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Daniel Krueger
Western Michigan University

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Full Sequence Bleaching With Dimethyldioxirane

by

Daniel Krueger

Advisor: Raja Aravamuthan

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Abstract

Research work to date has shown dimethyldioxirane to be a very powerful, yet highly selective oxidant. Dimethyldioxirane bleaching may become more important in the future with legislative restrictions on chlorine based bleaching agents as it contains no chlorine. Most work with dimethyldioxirane to date has concentrated on short sequence bleaching, or the use of peroxymonosulfate as a pre-treatment to improve oxygen delignification. The goal of this study was to develop a full sequence bleaching containing only dimethyldioxirane and other chlorine free bleaching agents that matched the brightness and strength characteristics of comparable chlorine dioxide based full sequences. Dimethyldioxirane was found to match the strength, but not the brightness of, chlorine dioxide. As well, dimethyldioxirane may be harsher on cellulose than chlorine dioxide. Additional optimization may allow dimethyldioxirane to perform as well as chlorine dioxide. It was seen that increased brightnesses were achieved by using optimum conditions and a step-wise chemical addition. As well, the addition of peroxide to dimethyldioxirane stages may increase brightness.

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Introduction

Research work to date has shown dimethyldioxirane to be a very powerful, yet highly selective oxidant. It has the advantage of being mild toward the oxidized products and reacting under neutral conditions. Earlier research has suggested that dimethyldioxirane may produce pulps of equal brightness to conventional chlorine based bleaching processes, but with greater strength and possibly reduced effluent loads. Dimethyldioxirane bleaching may become more important in the future with legislative restrictions on chlorine based bleaching agents. Since dimethyldioxirane contains no chlorine, it is an option for mills that are heading toward chlorine free bleaching. An additional advantage to dimethyldioxirane bleaching is that the effluent can be handled in conventional recovery furnaces, which can reduce waste treatment loads.

Though some research has been done with dimethyldioxirane bleaching, little has been done in regards to full sequence bleaching. Most work has concentrated on short sequence bleaching, or the use of peroxymonosulfate as a pre-treatment to improve oxygen delignification. A goal of this study was to develop a full sequence bleaching containing only dimethyldioxirane and other chlorine free bleaching agents that matched the brightness and strength characteristics of common chlorine dioxide based full sequences.

Literature Survey

Though the reaction of Caro's acid (peroxymonosulfate) and a ketone (Baeyer-Villiger reaction) has been known since the early part of this century, applications in regards to the bleaching of wood fiber have only become realized in the past ten years.

A study presented by Montgomery(1) in 1974 suggested that acetone is the most effective catalyst for converting peroxymonosulfate into dimethyldioxirane. Dimethyldioxirane is the active bleaching agent. Though acetone does not have the highest oxidation reaction rate, there is no reactant loss. The rate law for the production of dimethyldioxirane has been found to be:

$$-d[HOOSO_3-]/dt = k_1[HOOSO_3-][ketone][OH-]$$

This reaction is pseudo-first order when the ketone is in excess. At low ketone concentrations, the reaction rate is proportional to the ketone concentration. Montgomery also suggested the pathway in which a ketone and peroxymonosulfate form dimethyldioxirane, as seen in figure 1 (page 9).

Dioxirane studies done by Murray and others(2)(3)(4)(5) have shown dimethyldioxirane to be a very useful compound for the synthesis of many important compounds such as epoxides, ozonides, esters, acids, trioxides, and many other compounds which typically arise from carbonyl oxide. Dimethyldioxirane has also been studied for the control of sulfur oxides in pollution streams. Edwards *et al.*(3) presented a strong case for the dimethyldioxirane intermediate being the powerful oxidant in the Baeyer-Villiger reaction. Edwards also identified the undesirable side reactions which occur above and below a pH of 7 to 7.5 (see figure 1). Pioneering work done by Edwards in 1979 isolated dimethyldioxirane, though this was of more interest to research chemists. Additional work has shown many possible applications for dimethyldioxirane, including bleaching. One useful physical characteristic of dimethyldioxirane is that it is yellow in solution with a UV absorption of λ_{max} 335 nm. Consequently, the concentration of dimethyldioxirane in a solution could be determined by light absorbance at this wavelength.

In 1986 Springer and McSweeny(6) published a paper in which calcium sulfite and air was used to bleach delignified aspen pulp. This reaction forms calcium peroxymonosulfate, which is similar to a peroxymonosulfate salt commercially known as Oxone. Springer and McSweeny compared bleaching with this calcium salt to bleaching with peroxide and Oxone. Based upon percent active oxygen, they found that the calcium peroxymonosulfate performed as well as Oxone, while both performed significantly better than peroxide. Springer and McSweeny concluded that the conversion of calcium sulfite and air into calcium peroxymonosulfate is quite high. Brightnesses five to ten percent higher were achieved with Oxone over peroxide, with brightness increasing as percent active oxygen increased. Springer and McSweeny suggested that more work was needed to investigate the effectiveness of other catalysts, higher consistencies, and shorter bleaching times.

In 1990, Springer(7) published another paper that investigated the delignification of aspen using hydrogen peroxide and peroxymonosulfate. He concluded that at low pH, solutions of peroxymonosulfate are much more effective in delignification than peroxide. Consequently, peroxymonosulfate is a stronger oxidizing agent than peroxide. Springer also suggested that increasing the pH with sodium hydroxide may reduce attacks on carbohydrates (cellulose) without reducing the lignin removal effectiveness. He found that dimethyldioxirane delignification occurred most effectively at a pH of 11. Under this alkaline condition, however, cellulose was degraded and the delignification of aspen was found to be inadequate. Peroxymonosulfate reactions can occur at lower pHs, reducing degradation. Springer's work suggested that the source of the peroxymonosulfate ion does not affect bleaching ability. He also suggested that peroxymonosulfate could be generated *in-situ* with hydrogen peroxide and sulfuric acid to improve the yield of mechanical, or semi-mechanical, or even possibly chemical pulps. Consequently, peroxymonosulfate could be used to restore or enhance the strength of unbleached softwood kraft wastepaper. Peroxymonosulfate could be used as a replacement for chlorine based bleaching, and to deligninify many agricultural residues.

Springer and McSweeny(8) in 1993 investigated the usefulness of treating pulps with peroxymonosulfate before oxygen delignification. This was done to improve delignification without the use of chlorine and to prevent cellulose degradation from excessive oxygen delignification. In this study, they concluded that pretreatment with peroxymonosulfate was as effective as chlorine pretreatment, as long as transition metals were removed before hand. DTPA was used as a chelation agent, though they suggested that mineral acid treatments would be as effective for metal ion removal. They theorized that metal ions cause peroxymonosulfate to form radicals which attack cellulose. Thus, chelation may prevent excessive cellulose degradation. This study also suggested that peroxymonosulfate pretreatment is preferable to chlorine as no chlorinated organic compounds are formed. Dimethyldioxirane is more desirable than nitrogen dioxide as an oxygen delignification pretreatment because there is no gaseous phase. The peroxymonosulfate pre-treatments were done at a pH of 5.

Ragauskas(9) in 1993 suggested that the bleaching of softwood kraft pulps with monopersulfate compounds is significantly improved when acetone is used as a catalyst. The viscosity of water/acetone bleaching with peroxymonosulfate was greater than the viscosity of water/no acetone bleaching, suggesting lower degradation. For example, in the water only system, the kappa number was reduced 6.4 points. In the water/acetone system the kappa number was reduced 13.6 points. When water and acetone is used, most of the lignin is removed during bleaching rather than extraction. It was also found that dimethyldioxirane can be generated *in-situ* before the addition of pulp. Thus the need for aqueous acetone slurries with pulp is eliminated, reducing acetone requirements. The most effective pre-mixing time for the bleaching liquor was 5 minutes. Additional pre-mixing actually reduced bleaching effectiveness.

In 1993 Lee, Hunt, and Murray(10) showed that dimethyldioxirane (they refer to it as activated oxygen, or 'A') reacts with lignin through an electrophilic oxidation, similar to elemental chlorine and chlorine dioxide. Since the reaction is similar, residual lignins can be rendered soluble for caustic extraction. They also concluded that dimethyldioxirane can completely replace chlorine based bleaching agents, is effective on both hardwood and softwood kraft pulps, and there is little yield loss in the activated oxygen stage (dimethyldioxirane). There was a greater reduction in kappa number, with greater strength, using activated oxygen rather than oxygen delignification. The activated oxygen pulp had similar performance with a chlorine based bleaching on the same pulp. In this study, however, extraction after activated oxygen bleaching reduced the kappa number further. It was also found that the charge of acetone is directly proportional to the amount of dimethyldioxirane formed *in-situ*. Sequences studied were OAE, AEDED, OAEP, AEP, and (C+D)ED. This work is a basis for similar full sequence studies.

In May 1994, Lee, Hunt, and Murray(11) presented another article on activated oxygen bleaching. This work was conducted on unbleached and oxygen delignified kraft pulps. It was suggested that electrophilic reagents (such as dimethyldioxirane) react with the electron-rich aromatic and olefinic structures present in lignin, but not with electron poor cellulose. This is probably why dimethyldioxirane is such a selective bleaching agent. This work supported their earlier statements that dimethyldioxirane can equal the performance of chlorine based compounds. Some sequences tested in this study included OAEopQP, OAEoP, AD, and AO (Q is chelation). A peroxide brightening stage used after activated oxygen (dimethyldioxirane) bleaching gave final pulp brightnesses near ninety percent compared to eighty percent when activated oxygen was not used. However, the authors suggest that a final peroxide bleaching stage on low kappa number pulps can reduce strength. They suggested further research in this area.

A study recently published by McGrouther and Allison(12) suggests that pretreatment with dimethyldioxirane greatly enhances oxygen delignification of kraft pulps. Dimethyldioxirane was found to be quite selective in lignin removal, and pretreatment with dimethyldioxirane improved later oxygen stage selectivity. This is important as oxygen delignification can only remove about 50% of the lignin before the pulp is excessively degraded. McGrouther and Allison found that the absence of interstage washing allowed peroxide and dimethyldioxirane to be carried over to the next stage, improving bleaching performance. They also learned that chelation is necessary to minimize cellulose degradation. When dimethyldioxirane is decomposed by metal ions, free radicals are formed which attack cellulose. Chelation reduced peroxymonosulfate consumption by 50%. It was also found that increasing peroxymonosulfate charge improves overall delignification selectivity. High temperatures and long reaction times increase peroxymonosulfate consumption. Though a moderate reaction temperature and a short reaction time are optimum pre-treatment conditions. Increased pH will improve later oxygen delignification due to less acid carry over. However peroxymonosulfate consumption increases. The authors suggest that additional work is needed to study this. It was also found that the addition of hydrogen peroxide during the dimethyldioxirane stage reduced selectivity (especially at low concentrations of peroxymonosulfate), but increased lignin removal. However, peroxide in a subsequent oxygen stage improves selectivity. An unusual comment was that chlorine dioxide was better at removing lignin while maintaining pulp viscosity than dimethyldioxirane. The authors suggested that more work is required to develop improved peroxymonosulfate treatments to achieve the same effectiveness and selectivity of chlorine dioxide.

At the 1994 Executives' Conference in Atlanta, McDonough(13) presented a report on the Institute of Paper Science and Technology's progress in the area of environmentally friendly bleaching processes. Their work has suggested that the dimethyldioxirane stage leads to much brighter pulps when placed early on in bleaching sequences. Dimethyldioxirane was found to give the highest level of brightness compared to any totally chlorine free sequences while maintaining pulp quality. Sequences that were compared were OAQP and OQPA. The OAQP had much higher brightnesses and increased lignin removal, with a higher effectiveness at higher dimethyldioxirane charges. (Q is a metal removal stage, A is a dimethyldioxirane stage.)

Francis *et al.*(14) in 1994 presented a comprehensive study on the effect of metal ions on peroxymonosulfate decomposition. This study suggests that there is a significant increase in peroxymonosulfate decomposition when metal ions are present, especially cobalt. Peroxymonosulfate decomposition is more significant when the pH is less than six.

Lorås(15) gives specific details on peroxide and dithionite bleaching. It has been found that dithionite reductive bleaching is most effective at 70°C, 4% consistency, and a pH of 5-6. A buffer is required to prevent the pH from dropping during bleaching. Bleaching is quite quick (10-15 min), and subsequent bleaching with SO_2 increases brightness. Though iron will discolor pulp in dithionite bleaching, earlier chelation should prevent this problem. Dithionite mixtures need to be made just before bleaching as they quickly degrade with oxygen. Peroxide bleaching is improved at higher consistencies (10-20%) and at a pH of 10-11. As with peroxymonosulfate, chelation is required to improve peroxide bleaching.

