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The Use of Dimethyldioxirane in Refiner Bleaching of High-Yield Pulps

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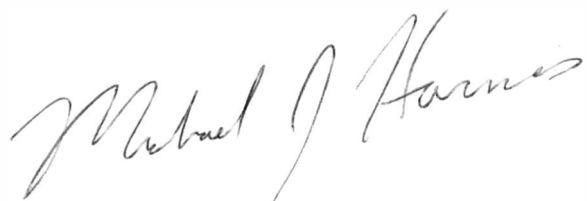
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Western Michigan University, 1996

In the attempt to find improved bleaching chemicals for the bleaching of high-yield pulps, dioxiranes may prove to be the solution. Unlike hydrogen peroxide, which has been introduced to a refiner environment in the past, dimethyldioxirane (DMD) does not require the use of sodium silicates. This is very beneficial due to the fact that silicates have a highly undesirable side effect of causing excessive refiner plate wear.

The experimentation was constructed to determine the exact feasibility of the use of dimethyldioxirane as a refiner bleaching agent. This was completed through the comparison of the pulp strength and brightness values of refiner bleached stock using a PFI mill to simulate refiner action. Hydrogen peroxide and dimethyldioxirane generated *in-situ* were used as the bleaching agents.

Dimethyldioxirane was found to produce a brightness increase of 8.5 points in comparison to the reference pulp. Low concentrations of DMD were found to be sufficient, with a charge of 2.0% DMD producing equivalent brightness values to higher concentrations. A 17 brightness point increase was obtained while utilizing a 2-stage refiner bleaching sequence, with the first stage being 3.0% DMD, and the second being 2.5% hydrogen peroxide without silicates.

ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION

Bleaching within a refiner environment provides the benefits of high bleaching consistency, vigorous mixing, and high temperatures for quick chemical reactions. Hydrogen peroxide, which is the current standard bleaching chemical for high yield pulps, cannot be used alone in the refiner due to decomposition reactions that take place at high temperatures for this chemical. Sodium silicate, which is typically used to stabilize this decompostion reaction, cannot be used in a refiner setting because it causes scaling on the refiner plates. Dimethyldioxirane (DMD), which has shown good results on the bleaching of chemical pulps, does not require a stabilizer due to its stability to temperature, and can therefore can make use of the bleaching advantages in a refiner.

No previous work had been found on using DMD as a refiner bleaching agent, or as a bleaching agent for high-yield pulps during a literature search. It was the goal of this experiment to determine if dimethyldioxirane is an effective refiner bleaching agent. This was done in comparison to two stages of hydrogen peroxide bleaching, with the first stage being a conventional bleaching using silicates, and the second stage being a refiner bleaching sequence using DTPA as a stabilizer.

CHAPTER II

LITERATURE SEARCH

Bleaching Chemistry

According to C.-L. Lee, et al. (1), three basic categories can be created for bleaching agents. These categories include: (A) cationic, (B) anionic, and (C) radical. These categories are defined by the bleaching agents electrophilicity (ρ). The electrophilicity value predicts the selectivity of the bleaching agent.

Cationic bleaching agents, known as electrophiles, have a negative electrophilicity value. This allows the bleaching agent to act upon the electron rich aromatic and olefinic structures found in lignin, causing delignification. However, electrophiles will leave the electron poor structure of cellulose alone, which is desired. Ozone is an example of a cationic bleaching agent (1).

Anionic bleaching agents are known as nucleophiles, and have a positive electrophilicity. They are noted for their ability to remove chromophores, which color pulp, and therefore are referred to as brightening agents. However, nucleophiles do not exhibit any delignification reactions (1).

2

Radicals can either be cationic or anionic depending on the pH of the bleaching solution. Hydrogen peroxide is an example of a radical, due to its varying electrophilicity with different pH values (1).

Hydrogen Peroxide

At alkaline conditions, hydrogen peroxide has a ρ of +1.54 mV. However, under acidic conditions, hydrogen peroxide has a ρ of -1.13 mV (1). This study will be focused upon hydrogen peroxides effectiveness at alkaline pH, and therefore, its cationic properties.

In a conventional bleaching system, hydrogen peroxide is added to the pulp at a alkaline pH in order to create the perhydroxy ion:

$$H_2O_2 + OH^- \rightarrow OOH^- + H_2O$$
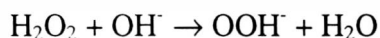
This reaction is favorable since the perhydroxy ion is responsible for the bleaching of the pulp (2).

Strunk, et al. (2) reported that at high temperatures, thermal decomposition of hydrogen peroxide can take place, which leads to the following undesired reaction:

$$H_2O_2 \rightarrow H_2O + 1/2\ O_2$$
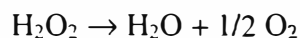
The rate at which this decomposition occurs is increased by both an increase in temperature and in pH. Because of this, conventional bleaching systems use an

alkaline system. A typical pH range at the beginning of the bleaching cycle is 10.5 to 11.0. This pH is reduced to a range of 9.0 to 10.0 by the end of the cycle.(2).

Not only does hydrogen peroxide thermally decompose, but it also catalytically decomposes via the second reaction in the presence of heavy metals. These compounds, such as manganese, iron, or copper, are introduced to the bleaching system through water, other chemicals, or the wood itself. It has been noted that 100 PPM of manganese is sufficient to cause significant decomposition (2).

Burton (3) reports that in order to inhibit catalytic decomposition, hydrogen peroxide stabilizers are added in storage and in the bleaching process . These stabilizers include sodium silicate, diethylenetriaminepenta-acetic acid (DTPA), diethylenetriaminepenta-monophosphonic acid (DTMPA), and magnesium sulfate (Epsom salt). Strunk, et al. (2) reported sodium silicate as one of the more effective stabilizers.

Not only does sodium silicate stabilize, but it also acts as a source of alkali for the bleaching process. It has also been shown that the prescence of sodium silicate also increases the resulting brightness of the pulp during the bleaching process (3). These characteristics, as well as being relatively inexpensive, makes sodium silicate the stablizer of choice for hydrogen peroxide bleaching.

<u>Dimethyldioxirane</u>

Dioxiranes are three membered ring cyclic peroxides (4). They are a class of powerful electophilic oxidants possessing a readiness to transfer a single activated oxygen atom (1). Dimethyldioxirane (DMD) has shown to be very efficient in its oxygen transfer ability and selectivity in its reactions (1). Because of this ability, dimethyldioxirane is often referred to as activated oxygen (1,5). DMD has also shown to have a ρ value of up to -1.53 mV in reaction with lignin (1). This ρ values would make DMD a powerful delignifier.

<u>Generation</u>

The structure of dioxiranes consists of a cyclic three-member ring containing two oxygen and one carbon atom, as shown by Figure 1 (1).

Figure 1.   The Chemical Structure of Dimethyldioxirane

According to Murray et al. (6), DMD is a peroxidic intermediate the ozonolysis reaction. Montgomery (7) had first suspected this by observing that

ketones reacted with monoperoxysulfuric acid, known as Caro's acid, to form an intermediate. This intermediate, known as the "Criegee" intermediate, reacts further to form a dioxirane (6).

