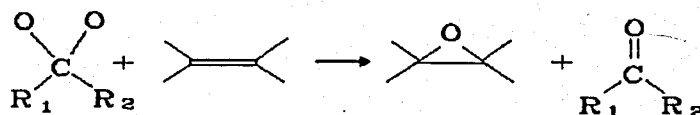
Dimethyldioxirane has the ability to readily transfer oxygen atoms and oxidize many organic compounds (9). More importantly, this relatively new oxidant has been shown to be a selective oxidant in delignification reactions (2,6,8).

## Dioxirane Bleaching Wood Pulp

### Background

The ability of pure peroxymonosulfuric acid ( $\text{HSO}_5^-$ ) to bleach or delignify kraft pulp has already been established (12,13,14). However, dimethyldioxirane has only been recently investigated as a bleaching or delignifying agent for kraft pulps (2,6,8). Preliminary results suggest that DMD acts both as a brightening and as a selective delignifying agent for wood pulps.

The most efficient way to produce DMD for pulp bleaching is in-situ with a 1.5 mol ratio of acetone to caroate (2,6). Sodium bicarbonate ( $\text{NaHCO}_3$ ) is used as a buffer to control the pH between 7.0-7.5. This pH range maximizes oxidation yield (15). Above this range, the dioxirane intermediates are decomposed by the large numbers of caroate anions ( $\text{SO}_5^{--}$ ) present in solution. A general delignification/bleaching reaction mechanism is shown by Equation II.



Equation II: General Dioxirane Oxidation Reaction (6)

As shown in Equation II, the DMD transfers a single oxygen to oxidize the substrate before reverting back to acetone.

Therefore DMD is also termed "activated oxygen" or the "A" stage in a bleaching sequence (6). DMD has been shown to react readily with the numerous carbon-carbon double bonds in residual lignin. Therefore DMD is selective towards cellulose because electron-rich carbon-carbon double bonds are not abundant in cellulose and hemicelluloses.

#### Using DMD in Single-Stage Bleaching

Ragauskas (8) experimented with single-sequence DMD bleaching of softwood kraft pulps (Kappa No. 39.5-27.6). He isolated DMD and applied it (5% chemical concentration) on 3% consistency pulp for 1.5 hours at room temperature to determine its bleaching potential. A 66% drop in Kappa No. was observed (39.5 to 11.9) after a final alkaline extraction. He then bleached pulp with in-situ DMD using a buffered acetone and OXONE solution on pulp slurries of less than 4% consistency. Delignification was directly related to chemical charge. Lignin removal (Kappa No. reduction) maximized at about 75% with a 145% (on pulp) monopersulfate charge. He also found that Kappa No. decreased after a 1.5% caustic extraction, indicating that DMD leaves soluble lignin residuals. This gives evidence that DMD creates soluble lignin fragments in a way similar to chlorine compounds (2,6).

Lee, et al. (2,6), used isolated DMD to bleach an aspen kraft pulp (Kappa No. 16.4). A 0.55% activated oxygen charge was used on a 14.2% consistency pulp for one hour at room

temperature. Activated oxygen charge was based on one available oxygen per monoperoxysulfate molecule. A 79% delignification was achieved and brightness increased about 19% (40.6% to 59.4% ISO). Zero-span tensile strength was much higher than a comparably bleached oxygen pulp (17.0 vs. 10.6 km) and only slightly lower than a conventional (C+D)ED pulp (17.0 vs. 17.4 km). This result relates to the selective nature of DMD (2). Bleaching at 7.6% consistency under the same conditions reduced Kappa No. by 68%.

Lee (6) also used in-situ generated DMD in a single-stage bleaching of a softwood kraft pulp (Kappa No. 31.5). The AE bleaching was carried out at 13.6% consistency and 25°C for one hour. His results were similar to what Raguaskas (8) had reported: delignification increased with chemical charge, and a caustic extraction (1%) removed residual lignin. Viscosity also decreased with delignification, but not to a critical extent. Extracted viscosity dropped 46% (33.5 to 18.2 mPa·s) with 85% delignification (Kappa No. 31.5 to 4.8). These trends were similar to a (C+D)E pulp. Lee found similar results with a softwood oxygen-delignified kraft pulp (Kappa No. 12.6) using oxygen to reinforce the extraction stage.

#### Using DMD in a Bleaching Sequence

The use of an A (DMD) stage in a typical bleaching sequence was also studied by Lee (2,4). A softwood pulp (Kappa No. 31.5) was AE-bleached to a Kappa No. of 5.4 (2). The resulting pulp



was then bleached with a DED sequence to a 90.9% ISO brightness. Final strength properties of the AEDED pulp were nearly identical to conventional sequences such as (C+D)EDED and O(C+D)EDED. Totally-chlorine-free sequences such as AEP and OAEP were used to bleach an aspen kraft pulp to above 85.0% ISO brightness. Strength and viscosity of these bleached pulps were comparable to each other and conventional pulps. However, final brightness of these TCF sequences averaged about 5% less than conventional chlorine sequences.

## LITERATURE ANALYSIS

The reported work on dioxirane bleaching has shown that the process can be used to effectively bleach papermaking wood fibers (2,6,8). Dioxiranes can selectively delignify both softwood and hardwood sources in a way similar to chlorine compounds, and produce pulp comparable with conventional sequences. Despite its promise, much of the required research work on applying this technology as a practical process for the paper industry remains to be done.

Only a small amount of literature exists on this process, and not much information is available regarding the effects of process variables or the interactions between variables. This information will be required to optimize the bleaching process to obtain desired pulp qualities and favorable economics. The reported knowledge regarding process variables is summarized below.

### The Effect of Time

The effect of time on dioxirane bleaching has only been reported with bleaching times between 1-1.5 hours (2,6,8). However, it is widely accepted that the extent of chemical reactions increase with time. Therefore, the extent of dioxirane bleaching should vary with time.

### The Effect of pH

The effect of pH is already well established (9). The pH for the in-situ carboate/ketone process must be between 7.3-7.5 or undesirable side reactions occur (9).

### The Effects of Chemical Concentration, Consistency, and Temperature

The literature suggests that higher chemical applications on pulp increase bleaching reactions (2,6,8). It also appears that higher consistencies may improve the degree of bleaching (2,8). However, the extent to which these variables affect bleaching is not known. The effect of temperature is also not known. Studies to date were conducted only at about room temperature (25°C) (2,6,8).

### The Effect of Metal Ion Removal

Another parameter in question is the effect of metal ion removal. It is known that bleaching with conventional peroxides requires sequestering of metallic ions (3). Presence of metal ions degrade the stability of peroxide, so they must be inactivated with a chelating agent such as DTPA or EDTA. Although reports have indicated that chelation may improve peroxymonosulfate stability (4,5,13,16), no significant effects were reported using chelation before a DMD stage (1).

## PROBLEM STATEMENT

The paper industry is in need of finding alternative, environmentally-friendly methods to bleach wood pulps. Conventional bleaching with chlorine compounds produces by-products which are under strict environmental regulation. Therefore, bleaching with chlorine compounds may someday become too uneconomical or technically difficult to meet eventual tighter limitations on by-product effluent.

Bleaching with organic peroxides, or dioxiranes, may hold opportunity as a feasible environmentally-friendly bleaching process for the paper industry. One dioxirane in particular, dimethyldioxirane (DMD), has shown promise as a selective delignifying and brightening agent for wood pulps. However, work needs to be done to help determine the effects of typical bleaching variables on this process. This knowledge will help locate the optimum process conditions in terms of desired pulp properties and favorable economics. This information is required to help implement this bleaching technology as a practical industry operation.