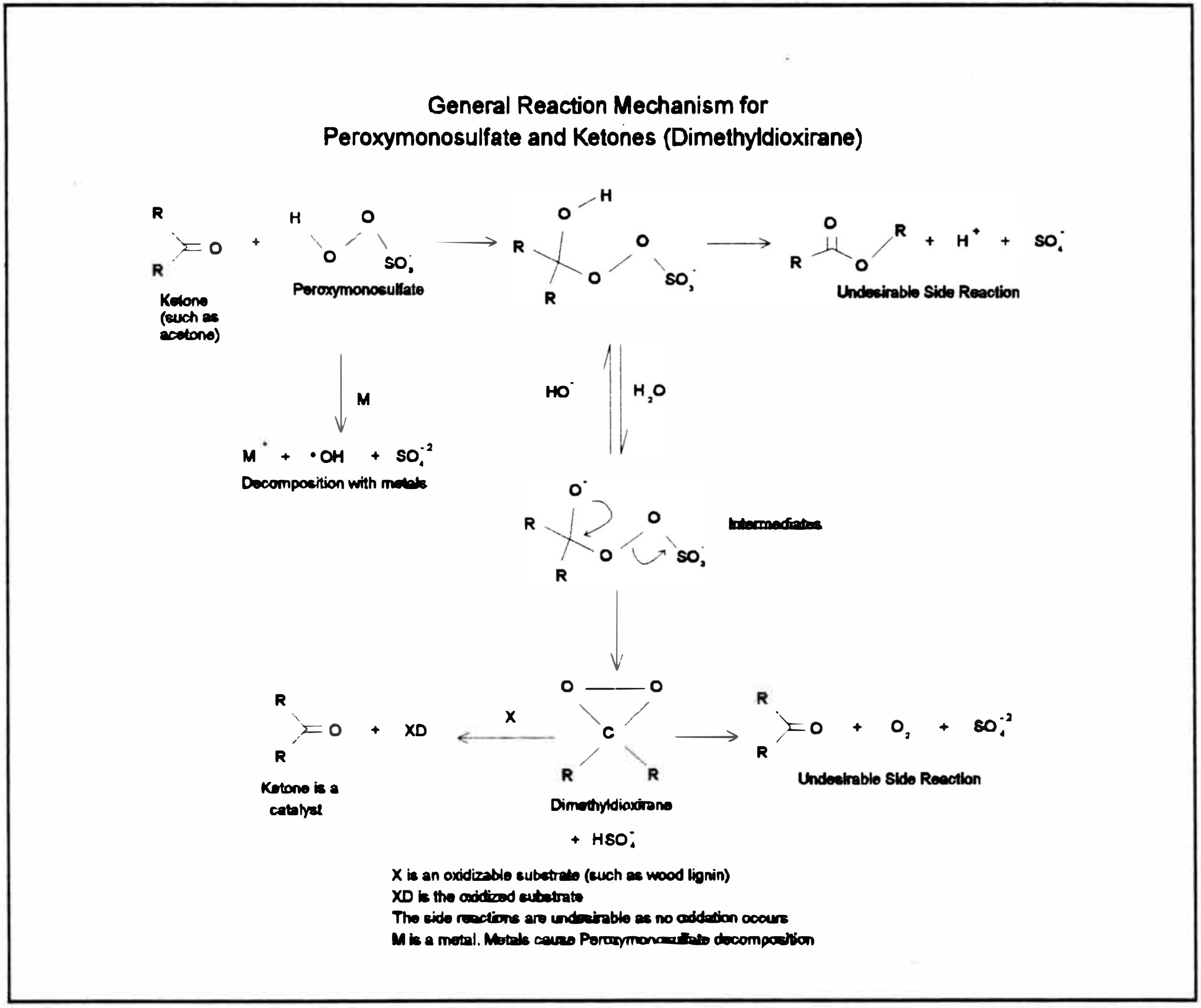
Problem Statement & Objective

This study was conducted to determine if dimethyldioxirane can be used to replace chlorine dioxide in full sequence bleaching with comparable increases in brightness, and low losses in strength. The main goal was to find a full sequence bleaching utilizing peroxide, caustic, dithionite, and dimethyldioxirane that matched the performance of a similar chlorine dioxide sequence.

Literature Analysis

From these studies, it is seen that a general reaction pathway has been determined for the electrophilic oxidation of lignin by dimethyldioxirane. This pathway is shown in figure 1.

Figure 1 (9, 12)


General Reaction Mechanism for Peroxymonosulfate and Ketones (Dimethyldioxirane)

X is an oxidizable substrate (such as wood lignin)
XD is the oxidized substrate
The side reactions are undesirable as no oxidation occurs
M is a metal. Metals cause Peroxymonosulfate decomposition

Dimethyldioxirane can be produced from the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (commercially known as Oxone, produced by DuPont). This salt is a source of the peroxymonosulfate ion ($HOOSO_3^-$) which then reacts with acetone through various intermediates to give dimethyldioxirane. The formation and subsequent reduction of dimethyldioxirane is exceedingly quick. In the presence of an oxidizable substrate (such as lignin), the dimethyldioxirane becomes an effective oxidant.(9) Peroxymonosulfate will preferentially react with the electron-rich structure of lignin over the electron-poor structure of cellulose. The side reactions can be controlled by pH. Another significant reaction is the decomposition of peroxymonosulfate with metal ions. This is a preferred reaction for peroxymonosulfate; so metal ions significantly increase chemical consumption. The free radicals that are formed attack cellulose, degrading the pulp. Consequently, chelation may increase selectivity. Side reactions need to be minimized to reduce reactions which consume chemical, but do no useful bleaching.

Most of the studies done thus far have investigated the usefulness of dimethyldioxirane as either a pre-treatment for oxygen delignification or as a short sequence bleaching agent. Some work has been done in regards to utilizing dimethyldioxirane for full sequence bleaching (such as the work done by Lee *et al.*(10,11)). However, in Lee *et al.*'s study, chlorine dioxide was used, which is chlorine based. Though many authors suggest that dimethyldioxirane can be as effective as full sequence chlorine based bleaching, few have actually done anything along that line. McGrouther and Allison(12) commented that chlorine dioxide was better at removing lignin while maintaining pulp viscosity than dimethyldioxirane. This is contrary to the comments of the other authors.

The objective of this project was to use chlorine free compounds for full sequence bleaching. It was hoped that dimethyldioxirane bleaching is an effective alternative to chlorine dioxide in full sequence bleaching. It is a goal of this study to investigate if dimethyldioxirane can perform as well as chlorine dioxide. The elimination of chlorine based bleaching agents is becoming a significant concern due to public pressure and possible legislation.

Experimental

Oxone (peroxymonosulfate, produced by DuPont) was used to produce the dimethyldioxirane used for bleaching. Other methods of generation, while possibly more cost effective, have not been perfected and may not always form dimethyldioxirane.

For this study, a commercial oxygen delignified hardwood kraft pulp was donated by Consolidated Papers in Wisconsin Rapids, WI. Oxygen delignification was chosen as the first bleaching stage because approximately half of the lignin was removed without the use of chlorine. A sample of unbleached kraft from the same process was also donated.

Based upon the work of Murray and others (2-5), the pH for this study was set at 7.0 to 7.5. Though Springer's(7) work suggested that peroxymonosulfate has greater oxidizing power at lower pHs (from 2 to 5), he found that a pH around 7 reduces carbohydrate attack. A bicarbonate buffer was created to keep the pH in the desired range. The amount of bicarbonate required for buffering was determined experimentally. This pH was selected as it minimizes the undesirable side reactions which consume peroxymonosulfate (as seen in figure 1).

Springer, McSweeny, Francis, and others saw that metal ions will significantly decompose peroxymonosulfate. McGrouther and Allison(12), for example, found that chelation decreased peroxymonosulfate consumption by 50%. Peroxymonosulfate decomposition does no useful bleaching, and McGrouther and Allison(12) suggested that the free radicals formed can actually be destructive toward cellulose. To ensure that complete chelation occurred, EDTA was used remove the metal ions. Chelation was done by adding EDTA to the pulp during dimethyldioxirane (A) and peroxide (P) bleaching stages. EDTA was added at 0.5% on OD fiber in with the acetone and dilution water for the dimethyldioxirane stages, and was added to the dilution water for peroxide stages. Deionized water was used in all stages for dilution and washing to minimize metal ion introduction. An additional side study was performed to look at the effects of chelation. Single stage DMD bleaching (OAE) was done using different chelation conditions and addition rates. Four DMD stage bleachings were done in which the pulp was initially washed, but no EDTA was added; no wash and no EDTA; no wash and 1% EDTA; and no wash and 5% EDTA.

Though consistency is a factor that could affect bleaching effectiveness, this study used a dimethyldioxirane stage consistency of 6%. Other stages were run at 8% consistency (except for dithionite which was run at 4%). 8% is considered the maximum consistency that can be thoroughly mixed in plastic bags by hand.

Lee *et al.*(10) suggested that the charge of acetone present before peroxymonosulfate addition is proportional to the quantity of dimethyldioxirane formed. Though one could add far excess acetone, this would not be cost effective. Initial laboratory work suggested that mixing the acetone and bicarbonate with the dilution water, then mixing the dilution water with the pulp for 5 minutes, and then adding dry Oxone to the pulp gave the greatest bleaching effectiveness. DMD stages had a 1.5 mole ratio of acetone to peroxymonosulfate.

The temperature for the dimethyldioxirane (A) stages was 45°C. All other stages were run at 65°C, which is typical. Dilution water for all stages was heated to around 65°C before addition. The dimethyldioxirane stage was run for one hour as Springer and McSweeny(8) found that most lignin reduction occurs during the first hour.

Oxone was added at three percent activated oxygen concentration (not Oxone) on dry fiber. It was assumed that each peroxymonosulfate molecule gives up two activated oxygen molecules in the conversion calculation. Work done by Springer *et al.*(8), Lee *et al.*(11), and McGrouther and Allison(12) suggested that this charge gives excellent performance. After this point, the marginal returns diminish. One percent NaOH extractions for 30 minutes at 65°C were used after the dimethyldioxirane stages. Four percent NaOH extractions run for 1.5 hours at 65°C were used after the other stages. Extractions after dimethyldioxirane stages were at a lower percent NaOH because Ragauskas(9) had observed that most lignin is removed in dimethyldioxirane bleaching, rather than extraction. The Oxone was added to the pulp slurry as a dry powder because initial work suggested that this gave the greatest brightness increase.

Since dimethyldioxirane is an oxidative bleaching agent, subsequent reductive bleaching with dithionite was used to prevent later color reversion and consume any residual oxidizing agents. Dithionite bleaching was conducted at 4% consistency and a pH of 5-6. It was done at 65°C for 15 minutes. Dithionite mixtures were made just before bleaching as they quickly degrade in the presence of oxygen.

Chlorine dioxide was prepared by dissolving 6.7 g of sodium chlorite into 1000 ml of ice cold water. Fifty ml of 4 N sulfuric acid was added to the sodium chlorite solution over a 10 minute time span. After the solution was prepared, the strength of the chlorine dioxide solution was determined. This was done by adding 10 ml of the chlorine dioxide solution, 150 ml of distilled water, 10 ml of 4 N sulfuric acid, and 20 ml of 1 N KI solution to a flask. This mixture was then titrated with 0.2 N $Na_2S_2O_3$ to a pale yellow color. Starch indicator solution was then added, and the titration continued until the solution was colorless. The concentration in equivalent Cl_2 was calculated. All chlorine dioxide stages were run at 8% consistency, 2% Cl_2 equivalent on OD fiber, at a pH of 3 to 5, and at 65°C for 1.5 hours. The strength of regular household bleach was determined like above for the one hypochlorite stage. It was run at 8% consistency, 2% Cl_2 equivalent on OD fiber, at a pH of 8.5 to 9, and at 65°C for 1.5 hours.

All peroxide stages were run at 8% consistency, 2% Cl_2 equivalent on OD fiber, at a pH of 10.5 to 11, and at 65°C for 1.5 hours. The peroxide stage also contained 0.5% EDTA on OD fiber for chelation.

Using the work of Eric Thompson(16), who optimized a single DMD stage bleaching sequence, optimizations were applied to an OAEP sequence. This sequence was chosen as it had the best performance of all the earlier DMD sequences. These optimum conditions consisted of initially adding 2% EDTA and dilution water to the fiber at 5.5% consistency. This mixture was allowed to sit at room temperature for 15 minutes, and then the pulp was washed. Optimum conditions for the DMD stage were 2.8% peroxymonosulfate on OD fiber, at 55°C, at a pH of 7 to 7.5, at 5.5% consistency for 0.5 hours. In the step-wise optimization, the Oxone charge was added in three steps. One-third was added at 0 minutes, one-third at 15 minutes, and one-third at 30 minutes. The total bleaching time was 1 hour.

All bleaching experiments were done in Zip-lock plastic bags. The bags were doubled to ensure no leakage into or out of the baggies. To give greater experimental precision, two identical bleachings were run side by side for each sequence studied. For each stage, the chemicals and dilution water required were added to the pulp and thoroughly kneaded to mix. During any bleaching stage, the bags were kneaded, and pH checked and adjusted if necessary, every 15 minutes. NaOH and acetic acid were used to adjust the pH. After each bleaching stage in the sequence, a portion of the pulp was removed from each bag to make handsheets for brightness, viscosity, and strength determination. The pulp was washed with a large quantity of distilled water in a Buchner funnel after each stage. By taking these samples, each bleaching stage could be evaluated for brightness increase and pulp degradation. 1.2 g handsheets (approximately 40 lb sheets) were made from the pulp samples on a British Sheetmaker according to TAPPI Standards. The basis weight of each sheet was determined. All pulp samples were refrigerated if handsheets were to be made at a later time. After drying to a constant dryness in constant humidity room, the brightness (Tappi Standard T425 om-92) and strength was measured. Strength was quantified through the tensile measurements (Tappi Standard T 404 cm-92). Samples of the pulp were dried after an acetone wash for viscosity determination (Tappi Standard T230). A 150 ml viscometer was used for the viscosity measurements. Two viscosity measurements, within 1 second of each other, were taken for each sample. After testing, all the data was collected and organized in a database. Strength indexes were calculated for each sample. Statistical analyses, such as t-tests, were used to determine if there were any significant differences in strength and optical properties between the various bleaching sequences. The calculations for these analyses were done using Quattro Pro Win 6.0. All optical and strength testing was done following TAPPI standards.

