

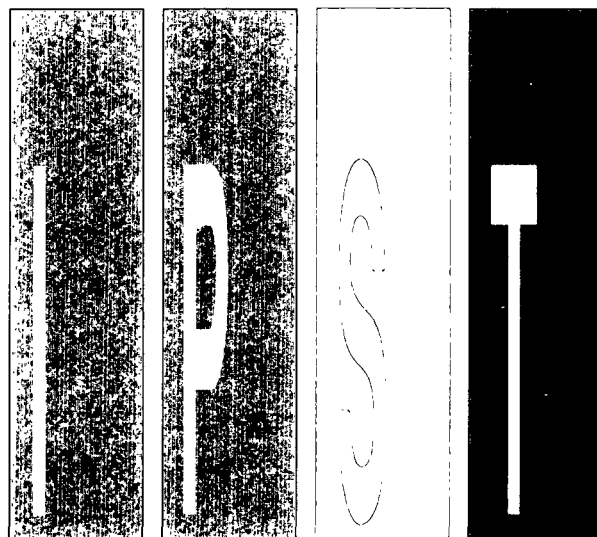


*Institute of Paper Science  
and Technology*

**MECHANICAL PULPING  
PROJECT ADVISORY COMMITTEE  
MEETING**

**AUGUSTA, GEORGIA**

**SEPTEMBER 28, 1994**



*Atlanta, Georgia*

# MECHANICAL PULPING PROJECT ADVISORY COMMITTEE

## TENTATIVE AGENDA

WEDNESDAY, SEPTEMBER 28, 1994

SHERATON AUGUSTA HOTEL  
AUGUSTA, GEORGIA

12:00	Lunch - Introductions and Assignment of Projects to Committee Members	All Frazier
12:30	Project 3694 - Brightness	Rudie
1:15	Project 3729 - Strength	Rudie
1:45	New Project - Experimental Plan	Rudie
2:15	Break	
2:30	Project 3524 - Brightness Stabilization	Ragauskas
3:30	Student Research: An Evaluation of Strain Distribution in Loblolly Pine Fibers Under Cyclic Compression	Rueckert
4:00	Student Research: The Effect of Ophiostoma Piliferum on the Strength Properties of Mechanical Pulp	Forde/Rudie
4:15	Future Directions	All
4:30	Project Selection Criteria	McDonough
4:45	Other Business	All
5:00	Adjourn	

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Revised 9.14.94

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**Project 3694**  
**High Brightness High Yield Pulps**

Alan W. Rudie

Chemical & Biological Sciences Division

Institute of Paper Science and Technology  
Atlanta, GA

September 28, 1994

**PROJECT:** 3694

**TITLE:** HIGH BRIGHTNESS HIGH YIELD PULPS

**TASK:** An Evaluation of the Influence of pH Profile on Peroxide Bleaching.

**Summary:**

Three sets of experiments have been performed in an effort to establish an ideal time/pH relationship for peroxide bleaching. The first set of experiments looked at the BTG probe brightness response and pulp bleaching response at different peroxide charges. This culminated in an attempt to identify the optimum sodium hydroxide charge for bleaching with 4% peroxide at 10% consistency and 50° C. Experiments carried out with 3%, 3.4% and 4% NaOH all gave about 15 points brightness gain. At 5% NaOH, about 14 points in brightening were achieved.

The second series of experiments evaluated a split sodium hydroxide charge. The hypothesis being tested was that peroxide was subject to slower diffusion than hydroxide, and adding the caustic after a time delay might decrease alkaline reversion at the beginning of the reaction. Some sodium hydroxide was added at the beginning of the bleaching process to prevent premature precipitation of the sodium silicate in the peroxide bleach solution. Maximum brightness gain was 15.9 points, achieved with two sodium hydroxide charges of 2% each spaced five minutes apart.

The third series of experiments was designed to determine if the optimum maximum pH was higher than the optimum pH for residual bleaching. This was carried out with a series of experiments where the sodium hydroxide was either singly charged with the peroxide, or split between two additions five minutes apart. The total sodium hydroxide charged exceeded the optimum determined in the first two sets of experiments, but was partially neutralized with sulfuric acid twenty minutes into the bleaching process. The best brightness gain was obtained with 1% sodium hydroxide added with the hydrogen peroxide, 4% added five minutes later and 1% of equivalent acid added at 20 minutes. Nearly identical results were obtained with 2.5, 2.5 and 1 and 3, 3 and 1 (% caustic, % caustic and % acid) addition methods. Maximum brightness obtained here was 15.4 points, slightly less than the split addition case without excess caustic. The difference in brightness obtained is not due to a loss in bleaching efficiency at the high maximum pH, but rather is due to an estimated 1.5 points in brightness lost on the addition of acid. There was insufficient time to determine if this loss could be reduced or eliminated using acids other than dilute sulfuric acid.

**Introduction:**

At the March PAC meeting, the project was still encountering start-up difficulties, primarily related to the difficulty mixing 10% consistency pulp. At that time I showed a slide with a series of step changes in base and acid addition, and evidence that the pH did not follow

appropriately, and abruptly. High concentrations of pulp and chemicals were forming in the middle of the mixer, between the top and bottom sets of agitators and there was not sufficient pulp movement out of this middle zone to complete the mixing. At the closed PAC meeting, I showed a second graph where a mixer had been placed in the center of the reactor, and the mixing behaved quite nicely through two step changes in pH.

We proceeded with the experimental work using this configuration and did not experience serious mixing problems.

The experimental sequence was designed to evaluate two hypothesis.

1. Typically hydroxide ions (and protons) have much faster diffusion rates in protic media than other molecules. This presents the possibility that in a single charge of sodium hydroxide and hydrogen peroxide, the local hydroxide concentration may rise high enough to induce alkaline reversion reactions, before the peroxide is evenly mixed to prevent them.

The proposed solution (test of the hypothesis) was to charge all or part of the sodium hydroxide a few minutes after the peroxide was added. To avoid potential problems with precipitation of silicate, the sodium hydroxide was split evenly with half charged with the peroxide, and half added five minutes later. It should also be noted that this method reduces the maximum pH but prolongs the time at the high pH.

2. Peroxide reacts most readily with the phenolate ion. Note, this hypothesis is in disagreement with most of the reaction schemes suggested for peroxide bleaching, but really cannot be ruled out with the existing data and is compatible with the pH behavior of the reaction showing a maximum rate in the 11 to 12 pH range.) There is a range of pKa's for the various phenols in lignin due to differences in ring substituents and the proximity of the phenolic groups relative to each other. Some phenolic groups may require very high pH to deprotonate, higher than can be obtained and maintained for a suitable period of time with the sodium hydroxide charge limited by the need to maintain a peroxide residual.

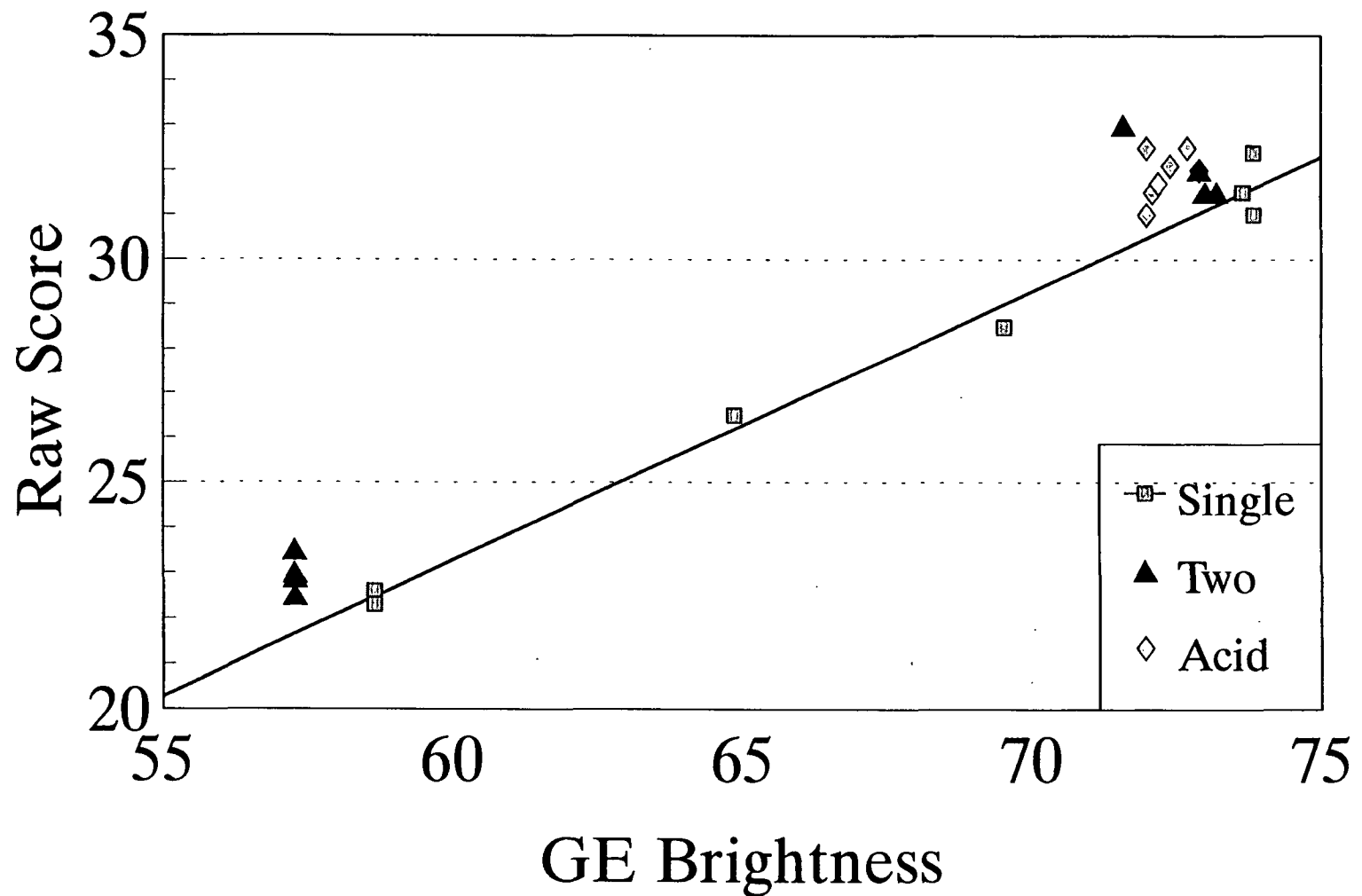
The proposed test of this hypothesis is to add excess sodium hydroxide at the beginning of the bleaching process and control the peroxide residual by neutralizing some of the caustic with acid some time after the initial chemical addition.