## OBJECTIVES

The aim of this research will be to characterize and optimize the bleaching potential of a single-stage in-situ generated dioxirane on a kraft pulp. In particular, the goals of this research are listed below:

1. To help determine the relationship of and interaction between bleaching variables on bleaching effectiveness. The studied variables include chemical concentration, bleaching consistency, bleaching temperature, and metal-ion removal on pulp.
2. To help optimize the bleaching process in terms of desired pulp properties. Bleaching conditions will be cross-referenced with bleached pulp viscosity, delignification, strength, and brightness.

## EXPERIMENTAL DESIGN

This research utilized statistically designed experiments and response surface methodology (RSM) to determine the effects of and interactions between process variables. In the search for optimum conditions, the region of optimum response is not likely to be known at first. Initial screening experiments provide information relating to which directions the studied conditions should change to locate the desired optimum. This procedure of following the path of optimum response is the method of steepest ascent. When the conditions are near an optimum, a rotatable central composite design is utilized. These techniques describe the response surface (relationship between variables) and help establish the location of optimum response.

### Initial Experimentation

The initial experimentation will, of course, be used to determine the ideal methods to perform the bleaching trials. It will also provide information of where to proceed to find the optimum conditions. Three primary bleaching variables will be studied at first: chemical concentration, consistency, and temperature.

Initially, a three-factor orthogonal first-order factorial design with three center points will be utilized. This method

studies all the variables simultaneously to describe the response surface. The coded design structure is shown in Figure 2. High-level and low-level conditions are coded as "1" and "-1", respectively, with the center points coded as "0". This design is chosen so that the estimated first-order response of each variable is not confounded with any other variable or combination of variables. The center points provide an estimate of the experimental error (17). Stepwise regression is used to fit the data to the following first order model:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3$$

Equation III: 1st-Order Response Model

where "y" is the measured response, " $x_n$ " are the coded variables, and " $\beta_n$ " are the fitted coefficients [ $n=1,2,3\dots$ ]. Analysis of variance is then used to check to adequacy of the model.

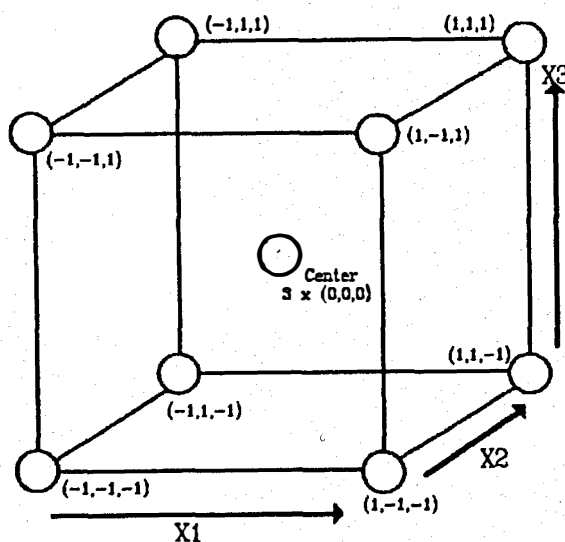


Figure 2: 1st-Order  
Three-Factor Model

If the data fits the model, the center point is moved in the direction of steepest ascent (maximum response) and another experiment is performed. This process continues until the first-order model does not fit the data. The model is then changed to a second-order central composite design by the addition of more points to the first-order system.

### The Method of Steepest Ascent

The method of steepest ascent is a sequential procedure where information from a first-order model is used to find the path of maximum response (17). By following this path, the experiment can quickly be brought near the region of optimum response.

This path can be determined by the relative magnitudes of the model coefficients ( $\beta_j$ ) in Equation III. In general, the path of steepest ascent is defined by incremental changes in the studied variables:

$$\Delta X_j = \frac{\beta_j}{2\mu}$$

where " $X_j$ " is the coded response of the  $j$ th variable, and " $\mu$ " is a factor which depends on the desired conditions of the path. If the path is conveniently chosen so that  $X_j$  increases one unit from its initial base value ( $\Delta X_j = 1$ ), then  $\mu$  will be  $\beta_j/2$ . Therefore, the other coded changes along the response path will



be  $\Delta X_{j+n} = (\beta_{j+n})/(\beta_j)$  [ $n=1,2,3\dots$ ]. All changes are relative to the initial coded values of the variables at the center point. This concept is shown in Figure 3 for a system of three factors.

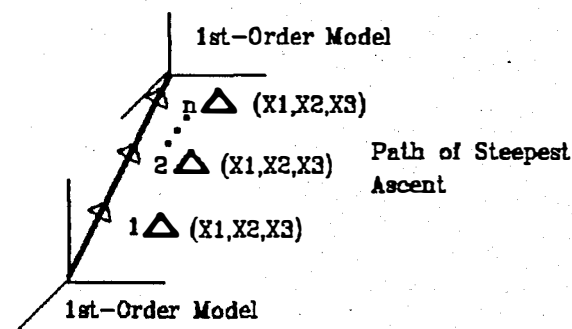


Figure 3: Method of Steepest Ascent with Three Factors

This path is followed by multiples of the coded increments until the response does not significantly change toward the maximum response. When further experimentation along the path yields little or no response change, another first-order model is fitted around the new center point. If curvature is present, a central composite design is implemented. If the surface remains first-order, a new path is obtained and the procedure is started again.

### The Central Composite Design

When the model described by Figure 2 does not adequately fit the first-order equation (Equation III), the experiment is in a region of curvature. That is, the measured response (e.g. strength, brightness, etc.) strongly depends on higher-order

terms of and interactions between the studied variables. The central composite design is used to fit a second-order response surface. For an experiment of three factors, this design can be implemented by additional points on the face-centered cube of Figure 2. Axial points and additional center points are added, as shown in Figure 4. The design is rotatable because all the points geometrically lie on the surface of a sphere (18). Therefore, each point is equally important in the estimate of experimental variance.

The data is fit to the second-order model:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_1^2 + \beta_5 x_2^2 + \beta_6 x_3^2 + \beta_7 x_1 x_2 + \beta_8 x_1 x_3 + \beta_9 x_2 x_3$$

Equation IV: 2nd-Order Response Model

Analysis of variance is applied to check the adequacy of fit. If the model applies, the optimum response is near. A method called canonical analysis is used to determine the shape and properties of the response surface (17).