Definition of sequence terms:

O = Oxygen Delignification stage
A = Dimethyldioxirane stage (DMD)
D = Chlorine dioxide stage (ClO_2)
H = Hypochlorite stage (bleach - HOCl)
P = Hydrogen peroxide stage (H_2O_2)
E = Extraction stage (NaOH)

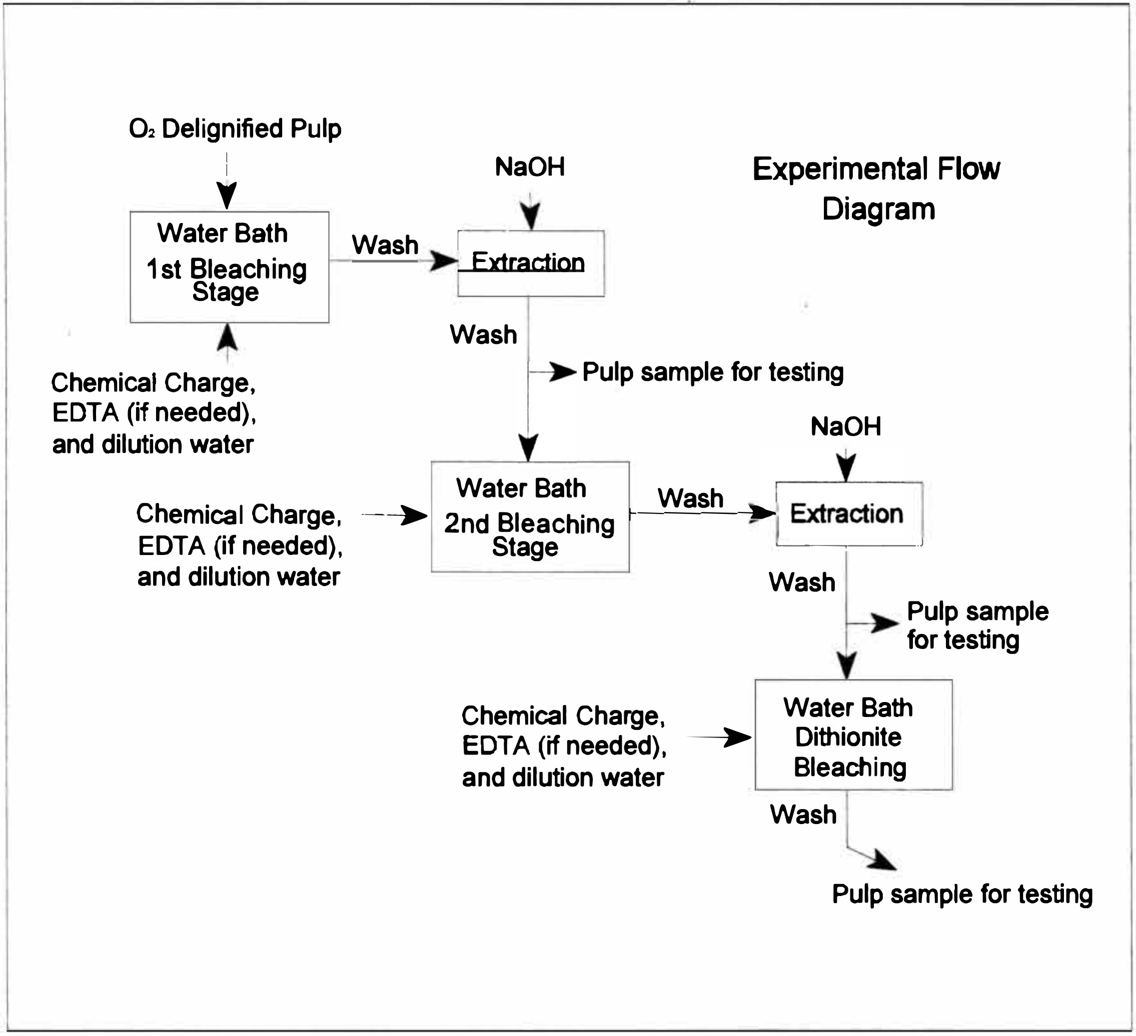
Table 1 - Experimental Conditions Summary

Stage	Temp °C	pH	% Consistency	Chemical on OD fiber %	Reaction time hr	Chelation on OD fiber
O	from Consolidated Paper					
A	45	7-7.5	6	3[†]	1.0	0.5% EDTA
D	65	3-5.5	8	2[*]	1.5	None
H	65	8.5-9	8	2[*]	1.5	None
P	65	10.5-11	8	2[*]	1.5	0.5% EDTA
E	65	11	8	8	1.5	None
after A	65	11	8	1	0.5	None
Dithio	65	5-6	4	2	0.25	None

[†] Percent activated oxygen (see calculations)
[*] Percent equivalent Cl_2 (see calculations)

The chlorine based sequences run were DED, OHEP, ODED, and ODEP. The DMD based sequences run were OAEP, OPAE, OPEAE, OEAEP, O(A/P)E, and OAEA. Some DMD plus chlorine dioxide sequences were run and they were DEAE and AEDE. A chelation side study was run using an OAE sequence. Optimized conditions were applied to an OAEP sequence.

Figure 2


O₂ Delignified Pulp
NaOH
Experimental Flow Diagram
Water Bath
1st Bleaching Stage
Wash
Extraction
Chemical Charge, EDTA (if needed), and dilution water
Wash
Pulp sample for testing
NaOH
Chemical Charge, EDTA (if needed), and dilution water
Water Bath
2nd Bleaching Stage
Wash
Extraction
Wash
Pulp sample for testing
Chemical Charge, EDTA (if needed), and dilution water
Water Bath
Dithionite Bleaching
Wash
Pulp sample for testing

Results

Table 2 - Data Summary

Sequence	Brightness %	Tensile Index $N \cdot m^2/g$	Viscosity cP
O_2 Delignified	43.7	32.3	18.0
OHEP	72.5	24.02	
ODED	82.1	25.2	
ODEP	81.2	25.46	
OAEP after OA	70.4	24.43	10.7
OAEP	77.1	22.74	10.2
OAEP(dithionite)	78.5	23.51	
OPAE after OP	54.0	25.12	15.4
OPAE	74.5	21.25	9.9
OPAE(dithionite)	76.5	25.16	
OPEAE after OPE	54.2	17.92	17.1
OPEAE	74.3	17.04	10.9
OPEAE(dithionite)	75.6	18.55	
OEAEP after OEAE	72.0	17.75	12.0
OEAEP	75.4	18.58	11.0
OEAEP(dithionite)	77.2	19.11	
OAEA after OAE	72.1	16.35	10.0
OAEA	78.2	19.58	8.4
OAEA(dithionite)	81.4	13.52	
O(A/P)E	72.4	18.03	8.3

Sequence	Brightness %	Tensile Index $N{\cdot}m^2/g$	Viscosity cP
Kraft Unbleached	29.4	20.7	
DED	80.0	17.73	
DEAE after DE	65.9	10.12	15.7
DEAE	77.9	15.02	10.8
DEAE(dithionite)	78.5	16.15	
AEDE after AE	64.2	11.76	11.9
AEDE	79.9	12.73	10.9
AEDE(dithionite)	81.2	17.98	
Optimized			
OAEP after OA	70.2	15.23	12.9
OAEP	75.5	18.68	11.2
OAEP(dithionite)	76.9	17.29	
Step-Optimized			
OAEP after OA	73.2	17.48	10.0
OAEP	75.2	18.25	9.9
OAEP(dithionite)	78.9	17.82	
Chelation Study	OAE	Sequence	
No wash No EDTA	71.0	16.45	10.9
Wash No EDTA	72.4	18.94	9.8
No wash 1% EDTA	71.4	20.45	10.3
No wash 5% EDTA	71.0	16.37	10.8

Table 3 - Brightness Statistical Summary (t-test comparisons)

	t Brightness	Conclusion
ODED vs OAEP	10.52	S,5% ODED Significantly Brighter
ODED vs OPAE	16.76	S,5% ODED Significantly Brighter
ODED vs OPEAE	22.58	S,5% ODED Significantly Brighter
ODED vs OEAEP	16.55	S,5% ODED Significantly Brighter
ODED vs OAEA	4.11	S,5% ODED Significantly Brighter
ODEP vs OAEP	9.40	S,5% ODEP Significantly Brighter
ODEP vs OPAE	16.93	S,5% ODEP Significantly Brighter
ODEP vs OPEAE	25.59	S,5% ODEP Significantly Brighter
ODEP vs OEAEP	17.45	S,5% ODEP Significantly Brighter
ODEP vs OAEA	1.35	NS,5% ODEP's Brightness = OAEA's
DED vs DEAE	6.04	S,5% DED Significantly Brighter
DED vs AEDE	-5.48	S,5% AEDE Significantly Brighter
OAEP vs OAEP Opt	3.76	S,5% OAEP Significantly Brighter
OAEP vs OAEP Step-Opt	-1.00	NS,5% OAEP's Brightness = OAEP Step-Opt's
OAEP Opt vs OAEP Step-Opt	-4.43	S,5% OAEP Step-Opt Significantly Brighter
Chelation	OEA	Sequence
Regular vs No wash No EDTA	-2.10	NS,5% Regular's Brightness = No Wash No EDTA's
Regular vs Wash No EDTA	-6.19	S,5% Wash No EDTA Significantly Brighter
Regular vs No wash 1% EDTA	-3.54	S,5% No Wash 1% EDTA Significantly Brighter
Regular vs No wash 5% EDTA	-1.94	NS,5% Regular's Brightness = No Wash 5% EDTA's
F-test analysis comparing the chelation groups suggests that there was a significant brightness difference between the groups. F=9.03 > F-critical=3.09 Washing had the largest affect of increasing brightness.		

See appendix 2 for t-test calculations. If the calculated t is less than the two-tailed critical t, then there is no significant difference between the two sets of data (NS).

Table 4 - Tensile Statistical Summary (t-test comparisons)

	t Tensile	Conclusion
ODED vs OAEP	2.05	NS,5% OAEP's Strength = ODED's
ODED vs OPAE	0.05	NS,5% OPAE's Strength = ODED's
ODED vs OPEAE	11.60	S,5% ODED Significantly Stronger
ODED vs OEAEP	5.71	S,5% ODED Significantly Stronger
ODED vs OAEA	7.30	S,5% ODED Significantly Stronger
ODEP vs OAEP	1.80	NS,5% OAEP's Strength = ODED's
ODEP vs OPAE	0.41	NS,5% OPAE's Strength = ODED's
ODEP vs OPEAE	12.23	S,5% ODEP Significantly Stronger
ODEP vs OEAEP	5.98	S,5% ODEP Significantly Stronger
ODEP vs OAEA	7.63	S,5% ODEP Significantly Stronger
DED vs DEAE	0.55	NS,5% DEAE's Strength = DED's
DED vs AEDE	-0.96	NS,5% AEDE's Strength = DED's
OAEP vs OAEP Opt	4.73	S,5% OAEP Significantly Stronger
OAEP vs OAEP Step-Opt	3.91	S,5% OAEP Significantly Stronger
OAEP Opt vs OAEP Step-Opt	-0.66	NS,5% OAEP Opt's Strength = OAEP Step-Opt's
Chelation	OEA	Sequence
Regular vs No wash No EDTA	4.31	S,5% Regular Significantly Stronger
Regular vs Wash No EDTA	4.12	S,5% Regular Significantly Stronger
Regular vs No wash 1% EDTA	3.72	S,5% Regular Significantly Stronger
Regular vs No wash 5% EDTA	5.94	S,5% Regular Significantly Stronger
F-test analysis comparing the chelation groups suggests that there was no significant tensile strength difference between the groups. F=2.09 < F-critical=3.09		

