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Washing Between and After a Two Stage Hydrogen Peroxide Bleaching Sequence to Reduce Reversion and Increase Brightness

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**Washing Between and After A Two Stage
Hydrogen Peroxide Bleaching Sequence
To Reduce Reversion and Increase Brightness**

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**Course: Paper 473, Senior Engineering Problem 2
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ABSTRACT:

Even though a fairly high brightness can be obtained, mechanical pulps, such as refiner mechanical pulp, contain all of the color forming groups found in the wood. This limits its use because these groups revert back to a yellow color over time. If they could be removed by washing, RMP could be used in a wider variety of grades. This project will discuss background on the subject, followed by a design and procedures to try and accomplish this goal.

It was found that excessive washing will give a temporary increase in brightness, however no statistical change in reversion is seen.

INTRODUCTION.

Even though a fairly high brightness can be obtained, mechanical pulps still contain all of the color forming groups present in the wood. This limits the use of mechanical pulp in quality publication grades because these color groups revert to a yellow color upon aging.

In the environmentally conscious world of today, most companies would like to get the maximum use of their wood. High yield pulping is one solution to this. It is also less expensive because fewer chemicals are used. The yellow color reversion is a problem with mechanical pulp, however. This is aesthetically unacceptable in the high quality papers of today's market. If the color groups could be removed, lessening reversion, mechanical pulps could be used in a wider variety of grades.

This project shows that it may be possible to use large quantities of water to wash the reverting groups from the pulp. This paper will go into some background material, followed by the experimental design. After the design is reviewed, the procedures, results and conclusions will be discussed. The finishing note will be recommendations for further study in this area.

BACKGROUND.

The base stock for all of the work done in this project was 100% aspen RMP. RMP stands for refiner mechanical pulp. This process incorporates the mechanical action of refiner plates to tear the fiber from the wood chips. The lignin present in the chips also stays with the pulp suspension. The lignin contains color forming groups. These groups give lignin its initial brightness as well as cause reversion.

In order to raise the brightness of the pulp to an acceptable level for paper manufacture it must be bleached to a higher brightness. A typical bleach for a high yield pulp, such as RMP, is of oxidative nature. The bleaching agent used in this project is hydrogen peroxide, an oxidative bleach.

Oxidative Reaction on Lignin.

Finding out the exact reactions that peroxide has on the color forming groups has been taking place for several years. In the early 50's, it was indicated that the peroxide attacked the lignin through the carbonyl groups, color forming groups, in the molecular structure of lignin (1).

Andrews believes that the peroxide is capable of breaking down lignin like structures to yield colorless substances by alternate routes which involve demethylation, quinone formation, cleavage of side chains and ring rupture (2). In another work he has presented a possible reaction in which is seen in Figure 1 (3).

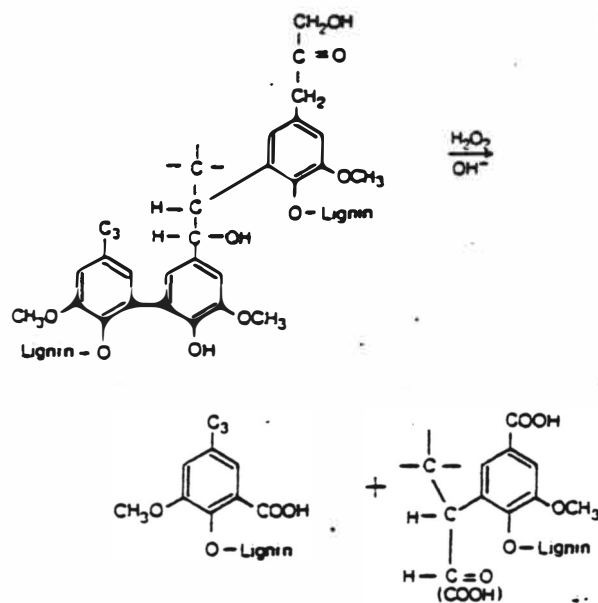


Figure 1. Oxidative reactions on lignin.

In recent work Strunk also proposed that the peroxide bleaching power was used to cleave chromophoric groups from the lignin structure (4). This work was done on a kraft pulp and peroxide was used as a brightness enhancer. The fact is if the color forming bodies are removed from the lignin structure extensive washing may remove them.

Another reaction which has also been shown indicates that a high alkali environment produces oxygen which will combine with the fragments from the lignin and form chromophoric structures. This is being done as the peroxide removes similar structures (2). In essence, new color forming groups are being formed as current ones are being deactivated.

Reversion.

It has been shown that there are several color forming groups found in lignin. Among these are carbonyl structures and quinone groups. The actual process taking place is the consumption of peroxide to break down the carbonyl structure while at the same time quinone groups are being made (5). These quinone groups are further broken down into carboxylic acids and hydroxy-quinones (5). All of these aid in the reversion process.