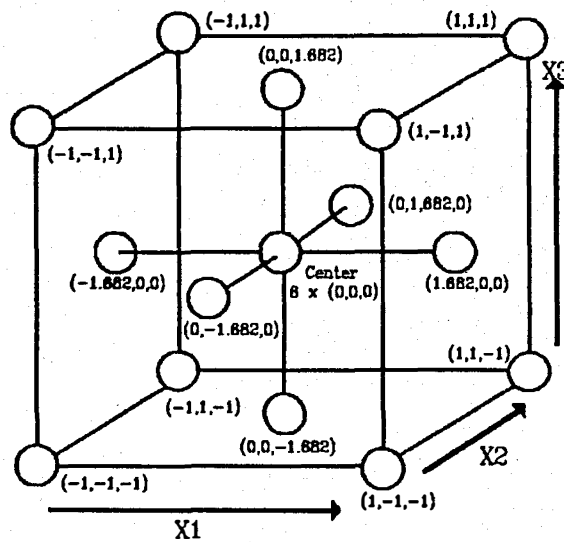


Figure 4: Central Composite Model with Three Factors

Canonical analysis consists of determining the eigenvalues of the  $B$  matrix of the second-order model in matrix notation:

$$\hat{y} = \beta_0 + X'b + X'BX$$

where  $b$  is a  $(k \times 1)$  vector of the first-order regression coefficients, and  $B$  is a symmetric  $(k \times k)$  matrix whose diagonal elements are the quadratic coefficients and whose off-diagonal elements are one-half of the interaction coefficients of the second-order model representing the surface. The stationary point (point of extreme response) of the system is given by equating the derivative of  $Y$  with respect to the  $X$  vector:

$$\hat{y}_0 = \beta_0 + \frac{1}{2}X'_0b$$

where  $y_0$  is predicted response, and  $X_0$  is the stationary point. The system is transformed by moving the center to the stationary point, and rotating the axes so they correspond to the principle axes of the inflection point in the contour system. This eliminates interaction terms. The new translated system of three variables is then described by:

$$y = y_0 + \lambda_1 w_1^2 + \lambda_2 w_2^2 + \lambda_3 w_3^2$$

where  $y_0$  is the response at the stationary point,  $w_h$  are the transformed variables, and  $\lambda_h$  are the eigenvalues.

The nature of the eigenvalues determines the type of response system. If they are all negative, the stationary point is a maximum; if they are all positive, it is a minimum; if they have different signs, it is a saddle point. Ridge analysis must be applied if it is a saddle point.

Once the response surface has been described, additional experimentation around the region is performed to pinpoint the optimum.

### Coding of Variables

For the experimental procedures described above, the variables can be coded in reference to a center point. For the initial experimentation, the respective center points for chemical concentration, consistency, and temperature will be 2%, 4%, and 35°C. It is desired that each respective coded unit of

chemical concentration, consistency, and temperature is 1%, 2%, and 10°C. Therefore, the coding equations are as follows:

Chemical Concentration:  $X_1 = \frac{(\% \text{ AO}) - 2\%}{1\%}$

Consistency:  $X_2 = \frac{(\% \text{ Cy}) - 4\%}{2\%}$

Temperature:  $X_3 = \frac{(\text{Temp}) - 35^\circ\text{C}}{10^\circ\text{C}}$

For example,  $X_1$  (AO) will be coded as "0" when it is 2% (center point), and as "1" when it is 3% (high level).

## EXPERIMENTAL MATERIALS AND PROCEDURES

### Bleaching Materials

The pulp source used in this study was a commercial  $O_2$ -delignified hardwood kraft (Kappa No. 5.6) donated by Consolidated Papers in Wisconsin Rapids, Wisconsin. A representative pre-delignified sample (Kappa No. 11.5) was also obtained for comparison purposes if necessary.

The caroate (OXONE) was purchased through Aldrich Chemical Co. Reagent-grade sodium bicarbonate ( $NaHCO_3$ ) was obtained as a buffering agent. Acetone and EDTA (chelating agent) were also reagent grade.

### Bleaching Procedures

Representative 15 g (O.D.)  $O_2$ -delignified pulp samples were adjusted to the desired consistency with the proper amounts of distilled water, acetone, caroate, and sodium bicarbonate. The caroate/acetone/buffer solution was premixed for 5 minutes before addition on pulp, at a buffered pH between 7.0-7.5. A 1.5 mol ratio of acetone to activated oxygen (AO) was used. For experimental purposes, it was assumed that each  $KHSO_5$  molecule provided one molecule of AO.

The pulp slurry was mixed in a polyethylene bag under a water bath for one hour. The water bath was regulated to the desired temperature. At the end of the bleaching trial, the pulp was extracted for one-half hour at 1% NaOH, 8% consistency, and 65°C.

The bleached pulp was subsequently tested for viscosity (T230). The remainder of the pulp was made into handsheets of 60 g/m<sup>2</sup> in a British sheet-making mold (T205). The handsheets were tested for brightness (Technidyne, T454) and breaking length (T494).

## EXPERIMENTAL RESULTS

A total of 50 bleaching runs were made in this study. The first 43 runs were utilized in the application of RSM to locate the optimum conditions. The last seven runs (44-50) studied the effects of reaction time, metal-ion removal, and step-wise chemical addition on the optimized bleaching conditions.

The first 11 runs (No. 1-11) consisted of a first-order design of three variables. Using the first-order design results, the next 5 runs (No. 12-16) were applied using the method of steepest ascent to locate the next region of experimentation. Runs No. 17-36 formed a central composite design of three variables to describe the response surface and to locate the optimum region. Once the response surface was characterized, Runs No. 37-43 were used to pin-point the optimum conditions.

### Application of RSM

#### 1st-Order Design Runs

A first-order design was chosen to screen the experimental variables (chemical charge, consistency, and temperature) for significance and to help assess where the optimum conditions were located. These runs are numbered 1 to 11 in Table 1. The graphical layout of this experiment is shown in Figure 5, with eight runs around the center point of 2% AO, 4% Cy, and 35°C.



The center point was replicated three times to estimate experimental error and variance.

Table 1

## First-Order Design Runs

Run No.	Chem- ical AO (%)	Cons- istency Cy (%)	Temp. (°C)	Bright- ness (%)	Visc- osity (mPa·s)	Break- ing Length (km)
	Unbleached Pulp			43.20	18.03	2.57
1	2	4	35	69.53	15.26	2.67
2	2	4	35	69.63	15.42	2.44
3	2	4	35	69.10	14.41	2.65
4	1	2	25	60.05	17.65	2.30
5	3	2	25	67.62	16.39	2.56
6	1	6	25	67.50	16.96	2.59
7	3	6	25	72.42	13.76	2.57
8	1	2	45	66.11	16.35	2.52
9	3	2	45	72.77	14.06	2.19
10	1	6	45	70.84	14.97	2.60
11	3	6	45	72.20	12.22	2.69
Runs 1-3 denote the center point.						

ANOVA summaries for the yield values of brightness, viscosity, and breaking-length are shown in Tables 2 to 4, respectively. Analysis of variance revealed that all terms (linear, quadratic, and interaction) were significant with respect to brightness, although the linear term was the most significant. Viscosity followed the first-order model without significant curvature. Breaking-length did not fit the first-order model with any significance.