In the case of dimethyldioxirane, the ketone used to decompose the peroxymonosulfate is acetone. This reaction is catalytic since the ketone is not consumed (1). If an oxidizable substrate is present (X), dimethyldioxirane then becomes an effective oxidant (8). The ketone reaction with peroxymonosulfate is shown in Figure 2.
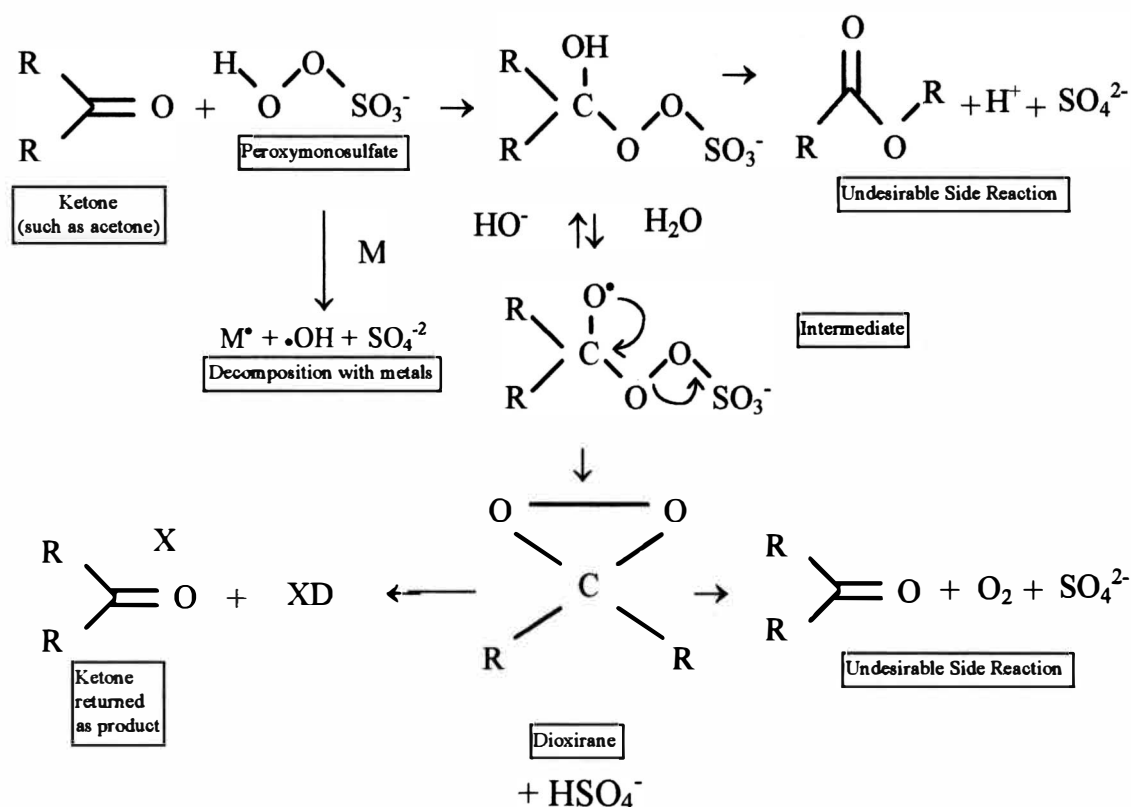
Figure 2. General Reaction for Peroxymonosulfate and Ketones

Springer and McSweeny (9) noted that although peroxymonosulfate was quite stable under acidic conditions, some decomposition did take place. Transition metals were found to react with the peroxymonosulfate and form hydroxyl radicals that are unbeneficial to the bleaching process, as noted by the first side reaction in Figure 2. By removing the metal ions in the pulp prior to peroxymonosulfate addition, with some type of chelation agent, this decomposition of peroxymononsulfate can be halted.

Murray (10) noted that at pH values higher than 7.5, the yield of oxidation products was greatly reduced. This phenomena was explained by an increased concentration of caroate dianion which would attack the dioxirane and generate oxygen.

Bleaching With Isolated DMD

DMD can be prepared in low yield through the gas-phase ozonolysis of alkenes (1). This involves adding a monopersulfate compound to an aqueous acetone solution of sodium bicarbonate and vacuum distilling the DMD (8). A 50 to 100 Torr vacuum is applied during the distillation process, and the DMD vapors are then condensed by cooling them to $-78^0 C$ (4).

Isolated DMD Bleaching of an Aspen Pulp. C.-L. Lee, et al. (1) conducted an experimentation on the effectiveness of isolated DMD on a lab generated aspen pulp with a initial kappa number of 16.4 . Bleaching was then carried out at room

temperature at .55% DMD on oven-dry pulp, with a 14.2% pulp consistency for 60 minutes.

The isolated activated oxygen was able to decrease the kappa number of the aspen pulp by 79% to 3.9, and had a superior tensile strength of 17 km. This tensile strength is comparable to pulp generated by (C+D)ED bleaching sequence. However, it was noted that the chemical yield of AO based on monoperoxysulfate charge was less than 1%. This is not practical for industrial purposes (1).

Bleaching With in Situ Generated DMD

DMD is prepared through in situ generation by mixing acetone with a monopersulfate compound, and sodium bicarbonate, which is used as a pH buffer (1, 5, 8). The monopersulfate compound can be generated by an "Adiabatic Caro's acid Unit" (11). However, the commercial product monoperoxysulphate (K_2SO_4 * $KHSO_4$ * $2KHSO_5$), which is derived from the potassium hydroxide neutalizaton of Caro's acid, is typically used (12). Besides being convenient, monoperoxysulphate is stable and easily transportable (11).

Bleaching of a Canadian Western Hemlock Pulp. C.-L. Lee, et al. (1) tested the bleaching potential of in situ generated DMD on Canadian western hemlock with a kappa value of 31.5, a viscosity of 33.5 mPa, and a 24.4% brightness. For the in-situ generation of DMD, the pulp was mixed with acetone at a 1.5 mole ratio to the AO

charge for 10 minutes, with $NaHCo_3$ added for pH control at 7 to 7.5 . OXONE, a trade name for monperoxysulphuric acid, was then added to the slurry at 25^0 C and at 13.6% pulp consistency for 45 minutes with only initial kneading. The chemical charge of the activated oxygen was based on one available oxygen molecule per $KHSO_5$ molecule used.

Activated oxygen charge was varied between 0 and 5% on percent oven-dry pulp. Results showed that as the percentage charge was increased, the kappa number and viscosity decreased. The greatest degree of delignification was obtained at a 5% charge, where a kappa number of 9.8, which is a 69% degree of delignification, was obtained. However, viscosity dropped to 20.9 mPa*s (1). This type of results lead to the conclusion that activated oxygen reacts with residual kraft lignin in a way similar to elemental chlorine/chlorine dioxide (5).

Refiner Bleaching

Refiner bleaching is a viable bleaching method for hydrogen peroxide to the conditions created in the refiner, according to Strunk, et al. (2). High consistency, vigorous mixing, and high temperatures for rapid reactions create optimal conditions inside the refiner for bleaching agents.

Hydrogen Peroxide

Although the conditions in a refiner are excellent for bleaching with hydrogen peroxide, according to Strunk, et al. (2), temperatures during refiner bleaching usually exceed 100^0 C, causing thermal decomposition of the agent. This results in unnecessary chemical consumption and decreased bleaching effectiveness.

Although sodium silicate is effective source of alkali and stabilization of hydrogen peroxide in conventional bleaching systems, it has an undesirable side effect of causing refiner plate scaling in refiner bleaching. Although many attempts have been made to reduce this scaling, it appears to be inherent with the use of sodium silicate (2).

Dimethyldioxirane

No previous literature was cited for the use of dimethyldioxirane as a refiner bleaching agent. Similarly, no previous work was found on the use of DMD as a bleaching agent for high yield pulps.

Literature Analysis

From the information gathered from previous experimentations, pH, not temperature, seemed to be the controlling factor in DMD bleaching effectiveness. DMD also does not require the use of silicates. Therefore, dimethyldioxirane should

be able to be added directly to the primary refiner in order to take advantage of the conditions in the refiner.

The literature found suggests that DMD is an excellent delignifier of pulp. Delignification is not desired for high-yield pulps, since it it decreases the percentage yield. It is hoped that the very long lignin chains of the high yield pulp are shortened, but not solubilized. This will hopefully lead to a brightness improvement through modification of wavelengths absorbed by the pulp.