The oxidative bleaching conditions also contribute to the formation of color groups (2). Andrews has shown that the high temperatures and pH help the formation of carbanions. These conditions have an effect on the initial pulp brightness as well as the reversion characteristics.

Peroxide Chemical Reactions.

Most of which has been previously discussed has been done on lignin models. The actual chemistry behind oxidative bleaching is very complicated and the identification of specific reactions which would account for the consumption of the peroxide are inconclusive (3). Much is known, however, on the dissociation of peroxide as well as the basic reactions during peroxide bleaching.

The preferred dissociation of peroxide in water is as follows:



The actual ion responsible for the bleaching action on the

pulp is the perhydroxyl ion (O_2H^-). This preferred dissociation is dependant on temperature, however, it relies more on the pH of the solution (3). This can be seen in Figure 2.

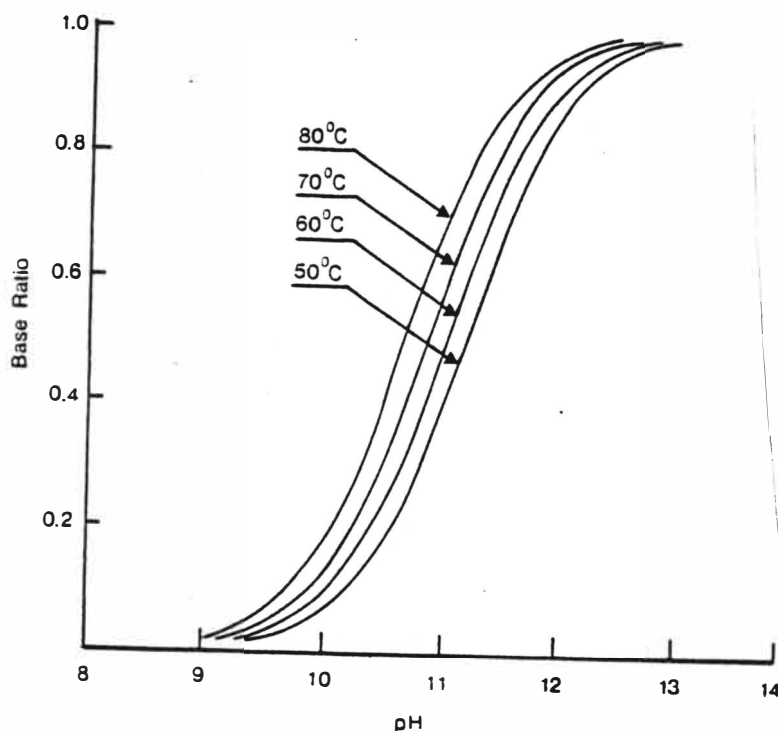
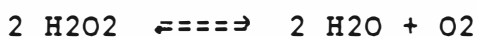


Figure 2. pH vs. Perhydroxyl Concentration.

As the pH drops below 10, the predominant dissociation that occurs to the peroxide is:



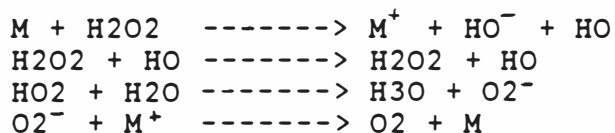
This shows peroxide decomposing into water and oxygen. This has no bleaching power thus it is best if the pH remains above 11.

Peroxide decomposition is the most prevalent reaction occurring and will reduce the bleaching potential drastically

if not prevented and monitored. Heavy metal ions are a major contributor to this reaction, catalyzing the peroxide.

In the past, Magnesium Sulfate was added to the Sodium Silicate to create Magnesium Silicate. This chemical will absorb trace metal ions such as Manganese, Copper, and Iron (3). Currently strong acids have been developed to deactivate metal ions in the pulp. The most common and widely used is Pentasodium Diethylenetriaminepentaacetic acid (Na₅DTPA or more commonly DTPA). This chemical is extremely efficient and is stable in strong oxidizing systems such as peroxide bleaching (7).

DTPA reacts by forming a complex ring structure with the reactive metal ions. Francis has shown that peroxide reacts with metal ions as follows:



Where M is a metal ion (8).

DTPA reacts with the metals before this reaction can occur.

External Factors Affecting Peroxide Bleaching.

Pulp consistency must be taken into account when performing peroxide bleaching. As the consistency increases, so does the increase in brightness. This can clearly be seen in Figure 3.