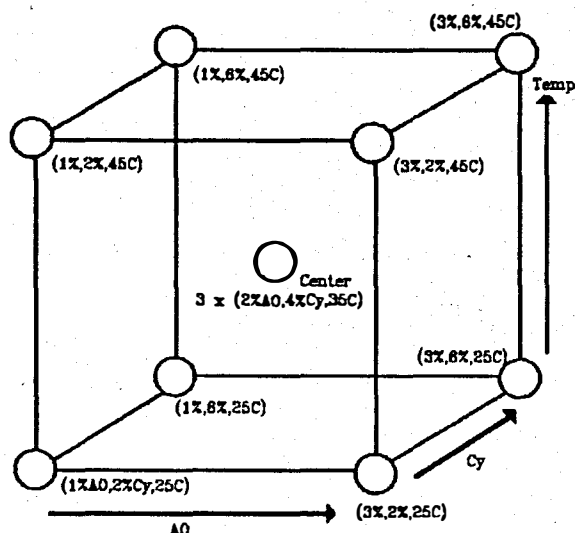


Figure 5: 1st-Order Region

Table 2

ANOVA Table for Brightness

SOURCE OF VARIATION	DF	SS	MS	F
Linear	3	111.866	37.2887	12.55 <sup>a</sup>
Residual Error	7	20.800	2.9715	
Quadratic	1	1.163	1.1627	14.66 <sup>b</sup>
Interaction	4	19.479	4.8698	61.41 <sup>c</sup>
Pure Error	2	0.159	0.0793	
Total	10	132.667		

<sup>a</sup> Significant at 1%<sup>b</sup> Significant at 10%<sup>c</sup> Significant at 2.5%

Table 3

ANOVA Table for Viscosity

SOURCE OF VARIATION	DF	SS	MS	F
Linear	3	23.0359	7.6786	30.20 <sup>a</sup>
Residual Error	7	1.7797	0.2542	
Quadratic	1	0.1532	0.1532	0.52
Interaction	4	1.0371	0.2593	0.88
Pure Error	2	0.5894	0.2947	
Total	10	24.8156		

<sup>a</sup> Significant at 1%

Table 4

ANOVA Table for Breaking-Length

SOURCE OF VARIATION	DF	SS	MS	F
Linear	3	0.09685	0.03228	1.50
Residual Error	7	0.15022	0.02146	
Quadratic	1	0.01546	0.01546	0.95
Interaction	4	0.10230	0.02558	1.58
Pure Error	2	0.03247	0.01623	
Total	10	0.24707		

The uncoded first-order regression equations for the first-order model are shown below:

$$\text{Brightness (\%)} = 53.4 + 2.56*(AO) + 1.03*(Cy) + 0.179*(Temp)$$

$$\text{Viscosity (mPa}\cdot\text{s)} = 22.4 - 1.19*(AO) - 0.41*(Cy) - 0.090*(Temp)$$

$$\text{Breaking Length (km)} = 2.31 + 0.00*(AO) + 0.06*(Cy) - 0.000*(Temp)$$

As expected, brightness response had a negative correlation with viscosity. Chemical charge (AO), consistency (Cy), and temperature (Temp) were all found to be significant to 2.5% with

respect to brightness and viscosity (see Appendix A). Breaking-length was not significantly affected in this region of experimentation.

Brightness was chosen as the optimization variable at this stage because it was closer to a region of curvature than viscosity. Also, no correlation apparently existed with breaking length. Therefore, brightness seemed to be a more reliable parameter to proceed with the optimization.

#### Method of Steepest Ascent Runs

Using the first-order regression equation for brightness, five experimental runs were made which followed the path of steepest ascent. These runs are summarized as Runs 12-16 in Table 5.

Table 5

Steepest-Ascent Runs

Run No.	Chem- ical AO %	Cons- istency Cy (%)	Temp. (°C)	Bright- ness (%)	Visc- osity (mPa·s)	Break- ing Length (km)
12	3.0	5.6	42	72.83	12.15	2.31
13	3.5	6.4	46	73.12	10.89	2.30
14	4.0	7.2	49	73.41	9.87	2.26
15	4.5	8.0	53	73.92	8.46	2.33
16	5.0	8.8	56	74.09	7.91	1.80

Figures 6 and 7 show a plots of brightness and viscosity with reference to the bleaching conditions. As shown, once out of the 1st-order experimental region, the brightness prediction

quickly became invalid. The brightness response levelled-off quickly near 73%. The viscosity prediction, however, was more reliable.

Since brightness response quickly levelled-off, indicating a region of curvature, the design center point was moved and a second-order design was implemented. The new center point was chosen as 3% AO, 6% Cy, and 45°C, which preserved a point on the first-order design.

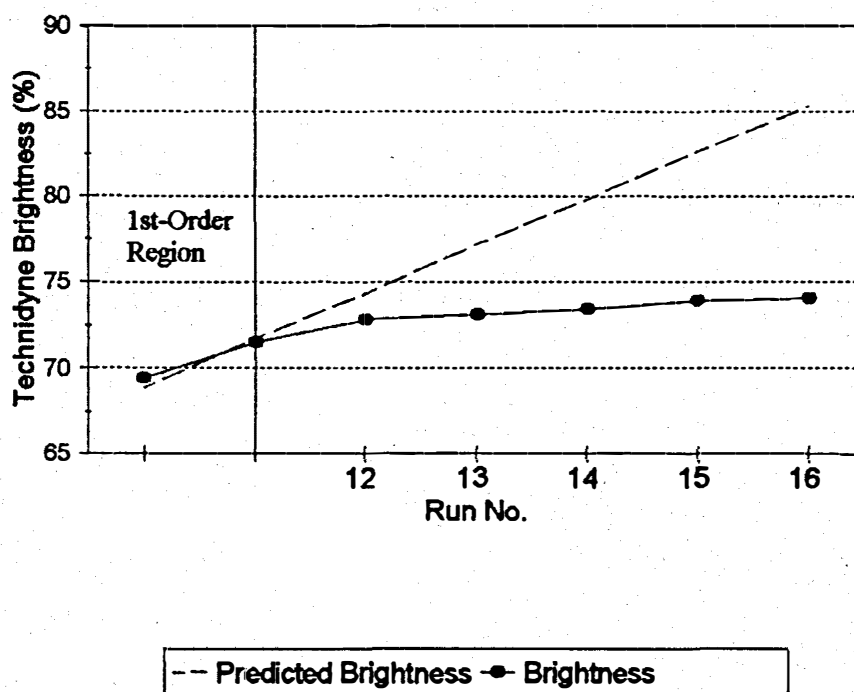


Figure 6: Steepest Ascent Runs (Brightness)

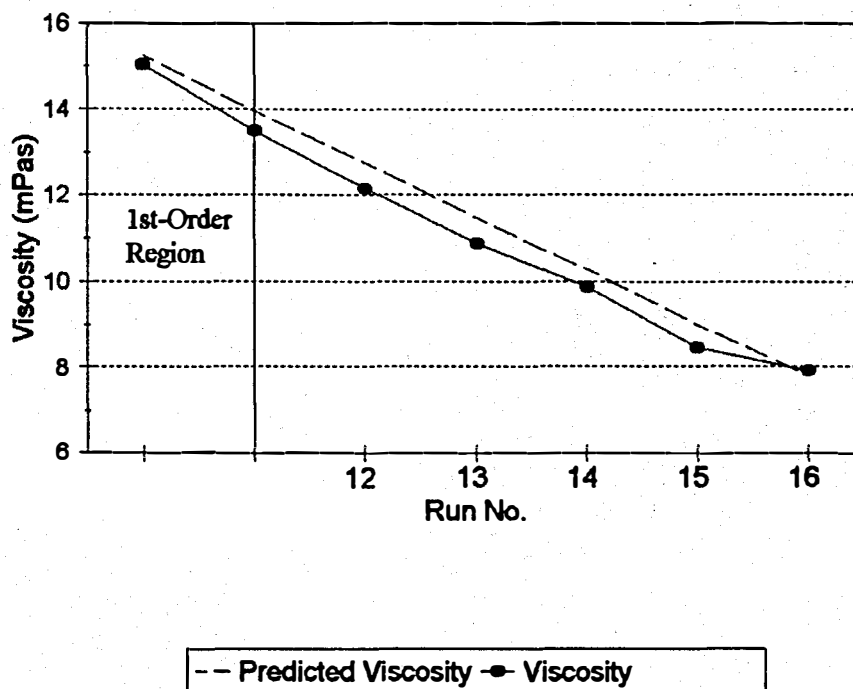


Figure 7: Steepest Ascent Runs (Viscosity)

#### Central-Composite Design Runs

Runs 17-36 consisted of a central composite design of three variables to estimate the second-order response. Table 6 summarizes the uncoded bleaching conditions. Figure 8 shows the graphical layout around the center point. Axial points are added, and the center point is replicated six times to estimate experimental error and variance.