Refiner bleaching with H_2O_2 in the presencce of silicates is not viable do to the scaling of the refiner plates. However, silicates main purpose is to be used as a stabilizer. If another stabilizer, such as magnesium sulfate or DTPA were used in its place, refiner bleaching experiments could be conducted.

Although the effectiveness of dimethyldioxirane may exceed hydrogen peroxide, cost has to be taken in as a factor. According to Rooks (12), the price of DMD has to drop 100 times in order to be feasible.

CHAPTER III

PROBLEM STATEMENT

The goal of this study was to determine if dimethyldioxirane is an effective

refiner bleaching agent in comparison to hydrogen peroxide. This comaparison of the

DMD bleached pulp was to be done against pulps bleached by (a) a conventional

peroxide bleaching sequence, and (b) a refiner peroxide bleaching sequence.

CHAPTER IV

EXPERIMENTAL

Experimental Design

To conduct the necessary experiment for this thesis, a PFI mill was used to simulate refiner conditions. Refiner bleaching was conducted in two phases, with the first phase utilizing dimethyldioxirane as a bleaching agent. The dioxirane was created through *in-situ* generation within the refiner in order to conduct the pulp bleaching. A super chelated version of the pulp was tested along with the original pulp to test the effect of metal ion removal. Bleaching agent concentrations were varied in order to maximize pulp properties.