## **Results and Discussion:**

The initial group of experiments varied the peroxide charge to obtain a comparison between the BTG optic probe and TAPPI directional brightness. At 4% peroxide, the sodium hydroxide charge was varied to help determine the optimum sodium hydroxide charge for the pulp in use, and evaluate the influence of the residual pH on the optic probe output. These results are summarized in table 1 and figure 1.

Figure 1. Brightness vs Blue Diode  
Raw Scores

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PAC, 9/94:  $R^2 = 0.96$

Table 1. Preliminary Experiments

ID	H <sub>2</sub> O <sub>2</sub>	NaOH	residual pH	Blue	Green	GE
Start			5.0	22.3	24	58.66
331	1.0	1.2	8.5	26.5	28	64.85
401	2.0	2.0	8.6	28.5	30	69.53
404	4.0	3.4	9.5	31.5	31.5	73.65
405	4.0	4.0	9.7	31	31	73.84
406	4.0	3.0	9.0	32.4	32	73.84

The TAPPI directional brightness has a high correlation with the blue diode ( $r^2 = 0.99$ ,  $se = 0.64$ ) and green diode ( $r^2 = 0.94$ ,  $se = 1.82$ ) of the optic probe. Addition of a term for residual pH is not statistically significant, and gives a negative coefficient (high pH decreases TAPPI brightness relative to BTG solution brightness) which is counter to the results of the early pH step change experiments.

The second group of experiments used a split charge of sodium hydroxide. One half the sodium hydroxide used in the experiment was mixed with the peroxide, sodium silicate and magnesium sulfate in the bleach solution before adding to the pulp in the mixer. The other half of the sodium hydroxide was added five minutes later. Using 1.7% sodium hydroxide in each stage (3.4% total) this produced two pH maxima, both at about 9.6. Using 4% and 4.5% (total) sodium hydroxide the pH maxima were approximately 11.5 followed by 12, in both cases. The highest brightness increase obtained in this project (15.9 points) was obtained using 4% total sodium hydroxide evenly split between the two additions. However, this brightness gain is not significantly greater than was obtained with an initial charge of 4% sodium hydroxide and an additional 1% added 5 minutes later (15.6 points) or the control bleaches in table 1 with 3 to 4% sodium hydroxide added with the hydrogen peroxide (15 points).

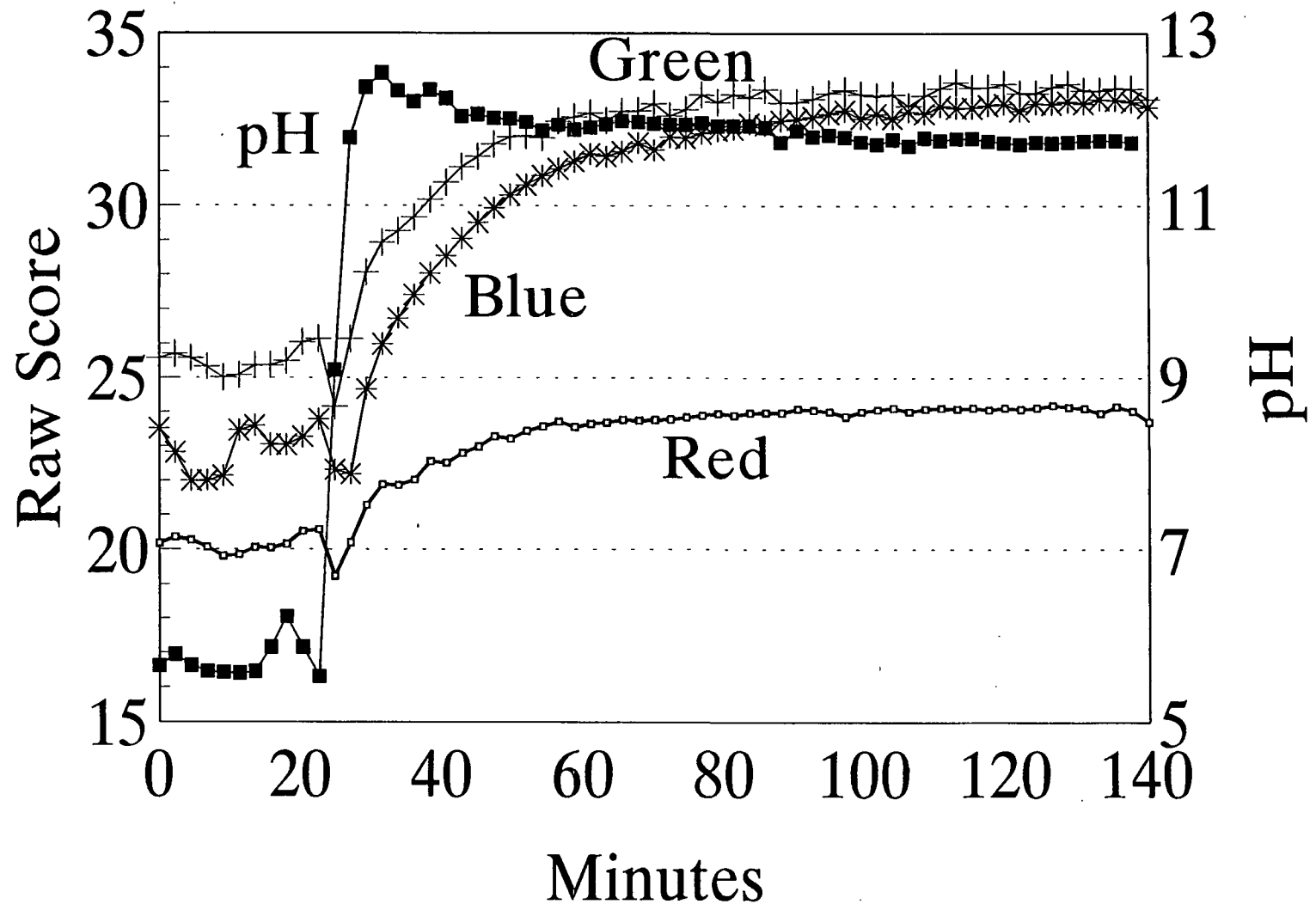
An analysis of the optic probe output in these experiments shows a slower initial rise in brightness with a steeper brightness gain during the residual phase of bleaching. This is most pronounced in the experiment with two 2% NaOH charges that resulted in the highest final brightness gain.

The final group of bleach experiments used both single addition and split additions for the sodium hydroxide, but included an acid addition after 20 minutes of reaction, to lower the pH during the residual phase of bleaching. Summary results for both the second and third sets of experiments are listed in table 2.

None of the experiments with acid addition gave higher final directional brightness than the split addition case, experiment 606. However, using the ISO brightness data, (not shown) experiments 608,609,613 and 623 all give higher final brightness than the split 4% sodium

Figure 2. Single Charge Bleaching  
4% Peroxide, 5% Sodium Hydroxide

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PAC, 9/94, Starting Brightness = 58, Final = 71.7

hydroxide experiment. Using the ISO brightness, experiments 613 and 623 gave the highest final brightness, 72.9 and 73.0 respectively.

Table 2.

ID	NaOH	NaOH	Acid	Residual pH	Blue	Green	GE
Start					23	25.5	57.3
524	1.7 <sub>0</sub>	1.7 <sub>5</sub>	0	9.0	33	32.6	71.6
606	2.0 <sub>0</sub>	2.0 <sub>5</sub>	0	10.3	31.5	32	73.2
607	2.25 <sub>0</sub>	2.25 <sub>5</sub>	0	10.1	31.5	32	73
608	2.5 <sub>0</sub>	2.5 <sub>5</sub>	1.0 <sub>20</sub>	9.68	32.1	33	72.4
609	3.0 <sub>0</sub>	3.0 <sub>5</sub>	2.0 <sub>20</sub>	9.8	31.7	31.8	72.2
613	1.0 <sub>0</sub>	4.0 <sub>5</sub>	1.0 <sub>20</sub>	9.75	32.5	31.6	72.7
614	5.0 <sub>0</sub>	0.0	0.0	10.41	33	33.5	71.8
615	5.0 <sub>0</sub>	0.0	1.0 <sub>20</sub>	9.9	31.5	32	72.1
616	2.5 <sub>0</sub>	2.5 <sub>5</sub>	1.0 <sub>60</sub>	9.8	32.5	32.5	72.0
622	4.0 <sub>0</sub>	1.0 <sub>5</sub>	1.0 <sub>20</sub>	9.7	31	31.7	72.0
623	4.0 <sub>0</sub>	1.0 <sub>5</sub>	H <sub>2</sub> O	10.3	32	32.5	72.9