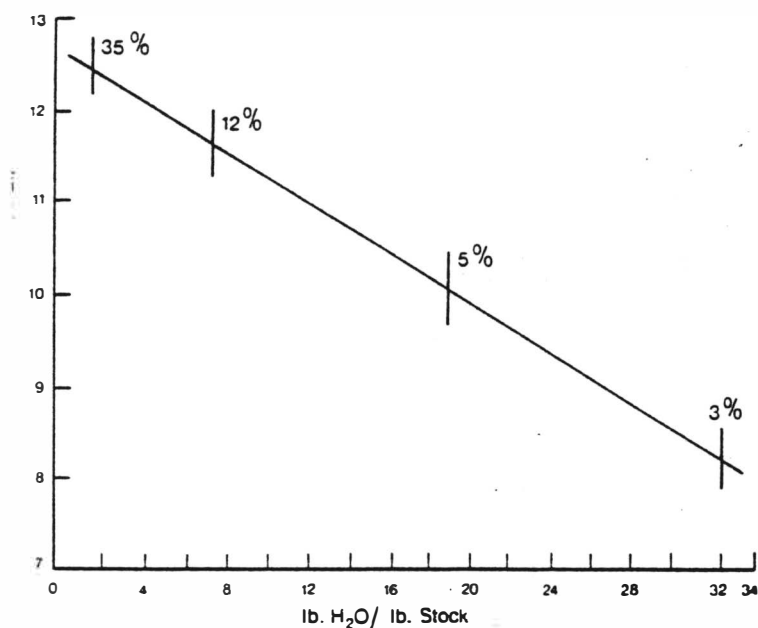


Figure 3. Brightness vs. Consistency.

Sjorgren indicates two possibilities for this increase. First, there may be an intermediate chemical produced during bleaching which transfers from fiber to fiber aiding in the oxidation reaction. The distance between the fibers is critical, and if the consistency is too low the benefits of this chemical are not seen (6). Another possible explanation is that increasing the consistency increases the probability that the perhydroxyl ion will react with the lignin in contrast to a non-bleaching reaction (6).

The second variable that effects the bleaching reaction is the peroxide charge. Figure 4 shows the relation of peroxide charge on the brightness of Poplar pulp (3). As you can see an increase in peroxide charge on the pulp will increase the brightness. This is due to the fact that increasing the peroxide level will increase the perhydroxyl ion concentration. Studies have been done and it is not possible to alter the consumption by forcing the level of

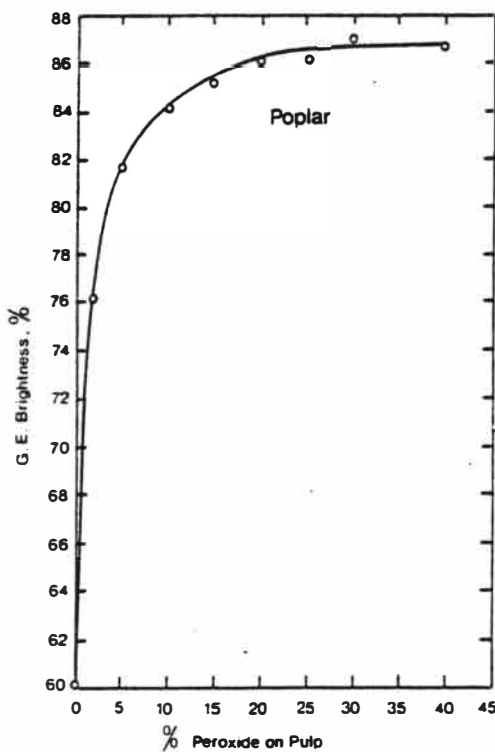


Figure 4. % Peroxide Addition vs. Brightness Gain

residual peroxide down by increasing temperature or alkali charge (9). Alkalinity and temperature do have an effect on the final brightness however.

Alkalinity of the solution during peroxide bleaching is extremely important. It has been shown that for every increase of 0.25% H_2O_2 there should be an adjacent increase in $NaOH$ of 0.20% (3). This is to insure that the pH is kept at the proper level. Increased alkalinity increases the bleaching rate up to 11.5. A further increase leads to a decreasing rate. At pH 12, the bleaching rate is about the same as pH of 10.5 (6).

If the pH falls, oxygen produced from the dissociation will generate chromophoric groups making them more resistant to the peroxide. For this reason the solution must be stabilized. Sodium Silicate is commonly used as a buffering solution in peroxide bleaching systems. It buffers by

assuming a complex formation between the peroxide and the silicic acids (3).

Aging of Paper.

No standard aging procedure has been developed for paper. This is due to the fact that no aging device can duplicate natural aging. Temperature, humidity, wave length, intensity and exposure are all variable in nature (10). MacMillan and Rapson found that good results for optical properties can be obtained using a light aging device (11). An estimate on approximate aging was done and it correlated to 3.3 days of aging to one hour in the Fade-Ometer, a light aging device (12). This was done for Chicago, Illinois, latitude in mid-January.

EXPERIMENTAL DESIGN

The purpose of this project is to use washing during a two stage hydrogen peroxide bleaching process to obtain higher brightness and lessen reversion.