The second phase (II) involved using hydrogen peroxide as a bleaching agent. This phase was broken down further into two different stage. In one of the stages, the pulp was bleached in the PFI mill with hydrogen peroxide in the presence of a chelation agent. In the other, pulp was first refined in a PFI mill in presence of a chelation agent, and was then treated with peroxide (after the refining) in plastic bags. In this second stage, peroxide bleaching was done with and without the use of a silicate stabilizer. A schematic of the experimental design is shown in Figure 3.

```
                              Pulp
            DMD                │              Peroxide
        ┌───────────┬─────────┴────────┬───────────────┐
    Normal      Superchelated    Conventional       Refiner
    Pulp            Pulp           Bleaching        Bleaching
      │               │         ┌──────┴──────┐         │
      │               │        With        Without      │
      │               │      Silicates    Silicates     │
      │               │      └────┬────────────┬───┘     │
  Bleached Pulp   Bleached Pulp   │            │     Bleached
                                  │            │       Pulp
                             Bleached Pulp  Bleached Pulp
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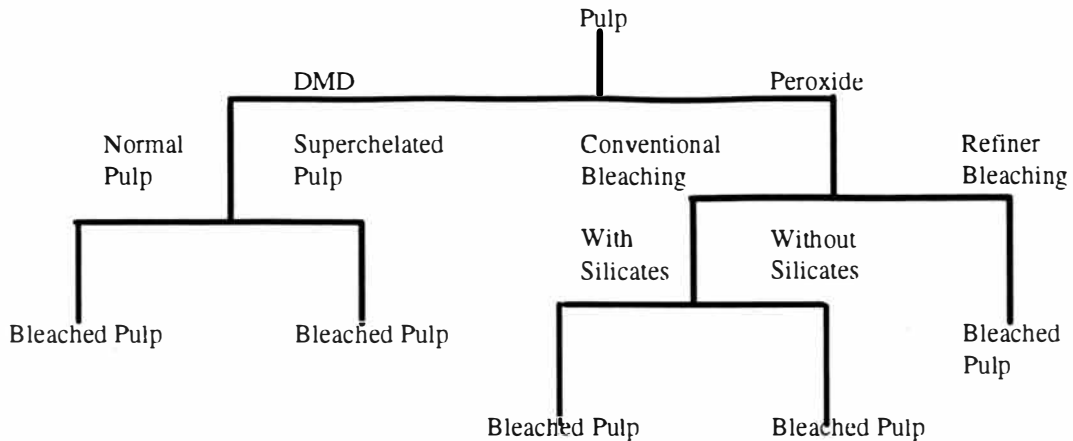
Figure 3. Schematic of the Experimental Design

The feasibility of using DMD as a refiner bleaching agent was determined

through a comparison of DMD bleached properties with those obtained with hydrogen

peroxide. These properties included brightness and zero-span tensile strength.

Experimental Procedure

Materials

Pulp Sample

The pulp used in this experimentation is thermo-mechanical pulp consisting of

100% softwood fibers. This pulp, which was donated by Abteco fiber company, had

been run through a refiner one time before being shipped. Therefore, this

experimentation will represent a two-stage refining sequence.

Chemicals

To complete the hydrogen peroxide refiner bleaching sequences, the following chemicals were needed: hydrogen peroxide, sodium silicate, sodium hydroxide, and EDTA.

The dimethyldioxirane refiner bleaching sequences were completed with the following chemicals: Oxone (monoperoxysulfate, produced by DuPont), acetone, sodium bicarbonate, and EDTA. For the DMD bleaching with superchelated pulp, triethanolamine, hydrochloric acid, and DTPA were also needed.

All of these chemicals were procurred from Fluka Chemical Corporation.

Methods

In order to complete refiner bleaching on a laboratory scale, a PFI mill was used to simulate a refiner. All refiner trials using the PFI mill were done in accordance with the TAPPI standard (T 248 cm-85). A standard freeness of 350 mL CSF was used in replacement of the suggested freeness of 300 mL CSF as a refining guide.

To ensure the same quality of pulp for each run, a two-attempt limit was set for the number of times the PFI mill could be stopped for freeness readings on the same pulp. If the pulp was not within the range of 340 to 360 CSF, it was to be discarded.

Phase I: Refiner Bleaching With Dimethyldioxirane

Peroxymonosulfate has been noted to decompose in the presence of heavy metal ions (11). This decomposition inhibits the bleaching effectiveness of DMD since it limits the amount of the intermediate formed. Therefore, to limit this nonbeneficial reaction, chelation was effected. This was done in two different methods; superchelation of the pulp, or addition of EDTA to the pulp.

Using Springer's (8) methodology, a superchelated pulp was made through sequentially treating a pulp sample with triethanolamine, hydrochloric acid, and three treatments of 10% DTPA on O.D. fiber. After treatment, the superchelated pulp was ready to be disintegrated according to PFI mill standards.

Lee *et al.* (5) suggested that quantity of dimethyldioxirane formed in *in-situ* is proportional to the charge of acetone present in the pulp prior to peroxymonosulfate addition. Therefore, after disintegration, both pulp types was diluted with a combination of acetone, sodium bicarbonate and deionized water, instead of using just deionized water, as described in the PFI mill standard. The acetone charge utilized was in a 1.5 mol ratio to the amount of peroxymonosulfate used in the trial. The pH will be maintained in a range of 7-7.5 with the bicarbonate. In the case of the non-superchelated pulp, 0.5% EDTA will also added at this point to remove the metal ions.

After dilution, the pulp was placed in the PFI mill along with the experimental amount of oxone. This experimental amount of oxone was determined by assuming

that each peroxymonosulfate molecule produces two activated oxygen equivalents. With all of the chemical reagents added to the pulp, the refining process was initiated, allowing for *in-situ* generation of DMD in the refiner, and for bleaching to occur.

Previous work by Thompson (13) allowed for the determination of optimal brightness conditions for a single DMD bleaching stage. These conditions included the use of 2.8% peroxymonosulfate on OD fiber at 55^0 C at a pH of 7 to 7.5. The author used these initial conditions, except for temperature due to PFI mill standards, as an initial starting point. At this point, charge levels of 2.5%, 3.0%, 3.5%, 4.0%, 4.5%, and 5.0% were used to determine the effect of DMD charge level on pulp propeties. Replications were completed to these bleaching levels to determine reproducibility.

After the refining process is complete, the pulp was rinsed with a large quantity of deinonized water in a Buchner funnel. After being thoroughly rinsed, the pulp consistency was raised to around 18% using the Buchner funnel. The pulp was then stored at 4^0 C until needed for testing.

Phase II: Refiner Bleaching With Hydrogen Peroxide

In order to create a hydrogen peroxide refiner-bleached pulp with the highest qualities, the sequence was broken down in to two stages. The first stage used sodium