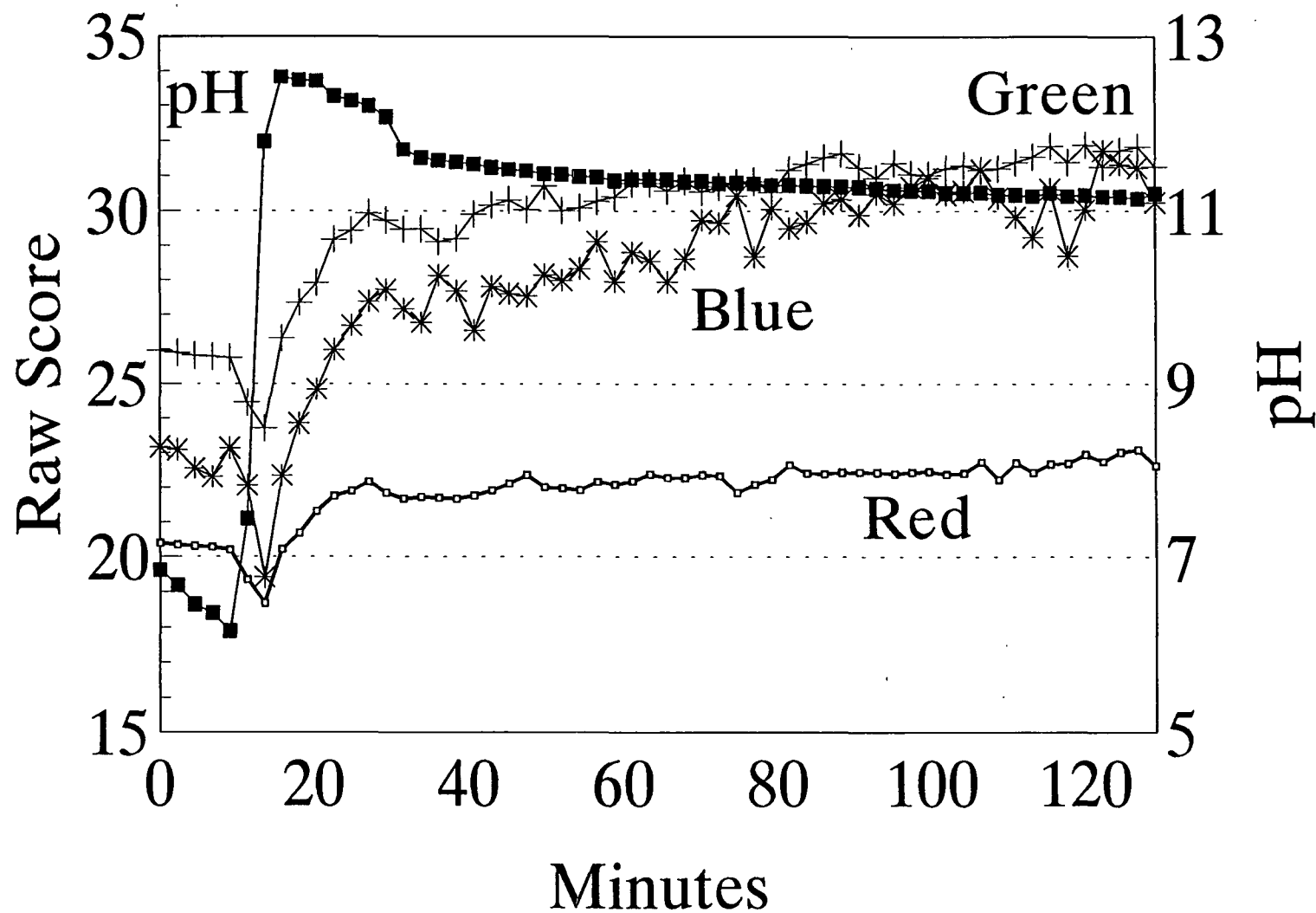
Subscripts indicate the time of addition relative to peroxide. Acid addition is sulfuric acid, and is expressed as equivalent sodium hydroxide neutralized.

**The conclusion reached from these 16 experiments, is that neither split addition of sodium hydroxide nor use of excess sodium hydroxide with subsequent addition of acid gives a statistically significant improvement in brightness over conventional peroxide bleaching.**

Typical bleach response curves are shown in figure 2 for experiment 614 as a single sodium hydroxide charge case and in figure 3 for experiment 615 as an example of a single charge of sodium hydroxide with acid addition after 20 minutes. The blue diode output for experiment 614 was fit to an inverse time relationship ( $\text{Blue} = 34,240 - 134,814/(\text{Time} - 15.85)$ ) giving an  $r^2$  of 0.99. This relationship been time shifted to match the initial bleach response of the acid adjusted experiment and the results are shown in figure 4. The conventional bleach response is for 4% peroxide and 5% sodium hydroxide. The acid addition case is also 4% peroxide and 5% sodium hydroxide, but the pH was reduced at 20 minutes after peroxide addition by adding 1% acid. This shows as a drop in pH from about 12 to about 11.5 at 30 minutes. Simultaneous to the drop in pH, the output of the blue diode drops and levels off, never regaining the brightness lost on addition of acid. Final brightness for these two cases were 71.8 without acid,

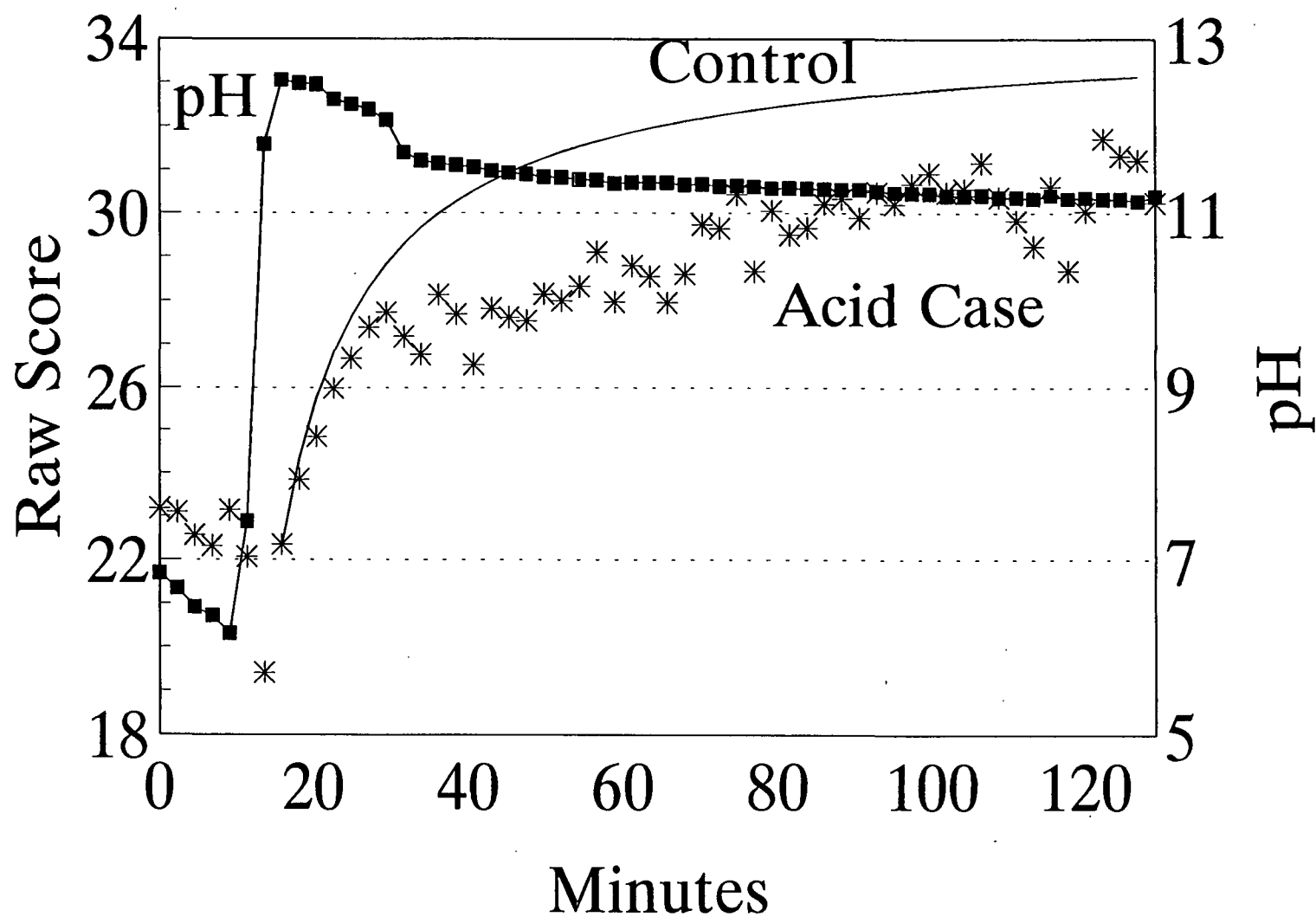
Figure 3. Acid Adjust Bleaching  
4% Peroxide, 5% Sodium Hydroxide, 1% Acid

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PAC, 9/94, Starting Brightness = 58, Final = 72.7

Figure 4. Acid Adjust Bleaching  
5% Sodium Hydroxide Standard



PAC, 9/94, 4% Peroxide, 5% Sodium Hydroxide, 1% Acid

and 72.1 with the addition of acid.

Several features of this graph are significant:

First, although the case without acid addition has the higher final blue diode response, it has the lower brightness. This suggests that factors such as pH, consistency or residual peroxide are influencing the probe brightness and in a more complete evaluation would need to be accounted for.

Second, the brightness curve drops after addition of acid and the rate of brightness gain decreases. The gap between the acid addition case and single charge case does not begin to narrow until around 80 minutes into the reaction.

Third, the addition of acid has increased the variability of the optic probe output signal. This occurs in about half the cases on addition of the acid.

The blue diode response of experiment 615 appears low relative to experiment 614, but the final brightness obtained in the case of 615 is close to the predicted value. On the other hand, the final brightness obtained in experiment 614 is two standard errors below the value predicted from the blue diode response. One possible explanation is that alkaline reversion reactions have started because of the low residual peroxide level (0.6 % on pulp in experiment 614). If this is the case, they are not detected by any of the optic outputs of the BTG probe. It is possible these reactions are pH sensitive and only produce chromophores when the pulp is neutralized to make handsheets. This is opposite to what is normally experienced with lignin, but is consistent with the data, and the response of the optic probe on addition of acid *vide infra*.

The sudden drop in brightness seen on addition of acid is more obvious in some reactions than others. It appears that the optic probe recovers this brightness response after 5 to 10 minutes, but does not recover the brightness gain that would be projected to occur during the recovery period. In one case, water was added instead of acid and although the brightness drop was observed, the bleach response returned to the original curve after 10 minutes. The decrease in the rate of brightness increase after acid addition is consistent with the known pH requirements of peroxide reactions. As the peroxide charge is consumed, the rate of reaction also decreases, and for experiment 615 with 5% NaOH without pH adjustment, this appears to be occurring.

The increased variability of the optic probe output after acid addition is disconcerting. One possibility is that the low pH at the point of addition has precipitated something on the fibers which does not dissolve as the solution is mixed. The mixing evaluations conducted to date only demonstrate that the filtrates are evenly mixed throughout the fiber, no experimental work has been performed to evaluate if fibers are evenly blended as well. In these cases the increased variability is specific to the optic output and does not appear in the pH which is consistent with a good mixing/poor fiber blending hypothesis. This hypothesis is also consistent with the concept that post bleaching alkaline reversion is not fully apparent until the pulp is neutralized.