All bleaching parameters were held constant for each of the pulp samples. The actual bleaching conditions are found in Table 1.

The controlled variable that was used in this project was the amount of wash water used and when it was applied. The rates of addition can be found in Table 2.

The main reason for the different washing rates is to observe the amounts of color forming bodies which will be washed from the pulp. A decrease in reversion should be linearly related to the number of color bodies removed.

Effluent from each of the washing stages will be collected and used to determine the various organics present. Once these organics are known experimentation can be done to optimize the washing ratios needed for good removal. Cost analysis will then be done to see if any benefits from the washing are economical. If results are good, plans will be made for the modification of a two stage bleaching system.

Table 1. Bleaching Conditions

Stage	Pretreat	% Chem		pH	Time
1	wash .5% DTPA	H2O2	3.5%	11.2	3 hr
		Na2SiO3	3.0%		
		NaOH	to pH		
		MgSO4	0.5%		
		NaHSO3 15% soln. (neutralize)			
2		H2OH	3.0%	11.4	2.5 hr
		Na2SiO3	2.5%		
		NaOH	to pH		
		MgSO4	0.5%		
		NaHSO3 15% soln. (neutralize)			

Table 2. Wash Ratios

- I. No washing.
- II. Washing between stages 50:1 weight ratio.
- III. Washing between stages 100:1 weight ratio.
- IV. Washing between and after stages 50:1 weight ratio.
- V. Washing between and after stages 100:1 weight ratio.

EXPERIMENTAL PROCEDURES.

This project was done in laboratory scale and the bleaching done in air tight bags.

The experimental procedures will be divided into sections and summarized as follows:

- Section 1: Material Gathering.
- Section 2: Pre-Bleaching Preparation.
- Section 3: Bleaching / Washing.
- Section 4: Brightness Pad and Handsheet Forming.
- Section 5: Reversion Analysis.
- Section 6: Data Analysis.

Section One.

The material gathering began by obtaining a base stock. 100% Aspen refiner mechanical pulp was used. This pulp was donated by a Northern Michigan mill. It had been screened and treated for bacterial growth. The pulp was stored in five gallon buckets at 5-6% consistency. The storage room was dark and approximately 50 degrees F.

Two chemicals, either not found in the department or the shelf life had expired, had to be obtained from outside companies. These chemicals included hydrogen peroxide and a sequestering (chelating) agent.

The hydrogen peroxide was donated by General Chemical. A fifteen gallon drum of industrial grade H₂O₂ was sent at 35% concentration. The chelating agent was supplied by Dow Chemical Company. The product name is Versene 80. This is DTPA.

Several chemicals needed were readily accessible in the

department. Sodium Silicate, used for a buffering agent, was found in the chemical stock room. It was in dry form and dispersed into a 35% solution. Sodium Hydroxide, and Magnesium Sulfate were also found there in power form. These were dispersed into 20% and 10% solutions respectively. The final chemical, the neutralizing agent, was Sodium Bisulfite. This was obtained from the chemistry stock room and dispersed into a 15% solution. All dilutions were done with distilled water using a magnetic stirring device.

Section 2.

After consulting Donald Kasics thesis, which was done in 1990, I found it in my best interest to pre-wash the pulp before bleaching. Distilled water, weighing 100 times that of the pulp, was used for washing. Any gross contaminants such as bark and large dirt particles were removed at this time. The pulp was thickened and re-diluted to 1.5% consistency.

After the dilution 0.5% DTPA (based on oven dry fiber weight) was added to the pulp solution as a chelating agent. After being added the pulp was mixed for three minutes with a small Lightning Mixer. This being accomplished, the pulp was allowed to stand for thirty minutes to insure complete reaction of the DTPA. From here the pulp was re-thickened to a 12% consistency mat and prepared for bleaching.

Section 3.

The bleaching portion of the experiment was held constant. All chemical additions remained consistent for each batch and are found in Table 1. of the Experimental Design section. All of the percentages were done based on oven dry fiber weight.

The order in which the chemicals were added is as follows: Sodium Hydroxide was added to raise the pH above 11. Sodium Silicate was then added as a buffering agent. Magnesium Sulfate was also added to insure complete chelation. Finally the peroxide was added to the sample. After all of the chemicals were added the bags were sealed and mixed thoroughly for a minimum of two minutes.

After mixing the sample was placed in a 60 C water bath for three hours. Every five minutes during the holding time the pulp was agitated to insure good chemical mixing. Once the bleach had been completed the pH was recorded and the pulp was neutralized to a pH of 6. This was done using a Sodium Bisulfite solution.

The next stage was to then wash the pulp according to the schedule found in Table 2. Once washed, the pulp was re-thickened to 12%, charged with the second stage chemicals, and bleached. Neutralization followed by washing, if necessary, was done again.