Tables 7-9 are ANOVA summaries with respect to brightness, viscosity, and breaking length. Brightness had significant curvature in both quadratic and interaction terms. Viscosity response, however, was still in a linear region.

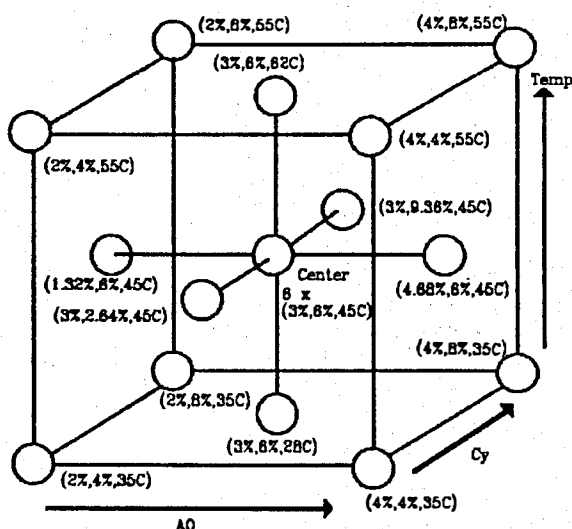


Figure 8: Second-Order Region

Table 6

## Central-Composite Design Runs

Run No.	Chemical AO (%)	Consistency Cy (%)	Temp. (°C)	Brightness (%)	Viscosity (mPa·s)	Breaking Length (km)
17	3	6	45	71.37	12.46	2.43
18	3	6	45	72.33	12.10	2.53
19	3	6	45	72.39	12.22	2.03
20	3	6	45	72.27	12.44	2.35
21	3	6	45	72.16	12.83	2.48
22	3	6	45	72.02	12.26	2.43
23	2	4	35	69.77	15.10	2.07
24	4	4	35	72.23	12.46	2.29
25	2	8	35	71.19	13.76	2.33
26	4	8	35	71.94	12.26	2.55
27	2	4	55	72.43	13.60	2.47

Table 6 - Continued

Run No.	Chem- ical AO (%)	Cons- istency Cy (%)	Temp. (°C)	Bright- ness (%)	Visc- osity (mPa·s)	Break- ing Length (km)
28	4	4	55	72.64	11.94	2.20
29	2	8	55	72.21	12.71	2.15
30	4	8	55	70.87	10.28	2.26
31	1.32	6	45	70.62	14.12	1.90
32	4.68	6	45	71.26	11.49	2.17
33	3	2.64	45	70.77	13.36	2.30
34	3	9.36	45	72.20	9.39	2.41
35	3	6	28	72.03	13.70	2.48
36	3	6	62	72.02	10.60	2.39

Runs 17-22 denote the center point.  
Runs 31-36 denote the axial points.

Table 7

ANOVA Table for Brightness

SOURCE OF VARIATION	DF	SS	MS	F
Linear	3	1.5647	0.5216	2.27
Quadratic	3	2.2128	0.7376	3.22 <sup>a</sup>
Interaction	3	4.8997	1.6332	7.12 <sup>b</sup>
Residual Error	10	2.2929	0.2293	
Lack-of-Fit	5	1.5847	0.3169	2.24
Pure Error	5	0.7082	0.1416	
Total	19	10.9701		

<sup>a</sup> Significant at 10%

<sup>b</sup> Significant at 1%



Table 8

ANOVA Table for Viscosity

SOURCE OF VARIATION	DF	SS	MS	F
Linear	3	27.924	9.30825	22.23 <sup>a</sup>
Quadratic	3	2.1203	0.70678	1.69
Interaction	3	0.1449	0.04831	0.12
Residual Error	10	4.1869	0.41869	
Lack-of-Fit	5	3.8561	0.77122	11.66 <sup>a</sup>
Pure Error	5	0.3307	0.06615	
Total	19	34.3769		

<sup>a</sup> Significant at 1%

Table 9

ANOVA Table for Breaking-Length

SOURCE OF VARIATION	DF	SS	MS	F
Linear	3	0.06106	0.020352	1.09
Quadratic	3	0.21366	0.071221	3.81 <sup>a</sup>
Interaction	3	0.13910	0.046367	2.48
Residual Error	10	0.18716	0.018716	
Lack-of-Fit	5	0.02641	0.005282	0.16
Pure Error	5	0.16075	0.032150	
Total	19	0.60098		

<sup>a</sup> Significant at 5%

Canonical analysis, with respect to brightness, revealed that the response region had a critical point near 3.45% AO, 5.86% Cy, and 43.8°C. The transformed response equation is shown below:

$$\text{Brightness} = 72.12 + 0.188 \text{ AO}'^2 - 0.655 \text{ Cy}'^2 - 0.041 \text{ Temp}'^2$$

where AO', Cy', and Temp' are the transformed variables and the

coefficients are the eigenvalues. Since the eigenvalues included both positive and negative terms, the response-surface shape is a saddle. This is shown graphically in Figure 9 with temperature held constant at 55°C.

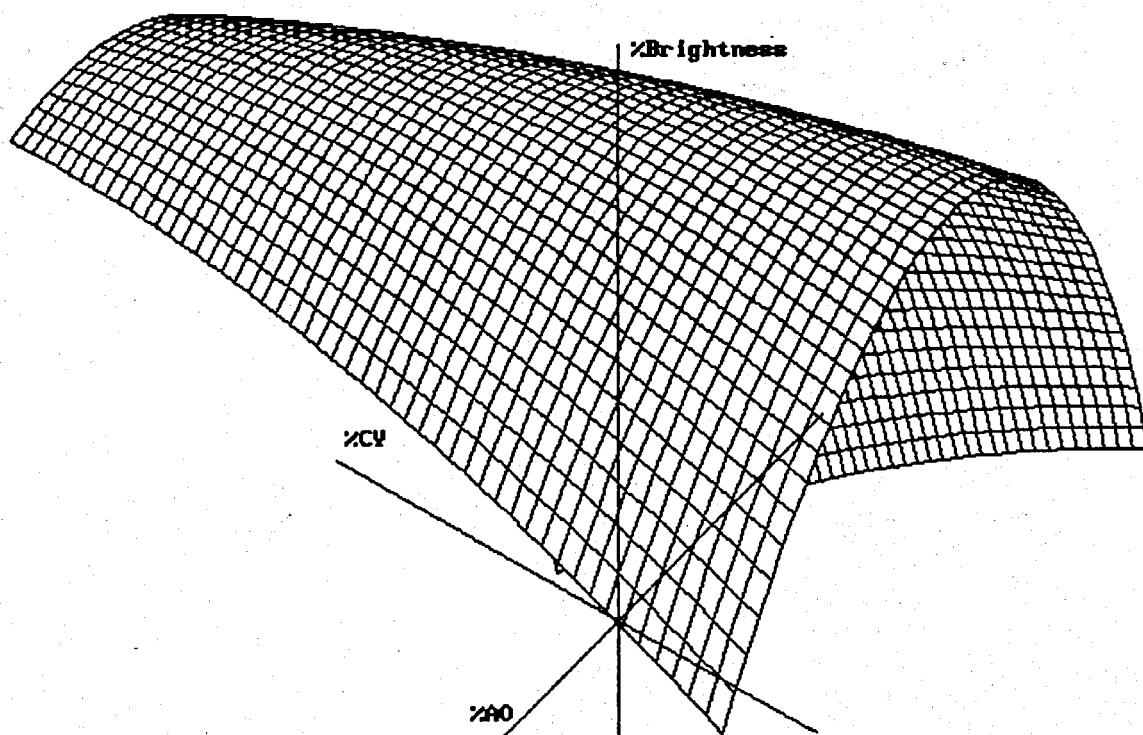


Figure 9: Brightness Response Surface  
With Temperature Constant at 55°C

Ridge analysis was applied and located the optimum conditions near 2.84% AO, 5.51% Cy, and 54.6°C. Ridge analysis outputs are shown in Appendix C.