## **Conclusions:**

The experimental work reported has raised a number of interesting issues, but there is insufficient data to resolve them. It does not appear that there is a large amount of brightness gain to be achieved by adjusting the pH and several replicate experiments would be required to determine if the modest brightness increases observed are real or just caused by normal experimental variation. The 1 point increase in brightness gain observed with split caustic addition would probably not justify the capital expense of adding a second mixer to the bleach process, but larger gains may be observed at 20 to 30% consistency where the sodium hydroxide concentration is higher and mixing is more difficult. In addition, a total brightness gain of about 2 points is potentially available if the brightness drop on the addition of acid can be avoided.

**Project 3729**  
**Improved Chemithermomechanical Pulp**

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September 28, 1994

**PROJECT:** 3729

**TITLE:** IMPROVED CHEMITHERMOMECHANICAL PULP

**Summary:**

Since the March meeting, we have completed the analysis of the Winter 94 wood sample to provide additional background information on the influence of the chlorite holopulping variables on the pulp handsheet strength. In particular, we were concerned about the effect air drying the pulp and the number of chlorite and extraction treatments have on the zero-span, tear and tensile indexes. In addition, there was a concern about whether wood chip zero-span tensile index was representative of the native fiber strength, or was artificially low because of the limited bonded area of unbeaten fibers. Since the Bowater Calhoun mill did not experience a significant strength loss this last winter the samples sent last February were not collected during a period of low pulp strength. It was decided to do more extensive testing on the wood chips and not test the refiner samples. In hindsight, there was an obvious error in the logic of this, which of course has become apparent with our testing. The winter 94 samples have shown low native fiber strength and it would have been interesting to see how the fiber behaved in the refining line. There is little point in testing these samples now since they have begun to decay.

This issue aside, the testing of the winter wood samples has largely confirmed our initial assumptions and has not materially changed the conclusion reached last March. In these experiments, the holopulping was carried out exactly as in the previous sets of samples, but with sufficient numbers of replicates to provide pulp for PFI beater runs. The chlorite holopulping was terminated with one group of samples after four treatment cycles and was extended to 5 treatments with the other group.

The unbeaten zero-span tensile index does appear to be representative of the native fiber strength, particularly in the case of the air dried pulp samples. For the never dried-pulps, the unbeaten zero-span tensile index is not the maximum zero-span and under these conditions the zero span test might be less reliable. The process of air-drying the pulp samples before making handsheets reduces the tested zero-span tensile index by 8.5% but the loss is largely independent of freeness. The additional chlorite treatment step also reduces zero-span slightly, with an average loss of 3.5%. Tensile index gives similar results with the air-drying process reducing tensile by about 24% and the additional treatment reducing the tensile index by 4%. On the other hand, the tear index increased by about 5% after air drying with the fifth treatment stage reducing tear index by about the same amount.

Using this data to provide a base line for evaluating the samples from the other three seasons, spring 93 had the strongest initial fiber strength, winter 92/93 and summer 93 were both weak. The weakest native pulp strength of the four periods was the Winter 93/94 sample. Although unexpected, this is an encouraging result since it suggests that the Bowater mill was able to compensate for the initial weakness of the fiber to minimize the impact on the mill.

**Introduction:**

As of the March annual meeting, we had tested samples of wood chips and pulp from the Bowater Southern Mill in Calhoun, Tennessee for the Winter of 92/93, Spring 93 and Summer 93. The mill had sent two sets of samples for each period and each set contained a sample of wood chips, primary refiner discharge, secondary refiner discharge, and a sample collected from the latency chest. A portion of the secondary refiner samples was latency relieved and made into handsheets for direct testing, and samples of all the sets were treated with sodium chlorite to delignify the wood. The pulps obtained from the chlorite process were also made into handsheets and tested. The conclusions based on the three periods was that the winter period did indeed show low strength which could be traced to the starting wood chips. The springs samples gave high strengths, but the summer samples gave low strengths, possibly less than the Winter samples. This was a little surprising to the mill because they had not been experiencing low paper strengths when the samples were collected.

There were a few concerns expressed about some of the testing:

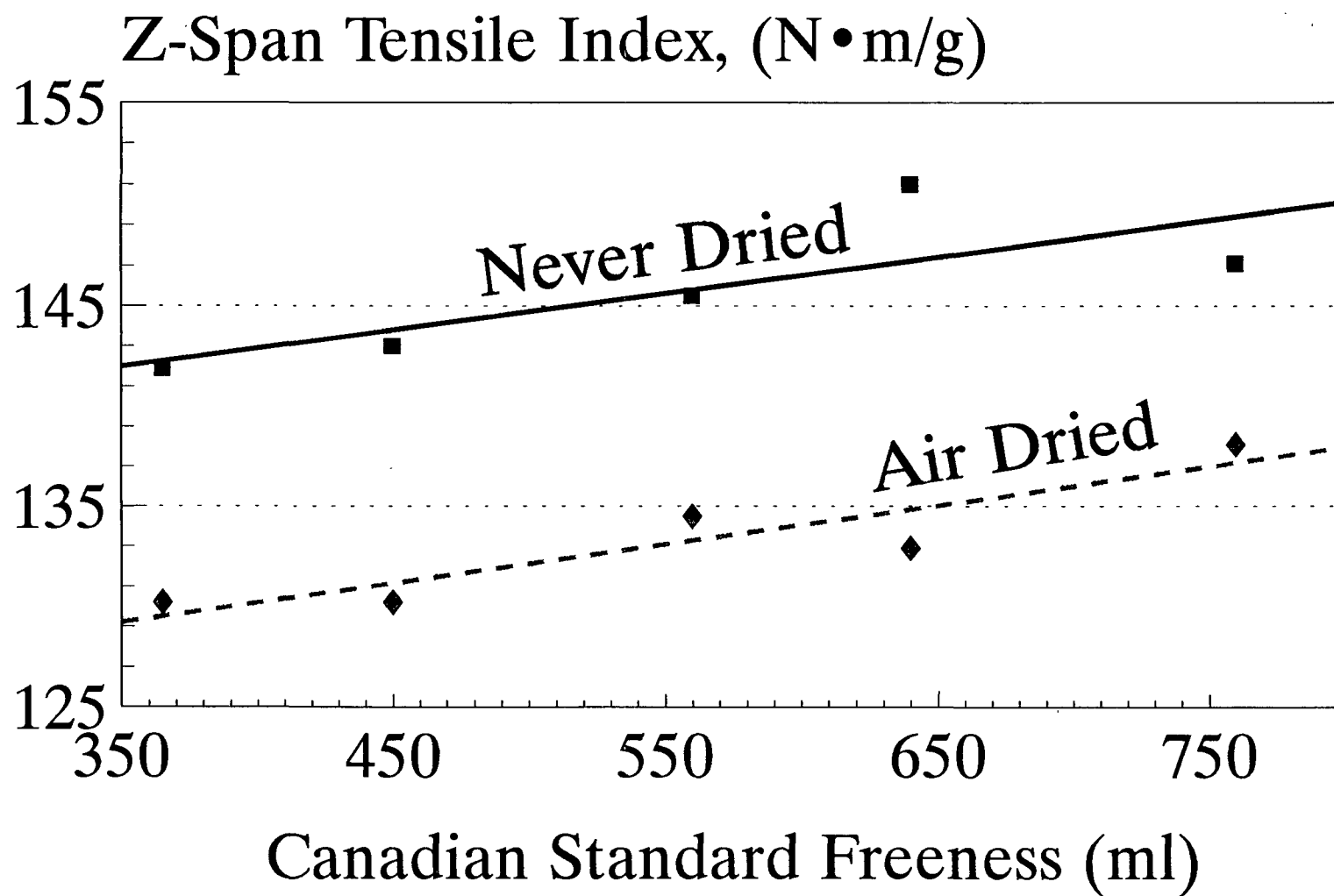
- The original winter sample was tested as is. The spring and summer samples were air-dried prior to re-slushing the samples to make handsheets for testing.
- The samples were treated with chlorite followed by alkaline extractions until the fibers were easily liberated with 1,000 revolutions in the British Disintegrator. There was a question as to how the additional treatments and reduction in yield affected pulp strength.
- There was a question as to whether the holopulped wood chip samples gave the highest possible zero span tensile strength or whether some beating was required to attain the maximum z-span tensile.

The mill failed to experience a period of low pulp strength in the winter of 93/94. They eventually sent a set of samples thought to be representative of normal production. It was decided not to test the pulp samples and do extensive testing of the wood chips to answer some of the remaining questions. The sample size used in the previous testing was small enough to fit in a 500 ml Erlenmeyer flask for holopulping. It was decided to continue with this sample size since it offered some additional security if a chlorine dioxide buildup should occur and detonate. (It should be emphasized that we have checked the chlorine dioxide concentration under worst case conditions. The maximum concentration of chlorine dioxide is well below the levels thought to be required for detonation.) Twentytwo 30 OD gram samples were delignified with sodium chlorite as indicated in the previous reports. Half were treated to three cycles of acid chlorite followed by alkaline extraction, and a final fourth chlorite stage. The other half were treated to an additional extraction and chlorite stage. The four stage treatment gave a final pulp yield of 64% with a brightness of 80. The additional stages reduced the yield to 63.2% and increased the brightness to 84%.

Pulps were treated to 0, 2300, 4000, 6500, and 9000 revolutions in the PFI mill giving freeness levels ranging from 760 to 355. Approximately half the sample at each freeness level was air dried. TAPPI handsheets were then made from each sample giving sets for two yield levels,

Figure 1. Zero Span Tensile

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5 freeness levels and air dried vs. never dried. Handsheets were tested for zero-span tensile, tensile, tear and burst and optical properties. Pulps were tested for Canadian Standard Freeness (before drying) and Kajaani fiber length.

## Results and Discussion:

The number of chlorite treatment stages and the air drying process proved to have a significant effect (95% confidence) on all the handsheet tests. The pulp freeness had a significant influence on all variables except the zero-span tensile index. The number of treatment cycles was significant in all cases except for Burst Index. Fiber length was reduced about 3% in the air drying process and decreased by about 7% in beating.