Figure 3

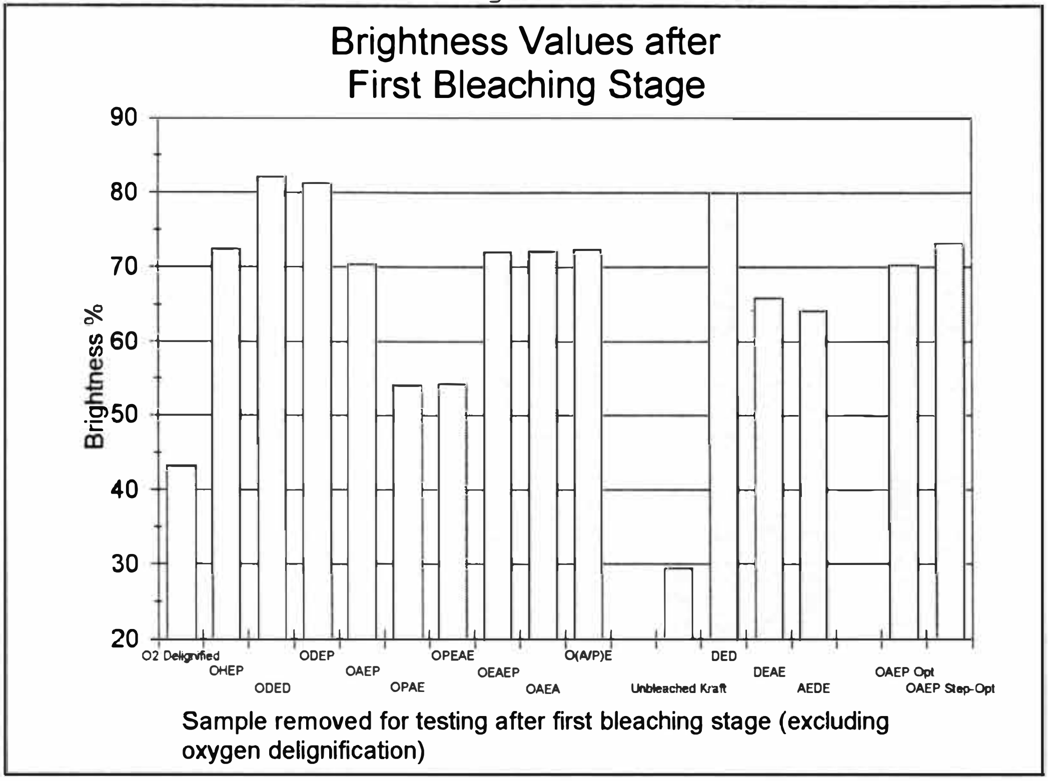


Figure 4

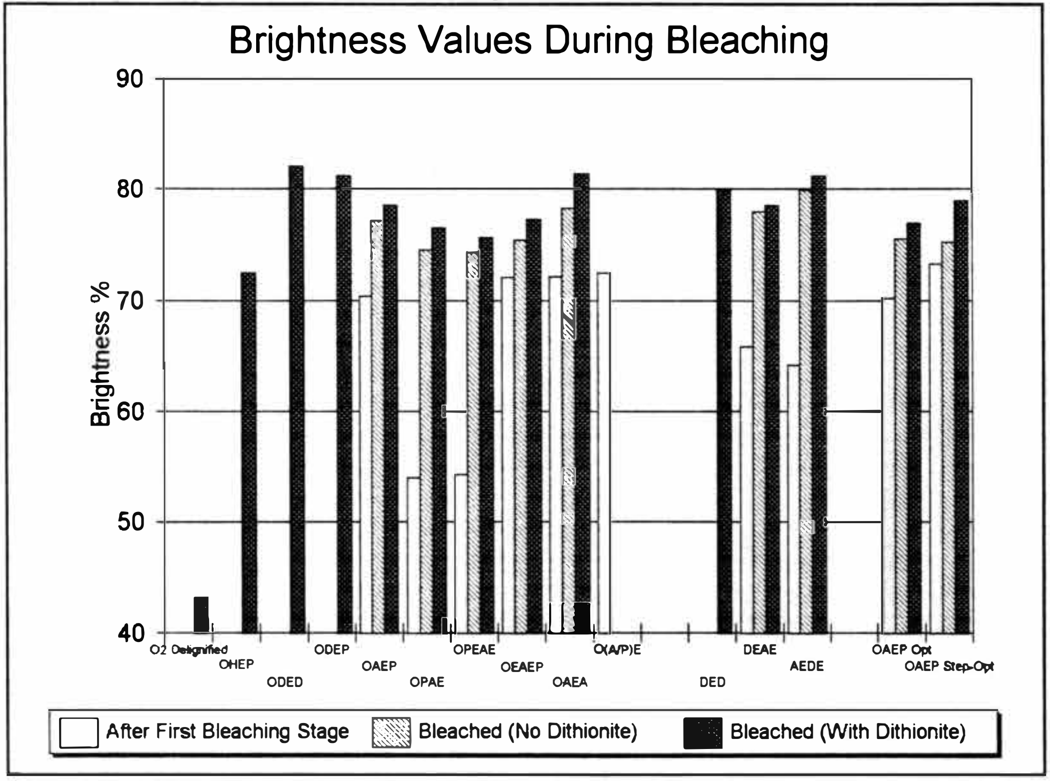


Figure 5

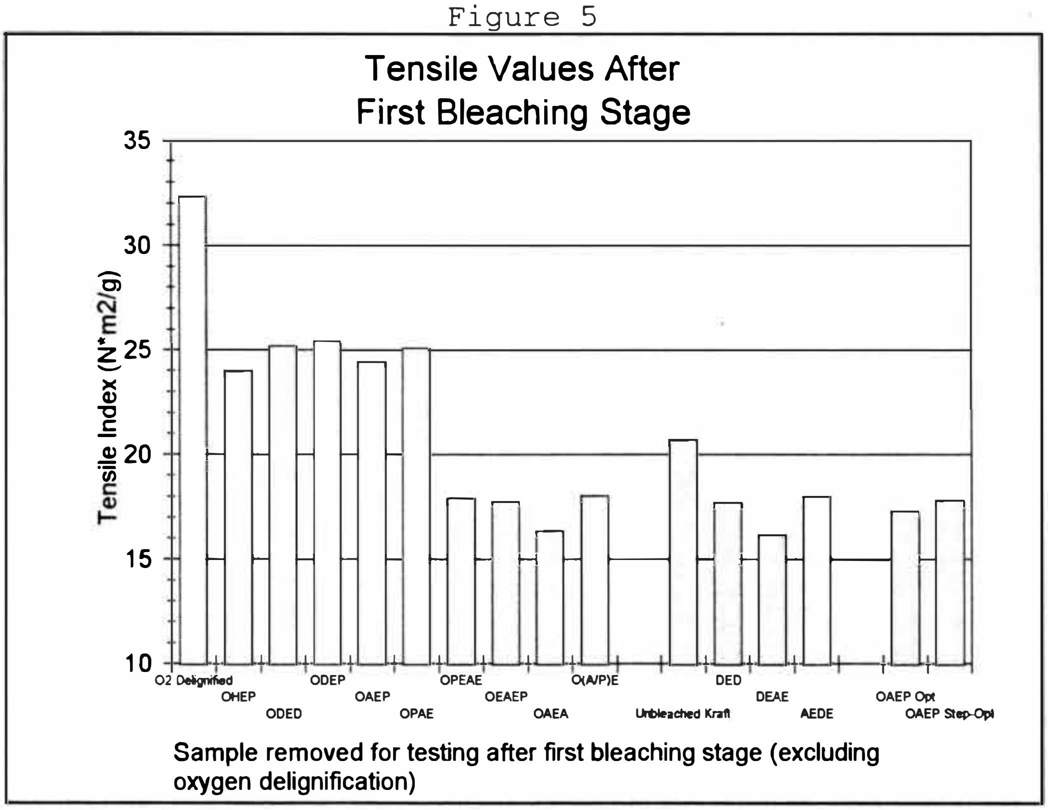


Figure 6

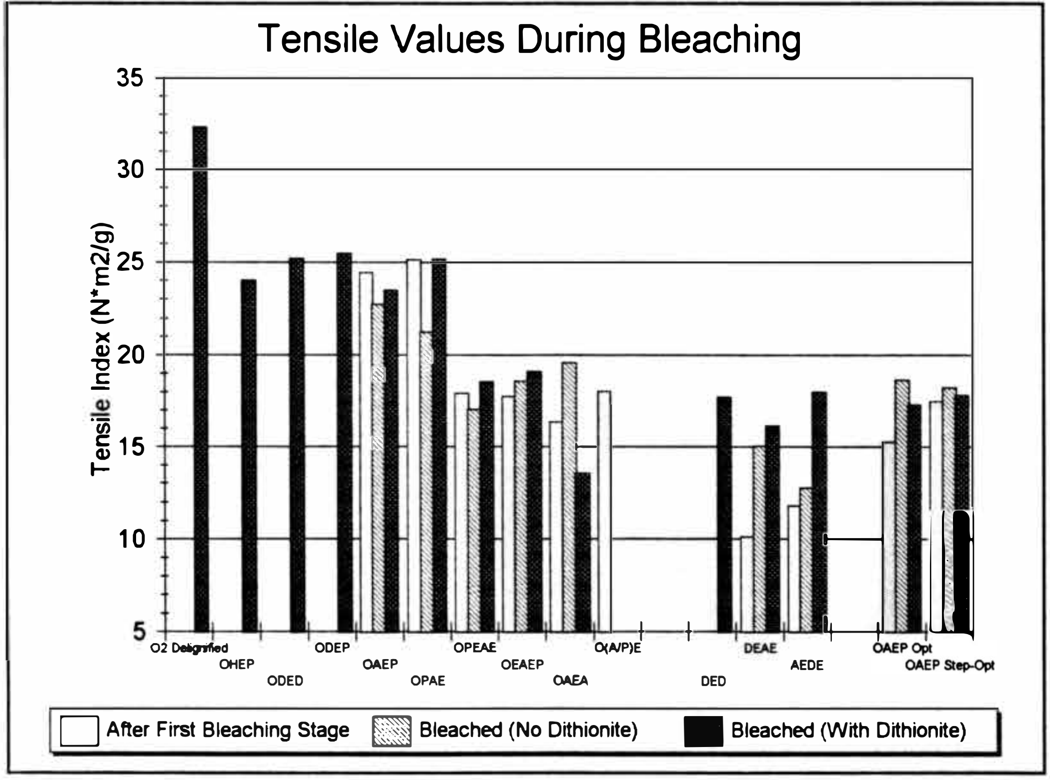


Figure 7

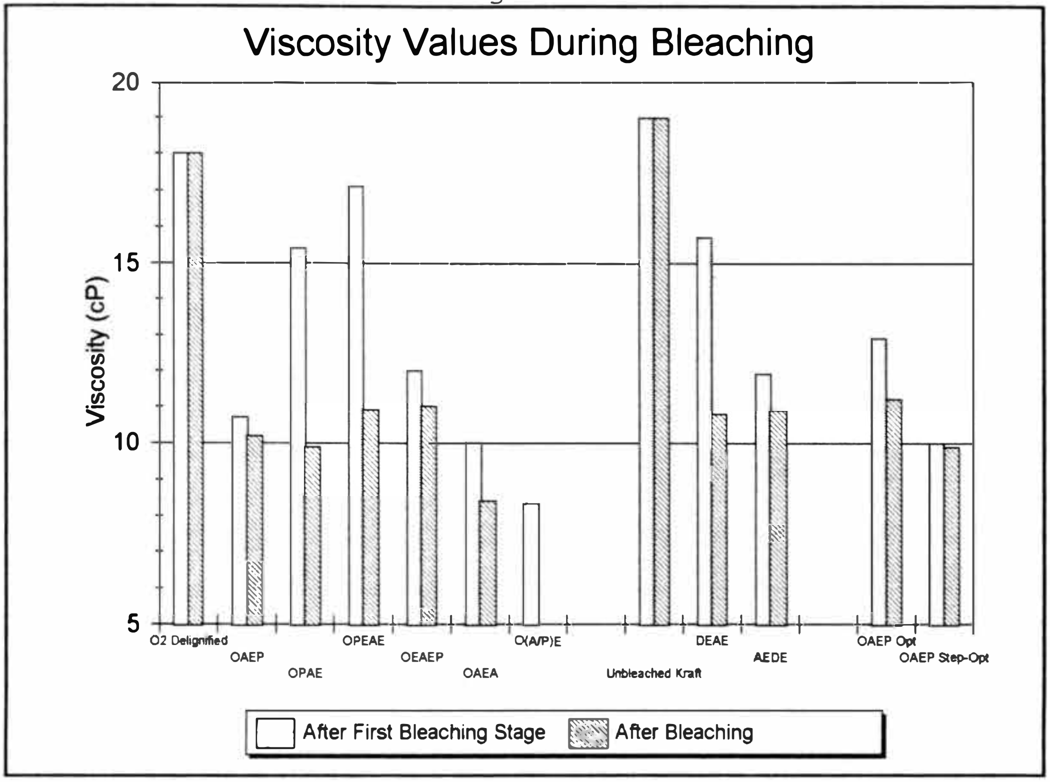
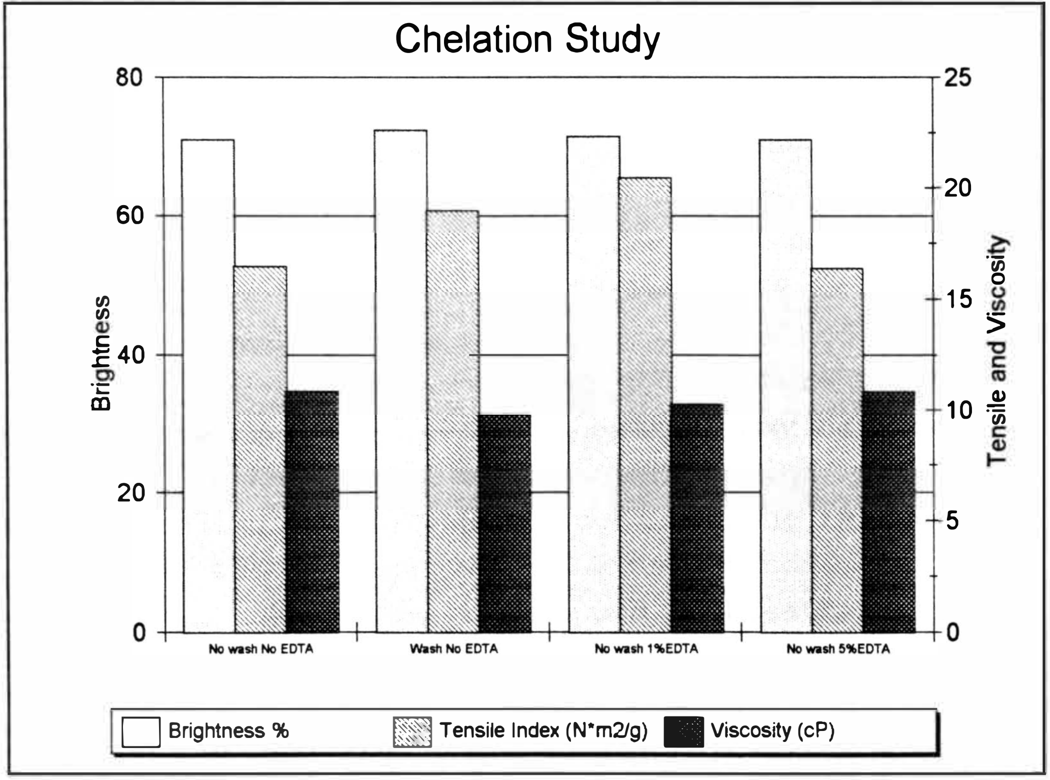


Figure 8



Discussion

t-tests were utilized to determine whether the different data sets belong to the same populations. If a data set belongs to the same population as another data set, the result is a non-significant (NS) difference. Thus statistically the data sets are equivalent. The calculations can be seen in appendix 2. To reach the conclusions seen in tables 2 and 3, the calculated t value for the two-tailed test was compared to the critical value. If the calculated t is larger than the critical value, then the data sets are statistically significantly different (S) at the given confidence level. All analyses were run at 95% confidence (α = 5%).