silicate along with magnesium sulfate for chelant control during the bleaching trial. The second stage used no sodium silicate but DTPA and magnesium sulfate as chelation agents.

Stage I: Sodium Silicate Addition. In order to complete high-yield pulp bleaching with hydrogen peroxide while utilizing a silicate stabilizer, bleaching must occur outside of the refiner. This procedure was simulated during this stage of hydrogen peroxide bleaching.

In accordance with the standards developed for the PFI mill, a 30 gram sample of the original pulp sample was disintegrated in a TAPPI disintegrator to disperse fiber bundles. After adjusting the consistency to 10%, the pulp was placed in the PFI mill. The pulp sample was then refined inside the mill to a freeness of 350 mL CSF.

Bleaching with hydrogen peroxide in the presence sodium silicate was completed as follows. The pulp, in a polyethylene bag, was warmed to 50^0 C by suspending the bag in a hot water bath for 30 minutes. The required amount of hydrogen peroxide and sodium silicate was then added to the pulp suspension. The bleaching agents and the pulp were then mixed by hand. A final bleaching consistency of 8% was maintained, as well as a pH range of 10.5 to 11. The sample was then retained in a 50^0 C hot water bath for 2 hours. The suspension was kneaded by hand once every 15 minutes during the 2 hour time interval to stimulate mixing of the pulp and the bleaching agent. At the end, the sample was then be removed from the hot water bath and drained of all excess liquid.

Previous refiner bleaching experiments have been completed by Perkins (14) by using varying amounts of sodium silicates with a bleaching liquor containing .5% H_2O_2, .05% $MgSO_4$, and having a 1.3% total alkalinity. Her work showed that it was not possible to reduce the silicate level below 4 to 5% without seriously affecting brightness. The author used Perkins bleaching formulation along with a silicate dosage of 4.5% as initial conditions in his experimentation.

Stage II: Chelant Addition. With the use of a chelant, bleaching of high-yield pulp with hydrogen peroxide was conducted within the refiner. This stage facilitated the pulp bleaching with hydrogen peroxide in a refiner setting.

The pulp sample (30 g) was then added to the PFI mill, along will the bleaching agents of hydrogen peroxide, sodium hydroxide, magnesium sulfate, and DTPA. The pulp (at 10% consistency) was then refined in the PFI mill, in the presence of the bleaching agents, to a freeness of 350 mL CSF.

Work was conducted by Perkins (14) using 2.5% hydrogen peroxide in addition with .5% $MgSO_4$ and 5% SiO_3 with varying amounts of alkalinity to bleach pulp in the refiner blow-line. Her experimentation showed that under these conditions, a total alkalinity of 2.5% was optimal. Initial conditions used by the author for this stage were Perkins optimal conditions with the substitution of 0.2% DTPA for the silicate.

Pulp Rinsing. After the pulp has been bleached by either of the peroxide stages, it was diluted with deionized water and mixed thoroughly. The dilution of the pulp allows for the halting of the hydrogen peroxide bleaching reaction. The pulp was then drained of excess liquid using a Buchner funnel, and then stored at 4^0 C until needed for testing.

Pulp Testing

Several tests are to be completed on the bleached pulp produced by the hydrogen peroxide and DMD bleaching stages in order to characterize their properties. Hypo number determinations were made on selected bleached pulp samples according to TAPPI Standard T253. Handsheets, weighing 1.2 g handsheets (40 lb sheet equivalent), were prepared on the British Sheetmaker for brightness and strength determination.

Handsheets were then conditioned in a constant humidity room for a 24 hour period. Tensile tests were completed on the cured handsheets (TAPPI standard T404 cm-92) as well as brightness (T452 om-92).

CHAPTER V

RESULTS AND DISCUSSION

Statistical Analysis

To verify a given set of data was significant in comparison to other data points, the margin of error was computed for all averaged results. This was completed by determining the standard deviation (sigma) for the sample group, and then multiplying this sigma value by two. According to the 65-95-99.7 rule of statistics, this two sigma range will result in an interval that we can be 95% confident that the true mean lies within. Due to the high probability that the true mean lies within the computed confidence interval, the author will note a significant difference in a comparison of data points if the intervals for each data point do not overlap.

Refiner Bleached Pulp At 350 mL CSF

Brightness

Following the procedure outlined in the experimental design, dimethyldioxirane was used as a refiner bleaching agent while the pulp sample was refined to 350 CSF. Figure 4 shows the brightness results obtained during this portion of the experiment.

From the figure, it can be noted that dimethyldioxirane does result in a brightness increase when used as a refiner bleaching agent. A significant brightness increase of 7.6 brightness points can be noted between the control pulp and the 2.5% DMD addition. This equates to a 29.3% increase in brightness with the DMD addition.

Brightness Of DMD Refiner Bleached Pulp At 350 CSF Freeness
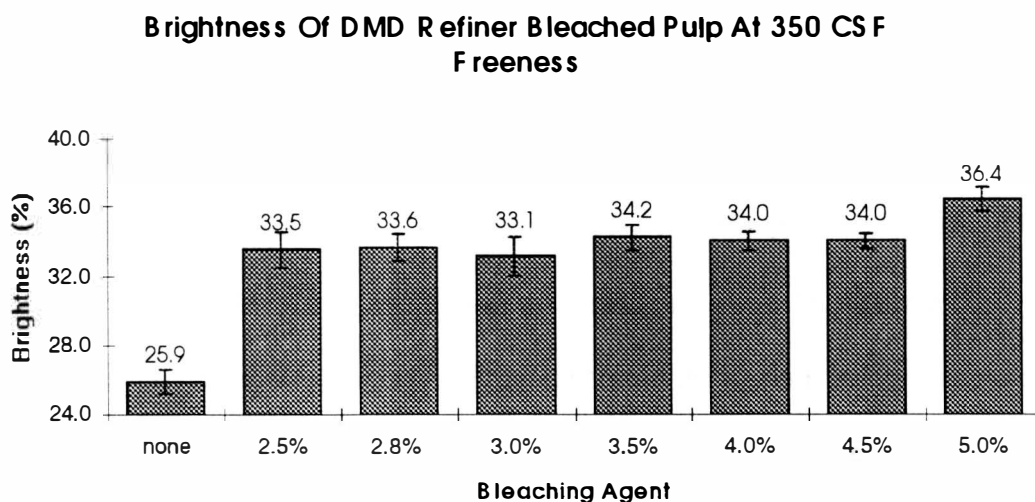
Figure 4.   Brightness of DMD Refiner Bleached Pulp at 350 mL CSF Freeness.

The brightness values obtained between the 2.5% DMD addition and the 4.5% DMD addition were not significantly different from each other. This means that no further improvement in brightness is occuring after a 2.5% addition of DMD in a refiner setting until the charge is increased to 5.0% DMD. At this charge addition, a brightness increase of 10.5 points was noted over the control pulp.