After the entire sequence of bleaching and washing was preformed, the pulp was pressed into a 10-12% pad and stored for brightness evaluation.

Section 4.

After the pulp had been bleached, brightness pads were made using the British Handsheet former. Four gram pads were made according to the TAPPI Standard. These sheets were then air dried for 24 hours at standard conditions. Once conditioned, brightness was recorded: 15 measurements on each of 10 sheets equalling 150 measurements for each sample. The measured pads were then stored in a freezer to minimize reversion while the other pads were being made.

Section 5.

Using all of the brightness pads, samples were cut for aging. The Fade-Ometer, a light aging device, was used for reversion analysis. The samples were put into the chamber and it was held at 100 degrees and constant humidity (100%). The carbon cores in the chamber were changed every 12 hours. The bulb was also cleaned at this time to insure good light transmission. The samples were aged for intervals of one, ten, and one hundred hours. After the samples were aged, they were re-conditioned at standard conditions and brightness was re-measured. The second brightness measurement was used in combination with the first to obtain a post color number according to the following equation:

$$\text{p.c. \#} = [(k/s) \text{ after aging} - (k/s) \text{ before aging}]$$

where: k = absorbtivity coefficient
 s = scattering coefficient

A similar equation that was used to obtain (k/s) values is found in TAPPI Standards for the coloring of paper:

$$k/s = [1-R]^2 / 2R$$

where: k = absorbtivity coefficient
s = scattering coefficient
R = Reflectivity of an " infinite pile of sheets
(brightness)

Section 6.

Data analysis included doing statistics on all of the numbers which were gathered in the results section of this paper. Both the standard deviation as well as the standard error of the mean are recorded with the average measurement. These statistics were used to compare the averages from stage to stage as well as comparing the different aging intervals.

RESULTS AND DISCUSSION

Tables 3 and 4 as well as figures 6 through 9, illustrate the results of the experimental design and procedure.

These results include the standard deviation as well as the standard error of the mean. Standard deviation is a common calculation used in nearly all statistical equations. Standard error of the mean (SEM) is calculated as follows:

$$\text{SEM} = \text{Std Deviation} / \sqrt{N}$$

where: N = number of samples.

This indicates the 95% probability of a value falling into the standard confidence level. The data point is recorded + or - 1 SEM.

Brightness.

Looking at the brightness data as well as the graphs one can see that there is statistical significance between the samples. Looking at Figure 8, the standard error bars do not overlap, thus making the data statistically significant.

After one hour of aging, the order of brightness remains the same, however, looking at figure 9, it is seen that the error bars do overlap thus removing any statistical significance.

At ten as well as one hundred hours of aging brightness is relatively the same for all of the samples. So

statistical evidence can be obtained from the data collected.

The initial significance could be due to the fact that all of the small impurities and residual chemical were removed through the washing stages. As aging continued the color bodies consumed this initial increase making all of the pulps relatively the same brightness.

Reversion.

The tables and graphs show that there is no decrease in reversion as hoped for. After one hour of aging all of the post color numbers are essentially the same. There must be a minimum of two post color numbers difference before any statistical significance is produced. As aging increases, so do the post color numbers. There is a significant increase in post color numbers with every increment of aging.

After ten and one hundred hours of aging, there are significant differences between the washed and unwashed p.c. numbers. The difference is going in the wrong direction however. Larger post color numbers indicate that there are more color forming bodies present in the pulp. From the data, the excessively washed pulp shows that they contain more color bodies when compared to the unwashed pulp. This may be due to the fact that the high amounts of wash water displaced ions that retard yellowing. An example of such an ion is calcium. If in fact this is the case p.c. numbers would increase for the highly washed pulp.

The effluent of the wash stages as well as a cost analysis was not performed because experimental data showed that this process did not work.

Table 3. Brightness

Aging Hr.	Batch	Brightness	Std. Dev.	STM
0	1	71.0	.86	.14
	2	72.1	.57	.09
	3	73.6	1.10	.08
	4	74.7	.91	.17
	5	75.6	.34	.30
1	1	63.9	.32	.38
	2	64.7	.20	.25
	3	65.0	.19	.49
	4	65.5	.35	.41
	5	67.1	.67	.43
10	1	50.7	.47	.21
	2	51.7	1.28	2.86
	3	51.6	.83	.37
	4	50.7	.93	.42
	5	51.0	.47	.21
100	1	40.5	.19	.08
	2	40.7	.11	.05
	3	40.3	.23	.10
	4	40.6	.27	.12
	5	40.7	.11	.05

Table 4. Post Color Numbers

Aging Hrs.	Batch	Post Color #	Stat. Sig.
1	1	4.27	
	2	4.23	
	3	4.69	
	4	4.80	
	5	4.13	
10	1	18.05	
	2	17.16	
	3	17.96	
	4	19.69	X
	5	19.60	X
100	1	37.78	
	2	37.80	
	3	39.48	X
	4	39.17	X
	5	39.26	X

Figure 6.