Statistical analysis, as shown in table 3, suggested that only the DEAE and AEDE sequences matched the strength of the DED sequence. Only the OAEP and OPAE sequences matched the strength of the ODED and ODEP sequences. All other DMD full sequences had tensile strengths that were statistically significantly lower than the chlorine dioxide based sequences.

An interesting trend observed in figure 6 is that the tensile increased as the bleaching sequence progressed. For example, the OEAEP sequence had a tensile index of 17.75 $N \cdot m^2/g$ after OEAE, 18.58 $N \cdot m^2/g$ before dithionite, and 19.11 $N \cdot m^2/g$ after dithionite. One would expect the strength to drop with additional bleaching. It is possible that this trend is an artifact of the experimental procedures. Even though the pulp was carefully washed with large quantities of distilled water between stages, some residual bleaching chemical may have remained. Generally, the pulp was refrigerated two to four days before handsheets were made. During storage, the residual chemical may have continued to react, destroying cellulose. However, dithionite, which is a reductive bleaching agent, would neutralize the residual chemicals. Thus the strength would be unaffected.

As expected, the viscosity dropped as bleaching increased. For example, the viscosity of the OEAEP sequence was 12 cP after OEAE, and was 11 cP after the rest of bleaching. This trend is expected as additional bleaching is generally at the expense of cellulose degradation. It is known that the viscosity can drop a significant amount before strength is affected. In work done by Eric Thompson, it was observed that there was little correlation between the brightness increase and the strength drop. However, viscosity was strongly correlated. Thus, the viscosity data may be more useful in quantifying the effect of the bleaching and cellulose degradation.

It was also observed that an DMD stage reduces the strength more than a D stage (16.35 N·m^2/g vs 25.46 N·m^2/g). Also, an DMD stage reduces strength more than a P stage (16.35 N·m^2/g vs 17.92 N·m^2/g). An (A/P) stage reduced strength less than an A stage alone (18.03 N·m^2/g vs 16.35 N·m^2/g), however the viscosity was lower (8.3 cP vs 10 cP), suggesting more cellulose degradation.

As seen in table 2, only the OAEA sequence had a brightness as high as ODEP. No other DMD sequence matched the brightness of the ODED sequence. All other DMD sequences had brightnesses that were statistically significantly lower than the chlorine dioxide sequences. As seen in figure 4, as bleaching progressed, brightness increased. It can also be seen, comparing OPAE and OAEP after the first sampling, that DMD increases brightness more than peroxide (54.0% vs 72.1%). However, this is at the expense of strength as observed in figure 5. An interesting observation is that an (A/P) stage may increase brightness with less strength loss than an A stage alone.

Chelation was found to have little effect on strength or viscosity, suggesting that the metal ion decomposition radicals suggested by McGrouther and Allison (12), if they exist, did not attack cellulose significantly. However, it was found that chelation (using EDTA) increases brightness. This may be due to reduced decomposition of bleaching chemical. Also, washing the pulp before bleaching also increased brightness. This could be due to fines removal which reduces chemical consumption, or the removal of residual magnesium ions left in the pulp from the oxygen delignification process.

The optimum conditions, as determined by Eric Thompson, were applied to an OAEP sequence. The Oxone charge was also added to this sequence, under optimum condition, in steps. This was done because Oxone reacts quickly with the pulp. By adding the chemical charge in steps, the reaction efficiency may be increased. It was found that there was no strength difference between optimized and the step-optimized (in which optimum conditions were used, but the Oxone charge was added in steps) sequences. However, the step-optimized sequence had a higher brightness. It was also observed that the optimized sequences had lower strength and brightness than the unoptimized conditions. The first sequences done, OAEP and OPAE, had significantly higher brightnesses and strength properties than all other DMD sequences. Why this happened is not clear. Perhaps an optimum condition was accidentally achieved, and not reached in later work.

Dimethyldioxirane did not achieve both the strength and optical properties of chlorine dioxide. However, it is possible that it could perform better with additional optimization. This work suggests that additional work must be done to optimize full sequence bleaching with dimethyldioxirane.

Conclusions

Dimethyldioxirane was found to match the strength, but not the brightness of chlorine dioxide. As well, dimethyldioxirane may be harsher on cellulose than chlorine dioxide, as signified by lower viscosities. However, Eric Thompson's optimized conditions improved bleaching with out a great deal of strength loss. Other conditions, such as a step-wise addition of bleaching chemical and adding peroxide in with the DMD, also increased bleaching.

Recommendations

It was seen that dimethyldioxirane was able to match the strength, and came close to the brightness achievable with chlorine dioxide. Additional optimization may allow dimethyldioxirane to perform as well as chlorine dioxide. It was seen that increased brightnesses were achieved by using a step-wise addition under Eric Thompson's optimized conditions. As well, the addition of peroxide in with the dimethyldioxirane may increase brightness. These are areas that should be pursued to further the optimization process for a full sequence. Additional optimization may also reduce chemical usage.

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Appendix 1 - Raw Data

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g
DED-1-1	1.245	62.9	80	79.6	1.595	1.24	1.621	1.07	16.58	16.85
DED-1-2	1.169	59.1	79.8	79.7	1.323	0.84	1.031		14.64	11.41
DED-1-3	1.616	81.7	79.5	79.5	1.06	0.81	1.221		8.49	9.78
DED-1-4	1.196	60.4	79.8	79.4	1.922	2.05	1.358	1.37	20.79	14.69
DED-2-1	1.48	74.8	79.5	79.7	2	1.59	2.062	1.42	17.48	18.03
DED-2-2	1.239	62.6	80.9	81.1	1.885	1.45	1.919	1.54	19.68	20.04
DED-2-3	1.331	67.3	80.3	79.5	2.064	1.24	1.664	0.89	20.06	16.18
DED-2-4	1.24	62.7	80.4	79.3	2.024	1.74	2.089	1.28	21.12	21.80
DED-2-5	1.395	70.5	80.9	80.9	1.885	1.12	1.815	1.17	17.48	16.83
AVG		66.9		80.0						17.73
OHEP-1-1	1.257	63.5	70.4	71.3	2.118		1.721	1.8	21.80	17.71
OHEP-1-2	1.246	63.0	71.5	71.8	2.387	1.54	2.432	2.04	24.79	25.25
OHEP-1-3	1.225	61.9	72	71.5	1.638		2.153	1.41	17.30	22.74
OHEP-1-4	1.241	62.7	72.3	71.8	2.481	1.8	2.813	1.52	25.87	29.33
OHEP-1-5	1.295	65.4	71.7	71.2	2.778	1.83	2.51	1.89	27.76	25.08
OHEP-2-1	1.068	54.0	70.9	71.9	2.003	2.13	1.839	1.11	24.27	22.28
OHEP-2-2	1.074	54.3	72.4	82.4	1.672	1.23	1.852	1.91	20.14	22.31
OHEP-2-3	1.052	53.2	72.3	73.5	1.962	1.92	2.258	1.78	24.13	27.77
OHEP-2-4	1.068	54.0	73	72.9	2.056		1.868	1.35	24.91	22.63
OHEP-2-5	1.065	53.8	71.9	72.4	2.352	1.84	2.118	1.71	28.57	25.73
		58.6		72.5						24.02

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g
ODED-1-1	1.236	62.5	82.2	83	2.365	1.7	2.478	1.7	24.76	25.94
ODED-1-2	1.287	65.0	82.5	82.2	2.4	1.7	2.674	1.86	24.13	26.88
ODED-1-3	1.291	65.2	81.7	81.7	2.295	1.32	2.773	1.9	23.00	27.79
ODED-1-4	1.339	67.7	83.7	83.3	2.706	2.23	2.738	2	26.15	26.46
ODED-1-5	1.276	64.5	82.8	82.9	2.26	1.25	2.658	1.75	22.92	26.95
ODED-2-1	1.282	64.8	82.5	83.3	2.617	1.67	2.714	1.83	26.41	27.39
ODED-2-2	1.286	65.0	81.7	82.2	2.47	1.87	2.44	1.49	24.85	24.55
ODED-2-3	1.269	64.1	80.7	80.9	2.011	1.17	2.454	1.64	20.50	25.02
ODED-2-4	1.232	62.3	81.4	81.4	2.37	1.51	2.405	1.9	24.89	25.26
ODED-2-5	1.322	66.8	81	80.5	2.429	1.51	2.69	1.94	23.77	26.33
		64.8		82.1						25.20
ODEP-1-1	1.352	68.3	80.1	80.3	2.609	1.82	2.682	1.68	24.97	25.67
ODEP-1-2	1.373	69.4	81.8	81.4	2.285	1.3	2.534	1.84	21.53	23.88
ODEP-1-3	1.441	72.8	81.9	81	3.082	1.81	3.219	2.12	27.67	28.90
ODEP-1-4	1.415	71.5	81.3	81.1	2.832	1.74	2.719	1.52	25.90	24.86
ODEP-1-5	1.378	69.6	81.1	83.3	2.996	1.85	2.902	1.6	28.13	27.25
ODEP-2-1	1.336	67.5	81.1	80.6	2.634	2.11	2.668	1.88	25.51	25.84
ODEP-2-2	1.349	68.2	81.1	80.9	2.644	2.16	2.55	1.73	25.36	24.46
ODEP-2-3	1.399	70.7	81.5	81.5	2.529	1.55	2.714	1.53	23.39	25.10
ODEP-2-4	1.425	72.0	80.7	80.9	2.787	2.03	2.583	1.84	25.31	23.45
ODEP-2-5	1.411	71.3	80.8	81.1	2.746	1.74	2.918	2.25	25.18	26.76
		70.1		81.2						25.46

O2-Delignified

B.W. = 80.5 g/m2

Sheet ID	Brightness	Tensile kg	Tensile Index 1 N*m2/g	Viscosity cP
O2 1-1	33.7	3.554	28.86	18
O2 1-2	31.6	4.016	32.62	
O2 1-3	33.8	4.035	32.77	
O2 1-4	37.8	3.087	25.07	
O2 1-5	36.1	3.909	31.75	
O2 1-6	34.4	4.298	34.91	
O2 1-7	36.4	4.113	33.40	
O2 1-8	36.3	4.239	34.43	
O2 1-9	37.4	4.454	36.17	
O2 1-10	38.0	4.009	32.56	
	35.5		32.3	

Unbleached Kraft

B.W. = 75.5 g/m2

Sheet ID	Brightness	Tensile kg	Tensile Index 1 N*m2/g	Viscosity cP
Kraft 1-1	20.5	2.583	22.37	19
Kraft 1-2	24.4	2.899	25.10	
Kraft 1-3	21.2	2.883	24.97	
Kraft 1-4	21.9	2.784	24.11	
Kraft 1-5	22.3	2.725	23.60	
Kraft 1-6	23.0	2.574	22.29	
Kraft 1-7	23.2	2.365	20.48	
Kraft 1-8	19.7	2.913	25.23	
Kraft 1-9	25.0	2.199	19.04	
Kraft 1-10	23.0			
	22.4		23.0	

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g	Viscosity cP
After A											
OAEP 1	1.262	63.8	69.8	69.7	2.158	1.18	2.695	1.84	22.12	27.63	10.7
OAEP 2	1.286	65.0	71.4	71	2.384	1.65	2.542	1.71	23.99	25.58	
OAEP 3	1.313	66.3	70.5	71	2.787	2.2	2.242	1.54	27.46	22.09	
OAEP 4	1.27	64.2	69.3	70.5	2.258	1.8	2.217	1.69	23.00	22.59	
OPAE 5	1.307	66.0	69.9	70.4	2.263	1.46	2.776	1.85	22.40	27.48	
		65.1		70.4						24.43	
No Dithionite											
OAEP 1-1	1.425	72.0	76	76.7	1.917	1.18	2.102	1.25	17.41	19.09	10.2
OAEP 1-2	1.423	71.9	77.4	77.8	2.647	1.58	2.062	1.37	24.07	18.75	
OAEP 1-3	1.438	72.7	76.9	77.3	2.199	1.27	2.974	2.2	19.79	26.76	
OAEP 1-4	1.436	72.6	76.3	77.7	2.059	1.02	2.727	2.07	18.55	24.57	
OAEP 1-5	1.452	73.4	77.5	77.3	2.11	1.04	2.362	1.4	18.80	21.05	
OAEP 2-1	1.324	66.9	76.8	77.6	2.883	1.79	2.464	1.99	28.17	24.08	
OAEP 2-2	1.272	64.3	76.3	76.2	1.987	1.23	2.795	2.14	20.21	28.43	
OAEP 2-3	1.276	64.5	77.4	77.6	2.36	1.65	2.341	1.72	23.93	23.74	
OAEP 2-4	1.351	68.3	77.5	76.6	2.617	1.79	2.652	1.68	25.06	25.40	
OAEP 2-5	1.282	64.8	78	77.2	NA	NA	2.403	1.57	NA	24.25	
		69.1		77.1						22.74	
W/Dithionite											
OAEP 1-1	1.304	65.9	79.2	78.7	2.634	1.9	2.395	1.58	26.14	23.76	
OAEP 1-2	1.255	63.4	76.8	76.7	1.742	1.05	1.997	1.39	17.96	20.59	
OAEP 1-3	1.304	65.9	79.1	79.2	1.718	1.19	2.634	1.64	17.05	26.14	
OAEP 2-1	1.33	67.2	78.1	79.2	3.055	2.45	2.132	1.11	29.72	20.74	
OAEP 2-2	1.302	65.8	77.9	79	1.911	1.13	2.596	1.76	18.99	25.80	
OAEP 2-3	1.299	65.6	79.3	78.9	2.65	2.11	2.902	2.23	26.40	28.91	
		65.6		78.5						23.51	