The effect of air drying the pulp on zero span tensile relative to starting freeness is shown in figure 1 for the wood samples treated to four stages of sodium chlorite delignification. The trend line for the air dried pulp samples runs nearly parallel to the never dried response but is displaced to lower values of z-span tensile index by about 12 N·m/g. The data for the five chlorite stage case is plotted in figure 2 for comparison to the trend lines for the four stage case. Although these data points do not adhere to the slopes of the four stage data, nearly all the points for the five stage data fall below the trend lines of the four stage data. The average loss in zero span tensile index is 5.2 N·m/g for the fifth stage of chlorite treatment.

The data for the zero span tensile index of samples treated with four chlorite stages appears to be strongly correlated with freeness (figure 1), but the data for the samples treated with five chlorite stages (figure 2) is poorly correlated with freeness and as a result, this term drops out of a regression analysis for zero-span tensile strength.

The influence of the three variables on tensile index is shown in figure 3. The air drying process reduces the tensile index by about 20 N·m/g at all freeness levels. The fifth stage of chlorite treatment has a much smaller effect, reducing the tensile index by just 3.5 N·m/g. The graph for tear index relative to never-dried freeness is shown in figure 4. The fifth chlorite stage reduces the tear index by about 0.45 mN·m<sup>2</sup>/g and the air drying process increases the tear index by about the same amount.

The relationship of tear index to tensile index is generally considered to be a better measure of pulp strength than the individual measurements. This data is shown in figure 5. Lines are provided for the five stage never-dried and five stage air-dried data. The air drying procedure has clearly reduced the tensile index without a corresponding increase in tear. The fifth stage of chlorite treatment also appears to have reduced the fiber strength, particularly in the case of the air-dried pulp samples.

Since freeness was not a significant variable for zero span tensile testing, the data from the three previous seasonal samples was pooled and test for significant differences. This data is summarized in table 1. There are no significant differences between the control and normal production samples from each period, but the spring zero span tensile strengths are significantly greater than the winter 92/93 and the summer samples. The summer controlled production zero-

Figure 2. Zero Span Tensile  
Number of Treatments

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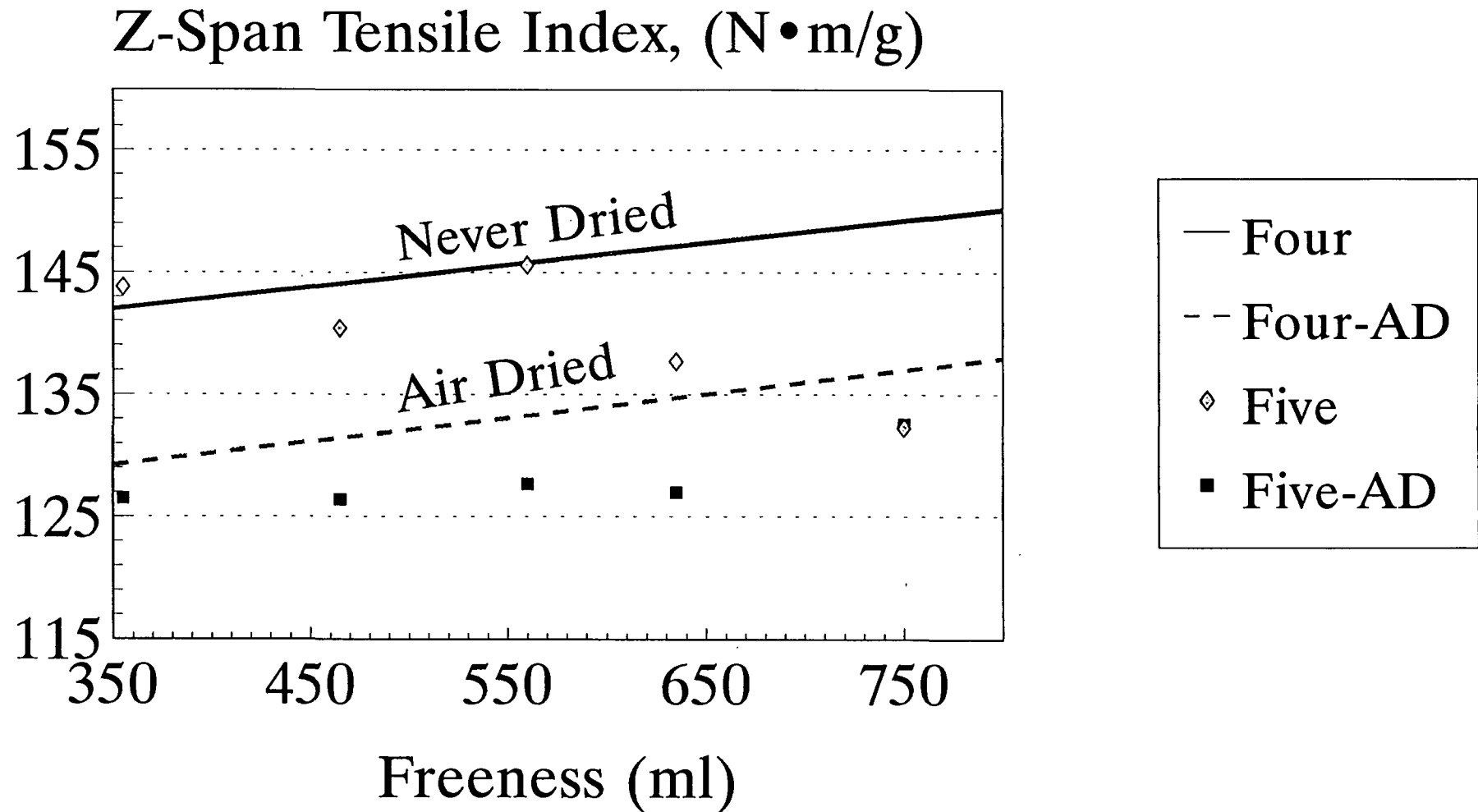