Brightness

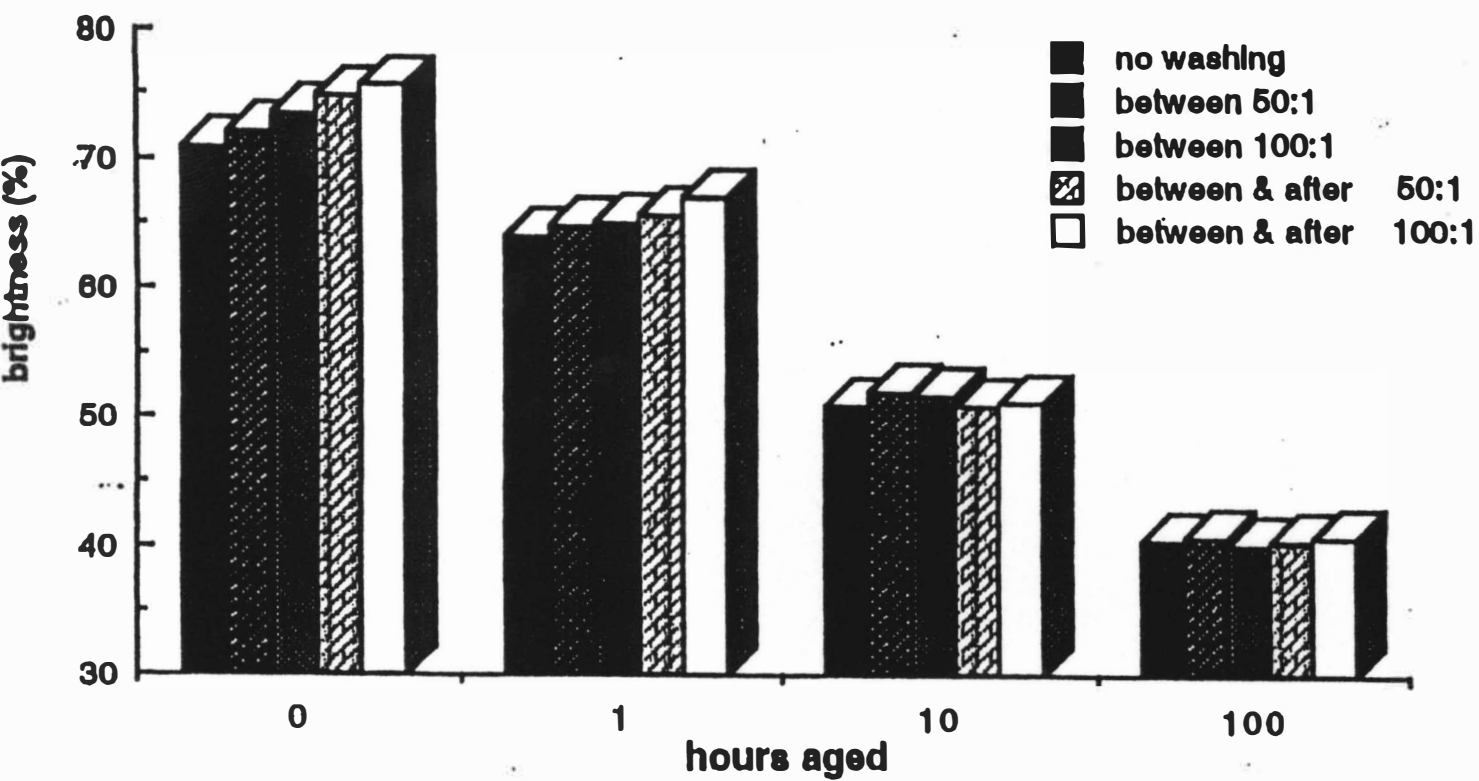


Figure 7.