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g	Viscosity cP
After P											
OPAE 1	1.237	62.5	53.5	53.2	2.389	1.78	2.8	2.02	24.99	29.29	15.4
OPAE 2	1.232	62.3	55.5	54	2.47	1.72	2.067	1.13	25.94	21.71	
OPAE 3	1.226	62.0	53.4	54.7	2.099	1.15	2.451	1.6	22.15	25.87	
OPAE 4	1.086	54.9	53.9	53.6	2.607	1.66	2.266	2.06	31.06	27.00	
OPAE 5	1.272	64.3	53.6	54.3	2.054	1.11	2.191	1.17	20.89	22.29	
		61.2		54.0						25.12	
No Dithionite											
OPAE 1-1	1.26	63.7	73.4	73.3	1.729	1.19	2.102	1.35	17.75	21.59	9.9
OPAE 1-2	1.276	64.5	74.8	74.2	1.893	1.21	1.978	1.13	19.20	20.06	
OPAE 1-3	1.331	67.3	74.4	74.3	2.553	1.62	2.37	1.28	24.82	23.04	
OPAE 1-4	1.311	66.2	74	75	1.965	1.31	2.172	1.31	19.39	21.44	
OPAE 1-5	1.298	65.6	73.8	74.6	2.287	1.53	2.585	1.87	22.80	25.77	
OPAE 2-1	1.308	66.1	75	75.2	2.47	1.73	1.863	1.15	24.43	18.43	
OPAE 2-2	1.289	65.1	74.2	74.5	1.936	1.06	1.756	1.02	19.43	17.63	
OPAE 2-3	1.282	64.8	74.6	75.1	2.013	1.12	2.411	1.97	20.32	24.33	
OPAE 2-4	1.29	65.2	75.6	74.3	2.097	1.23	2.04	1.27	21.03	20.46	
OPAE 2-5	1.331	67.3	74.9	75.3	2.532	1.59	1.906	0.92	24.61	18.53	
		65.6		74.5						21.25	
W/Dithionite											
OPAE 1-1	1.282	64.8	75.3	75	2.268	1.21	2.306	1.19	22.89	23.27	
OPAE 1-2	1.269	64.1	76.8	77.2	2.542	1.76	2.634	1.44	25.92	26.86	
OPAE 1-3	1.293	65.3	76.7	76.9	2.207	1.19	2.808	1.75	22.08	28.10	
OPAE 2-1	1.284	64.9	77.2	77.7	2.66	1.63	2.722	1.82	26.80	27.43	
OPAE 2-2	1.245	62.9	75.5	75.5	2.642	1.47	2.064	1.19	27.46	21.45	
OPAE 2-3	1.278	64.6	77	76.9	2.301	1.34	2.604	1.67	23.30	26.36	
		64.4		76.5						25.16	

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g	Viscosity cP
after OPE											
OPEAE 1-1	1.353	68.4	54.8	54.1	1.681	1.30	1.544	1.14	16.08	14.77	17.1
OPEAE 1-2	1.364	68.9	53.3	53.9	2.000	1.39	2.032	1.30	18.97	19.28	
OPEAE 1-3	1.357	68.6	54.0	53.4	1.885	1.46	1.922	1.26	17.97	18.33	
OPEAE 2-1	1.278	64.6	54.6	54.9	1.750	1.43	1.882	1.50	17.72	19.05	
OPEAE 2-2	1.335	67.5	53.9	54.2	1.600		1.925	1.26	15.51	18.66	
OPEAE 2-3	1.273	64.3	54.9	54.4	1.965	1.60	1.847	1.58	19.97	18.77	
				54.2						17.92	
No dithionite											
OPEAE 1-1	1.319	66.6	74.2	73.6	1.670	1.33	1.570	1.44	16.38	15.40	10.9
OPEAE 1-2	1.364	68.9	74.8	73.9	1.855	1.79	1.815	1.35	17.60	17.22	
OPEAE 1-3	1.398	70.6	74.1	74.7	1.903	1.39	1.723	1.27	17.61	15.95	
OPEAE 2-1	1.37	69.2	74.0	74.0	1.686	1.38	1.592	1.56	15.92	15.04	
OPEAE 2-2	1.36	68.7	74.3	74.3	1.970	1.43	1.893	1.32	18.74	18.01	
OPEAE 2-3	1.401	70.8	74.6	74.5	1.978	1.89	1.984	1.79	18.27	18.32	
				74.3						17.04	
With dithionite											
OPEAE 1-1	1.342	67.8	75.7	75.0	1.919	1.23	2.132	1.57	18.50	20.56	
OPEAE 1-2	1.325	67.0	75.7	76.0	1.823	1.25	1.887	1.39	17.80	18.43	
OPEAE 1-3	1.38	69.7	75.4	75.6	2.148	1.83	2.016	1.83	20.14	18.90	
OPEAE 2-1	1.335	67.5	75.5	75.4	1.852	1.44	1.761	1.40	17.95	17.07	
OPEAE 2-2	1.39	70.2	76.2	76.5	1.852	1.42	1.890	1.41	17.24	17.59	
OPEAE 2-3	1.328	67.1	75.3	75.2	2.048	1.78	1.901	1.18	19.95	18.52	
				75.6						18.55	

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g	Viscosity cP
after OEAE											
OEAEP 1-1	1.213	61.3	71.3	71.2	1.409	1.44	1.541	1.32	15.03	16.44	12
OEAEP 1-2	1.213	61.3	71.0	70.3	1.466	1.16	2.030	1.79	15.64	21.65	
OEAEP 1-3	1.227	62.0	72.0	71.1	2.024	1.61	2.086	1.63	21.34	22.00	
OEAEP 2-1	1.247	63.0	71.9	72.6	1.654	1.58	1.748	1.62	17.16	18.14	
OEAEP 2-2	1.269	64.1	72.0	72.4	1.989	1.39	1.863	1.39	20.28	19.00	
OEAEP 2-3	1.289	65.1	76.7	71.6	1.485	1.23	1.141	0.94	14.91	11.45	
				72.0						17.75	
No dithionite											
OEAEP 1-1	1.184	59.8	74.7	75.6	1.748	1.47	1.761	1.69	19.10	19.24	11
OEAEP 1-2	1.221	61.7	75.3	74.8	1.600	1.70	1.557	1.74	16.95	16.50	
OEAEP 1-3	1.301	65.7	75.3	75.0	1.866	1.45	1.893	1.54	18.56	18.83	
OEAEP 2-1	1.283	64.8	75.8	75.8	2.040	1.86	2.011	1.58	20.57	20.28	
OEAEP 2-2	1.318	66.6	75.0	75.9	1.796	1.48	1.850	1.51	17.63	18.16	
OEAEP 2-3	1.277	64.5	75.8	76.0							
				75.4						18.58	
With dithionite											
OEAEP 1-1	1.288	65.1	77.0	77.1	1.952	1.26			19.61		
OEAEP 1-2	1.261	63.7	77.1	77.3	2.164	1.60	2.118	1.51	22.20	21.73	
OEAEP 1-3	1.26	63.7	77.1	77.9	2.236	1.64	1.995	1.35	22.96	20.49	
OEAEP 2-1	1.219	61.6	77.0	77.1	1.136	1.24	1.624	1.62	12.06	17.24	
OEAEP 2-2	1.217	61.5	76.4	77.9	2.081	1.69	2.158	1.98	22.12	22.94	
OEAEP 2-3	1.226	62.0	78.2	76.8	1.670	1.45	1.063	1.23	17.62	11.22	
				77.2						19.11	

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g	Viscosity cP
After OAE											
OAEA 1-1	1.249	63.1	72.5	71.6	1.605	1.47	1.020	0.61	16.63	10.57	10.01
OAEA 1-2	1.288	65.1	71.6	71.3	1.871	1.49	1.356	0.95	18.80	13.62	
OAEA 1-3	1.288	65.1	72.3	72.3	1.713	1.32	1.587	1.21	17.21	15.94	
OAEA 2-1	1.2	60.6	72.2	72.7	1.726	1.26	1.922	1.41	18.61	20.72	
OAEA 2-2	1.223	61.8	72.0	72.7	1.592	1.06	1.466	0.99	16.84	15.51	
OAEA 2-3	1.216	61.4	72.4	71.6	1.407	0.86	1.573	1.30	14.97	16.74	
				72.1						16.35	
No dithionite											
OAEA 1-1	1.199	60.6	78.0	78.5	1.987	1.54	1.866	1.56	21.44	20.14	8.41
OAEA 1-2	1.272	64.3	77.7	77.7	2.059	1.45	1.995	1.35	20.94	20.29	
OAEA 1-3	1.214	61.3	78.4	78.9	1.581	1.14	1.474	0.97	16.85	15.71	
OAEA 2-1	1.276	64.5	78.3	78.9	1.925	1.24	2.040	1.50	19.52	20.69	
OAEA 2-2	1.255	63.4	79.1	77.9	2.032	1.96	2.030	1.87	20.95	20.93	
OAEA 2-3	1.279	64.6	77.8	77.1	2.019	1.35	1.686	1.04	20.42	17.06	
				78.2						19.58	
Dithionite											
OAEA 1-1	1.079	54.5	80.7	79.9	1.568	0.93	1.095	0.98	18.80	13.13	
OAEA 1-2	1.071	54.1	80.4	80.6	1.506	1.01	1.350	1.29	18.19	16.31	
OAEA 1-3	1.009	51.0	81.1	80.4	1.434	1.42	1.442	1.90	18.39	18.49	
OAEA 2-1	1.134	57.3	81.6	80.6	1.831	1.22	1.981	1.59	20.89	22.60	
OAEA 2-2	1.14	57.6	80.7	81.4	2.110	1.70	1.933	1.30	23.95	21.94	
OAEA 2-3	1.194	60.3	81.6	81.4	1.538	1.00	1.248	0.71	16.67	13.52	
				80.9						18.57	
O(A/P)E 1-1	1.226	62.0	72.0	72.6	2.005	1.48	2.134	1.55	21.16	22.52	8.34
O(A/P)E 1-2	1.277	64.5	72.3	72.6	1.766	1.07	1.823	1.72	17.89	18.47	
O(A/P)E 1-3	1.205	60.9	72.5	72.7	1.546	1.08	1.831	1.68	16.60	19.66	
O(A/P)E 2-1	1.205	60.9	71.4	72.6	1.463	0.75	1.444	1.28	15.71	15.50	
O(A/P)E 2-2	1.151	58.2	72.7	72.3	1.409	1.11	1.332	0.82	15.84	14.97	
O(A/P)E 2-3	1.205	60.9	72.5	72.9	1.809	1.32	1.734	1.30	19.42	18.62	
				72.4						18.03	

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g	Viscosity cP
after DE											
DEAE 1-1	1.399	70.7	65.9	66.4	1.632	1.06	1.662	1.38	15.09	15.37	15.7
DEAE 1-2	1.435	72.5	66.2	67.6	1.764	1.11	1.042	0.69	15.91	9.40	
DEAE 1-3	1.472	74.4	67.8	67.0	0.961		0.513		8.45	4.51	
DEAE 2-1	1.284	64.9	65.0	65.1							
DEAE 2-2	1.317	66.5	64.4	64.4	1.128	0.76	1.165	1.34	11.08	11.45	
DEAE 2-3	1.329	67.2	66.6	64.5	0.497		0.524		4.84	5.10	
				65.9						10.12	
No dithionite											
DEAE 1-1	1.4	70.7	77.3	78.0	1.834	1.26	1.699	1.07	16.95	15.70	10.8
DEAE 1-2	1.473	74.4	77.9	78.1	1.944	1.28	1.973	1.10	17.08	17.33	
DEAE 1-3	1.441	72.8	78.5	78.9	1.925	1.30	2.019	1.18	17.28	18.13	
DEAE 2-1	1.283	64.8	77.7	77.8	1.219	1.18	0.964		12.29	9.72	
DEAE 2-2	1.268	64.1	76.8	78.0	1.380	1.11	1.192	0.97	14.08	12.16	
DEAE 2-3	1.295	65.4	77.7	77.9	1.546	1.31	1.404	0.99	15.45	14.03	
				77.9						15.02	
With dithionite											
DEAE 1-1	1.25	63.2	78.7	78.3	1.501	1.19	1.643	1.42	15.54	17.01	
DEAE 1-2	1.328	67.1	78.5	79.5	1.466	0.95	1.485	0.98	14.28	14.47	
DEAE 1-3	1.312	66.3	78.4	79.7	1.710	1.11	1.686	1.20	16.86	16.63	
DEAE 2-1	1.35	68.2	78.0	78.4	1.705	1.19	1.595	1.14	16.34	15.29	
DEAE 2-2	1.313	66.3	77.1	77.8	1.595	1.24	1.627	1.21	15.72	16.03	
DEAE 2-3	1.306	66.0	78.8	79.1	1.820		1.774	1.25	18.03	17.58	
				78.5						16.15	