Figure 3. Tensile Index

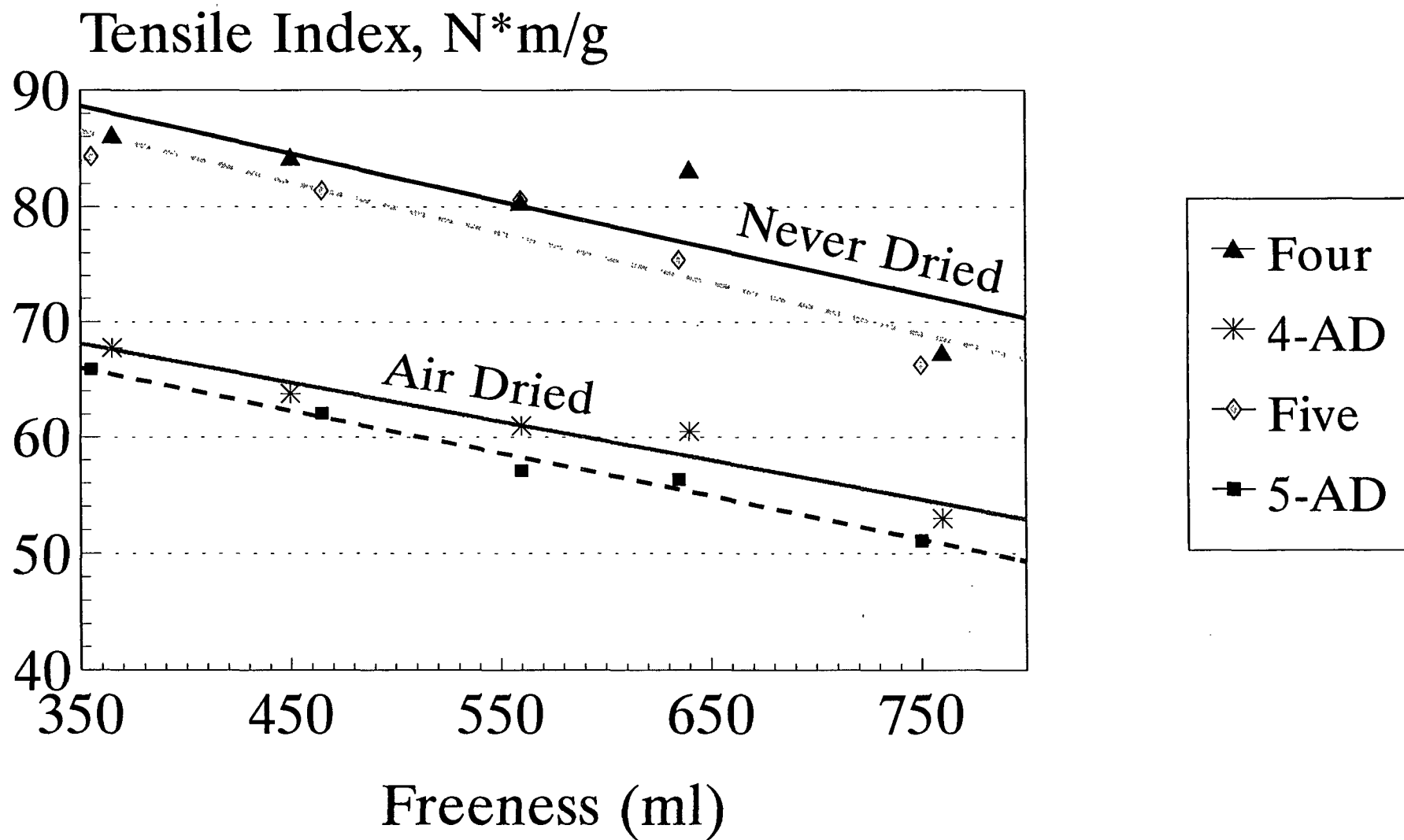


Figure 4. Tear Index

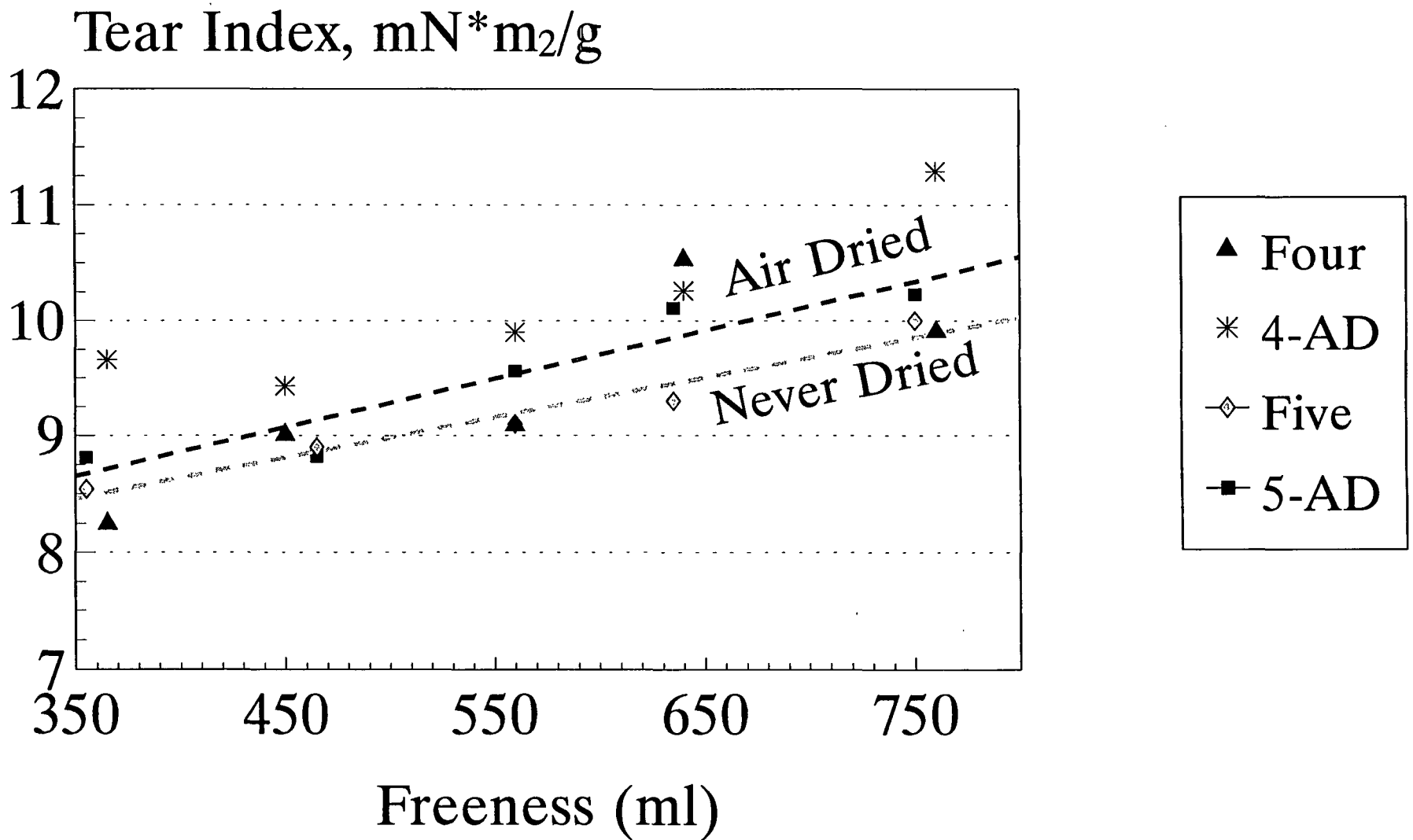
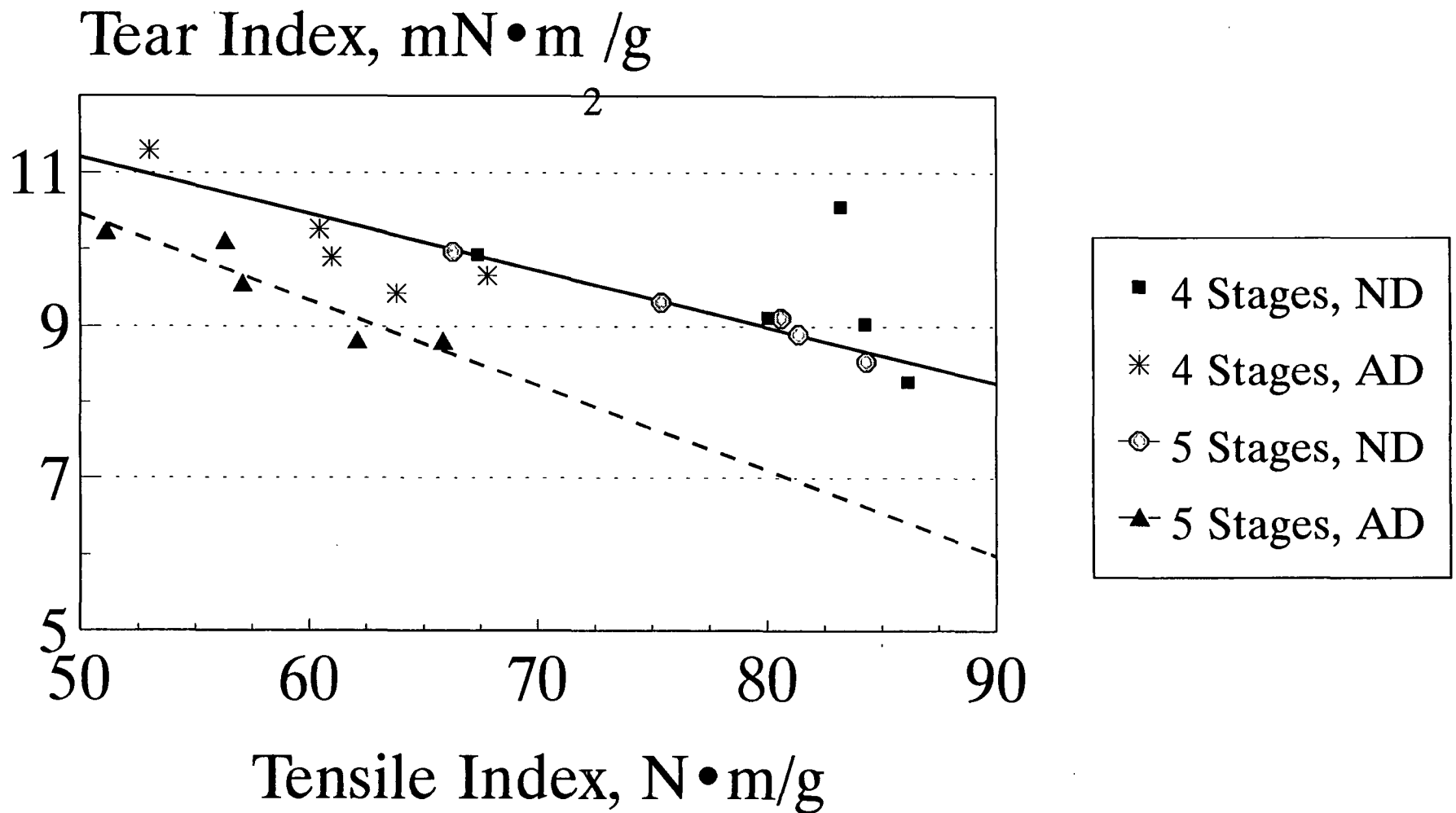


Figure 5. Tear/Tensile Data  
Chlorite Holopulps



Freeness from 760 ml to 365 ml.  
PAC, 9/94

span is significantly greater than the winter samples at a 90% confidence level (one tailed t-test). Since the Winter samples were not dried before making the handsheets, these zero-span tensile indexes should be about 12 N·m/g higher than would have been obtained with air dried samples. This would make both sets of summer samples significantly stronger than the Winter 92/93 samples.

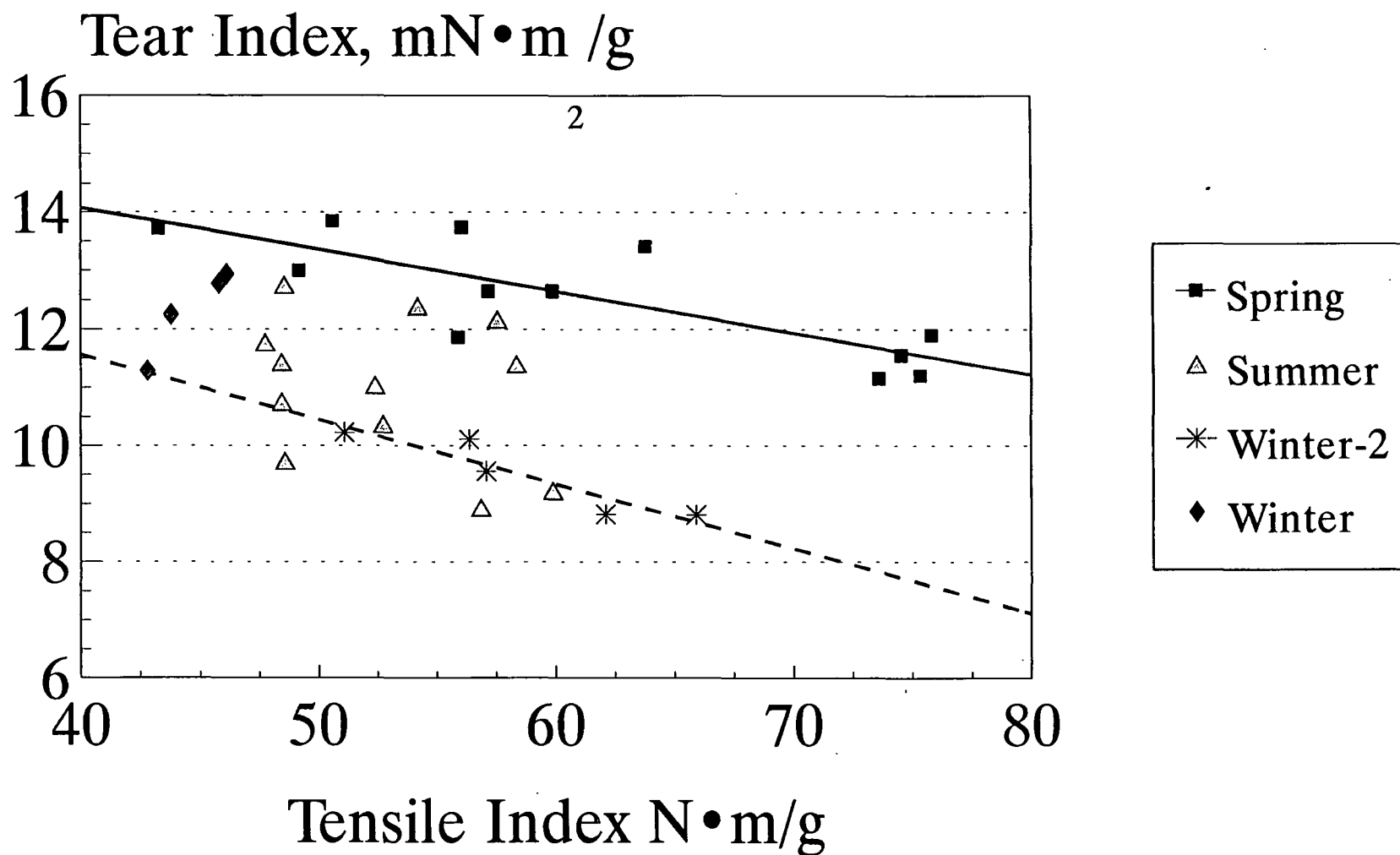
**Table 1.** Student *t* values for pooled Zero-Span Tensile Index data.