Post Color Numbers

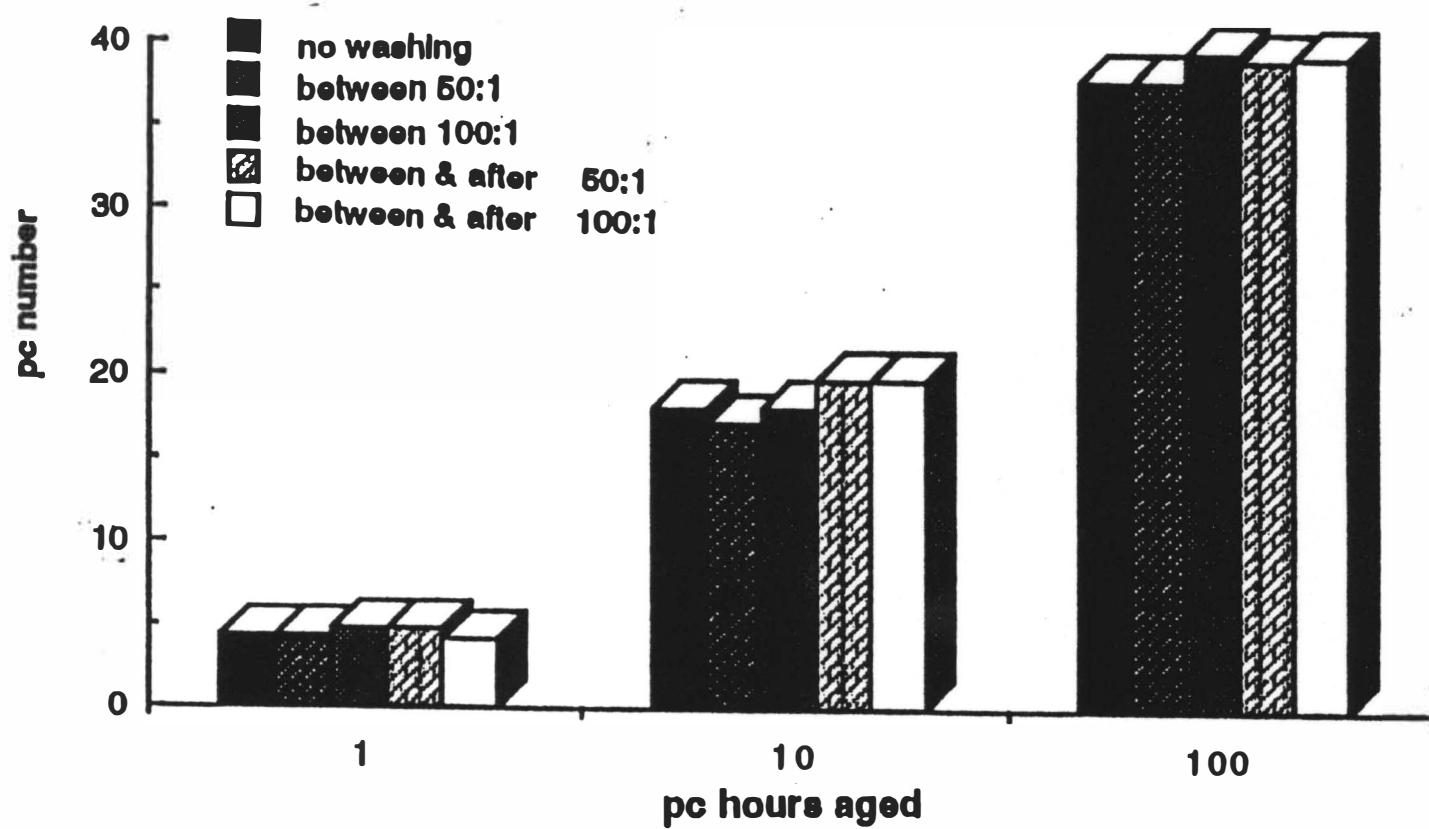


Figure 8.
BRIGHTNESS NO AGING

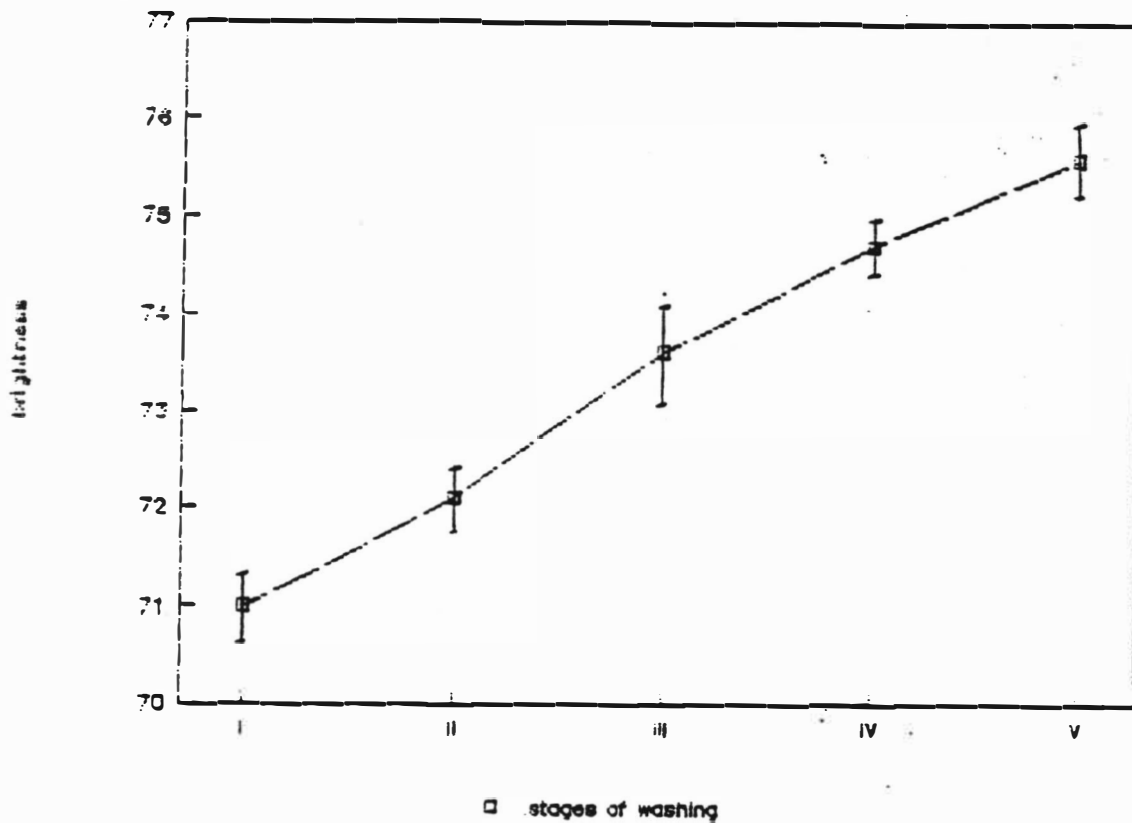
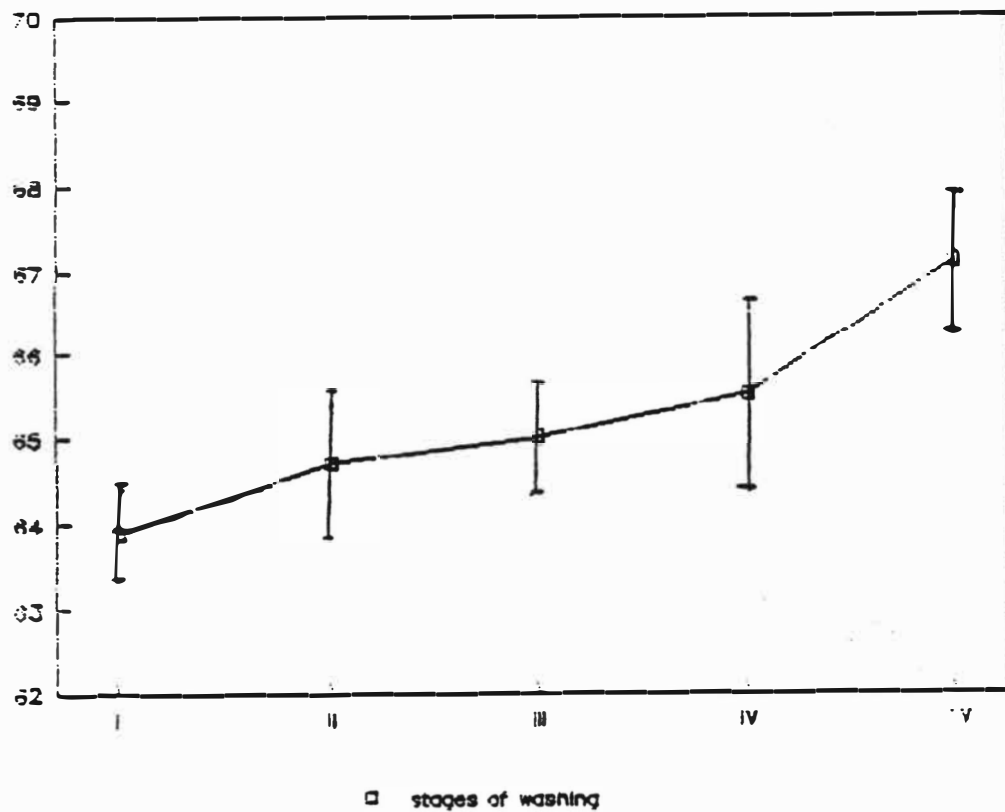


Figure 9
BRIGHTNESS AGING 1 HOUR



CONCLUSIONS.

Two-stage hydrogen peroxide is an effective bleaching sequence for refiner mechanical pulp. It has been shown that temporary increases in brightness can be seen if excessive washing is done between and after the stages of bleaching.

Even though excessive washing can increase brightness temporarily, this washing does not remove a detectable amount of the color forming bodies found in RMP. No significant change in reversion is seen between a pulp which has been heavily washed when compared to a pulp that has not been washed.

The conclusions of this experiment were not positive, however, they were statistically proven thus making this project a success.

RECOMMENDATIONS.

A recommended study for further evaluation of this matter includes another two stage bleaching sequence. This sequence would include an oxidizing bleach followed by a reducing bleach. The oxidative bleach may expose the color forming groups allowing the reducing bleach to eliminate them. Washing as well as a yield study should be included in this project.

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