To pinpoint the optimum conditions, Runs 37-43 were performed around the estimated optimum conditions with temperature constant at 55°C. Temperature had the smallest eigenvalue of -0.041 and therefore was the least significant variable. These conditions are summarized in Table 10. Analysis

with respect to brightness revealed that the runs were not statistically different. Therefore, the optimum conditions were defined at 2.8% AO, 5.5% Cy, and 55°C with an average brightness of 73.1% and viscosity of 12.76 mPa·s. This corresponds to a total brightness increase of 29.9 points and viscosity decrease of 5.27 mPa·s with respect to the original O<sub>2</sub>-delignified pulp.

Table 10  
Optimization Runs

Run No.	Chem- ical AO (%)	Cons- istency Cy (%)	Temp. (°C)	Bright- ness (%)	Visc- osity (mPa·s)	Break- ing Length (km)
37	2.8	5.5	55	72.63	12.87	2.23
38	2.8	5.5	55	73.06	12.30	1.94
39	2.8	5.5	55	73.53	13.11	2.04
40	2.6	5	55	72.73	12.59	2.19
41	3	5	55	72.39	12.34	2.11
42	2.6	6	55	72.75	12.22	1.96
43	3	6	55	73.26	11.78	1.91

#### The Effect of Time on Dioxirane Bleaching

Runs 44-46 observed the relative rate of the bleaching reaction by stopping the optimized process at 5, 15, and 30 minutes. These runs are summarized in Table 11. Brightness and viscosity are plotted with respect to time in Figure 10.

Table 11

The Effect of Time on the  
Optimized Bleaching Sequence

Run No.	Time	Brightness (%)	Viscosity (mPa·s)	Breaking length (km)
44	5	70.61	14.37	2.15
45	15	70.77	13.84	2.16
46	30	71.94	12.83	1.96
Optimum	60	73.07	12.76	2.07
All Runs at 2.8% AO, 5.5% Cy, 55°C.				

As shown, about 91.6% (27.4 points) of the total brightness increase of 29.9 points takes place in the first 5 minutes of reaction. The extent of reaction with respect to viscosity is about 69.4% (3.66 mPa·s) of the total decrease of 5.27 mPa·s. After the first five minutes, the extent of reaction proceeds more slowly.

These observations show that dimethyldioxirane reacts very quickly to whiten the colored components of the pulp. Cellulose-degrading reactions shown by viscosity reductions, however, proceed more slowly. Therefore, the total bleaching potential could be maximized with shorter reaction times to help preserve pulp viscosity if slightly less brightness is tolerable. This also suggests that DMD may be feasible in a short retention-time bleaching process. A possibility could be with bleaching high-yield pulps in refiners.

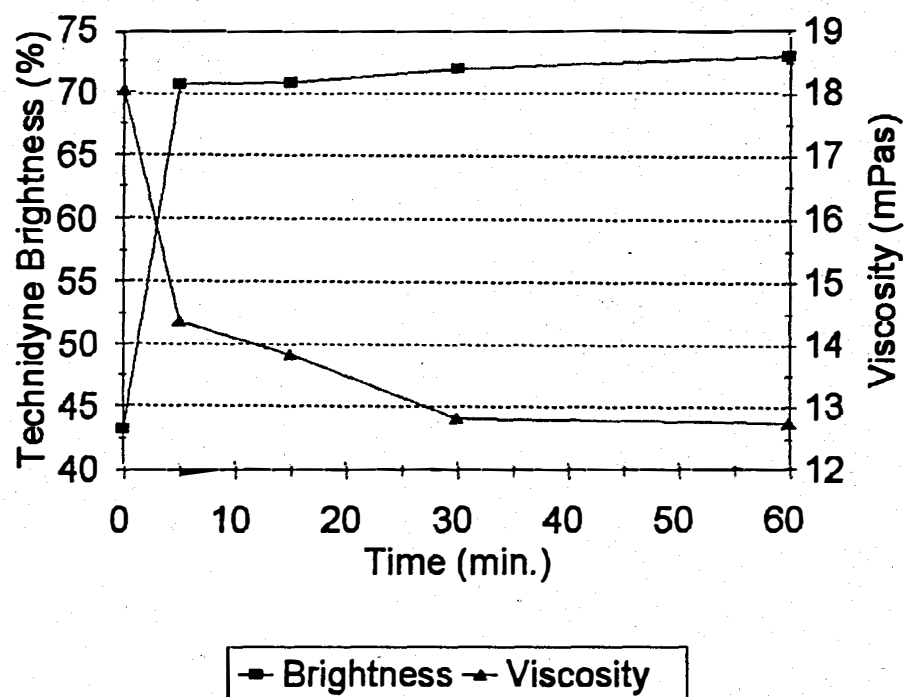


Figure 10: The Effect of Time on Dioxirane Bleaching

#### The Effect of Chelation on Dioxirane Bleaching

Runs 47-49 investigated the effect of chelation, or metal-ion inactivation, on the optimized bleaching process. These runs are summarized in Table 12. Run 47 had the pulp washed prior to the A stage with no chelant. Run 48 had 2% EDTA (chelating agent) added during the bleaching stage with no prior washing. Run 49 had 2% EDTA added prior to the DMD stage in a separate 'Q' stage with washing. This EDTA was mixed with the pulp at room temperature for 15 minutes with subsequent washing before the A stage. Results are shown in Figure 11.

Table 12

The Effect of Chelation and Chemical Addition  
on the Optimized Bleaching Sequence

Run No.	Sequence	Brightness (%)	Viscosity (mPa·s)	Breaking length (km)
Optimum	OAE	73.07	12.76	2.07
47	O(wash)AE	72.43	12.60	2.09
48	O(AQ)E	72.80	12.30	2.40
49	OQAE	74.57	13.60	2.25
50	OA(step)E	74.87	11.41	2.18
All Runs at 'A'-stage 2.8% AO, 5.5% Cy, 55°C.				

The OQAE process (Run 49) had about a 1.5 point brightness increase over the optimized OAE process. Pulp viscosity was about 1 mPa·s higher with the OQAE process. These results show that a separate metal-ion removal stage with washing may improve the bleaching potential of this process. Harmful impurities, which cause cellulose-degrading side reactions and DMD decomposition, are likely removed from the pulp during the Q stage.

The O(AQ)E process or the O(wash)AE process appeared to have no significant effect on the overall bleaching effectiveness. Metal ions or other impurities may need to be first inactivated with chelating agent and then removed with washing to prevent harmful side reactions.