	Winter		Spring		Summer	
	Normal	Control	Normal	Control	Normal	Control
WinNorm	0	-0.218	<b>3.230</b>	<b>3.668</b>	0.621	1.627
WinCont	-0.218	0	<b>3.693</b>	<b>4.130</b>	0.912	<b>2.059</b>
SprNorm	<b>3.230</b>	<b>3.693</b>	0	0.526	<b>-2.706</b>	<b>-1.918</b>
SprCont	<b>3.668</b>	<b>4.130</b>	0.526	0	<b>-3.169</b>	<b>-2.425</b>
SumNorm	0.621	0.912	<b>-2.716</b>	<b>-3.169</b>	0	0.994
SumCont	1.627	<b>2.059</b>	<b>-1.918</b>	<b>-2.425</b>	0.994	0

$t_{crit.} = 2.977$  for a 99% confidence level two tailed test, 2.145 for a 95% confidence level two tailed test and 1.761 for a 95% confidence level one tailed test.

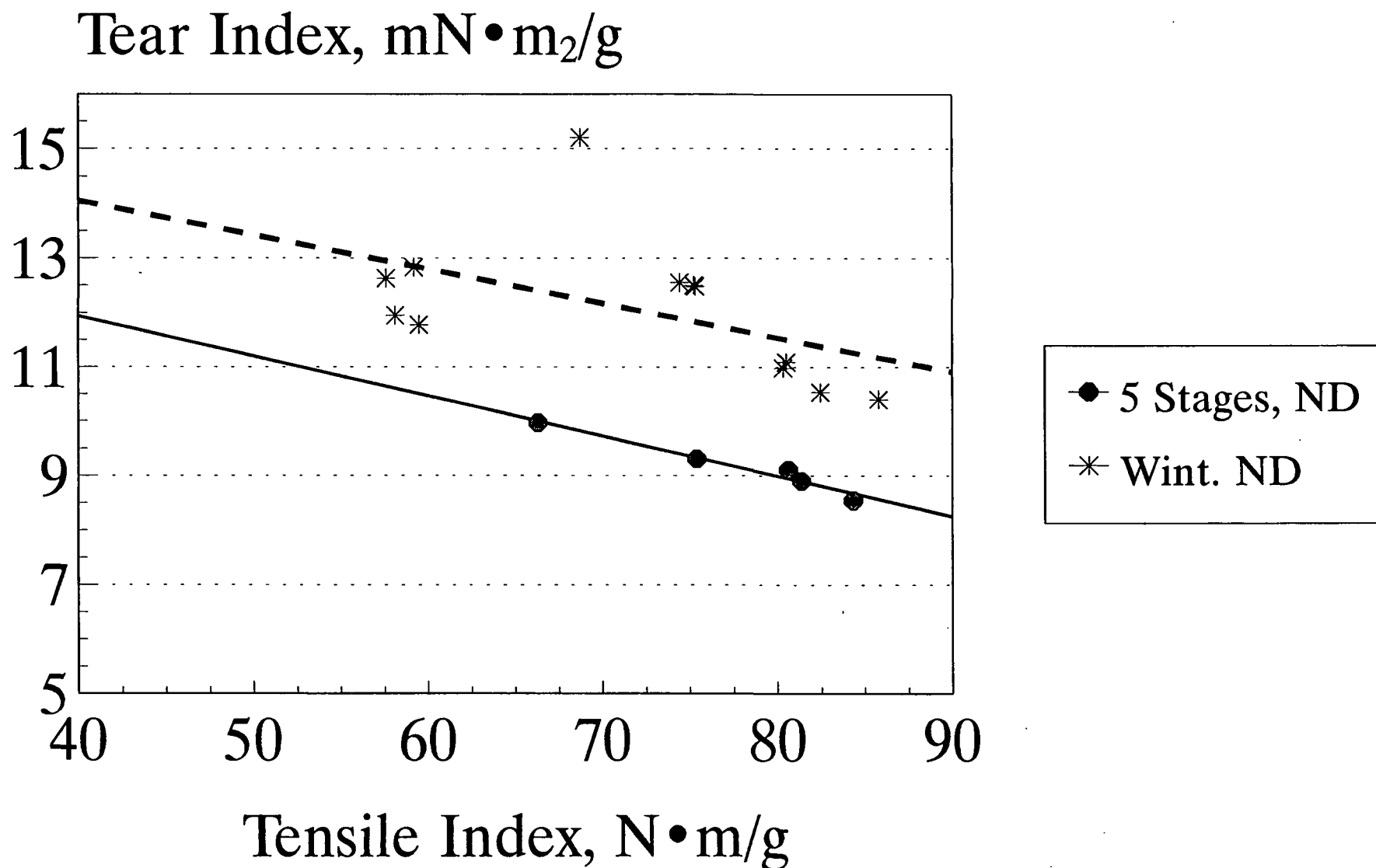
A tear/tensile graph for the four seasons is given in figure 6 using the 5 chlorite stage air-dried sample for the comparison. This is considered to be the most representative of the conditions used to prepare the spring and summer samples. A linear regression line is provided for the Winter air-dried data representing a PFI beater curve ( $r^2=0.87$ ), and the spring set of mill samples combining both the normal and controlled production periods ( $r^2= 0.64$ ). The four data points for the first winter samples are the results of retesting the chips with the spring samples. These are shown as diamonds. The original set of hopopulps were made into handsheets and tested without the air-drying step and are not directly comparable to this data. The four data point show an average 1.5 mN·m<sup>2</sup>/g lower tear index at a constant tensile index relative to the spring samples, and about a 1.5 mN·m<sup>2</sup>/g higher tear index at constant tensile than the data for the wood chips received in the winter of 93/94. The tear/tensile data for all 12 samples from the summer set of samples is shown as triangles. Although there is considerable scatter in this data, the average tear at a constant tensile is about 2 mN·m/g lower than the spring samples, and 1 mN·m<sup>2</sup>/g higher than the second set of winter samples. A similar graph for the never dried data is given in figure 7. The trend line for the Winter 92/93 data is very weak with an  $r^2$  of 0.25, but much of the error is contained in one point with an exceptionally high tear index. If this point is deleted, the  $r^2$  rises to 0.45, and the line falls about 0.25 mN·m<sup>2</sup>/g. This data shows that the tear index at constant tensile is about 1.75 to 2 mN·m<sup>2</sup>/g higher for the winter 92/93 than the PFI beater curve data on chips from the winter of 93/94. This is quite comparable to the 1.5 mN·m<sup>2</sup>/g difference observed in the air dried data shown in figure 6.

# Figure 6. Tear-Tensile Graph



Winter-2 is PFI data  
PAC, 9/94

Figure 7. Tear/Tensile Data  
Winter Never-Dry Samples



Although the regression line for the winter 92/93 never-dried tear/tensile data is nearly identical to the line for the spring air-dried tear/tensile data, the average  $1 \text{ mN}\cdot\text{m}^2/\text{g}$  loss in tear index on drying indicates that fiber strength of the winter 92/93 wood chips and pulp samples was indeed weaker than the fiber strength of the spring samples, confirming conclusions obtained from the zero-span tensile data.

### Wood Chip Analysis:

The wood chip size classification was reported last March and is included again as figure 8. It shows very modest increases in the larger size categories for both the Winter 92/93 samples and Summer 93 samples relative to Spring 93. Further analysis of this chips has been carried out with the intent of determining if there was a change in wood quality typical of a reliance on more plantation wood in Winter. The density and average growth increment were measured on the retained 1/2 and retained 3/4" size fractions. The average results are given in table 2.