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g	Viscosity cP
After AE											
AEDE 1-1	1.331	67.3	64.4	63.8	1.141	1.13	1.302	1.07	11.09	12.66	11.9
AEDE 1-2	1.33	67.2	63.7	63.3	1.541	1.25	1.479	1.03	14.99	14.39	
AEDE 1-3	1.311	66.2	63.4	63.7	1.536	0.88	1.772	1.41	15.16	17.49	
AEDE 2-1	1.344	67.9	64.3	64.1	0.507		0.725		4.88	6.98	
AEDE 2-2	1.319	66.6	64.8	63.5	0.679		1.246	1.12	6.66	12.22	
AEDE 2-3	1.346	68.0	65.5	66.0	1.340	0.98	1.213	1.09	12.88	11.66	
				64.2						11.76	
No dithionite											
AEDE 1-1	1.369	69.2	80.6	79.8	1.052	0.97	1.332	1.31	9.94	12.59	10.9
AEDE 1-2	1.289	65.1	79.0	78.4	1.184	0.78	1.238	0.98	11.88	12.43	
AEDE 1-3	1.306	66.0	80.2	79.6	1.262	0.94	1.364	1.37	12.50	13.51	
AEDE 2-1	1.311	66.2	79.5	79.7	1.468	1.38	1.399	1.30	14.49	13.81	
AEDE 2-2	1.299	65.6	79.9	80.0	1.651	1.43	1.568	1.30	16.44	15.62	
AEDE 2-3	1.311	66.2	81.6	80.2	0.722		1.264	1.18	7.13	12.47	
				79.9						12.73	
With dithionite											
AEDE 1-1	1.382	69.8	81.3	81.8	1.962	1.26	1.834	1.21	18.37	17.17	
AEDE 1-2	1.338	67.6	81.4	80.8	1.506	0.86	1.895	1.33	14.56	18.32	
AEDE 1-3	1.315	66.4	81.7	81.6	1.530	1.55	1.391	1.22	15.05	13.69	
AEDE 2-1	1.34	67.7	81.3	81.5	2.212	1.43	2.231	1.36	21.36	21.54	
AEDE 2-2	1.384	69.9	81.7	80.8	2.072	1.33	2.105	1.32	19.37	19.68	
AEDE 2-3	1.283	64.8	80.9	79.7	1.858	1.10	1.780	1.23	18.74	17.95	
				81.2						17.98	

CHELATION EXPERIMENT

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g	Viscosity cP
No wash No EDTA											
1-1	1.249	63.1	70.9	70.5	1.718	1.29	1.742	1.28	17.80	18.05	10.88
1-2	1.308	66.1	71.4	70.6	0.628	0.97	1.858	1.15	6.21	18.38	
1-3	1.202	60.7	71.1	71.4	1.874	1.43	1.683	1.03	20.17	18.12	
				71.0						16.45	
Wash No EDTA											
1-1	1.288	65.1	72.4	71.5	2.019	1.16	2.376	1.66	20.28	23.87	9.8
1-2	1.308	66.1	72.6	73.2	1.968	1.44	1.729	1.21	19.47	17.10	
1-3	1.245	62.9	72.0	72.7	1.648	1.18	1.522	1.41	17.13	15.82	
				72.4						18.94	
No Wash 1% EDTA											
1-1	1.298	65.6	71.3	71.9	2.016	2.00	1.804	1.23	20.10	17.98	10.25
1-2	1.34	67.7	70.9	71.7	2.268	1.51	2.140	1.28	21.90	20.66	
1-3	1.269	64.1	71.6	71.1	2.003	1.19	2.121	1.51	20.42	21.63	
				71.4						20.45	
No Wash 5% EDTA											
1-1	1.295	65.4	70.6	71.4	1.780	1.61	1.705	1.48	17.78	17.04	10.83
1-2	1.279	64.6	70.9	70.5	1.893	1.02	1.874	0.93	19.15	18.96	
1-3	1.241	62.7	70.5	72.3	1.128	1.07	1.297	1.23	11.76	13.52	
				71.0						16.37	

Sheet ID	Mass g	B.W.	Brightness 1	Using Optimim conditions Brightness 2	Tensile 1	Stretch 1	Tensile 2	Stretch 2	Tensile Index 1	Tensile Index 2	Viscosity
After OA					kg	%	kg	%	N*m2/g	N*m2/g	cP
OAEP 1-1	1.232	62.3	71.5	69.9	1.589	1.13	1.278	0.88	16.69	13.42	12.9
OAEP 1-2	1.243	62.8	72.0	70.7	1.493	1.19	1.570	1.03	15.54	16.34	
OAEP 1-3	1.226	62.0	72.2	71.2	1.299	1.13	BAD		13.71		
OAEP 2-1	1.214	61.3	69.1	68.9	1.538	1.05	1.329	0.88	16.39	14.16	
OAEP 2-2	1.235	62.4	70.5	71.1	1.425	0.99	1.509	1.20	14.93	15.81	
OAEP 2-3	1.284	64.9	67.4	68.3	1.501	1.07	1.533	1.25	15.13	15.45	
				70.2						15.23	
No dithionite											
OAEP 1-1	1.289	65.1	75.2	75.4	1.796	1.12	2.046	1.58	18.03	20.54	11.2
OAEP 1-2	1.282	64.8	74.9	74.5	1.978	1.48	1.941	1.47	19.96	19.59	
OAEP 1-3	1.294	65.4	75.7	75.7	1.670	1.11	1.828	1.23	16.70	18.28	
OAEP 2-1	1.363	68.9	77.3	74.7	1.777	1.24	1.820	1.27	16.87	17.28	
OAEP 2-2	1.402	70.8	75.3	76.4	1.764	0.96	2.376	1.57	16.28	21.93	
OAEP 2-3	1.261	63.7	75.4	75.1	1.820	1.34	1.954	1.55	18.67	20.05	
				75.5						18.68	
With dithionite											
OAEP 1-1	1.129	57.0	76.3	75.4	1.342	0.99	1.592	1.13	15.38	18.24	
OAEP 1-2	1.151	58.2	77.0	76.6	1.372	1.20	1.729	1.17	15.42	19.44	
OAEP 1-3	1.189	60.1	74.9	76.3	1.772	1.36	1.643	1.08	19.28	17.88	
OAEP 2-1	1.105	55.8	78.1	77.8	1.294	1.20	1.493	1.10	15.15	17.48	
OAEP 2-2	1.12	56.6	78.7	77.3	1.536	1.03	1.565	0.97	17.74	18.08	
OAEP 2-3	1.283	64.8	78.2	75.6	1.734	1.16	1.576	1.08	17.49	15.89	
				76.9						17.29	

Using Optimim conditions

Sheet ID	Mass g	B.W.	Brightness 1	Brightness 2	Tensile 1 kg	Stretch 1 %	Tensile 2 kg	Stretch 2 %	Tensile Index 1 N*m2/g	Tensile Index 2 N*m2/g	Viscosity cP
After OA				Step-wise Optimization							
OAEP 1-1	1.294	65.4	73.3	74.7	1.283	0.95	1.415	1.00	12.83	14.15	10.0
OAEP 1-2	1.189	60.1	74.7	73.7	1.984	1.49	1.519	1.14	21.59	16.53	
OAEP 1-3	1.267	64.0	72.3	72.2	1.801	1.56	1.471	1.56	18.39	15.02	
OAEP 2-1	1.227	62.0	73.6	71.7	1.992	1.42	1.681	0.97	21.01	17.73	
OAEP 2-2	1.232	62.3	73.8	73.8	1.605	1.31	1.804	1.22	16.86	18.95	
OAEP 2-3	1.214	61.3	72.9	72.2	1.777	1.38	1.672	1.24	18.94	17.82	
				73.2						17.48	
No dithionite											
OAEP 1-1	1.245	62.9	74.4	74.5	1.479	0.98	1.168	0.71	15.37	12.14	9.9
OAEP 1-2	1.273	64.3	74.7	76.9	1.788	1.47	1.785	1.24	18.17	18.14	
OAEP 1-3	1.196	60.4	73.6	76.9	1.683	1.58	1.842	1.55	18.21	19.93	
OAEP 2-1	1.229	62.1	76.2	75.6	1.812	1.59	1.836	1.32	19.08	19.33	
OAEP 2-2	1.229	62.1	76.2	73.3	1.895	1.17	1.807	1.13	19.95	19.02	
OAEP 2-3	1.266	64.0	74.5	75.4	1.850	1.50	2.027	1.79	18.91	20.72	
				75.2						18.25	
With dithionite											
OAEP 1-1	1.235	62.4	78.7	79.1	1.957	1.61	1.823	1.24	20.50	19.10	
OAEP 1-2	1.275	64.4	81.0	79.4	1.820	1.37	1.911	1.33	18.47	19.39	
OAEP 1-3	1.233	62.3	79.2	80.3	1.807	1.53	1.613	0.96	18.96	16.93	
OAEP 2-1	1.135	57.4	77.8	79.4	0.762	BAD	1.133	0.71		12.92	
OAEP 2-2	1.131	57.2	78.9	77.9	1.318	0.84	1.552	1.13	15.08	17.75	
OAEP 2-3	1.123	56.7	77.3	78.0	1.452	1.14	1.748	1.36	16.73	20.14	
				78.9						17.82	

Brightness

t-Test Two Sample Assuming Equal Variance

	ODED	OAEP		ODED	OPAE		ODED	OPEAE		ODED	OEAEP		ODED	OAEA
Mean	82.08	78.51	Mean	82.08	76.48	Mean	82.08	75.63	Mean	82.08	77.24	Mean	82.08	80.87
Variance	0.86	0.87	Variance	0.86	0.80	Variance	0.86	0.19	Variance	0.86	0.26	Variance	0.86	0.30
Observations	20	12	Observations	20	12	Observations	20	12	Observations	20	12	Observations	20	12
Pooled Var	0.86		Pooled Var	0.84		Pooled Var	0.61		Pooled Var	0.64		Pooled Var	0.65	
Hyp Mean Diff	0		Hyp Mean Diff	0		Hyp Mean Diff	0		Hyp Mean Diff	0		Hyp Mean Diff	0	
df	30		df	30		df	30		df	30		df	30	
t	10.52		t	16.76		t	22.58		t	16.55		t	4.11	
P(T<=t) 1-tail	0.000		P(T<=t) 1-tail	0.000		P(T<=t) 1-tail	0.000		P(T<=t) 1-tail	0.000		P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.70		t Critical 1-tail	1.70		t Critical 1-tail	1.70		t Critical 1-tail	1.70		t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.000		P(T<=t) 2-tail	0.000		P(T<=t) 2-tail	0.000		P(T<=t) 2-tail	0.000		P(T<=t) 2-tail	0.000	
t Critical 2-tail	2.04		t Critical 2-tail	2.04		t Critical 2-tail	2.04		t Critical 2-tail	2.04		t Critical 2-tail	2.04	

t-Test Two Sample Assuming Equal Variance

	ODEP	OAEP		ODEP	OPAE		ODEP	OPEAE		ODEP	OEAEP		ODEP	OAEA
Mean	81.18	78.51	Mean	81.18	76.48	Mean	81.18	75.63	Mean	81.18	77.24	Mean	81.18	80.87
Variance	0.45	0.87	Variance	0.45	0.80	Variance	0.45	0.19	Variance	0.45	0.26	Variance	0.45	0.30
Observations	20	12	Observations	20	12	Observations	20	12	Observations	20	12	Observations	20	12
Pooled Var	0.60		Pooled Var	0.58		Pooled Var	0.35		Pooled Var	0.38		Pooled Var	0.39	
Hyp Mean Diff	0		Hyp Mean Diff	0		Hyp Mean Diff	0		Hyp Mean Diff	0		Hyp Mean Diff	0	
df	30		df	30		df	30		df	30		df	30	
t	9.40		t	16.93		t	25.59		t	17.45		t	1.35	
P(T<=t) 1-tail	0.000		P(T<=t) 1-tail	0.000		P(T<=t) 1-tail	0.000		P(T<=t) 1-tail	0.000		P(T<=t) 1-tail	0.094	
t Critical 1-tail	1.70		t Critical 1-tail	1.70		t Critical 1-tail	1.70		t Critical 1-tail	1.70		t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.000		P(T<=t) 2-tail	0.000		P(T<=t) 2-tail	0.000		P(T<=t) 2-tail	0.000		P(T<=t) 2-tail	0.188	
t Critical 2-tail	2.04		t Critical 2-tail	2.04		t Critical 2-tail	2.04		t Critical 2-tail	2.04		t Critical 2-tail	2.04	