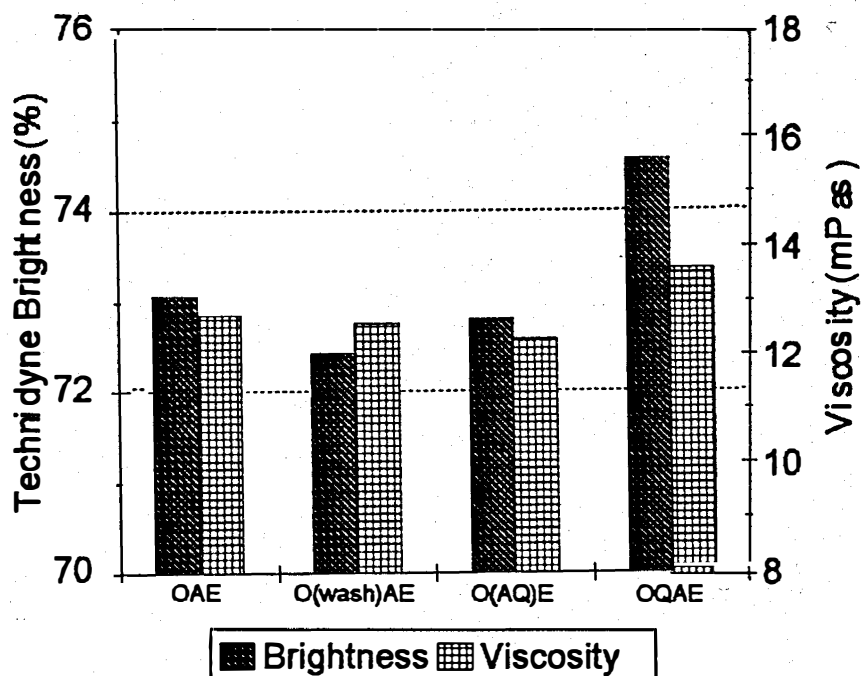


Figure 11: The Effect of Washing and Chelation on Dioxirane Bleaching

#### Step-wise Dioxirane Bleaching

Run 50 (refer to Table 12), was bleached at optimum conditions with the total chemical charge added in a step-wise manner in 20 minute intervals. This was done by adding the total Oxone charge in thirds at 0, 20, and 40 minutes.

As shown in Figure 12, brightness increased about 1.9 points and viscosity decreased about 1.3 mPa.s with respect to the optimized standard. This shows that adding the chemical in a step-wise manner may increase the bleaching driving force. It also shows that adding the bleaching chemical with residual chemical still present may be feasible. Therefore, extraction or

washing stages may not be required for back-to-back A-stages in a bleaching sequence. This possibility should be investigated further.

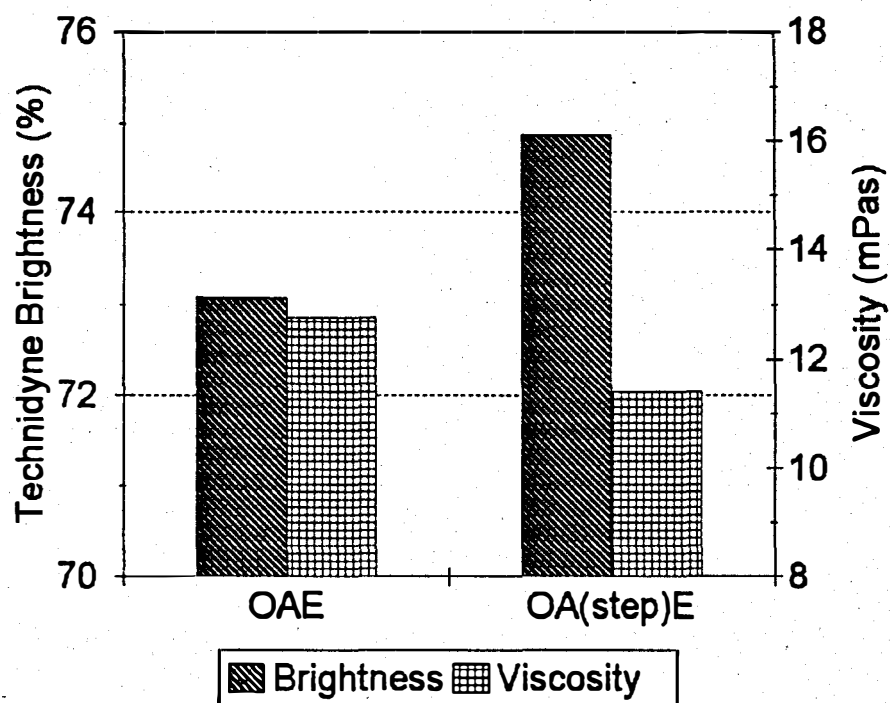


Figure 12: The Effect of Step-Wise Chemical Addition



## CONCLUSIONS

1. Dimethyldioxirane bleaching can be used to bleach  $O_2$ -delignified HWK pulps to over 70% brightness in a single stage with a viscosity drop of about 33%. However, overall effectiveness is significantly less than conventional chlorine compounds. For example, similar results on the identical pulp were obtained using  $ClO_2$  (19). A 2% equivalent  $Cl_2$  charge was used on the pulp at 8% consistency, 65°C, and 1.5 hours. The optimized DMD stage with 2.8% AO is equivalent to about 5.6%  $Cl_2$ . Therefore, in terms of oxidation potential, DMD was less than half as effective as  $ClO_2$  in this study.
2. Chemical charge, consistency, and temperature are important variables which affect dioxirane bleaching. Brightness response is in direct proportion to these variables, and viscosity response follows an inverse relationship.
3. Because over 95% of the brightness response occurs in the first 5 minutes of reaction, this process could be used to bleach wood fibers in short retention-time processes.
4. A metal-ion removal stage with washing before the dioxirane stage appears to improve bleaching efficiency. Removal of metal ions and other impurities may prevent dioxirane decomposition and other undesirable side reactions.
5. Adding the active bleaching chemical in intermittent steps increases the bleaching response to a small degree. This may show that washing or extraction is not needed between dioxirane stages in a bleaching process.
6. This research has shown that response surface methodology (RSM) can be used effectively to optimize a new bleaching process.

## RECOMMENDATIONS

1. This process should be studied with other types of pulp, such as high-yield and recycled furnishes. Other conditions than the relatively low consistency, unpressurized conditions of this analysis should also be considered.
2. The effect of metal-ion removal should be studied in greater detail. Specific ion types should be studied in terms of adverse effects on the bleaching mechanism. Also, the possibility of eliminating extraction stages between dioxirane stages should be further considered.