The results obtained during this experimental trial may be a result of the exstremely long lignin chains that high-yield pulps contain. Lignin is the portion of the pulp that contains chromophores, which darkens pulp. It is believed by the author that DMD is cleaving the doulble bonds within the long lignin chains that are found in high-yield pulps. Through the shortening of these lignin chains, the pulp becomes brighter as this dark portion is broken apart. This alteration allows for the reflection of more blue-white light that is measured as brightness, and causes the brightness increase.

Although the DMD is cleaving the double bonds contained within the lignin structure, the lignin molecule is still big and complex that it is still not solubilized in water. This is beneficial since it preserves the yield of the pulp. However, a limitation of brighness increase is being found because the lignin is being preserved within the pulp. Finally, at the 5.0% addition, enough chemical is present to cleave the lignin chain sufficiently to allow for the solubilization of the lignin itself.

Problems

Although positive results were being obtained from the original experimental design, modifications were needed to save on the large amount of time needed for each run. The cause of this problem was the difficulty in obtaining a 350 mL CSF freeness. The addition of chemicals was altering the amount of refining needed, as

would be expected. However, as shown in Figure 5, there was no clear trend showing

how the chemical addition was affecting the number of reveloutions needed. This

resulted in a lot of guessing at the number of reveloutions required to obtain the

proper freeness. Since the experimental design called for only two attempts with the

same pulp to hit a 350 mL CSF freeness, a lot of the runs ended up being discarded.

The Effect of DMD Concentration On Number Of PFI Mill Revolutions
(350 CSF)
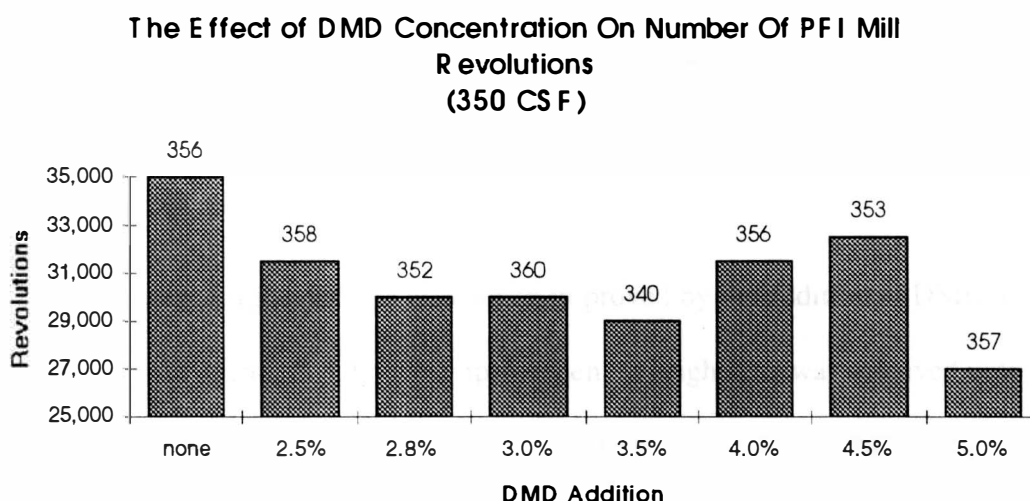
Figure 5.   The Effect of DMD Concentration on the Number of PFI Mill
             Revolutions.

It can be noted from Figure 5 that the average number or reveloutions required

appears to be around 30,000 reveloutions. From this information, the orignial

experimental design was altered to eliminate the 350 mL CSF target, and refine each

trial for 30,000 reveloutions in the PFI mill. Since dimethyldioxirane has been shown

to be very fast reacting (less than 10 minutes), the author felt that this modification

would not hamper the bleaching trials, since 30,000 reveloutions equates to over 30

minutes of refining.

Refiner Bleached Pulp At 30,000 Revolutions

Brightness

Based on the information obtained from the last bleaching trial, the author felt that modifications needed to be made in the DMD charge levels. A 1.0% and 2.0% DMD charge was added, and the 2.5% and the 4.5% DMD refiner charge levels were removed from the original experimental design. The results obtained are shown in Figure 6.

As shown, brightness was once again improved by the addition of DMD as a refiner bleaching agent. A 5.4 point improvement in brightness was achieved with a 1.0% addition, and a 8.7 point improvement was noted at the 2.0% DMD addition.

There was no statistical difference in the brightness between the 2.0% charge and the 5.0% charge of DMD. These results match those found in the previous set of experiments, further backing the previoulsy speculated method by which the DMD is acting under in the refiner.

Brightness of DMD Refiner Bleached Pulp at 30,000 PFI Mill Revolutions
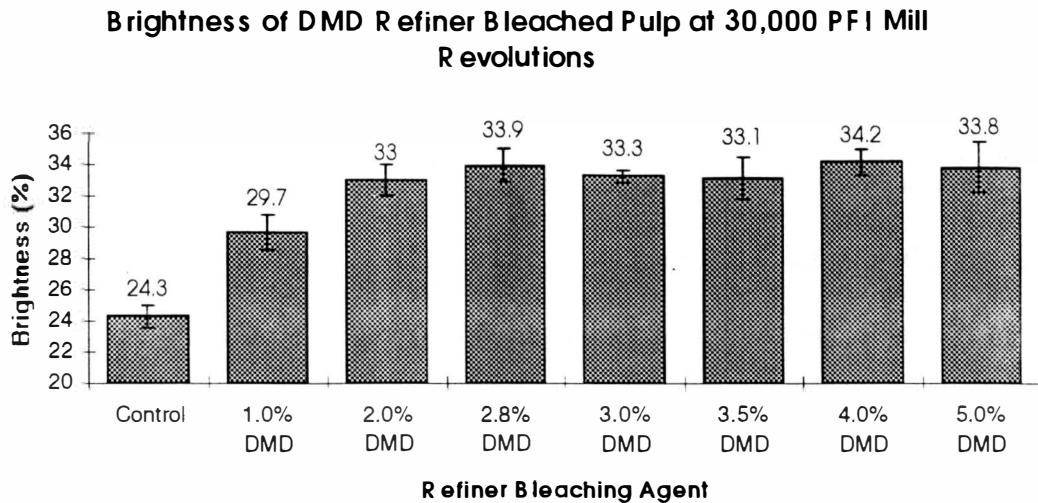
Figure 6.   Brightness of DMD Refiner Bleached Pulp at 30,000 PFI Mill Revolutions.

The only signifcant difference found in the comparison of the two trials is the brightness at the 5.0% DMD charge. The 350 mL CSF freeness had a brightness of 36.4 with a margin of error of 0.71. The 30,000 revolution pulp had a brightness of 33.8 with a margin of error of 1.63. This difference in brightness levels may be attributed to extra refining that the 30,000 revolution pulp under went. The 350 mL CSF pulp only went through 27,000 revolutions in the PFI mill. The extra 3,000 revolutions could have decreased the pulp brightness by increasing the fibrillation of the fibers. This increase fibrillation results in increased bonding, which hampers brightness since their are less air gaps in the sheet to aid in reflecting light.

Zero-Span Tensile

Zero-span tensile strength is a measurement of the average fiber strength found in a pulp. Through measurment of the zero-span tensile, it was the authors intent to determine whether the cellulose fraction of the pulp, which provides the strength of the fibers, is being damaged during the bleaching process. Figure 7 shows the results obtained.

Although a slight decreasing trend can be seen from the data, the results that were obtained for the zero-span tensile of the various pulps was not found to have a significant difference amongst themselves. This would mean that the addition of dimethyldioxirane was not degrading the strength of the fibers.
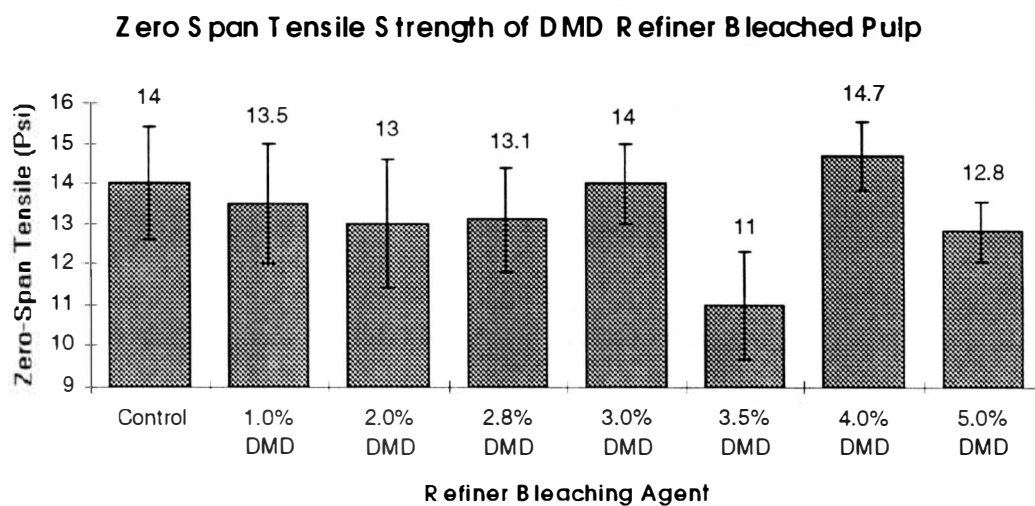
Figure 7. Zero-Span Tensile Strength of DMD Refiner Bleached Pulp

Hypochlorite Number

The hypochlorite ("hypo") number determines the degree of delignification of pulp. It can also be used as an estimation of the lignin content of the pulp being measured. The hypo number was determined for the control pulp along with the 1.0%, 3.0%, and 5.0% DMD addition at 30,000 PFI mill revolutions. The results are shown in Figure 8.

Hypo Numbers of Refiner Bleached Pulp
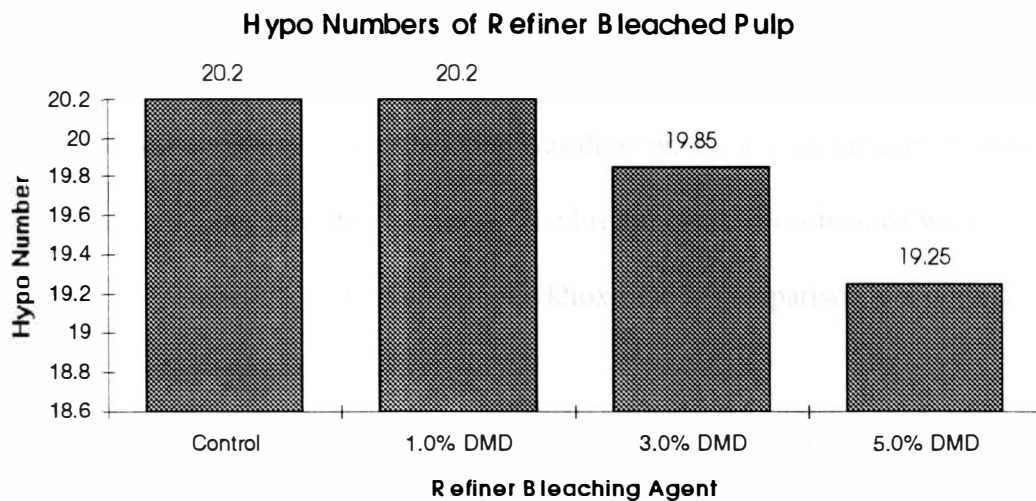
Figure 8. Hypo Numbers of DMD Refiner Bleached Pulp.

As shown by the data, a trend of a slightly decreasing hypo number with additional DMD charge is present. This rate of decrease appears to increase with the charge of DMD, illustrated with no change between the contol and 1.0% charge, a change of .35 units between 1% and 3.0% charge, and .60 units between the 3.0% and 5.0% DMD charge.