	DED	DEAE		DED	AEDE		O(A/P)E	OAE
Mean	79.99	78.53	Mean	79.99	81.21	Mean	72.43	70.35
Variance	0.36	0.52	Variance	0.36	0.35	Variance	0.16	0.45
Observations	18	12	Observations	18	12	Observations	12	10
Pooled Variance	0.42		Pooled Var	0.36		Pooled Var	0.29	
Hypothesized Mean Differenc	0		Hyp Mean Diff	0		Hyp Mean Diff	0	
df	28		df	28		df	20.00	
t	6.04		t	-5.48		t	9.024	
P(T<=t) one-tail	0.000		P(T<=t) 1-tail	0.000		P(T<=t) 1-tail	0.00	
t Critical one-tail	1.70		t Critical 1-tail	1.70		t Critical 1-tail	1.725	
P(T<=t) two-tail	0.000		P(T<=t) 2-tail	0.000		P(T<=t) 2-tail	0.00	
t Critical two-tail	2.05		t Critical 2-tail	2.05		t Critical 2-tail	2.086	

t-Test Two Sample Assuming Equal Variance

	OAEP	OAEP Opt		OAEP	OAEP Step Opt		OAEP Opt	OAEP Step Opt
Mean	78.51	76.85	Mean	78.51	78.92	Mean	76.85	78.92
Variance	0.87	1.46	Variance	0.87	1.15	Variance	1.46	1.15
Observations	12	12	Observations	12	12	Observations	12	12
Pooled Variance	1.17		Pooled Var	1.01		Pooled Var	1.30	
Hypothesized Mean Differenc	0		Hyp Mean Diff	0		Hyp Mean Diff	0	
df	22		df	22		df	22	
t	3.76		t	-1.00		t	-4.43	
P(T<=t) one-tail	0.001		P(T<=t) 1-tail	0.165		P(T<=t) 1-tail	0.000	
t Critical one-tail	1.72		t Critical 1-tail	1.72		t Critical 1-tail	1.72	
P(T<=t) two-tail	0.001		P(T<=t) 2-tail	0.330		P(T<=t) 2-tail	0.000	
t Critical two-tail	2.07		t Critical 2-tail	2.07		t Critical 2-tail	2.07	

Brightness
Analysis of Variance:One Way

Summary

Groups	*Count*	*Sum*	*Average*	*Variance*	
Column 1	6	425.9	71.0	0.150	No wash, No EDTA
Column 2	6	434.4	72.4	0.348	Wash, No EDTA
Column 3	6	428.5	71.4	0.146	No wash, 1% EDTA
Column 4	6	426.2	71.0	0.503	No wash, 5% EDTA

Analysis of Variance

Source of Variation

	SS	*df*	*MS*	*F*	*P-value*	*F-crit*
Between	7.77	3	2.59	9.04	0.0006	3.10
Within	5.73	20	0.29			
Total	13.50	23		S, 5%		

	Column 1	Column 2	Column 3	Column 4
Column 1				
Column 2	8.56			
Column 3	2.62	5.94		
Column 4	0.30	8.26	2.32	

Source of Error

	Regular **OA**	*No wash* **No EDTA**
Mean	70.35	70.98
Variance	0.45	0.15
Observations	10	6
Pooled Var	0.34	
Hyp Mean Diff	0	
df	14	
t	-2.10	
P(T<=t) 1-tail	0.027	
t Critical 1-tail	1.76	
P(T<=t) 2-tail	0.054	
t Critical 2-tail	2.14	

	Regular **OA**	*Wash* **No EDTA**
Mean	70.35	72.40
Variance	0.45	0.35
Observations	10	6
Pooled Var	0.41	
Hyp Mean Diff	0	
df	14	
t	-6.19	
P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.76	
P(T<=t) 2-tail	0.000	
t Critical 2-tail	2.14	

	Regular **OA**	*No Wash* **1% EDTA**
Mean	70.35	71.42
Variance	0.45	0.15
Observations	10	6
Pooled Var	0.34	
Hyp Mean Diff	0	
df	14	
t	-3.54	
P(T<=t) 1-tail	0.002	
t Critical 1-tail	1.76	
P(T<=t) 2-tail	0.003	
t Critical 2-tail	2.14	

	Regular **OA**	*No Wash* **5% EDTA**
Mean	70.35	71.03
Variance	0.45	0.50
Observations	10	6
Pooled Var	0.47	
Hyp Mean Diff	0	
df	14	
t	-1.94	
P(T<=t) 1-tail	0.037	
t Critical 1-tail	1.76	
P(T<=t) 2-tail	0.073	
t Critical 2-tail	2.14	

Tensile

t-Test Two Sample Assuming Equal Variance

	ODED	OAEP
Mean	25.20	23.02
Variance	3.12	17.26
Observations	20	11
Pooled Var	8.00	
Hyp Mean Diff	0	
df	29	
t	2.05	
P(T<=t) 1-tail	0.025	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.050	
t Critical 2-tail	2.05	

	ODED	OPAE
Mean	25.20	25.16
Variance	3.12	5.64
Observations	20	12
Pooled Var	4.05	
Hyp Mean Diff	0	
df	30	
t	0.05	
P(T<=t) 1-tail	0.480	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.960	
t Critical 2-tail	2.04	

	ODED	OPEAE
Mean	25.20	18.55
Variance	3.12	1.31
Observations	20	12
Pooled Var	2.46	
Hyp Mean Diff	0	
df	30	
t	11.60	
P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.000	
t Critical 2-tail	2.04	

	ODED	OEAEP
Mean	25.20	19.11
Variance	3.12	17.49
Observations	20	11
Pooled Var	8.08	
Hyp Mean Diff	0	
df	29	
t	5.71	
P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.000	
t Critical 2-tail	2.05	

	ODED	OAEA
Mean	25.20	18.57
Variance	3.12	11.45
Observations	20	12
Pooled Var	6.18	
Hyp Mean Diff	0	
df	30	
t	7.30	
P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.000	
t Critical 2-tail	2.04	

t-Test Two Sample Assuming Equal Variance

	ODEP	OAEP
Mean	25.46	23.51
Variance	3.01	18.57
Observations	20	12
Pooled Var	8.72	
Hyp Mean Diff	0	
df	30	
t	1.80	
P(T<=t) 1-tail	0.041	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.082	
t Critical 2-tail	2.04	

	ODEP	OPAE
Mean	25.46	25.16
Variance	3.01	5.64
Observations	20	12
Pooled Var	3.98	
Hyp Mean Diff	0	
df	30	
t	0.41	
P(T<=t) 1-tail	0.344	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.688	
t Critical 2-tail	2.04	

	ODEP	OPEAE
Mean	25.46	18.55
Variance	3.01	1.31
Observations	20	12
Pooled Var	2.39	
Hyp Mean Diff	0	
df	30	
t	12.23	
P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.000	
t Critical 2-tail	2.04	

	ODEP	OEAEP
Mean	25.46	19.11
Variance	3.01	17.49
Observations	20	11
Pooled Var	8.01	
Hyp Mean Diff	0	
df	29	
t	5.98	
P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.000	
t Critical 2-tail	2.05	

	ODEP	OAEA
Mean	25.46	18.57
Variance	3.01	11.45
Observations	20	12
Pooled Var	6.11	
Hyp Mean Diff	0	
df	30	
t	7.63	
P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.000	
t Critical 2-tail	2.04	

t-Test Two Sample Assuming Equal Variance

	DED	DEAE
Mean	16.77	16.15
Variance	14.62	1.34
Observations	18	12
Pooled Variance	9.40	
Hypothesized Mean Differen	0	
df	28	
t	0.55	
P(T<=t) one-tail	0.294	
t Critical one-tail	1.70	
P(T<=t) two-tail	0.588	
t Critical two-tail	2.05	

	DED	AEDE
Mean	16.77	17.98
Variance	14.62	6.28
Observations	18	12
Pooled Var	11.34	
Hyp Mean Diff	0	
df	28	
t	-0.96	
P(T<=t) 1-tail	0.172	
t Critical 1-tail	1.70	
P(T<=t) 2-tail	0.343	
t Critical 2-tail	2.05	

	O(A/P)E	OAE
Mean	18.03	24.43
Variance	5.73	5.62
Observations	12	10
Pooled Var	5.68	
Hyp Mean Diff	0	
df	20.00	
t	-6.274	
P(T<=t) 1-tail	0.00	
t Critical 1-tail	1.725	
P(T<=t) 2-tail	0.00	
t Critical 2-tail	2.086	

t-Test Two Sample Assuming Equal Variance

	OAEP	OAEP Opt
Mean	23.51	17.29
Variance	18.57	2.22
Observations	12	12
Pooled Variance	10.40	
Hypothesized Mean Differen	0	
df	22	
t	4.73	
P(T<=t) one-tail	0.000	
t Critical one-tail	1.72	
P(T<=t) two-tail	0.000	
t Critical two-tail	2.07	

	OAEP	OAEP Step Opt
Mean	23.51	17.82
Variance	18.57	5.20
Observations	12	11
Pooled Var	12.20	
Hyp Mean Diff	0	
df	21	
t	3.91	
P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.72	
P(T<=t) 2-tail	0.001	
t Critical 2-tail	2.08	

	OAEP Opt	OAEP Step Opt
Mean	17.29	17.82
Variance	2.22	5.20
Observations	12	11
Pooled Var	3.64	
Hyp Mean Diff	0	
df	21	
t	-0.66	
P(T<=t) 1-tail	0.258	
t Critical 1-tail	1.72	
P(T<=t) 2-tail	0.517	
t Critical 2-tail	2.08	

Tensile
Analysis of Variance:One Way

Summary

Groups	***Count***	***Sum***	***Average***	***Variance***	
Column 1	6	98.73	16.45	25.90	No wash, No EDTA
Column 2	6	113.67	18.94	8.56	Wash, No EDTA
Column 3	6	122.69	20.45	1.95	No wash, 1% EDTA
Column 4	6	98.21	16.37	9.24	No wash, 5% EDTA

Analysis of Variance

Source of Variation

	SS	***df***	***MS***	***F***	***P-value***	***F-crit***
Between Gı	71.55	3	23.85	2.09	0.134	3.10
Within Grou	228.23	20	11.41			
				NS, 5%		
Total	299.78	23				

	Regular **OA**	*No wash* **No EDTA**
Mean	24.43	16.45
Variance	5.62	25.90
Observations	10	6
Pooled Var	12.86	
Hyp Mean Diff	0	
df	14	
t	4.31	
P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.76	
P(T<=t) 2-tail	0.001	
t Critical 2-tail	2.14	

	Regular **OA**	*Wash* **No EDTA**
Mean	24.43	18.94
Variance	5.62	8.56
Observations	10	6
Pooled Var	6.67	
Hyp Mean Diff	0	
df	14	
t	4.12	
P(T<=t) 1-tail	0.001	
t Critical 1-tail	1.76	
P(T<=t) 2-tail	0.001	
t Critical 2-tail	2.14	

	Regular **OA**	*No Wash* **1% EDTA**
Mean	24.43	20.45
Variance	5.62	1.95
Observations	10	6
Pooled Var	4.31	
Hyp Mean Diff	0	
df	14	
t	3.72	
P(T<=t) 1-tail	0.001	
t Critical 1-tail	1.76	
P(T<=t) 2-tail	0.002	
t Critical 2-tail	2.14	

	Regular **OA**	*No Wash* **5% EDTA**
Mean	24.43	16.37
Variance	5.62	9.24
Observations	10	6
Pooled Var	6.91	
Hyp Mean Diff	0	
df	14	
t	5.94	
P(T<=t) 1-tail	0.000	
t Critical 1-tail	1.76	
P(T<=t) 2-tail	0.000	
t Critical 2-tail	2.14	

Appendix 3 - Sample Calculations

Determination of chlorine dioxide solution strength:

$$\text{g/L } ClO_2 = \text{titration} * \text{normality} * \frac{(67.46)}{(5 * 1000)} * \frac{(1000)}{\text{ml sample}}$$

$$= (7.6 \text{ ml } Na_2S_2O_3) * (0.200 \text{ N}) * \frac{(67.46)}{(5 * 1000)} * \frac{(1000)}{\text{5 ml sample}}$$

$$= 4.1 * 10^{-3} \text{ g/ml } (Cl_2 \text{ equivalent})$$

Calculation of required charge of chlorine dioxide:

$$40 \text{ g OD fiber} * 0.02 \text{ chemical} * (1/4.1 * 10^{-3} \text{ g/ml}) = 195.1 \text{ ml } ClO_2 \text{ water}$$

Calculation of required charge of peroxide:

$$30 \text{ g OD fiber} * 0.0096 * (1/0.030 \text{ g/ml}) = 9.6 \text{ ml } H_2O_2$$

Calculation of required charge of activated oxygen:

$$(0.03 \text{ chemical}) * 30 \text{ g OD fiber} * \frac{\text{mol O}}{\text{16 g}} * \frac{\text{614.9 g}}{\text{2 mol O}} \text{ Oxone} = 17.3 \text{ g Oxone}$$

Calculation of required charge of bicarbonate:

Determined experimentally that 14 g of $NaHCO_3$ is needed for every 7.68 g Oxone added to buffer solution around 7.5

$$(17.3 \text{ g Oxone}) * \frac{(14 \text{ g } NaHCO_3)}{\text{7.68 g Oxone}} = 31.54 \text{ g } NaHCO_3$$

Calculation of required charge of acetone:

$$(30 \text{ g OD fiber}) * (0.03 \text{ Oxone}) * \frac{\text{mol O}}{\text{16 g}} * \frac{\text{1.5 mol}}{\text{ratio}} * \frac{\text{58.1 g}}{\text{mol Ac}} = 4.90 \text{ g} = 6.2 \text{ ml}$$

Viscosity:

$$\eta = (\text{time sec}) * (1.052 \text{ density}) * (0.03847 \text{ viscometer constant})$$

$$\eta = (4.39 \text{ sec}) * (1.052) * (0.03847) = 10.7 \text{ cP (OAEP after A)}$$

Tensile Index:

Tensile Index = (tensile kg * 654 N/kg conversion)/(basis weight)
Tensile Index = $(1.605 \text{ kg} * 654)/(1.249 \text{ g/m}^2) = 16.63 \text{ N·m}^2\text{/g}$