## APPENDIX A

### Statistical Analysis of the First-Order Model

## VARIABLE CODING:

$$AO (\%) = \frac{\% AO - 2\%}{1\%}$$

$$Cy (\%) = \frac{\% Cy - 4\%}{2\%}$$

$$Temp (^\circ C) = \frac{Temp - 35^\circ C}{10^\circ}$$

## Estimated Effects and Coefficients for BRIGHTNESS

Term	Effect	Coef	Std Coef	t-value	P
Constant		68.889	0.5197	132.54	0.000
AO	5.125	2.563	0.6095	4.20	0.004
Cy	4.105	2.053	0.6095	3.37	0.012
Temp	3.580	1.790	0.6095	2.94	0.022

## Analysis of Variance for BRIGHTNESS

Source	DF	Seq SS	Adj SS	Adj MS	F
Main Effects	3	111.866	111.866	37.2887	12.55
Residual Error	7	20.800	20.800	2.9715	
Curvature	1	1.163	1.163	1.1627	14.66
Lack of Fit	4	19.479	19.479	4.8698	61.41
Pure Error	2	0.159	0.159	0.0793	
Total	10	132.667			

## Estimated Effects and Coefficients for VISCOSITY

Term	Effect	Coef	Std Coef	t-value	P
Constant		15.223	0.1520	100.13	0.000
AO	-2.375	-1.187	0.1783	-6.66	0.000
Cy	-1.635	-0.817	0.1783	-4.59	0.000
Temp	-1.790	-0.895	0.1783	-5.02	0.000

## Analysis of Variance for VISCOSITY

Source	DF	Seq SS	Adj SS	Adj MS	F
Main Effects	3	23.0359	23.0359	7.6786	30.20
Residual Error	7	1.7797	1.7797	0.2542	
Curvature	1	0.1532	0.1532	0.1532	0.52
Lack of Fit	4	1.0371	1.0371	0.2593	0.88
Pure Error	2	0.5894	0.5894	0.2947	
Total	10	24.8156			

## Estimated Effects and Coefficients for BREAKING LENGTH

Term	Effect	Coef	Std Coef	t-value	P
Constant		2.52545	0.04417	57.18	0.000
AO	0.00000	0.00000	0.05179	0.00	1.000
Cy	0.22000	0.11000	0.05179	2.12	0.071
Temp	-0.00500	-0.00250	0.05179	-0.05	0.963

## Analysis of Variance for BREAKING LENGTH

Source	DF	Seq SS	Adj SS	Adj MS	F
Main Effects	3	0.09685	0.09685	0.03228	1.50
Residual Error	7	0.15022	0.15022	0.02146	
Curvature	1	0.01546	0.01546	0.01546	0.95
Lack of Fit	4	0.10230	0.10230	0.02557	1.58
Pure Error	2	0.03247	0.03247	0.01623	
Total	10	0.24707			

## APPENDIX B

### Statistical Analysis of the Second-Order Model

## VARIABLE CODING:

$$AO (\%) = \frac{\% AO - 3\%}{1\%}$$

$$Cy (\%) = \frac{\% Cy - 6\%}{2\%}$$

$$Temp (^{\circ}C) = \frac{Temp - 45^{\circ}}{10^{\circ}}$$

## Estimated Regression Coefficients for BRIGHTNESS

Term	Coef	Stdev	t-ratio	p
Constant	72.0831	0.1953	369.102	0.000
AO	0.2311	0.1296	1.784	0.105
Cy	0.1131	0.1296	0.873	0.403
Temp	0.2199	0.1296	1.697	0.121
AO*AO	-0.3615	0.1261	-2.866	0.017
Cy*Cy	-0.1689	0.1261	-1.339	0.210
Temp*Temp	0.0221	0.1261	0.175	0.865
AO*Cy	-0.4075	0.1693	-2.407	0.037
AO*Temp	-0.5425	0.1693	-3.204	0.009
Cy*Temp	-0.3900	0.1693	-2.304	0.044

s = 0.4788

R-sq = 79.1%

R-sq(adj) = 60.3%

## Analysis of Variance for BRIGHTNESS

Source	DF	Seq SS	Adj SS	Adj MS	F
Linear	3	1.5647	1.5647	0.5216	2.27
Square	3	2.2129	2.2129	0.7376	3.22
Interaction	3	4.8997	4.8997	1.6332	7.12
Residual Error	10	2.2929	2.2929	0.2293	
Lack-of-Fit	5	1.5847	1.5847	0.3169	2.24
Pure Error	5	0.7082	0.7082	0.1416	
Total	19	10.9701			

## Estimated Regression Coefficients for VISCOSITY

Term	Coef	Stdev	t-ratio	p
Constant	12.3634	0.2639	46.848	0.000
AO	-0.9265	0.1751	-5.291	0.000
Cy	-0.7884	0.1751	-4.503	0.000
Temp	-0.7515	0.1751	-4.292	0.002
AO*AO	0.2900	0.1704	1.701	0.120
Cy*Cy	-0.2156	0.1704	-1.265	0.235
Temp*Temp	0.0584	0.1704	0.343	0.739
AO*Cy	0.0462	0.2288	0.202	0.844
AO*Temp	0.0062	0.2288	0.027	0.979
Cy*Temp	-0.1263	0.2288	-0.552	0.593

s = 0.6471      R-sq = 87.8%      R-sq(adj) = 76.9%

## Analysis of Variance for VISCOSITY

Source	DF	Seq SS	Adj SS	Adj MS	F
Linear	3	27.9247	27.9247	9.30825	22.23
Square	3	2.1203	2.1203	0.70678	1.69
Interaction	3	0.1449	0.1449	0.04831	0.12
Residual Error	10	4.1869	4.1869	0.41869	
Lack-of-Fit	5	3.8561	3.8561	0.77122	11.66
Pure Error	5	0.3307	0.3307	0.06615	
Total	19	34.3769			

## Estimated Regression Coefficients for BREAKING LENGTH

Term	Coef	Stdev	t-ratio	p
Constant	2.3743	0.05580	42.553	0.000
AO	0.0538	0.03702	1.452	0.177
Cy	0.0326	0.03702	0.880	0.399
Temp	-0.0228	0.03702	-0.616	0.552
AO*AO	-0.1158	0.03604	-3.212	0.009
Cy*Cy	-0.0026	0.03604	-0.073	0.943
Temp*Temp	0.0257	0.03604	0.712	0.493
AO*Cy	0.0475	0.04837	0.982	0.349
AO*Temp	-0.0750	0.04837	-1.551	0.152
Cy*Temp	-0.0975	0.04837	-2.016	0.071

s = 0.1368      R-sq = 68.9%      R-sq(adj) = 40.8%



## Analysis of Variance for BREAKING LENGTH

Source	DF	Seq SS	Adj SS	Adj MS	F
Linear	3	0.06106	0.06106	0.020352	1.09
Square	3	0.21366	0.21366	0.071221	3.81
Interaction	3	0.13910	0.13910	0.046367	2.48
Residual Error	10	0.18716	0.18716	0.018716	
Lack-of-Fit	5	0.02641	0.02641	0.005282	0.16
Pure Error	5	0.16075	0.16075	0.032150	
Total	19	0.60098			

## APPENDIX C

### Ridge Analysis

Ridge analysis is used when an unique extreme cannot be found in the second-order experimental region. This analysis is performed by taking spheres of increasing radii around the design's center point. The method of Lagrange Multipliers is used to find the maximum value falling on the sphere's circumference. The analysis shows which direction on the response surface one must proceed to find the optimum.

#### Ridge Analysis for Brightness

Coded Radius	Estimated Brightness (%)	UNCODED VARIABLES		
		AO (%)	Cy (%)	Temp (°C)
0.00	72.08	3	6	45.0
0.03	72.09	3.04	6.02	45.2
0.11	72.11	3.12	6.04	45.9
0.17	72.13	3.15	6.03	46.5
0.20	72.13	3.14	6.02	47.0
0.26	72.14	3.13	5.98	47.5
0.42	72.18	2.58	5.87	49.2
0.72	72.27	2.79	5.69	52.0
1.00	72.39	2.84	5.51	54.6

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