Since a relationship exists between hypo number and lignin content, a decrease in hypo number should correspond to a decrease in lignin content. This trend would then support earlier statements about the dimethyldioxirane cleaving the double bonds of the lignin chain, but not actually solubilizing the lignin untill a higher charge (5.0%) is used. This would lead to preservation of the yield and makes DMD well suited to bleach high-yield pulps.

Superchelation

Although dimethyldioxirane is stable in the presence of metal ions, peroxymonosulfate is not. Superchelation was done on a few pulp samples in order to remove the metal ions prior to bleaching. The brightness results obtained with bleaching a superchelated pulp with dimethyldioxirane in comparison to a normal pulp is shown in Figure 9.

As shown by the data, a trend does exist of higher brightnesses with superchelated pulps at higher DMD charge. However, statistically, there is no difference in brightness between the normal pulp and the superchelated pulp. Therefore, superchelation is not necessary for refiner bleaching of high-yield pulps with dimethyldioxirane.

Comparison of DMD Refiner Bleaching on Normal and Super Chelated Pulp At 30,000 PFI Revolutions
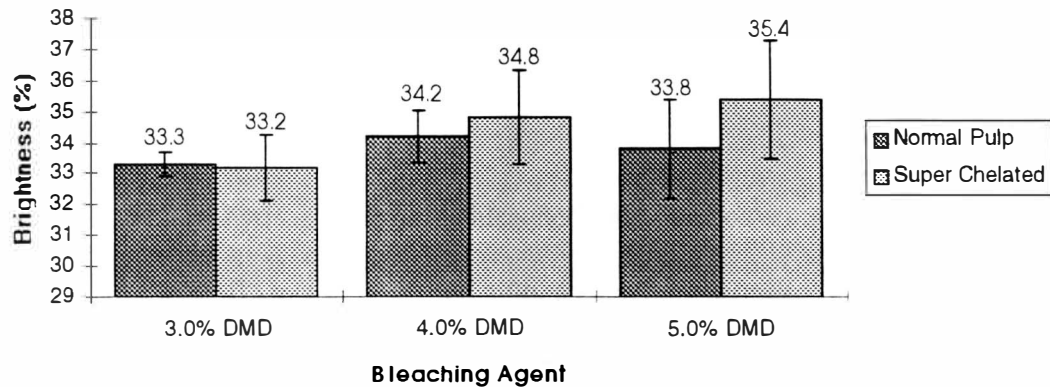
Figure 9.   Comparison of DMD Refiner Bleaching on Normal and SuperChelated Pulp.

Hydrogen Peroxide Bleaching

According to the experimental design, a conventional and refiner bleaching sequence was to be completed with hydrogen peroxide on the control pulp as a comparison to the DMD refiner pulp. It was also decieded at this time to perform a conventional hydrogen peroxide bleaching stage on previously DMD refiner bleached pulp to see if a two sequence refiner bleaching system would be feasible. If the results from the two sequence bleaching looked prominsing, a refiner bleaching sequence using DMD for the first half of the sequence and hydrogen peroxide without silicates for the second half of the refining period would be completed.

In determining the charge level of DMD to be used in the peroxide experiments, the author decided upon a 3.0% charge. Noting that the brightness

increase levels off at 2.0% from the past experiment, the extra percentage would ensure that the brightness plateau had been reached.

Conventional Bleaching Stage

To see how hydrogen peroxide bleached pulp in a conventional system compared to the DMD refiner bleached pulp, a bleaching sequence was carried out on the control pulp after it had been refined in the PFI mill. A hydrogen peroxide bleaching stage was also completed on previously refiner bleached pulp with a 3.0% DMD charge to see what type of results were obtainable. The results are shown in Figure 10.

Conventional Bleaching With 2.5% Hydrogen Peroxide
(Total Alkalinity = 2.5%)
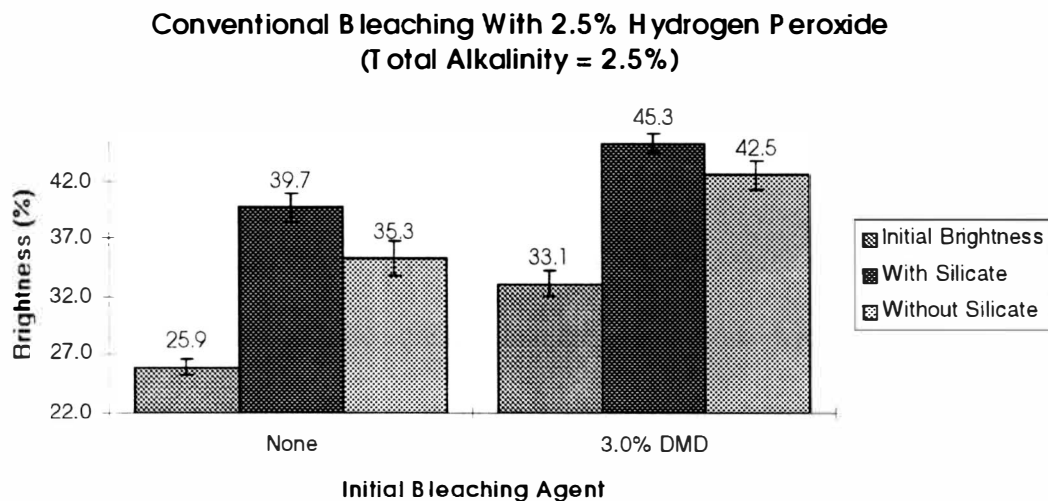
Figure 10.   Hydrogen Peroxide Bleaching in a Conventional System on Both a Control Pulp and a DMD Refiner Bleached Pulp.

As shown, a significant brightness improvement was obtained with the 2.5% hydrogen peroxide bleaching stage in all cases. A brightness improvement of 13.8 points was found when bleaching the contol pulp with hydrogen peroxide in the pressence of silicates. Only a 9.4 point increase in brightness was obtained on the control pulp when silicates were not used, showing silicate's ability to improve the brightness gain. In all cases, the hydrogen peroxide bleaching with silicates provides a significant increase in brightness over that obtained in refiner bleaching with dimethyldioxirane.

Bleaching a DMD (3.0%) refiner bleached pulp with hydrogen peroxide also produced positive results. Once again, the silicates presence gave a significant improvement in brightness gain, giving a 12.2 point increase compared to a 9.4 point increase.

Two-Stage Refiner Bleaching

It was noted that the brightness value obtained for 2-stage bleaching sequence without using silicates was much greater than the conventional hydrogen peroxide bleaching on the reference pulp. Encouraged by the results obtained with the convential bleaching stage with 2.5% hydrogen peroxide, the author proceeded with both a hydrogen peroxide refiner bleaching sequence (without silicates) and a two-stage refiner bleaching sequence. For the two-stage bleaching sequence, the first 15,000 revolutions of the PFI mill were completed with the addition of 3.0% DMD,

and the next 15,000 revolutions were completed with the addition of 2.5% hydrogen

peroxide. The pH was adjusted to 10.5-11.0 inbetween the two sequences. The

results from the experiment are shown in Figure 11.

Comparison Of Different Bleaching Agents And Bleaching Methods
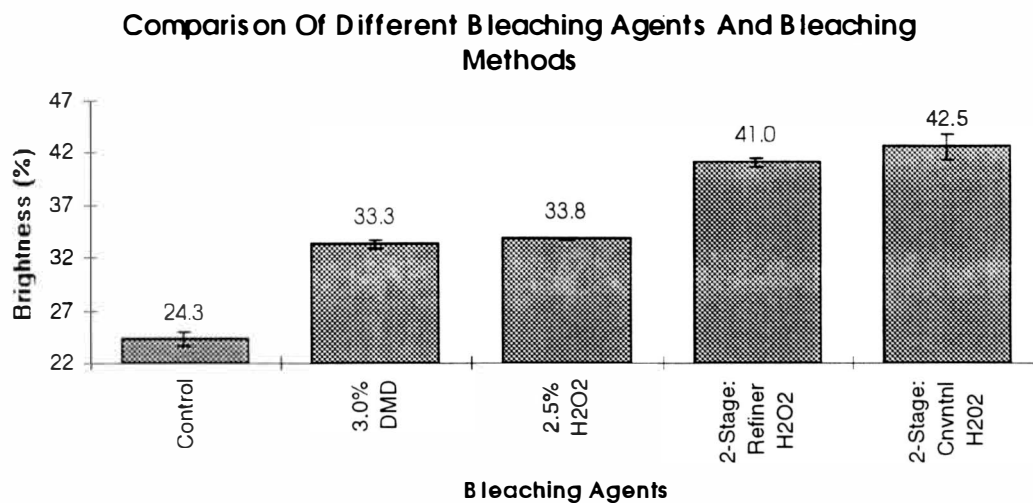
Figure 11.   Comparison of Different Bleaching Agents and Bleaching Methods.

As shown, the refiner bleaching with the hydrogen peroxide provide a very

small, significant brightness increase over what a 3.0% charge of DMD could

provide. But when used together as bleaching agents for half of the refiner run, a

brightness improvement of nearly 7.5 points results. This produces a significantly

brighter pulp.

In comparison to the addition of hydrogen peroxide in the refiner or in a

conventional bleaching system (no silicates), there was no significant difference

found. On the other hand, this 2-stage refiner bleaching sequence provided near a

16.5 point improvement over the control pulp. From these brightness data, it can be concluded that a refiner hydrogen peroxide bleaching sequence could be added after a refiner DMD bleaching sequence. Such a system could provide better brightness results than a conventional hydrogen peroxide bleaching sequence with silicates.

CHAPTER VI

CONCLUSIONS

Dimethyldioxirane was found to produce an increase in pulp brightness as a refiner bleaching agent. This increase was approximately 8.5 points from the control pulp when added to the refiner for 30,000 revolutions. Low concentrations of DMD, approximately 2.0% on O.D. pulp, was found to be sufficient for this brightness increase, since the brightness values leveled quickly.

Although superchelation of the pulp was theorized to improve pulp brightness by stopping the decomposition of peroxymonosulfate, the results showed that it was not mecessary. A trend was observed showing the superchelated pulps to be brighter than the normal pulps, but the difference between the two sets of values were statisticaly insignificant.

A large brightness increase (17 points) can be obtained using DMD and hydrogen peroxide in a 2-stage refiner bleaching sequence. This was accomplished using 3.0% DMD and 2.5% hydrogen peroxide, using DTPA as a stabilizer. Compared with earlier experimentation utilizing a conventional peroxide bleaching stage as the final stage, the results were statistically the same.

APPENDIX A

RAW DATA

Brightness

Run #	Description	Sheet 1 Bright 1	Bright 2	Sheet 2 Bright 3	Bright 4
8	Control-356 CSF	25.48	25.89	25.83	26.32
9	2.8% DMD-360 CSF	31.41	32.17	32.27	32.16
10	3.0% DMD-360 CSF	33.51	33.15	32.36	33.54
12	3.5% DMD-360 CSF	34.01	34.81	34.07	34.02
13	4.0% DMD-356 CSF	34.14	34.16	33.61	33.91
15	4.5% DMD-353 CSF	34.11	33.95	33.67	34.14
18	5.0% DMD-357 CSF	36.33	36.12	36.88	36.14
19	2.8% DMD-352 CSF	33.51	33.19	33.84	33.75
21	2.5% DMD-358 CSF	32.71	33.43	33.8	33.87
26	Run #8 + 2.5% H2o2 W/ Si	40.12		39.23	
27	Run #8 + 2.5% H2o2 W/O Si	34.51	34.68	35.81	36
28	Run #10 + 2.5% H2o2 W/ Si	44.89	45.38	45.09	45.86
29	Run #10 + 2.5% H2o2 W/O Si	41.91	42.46	43.34	42.28
33	Control	24.9	24.44	24.36	23.98
34	3.0% DMD	33.16	33.55	33.09	33.08
35	4.0% DMD	34.42	33.46	34.31	34.21
36	5.0% DMD	34.55	34.94	32.76	33.79
37	3.0% DMD on Super-K pulp	33.86	33.17	32.99	32.58
38	4.0% DMD on Super-K pulp	35.41	35.52	34.29	34.06
39	5.0% DMD on Super-K pulp	35.95	35.91		34.29
40	2-Stage: 3.0% DMD/2.5%H2O2	41.85	41.09	40.53	39.83
41	2-Stage: 3.0% DMD/2.5%H2O2	41.66	43.46	40.36	40.76
43	1.0% DMD	30.49	29.42	29.08	29.4
44	2.0% DMD	33.68	33.06	32.55	32.36
45	2.8% DMD	34.65	34.18	33.78	33.15
46	3.5% DMD	34.15	33.37	32.91	32.27
47	2.5% H2O2	33.79		33.73	

Run #	Description	Sheet 3 Bright 5	Bright 6	Average	Stdev	Error
8	Control-356 CSF			22.3	8.00	0.34
9	2.8% DMD-360 CSF			27.4	10.29	0.40
10	3.0% DMD-360 CSF			28.5	10.36	0.55
12	3.5% DMD-360 CSF			29.8	9.95	0.39
13	4.0% DMD-356 CSF			29.8	9.37	0.26
15	4.5% DMD-353 CSF			30.2	8.48	0.22
18	5.0% DMD-357 CSF			32.7	8.22	0.35
19	2.8% DMD-352 CSF			30.7	6.52	0.29
21	2.5% DMD-358 CSF			31.0	5.59	0.53
26	Run #8 + 2.5% H2o2 W/ Si			35.1	7.91	0.89
27	Run #8 + 2.5% H2o2 W/O Si			33.6	3.75	0.76
28	Run #10 + 2.5% H2o2 W/ Si			41.8	7.75	0.42
29	Run #10 + 2.5% H2o2 W/O Si			39.8	6.06	0.61
33	Control	24	24.13	25.5	3.30	0.29
34	3.0% DMD	33.37	33.32	33.4	0.33	0.15
35	4.0% DMD	34.72	34.35	34.4	0.48	0.34
36	5.0% DMD	33.21	33.65	34.1	1.11	0.66
37	3.0% DMD on Super-K pulp			33.9	1.78	0.53
38	4.0% DMD on Super-K pulp			35.5	1.56	0.75
39	5.0% DMD on Super-K pulp			36.3	1.97	1.09
40	2-Stage: 3.0% DMD/2.5%H2O2	40.51		40.6	0.74	0.67
41	2-Stage: 3.0% DMD/2.5%H2O2	40.36		41.3	1.18	1.17
43	1.0% DMD	29.87	30.23	31.6	5.03	0.44
44	2.0% DMD	32.97	33.47	34.6	4.18	0.42
45	2.8% DMD	33.94	33.45	35.5	4.24	0.43
46	3.5% DMD	32.69	32.94	34.9	4.93	0.53
47	2.5% H2O2	33.8		37.1	6.61	0.05

Zero Span Tensile Strength (PSI)

Run #	Description	Sheet 1			
33	Control	14.3	13.9	15.2	11
43	1.0% DMD	13.8	15.6	15.4	11.4
44	2.0% DMD	14.2	13.4	12	16.2
45	2.8% DMD	13	12.2	14.2	11.4
34	3.0% DMD	13.4	15.5	14	13.2
46	3.5% DMD	14.2	9.6	10.4	10.2
35	4.0% DMD	14.8	15.6	15.1	15.1
36	5.0% DMD	13.4	13.2	13.8	13.8
37	3.0% DMD on Super-K pulp	12.4	12	13.2	12.1
38	4.0% DMD on Super-K pulp	14.4	15.2	13.6	13.6
39	5.0% DMD on Super-K pulp	12	11.5	10.9	10.8
40	2-Stage: 3.0% DMD/2.5%H2O2	16.4	15.6	16.7	16.1
47	2.5% H2O2	11.6	14.9	15.2	13.7

Run #	Description	Sheet 2			
33	Control	13.2	15.8	14.6	13.60
43	1.0% DMD	14.2	14.6	11.1	14.60
44	2.0% DMD	13.5	15	13.4	11.50
45	2.8% DMD	13.7	14.6	12.2	13.70
34	3.0% DMD				
46	3.5% DMD	12.1	12.1	10.4	10.20
35	4.0% DMD	15.3	13.4	13.8	15.40
36	5.0% DMD	13	12.8	12.6	12.20
37	3.0% DMD on Super-K pulp	12.9	11.2	14.3	12.00
38	4.0% DMD on Super-K pulp	13	13	14.5	15.00
39	5.0% DMD on Super-K pulp	12.4	11.9	11.4	12.20
40	2-Stage: 3.0% DMD/2.5%H2O2	14.9	13.3	15.2	16.10
47	2.5% H2O2	15.3	14.2	14.2	15.40

Run #	Description	Sheet 3			
33	Control	15.00	13.4	14.3	13.9
43	1.0% DMD	11.80	14.2	12.6	12.8
44	2.0% DMD	12.50	10.55	10.9	13.2
45	2.8% DMD	15.30	11.5	12.1	
34	3.0% DMD				
46	3.5% DMD	9.30	10.7	11	11.6
35	4.0% DMD	13.30	15.1		
36	5.0% DMD	11.40	12	13.4	12.4
37	3.0% DMD on Super-K pulp	11.20	12.7	14.2	12.6
38	4.0% DMD on Super-K pulp	13.30	13.4	12.6	
39	5.0% DMD on Super-K pulp	10.60	12.2	13.2	12.9
40	2-Stage: 3.0% DMD/2.5%H2O2	13.10	13.7	14.9	14
47	2.5% H2O2	15.50	14.9	13.4	12.4

Run #	Description	Sheet 4				Average	Stdev	Error
33	Control	15.2	11	13.2	15.8	14.0	7.25	0.72
43	1.0% DMD					13.5	12.29	0.88
44	2.0% DMD					13.0	12.91	0.96
45	2.8% DMD					13.1	13.64	0.79
34	3.0% DMD					14.0	10.70	1.04
46	3.5% DMD					11.0	14.55	0.78
35	4.0% DMD					14.7	8.94	0.54
36	5.0% DMD					12.8	9.61	0.43
37	3.0% DMD on Super-K pulp					12.6	10.15	0.57
38	4.0% DMD on Super-K pulp					13.8	10.34	0.52
39	5.0% DMD on Super-K pulp					11.8	11.27	0.47
40	2-Stage: 3.0% DMD/2.5%H2O2					15.0	10.41	0.72
47	2.5% H2O2					14.2	13.62	0.72

APPENDIX B

SAMPLE CALCULATIONS

Calculation Of Required Charge Of Activated Oxygen

(.03 chemical) * 30 g OD fiber * $\underline{(1\ atom\ O)}$ * $\underline{(614.9\ g\ Oxone)}$
 16 g 2 atom O

 = 17.3 g Oxone

Calculation Of Required Charge Of Sodium Bicarbonate

Determined experimentally that 14 g of $NaHCO_3$ is needed for every 7.68 g Oxone added to buffer the solution to a pH of about 7.5

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

Calculation Of Required Charge Of Acetone

(30 g OD fiber) * (0.03 Oxone) * $\underline{atom\ O}$ * (1.5 mol ratio) * $\underline{58.1\ g\ acetone}$
 16 g mol acetone

 = 4.90 g acetone

 = 6.2 ml acetone

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