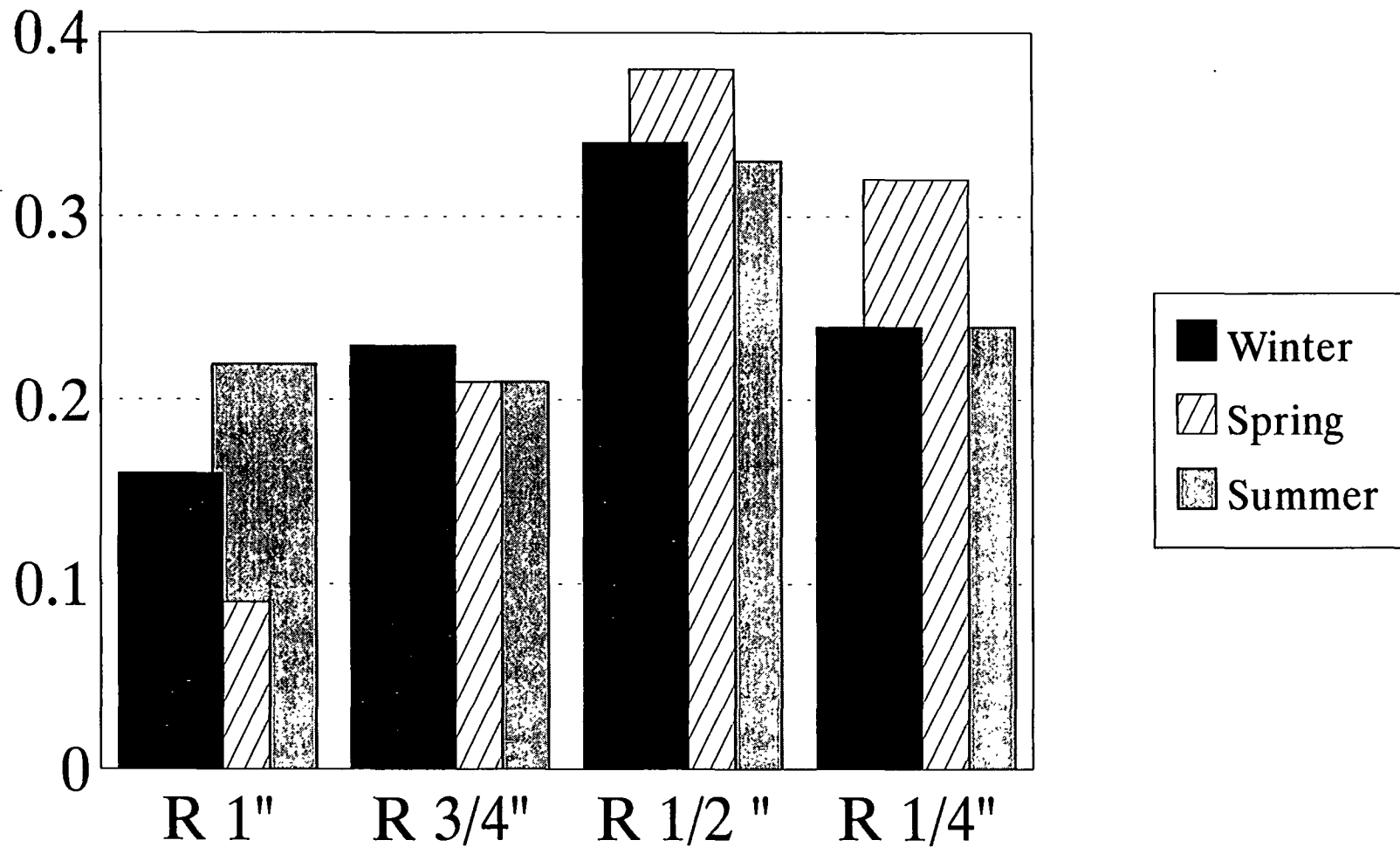
	Density g/cc	Growth Increment, mm			
		3/4" Average	RMSD	1/2 "Average	RMSD
Control	0.433	4.15	1.72	4.09	1.48
Winter	0.437	3.77	1.01	3.70	1.48
Spring	0.446	3.71	1.50	3.36	1.47
Summer	0.443	3.93	1.76	3.17	0.994

The difference in density between the three periods is small and not as large as would be expected with a significant shift in wood source. For example, in the juvenile wood project carried out by GT-CHYPS in 1990, wood density varied from 0.38 to 0.51 g/cc. The growth ring widths are also quite similar at 3 to 4 mm. One postulate as to the source of low strength wood was a shift to more plantation wood in winter. Plantation wood typically has a lower density and larger growth rings. Although the density is marginally lower during the winter periods, the growth ring widths are only significantly higher in the 1/2" size category. Typical plantation wood has growth rings of 6 mm or larger. Approximately 10% of the growth rings measured in the spring wood samples are in this size range compared to 12% for both winter and summer and 19% for the second winter sample used as a control.

Although none of these differences appear to be particularly significant, the ranking by percent of large growth rings matches ranking by wood densities, and both density and % of large growth rings match the relative order of native fiber strength for the four periods. On this basis we cannot rule out an increase in the amount of juvenile or plantation wood as the source of seasonal strength changes. Based on the results of the CHYPS project on the influence of wood growth and density on southern pine TMP (April 91 PAC), a 0.03 g/cc increase in wood density can increase burst index by 40 to 50% and tear by about 15%. The 0.01 g/cc change in density

Figure 8. Chip Size Distribution  
Bowater Seasonal Strength Data

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observed in the Bowater wood chips should change burst by 10 to 15% and Tear by about 5%. These changes are within the range observed in the Bowater samples.

## **CONCLUSIONS:**

Using the holopulping process to evaluate fiber strength losses in thermomechanical pulping has succeeded in tracing the seasonal strength loss observed by the Bowater TMP mills to a decrease in wood fiber strength during the winter and to a lesser extent the summer. This fiber weakness shows up as low wood chip and refiner holopulp zero-span tensile index and low holopulp tear index at constant tensile index for the winter samples. Fiber length is also lower in the winter and summer samples. An analysis of the wood chips for the three seasons evaluated shows a slight increase in oversized chips during the winter and summer periods, and a decrease in wood density of the winter and summer samples. In addition, there is an increase in the number of large growth rings observed in winter and summer, indicative of a higher juvenile wood or plantation wood content. The change in wood density observed is sufficient to induce the changes in strength observed in the mill.

This project has provided an excellent test of the chlorite holopulping technique and its utility on mill scale projects. The changes observed in pulp strength in this project appear to be at the resolution limits of the technique. However, the technique demonstrates low wood chip fiber strength during the periods of low TMP strength. The changes observed can be traced to changes in wood density and the size of the annual growth ring and are consistent with other observations on the influence of juvenile wood on pulp quality.

## **Acknowledgement:**

We would like to thank the Bowater TMP mill in Calhoun Tennessee for providing an interesting problem and the samples to study it. In particular, Bob Harley and John Griffey who have helped to manage and direct the project and Melanie Gray and Shawn Wendell who collected all the samples and mill data for the project.

**Project F012**  
**Improved High Yield Pulps from Dense Softwoods**

Alan W. Rudie

Chemical & Biological Sciences Division

Institute of Paper Science and Technology  
Atlanta, GA

September 28, 1994

## **Dues Funded Project**

### **Proposal**

<b>Project Title:</b>	Improved High Yield Pulps From Dense Softwoods
<b>Project Code:</b>	SPMP
<b>Project Number:</b>	F012
<b>Division:</b>	Chemical and Biological Sciences
<b>Project Staff:</b>	Alan W. Rudie, Blair Carter, Alex R. Shakhmet
<b>FY Budget:</b>	\$170,000

#### **OBJECTIVE:**

Improve the performance of southern pines in mechanical pulping processes.

#### **GOAL:**

An improved understanding of the performance limitations inherent in mechanical and chemimechanical pulping. The emphasis is on problem softwoods such as the southern yellow pines, and the interaction of wood structure and wood fiber morphology with the refining process.

#### **INTRODUCTION:**

During the last half century, the practice of short rotation forestry has become commonplace in the southeastern United States. This offers a unique opportunity to begin selecting tree variants more suitable for the products the wood is intended for. The paper industry is reaching a point where it can identify preferred features of wood fiber morphology that control paper quality in chemical pulps,<sup>1</sup> but has yet to identify the key features of wood and fiber structure that control energy requirements and pulp quality in mechanical pulps.

In the disk attrition or refining process, two metal disks rotate relative to each other. Each disk contains a pattern of raised bars and recessed grooves that help to transfer the energy to the wood chips.<sup>2</sup> As a wood particle passes between two bars, it is subjected to both shear and compressive forces. If the shear forces exceed the strength of the wood, the particle will fracture into two or more smaller particles. Particles that are not fractured by the shear are compressed in the bar crossing. Where the shear forces cause the wood fibers to separate and to break, the compression generates stresses that concentrate at the lumen wall and on the perimeter of the fiber where the filament (fibril) winding angle is larger. In a refiner, these processes are occurring at very high frequencies, ranging from a hundred hertz at the chip breakers up to  $10^6$  hertz at the perimeter of the disks. The cyclic stress initiates a fatigue failure, crack formation and crack propagation process which eventually causes a separation of

the  $S_1$  and  $S_2$  layers of the fiber wall. Unfortunately, at refining temperatures, wood is viscoelastic, and each stress cycle converts high cost mechanical (electrical) energy into lower valued thermal energy resulting in a high energy penalty for the process.<sup>3</sup> The development of whole fibers is enhanced by the fatiguing process, so in thermomechanical pulp manufacture for newsprint, a process attempting to develop strong, long fibered pulp needs to emphasize the cyclic compression mechanism of the refining process.

The force required to break fibers<sup>4</sup> is sufficiently close to the force required to separate fibers<sup>5</sup> that it is important for the wood to be stressed uniformly during the refining process. Unfortunately, there is a large non-uniformity in both the application of energy through disk refiners, and the strength of wood fibers.<sup>6</sup> Under typical commercial conditions many broken fibers and fiber fragments are produced resulting in decreased tear strength in the paper product.<sup>7,8</sup>

In producing printing papers, some fiber fragmentation is advantageous, but the optimization of paper strength and paper opacity requires that fiber fragmentation and whole fiber separation be controlled. In thermomechanical pulping, control is exercised by plate design,<sup>6</sup> adjusting the clearance between the refining disks, the amount of water present during the refining process<sup>9</sup> and the temperature of the preheater. These control methods change the average force per bar impact but the distribution of forces per bar impact is largely uncontrollable. Fibers on the surface of a wood chip or particle receive direct impact from the refiner bars whereas fibers inside the particle are stressed remotely through other fibers, a large particle forced between two refiner bars is subjected to more compression than a smaller particle and a fiber caught between two wood surfaces as they begin to separate is exposed to considerably more force than the wood fibers wholly contained in either part of the original particle. The frequency of broken fibers resulting from a refiner process is therefore dependant on the average force of a bar crossing and the distribution of forces in bar impacts, the average fiber strength and the distribution of fiber strengths. For these reasons, fiber (or wood pulp) quality in TMP shows a strong correlation to the intensity of the initial stages of refining<sup>10</sup> and the uniformity of the wood used in the process. The higher the average refining intensity, the greater the frequency at which the force of a bar impact exceeds the strength of the fiber and results in fiber fracture.

In addition to the variability in the forces exerted during refining, one must also consider the differences that exist in the strength of wood fibers. Wood is not a uniform material and differences in fibril angle and cell wall thickness<sup>11</sup> due to seasonal growth rate and year to year growth rate both influence the strength of fibers.<sup>4,12</sup> Recent research at the Institute of Paper Science and Technology has shown that when subjecting loblolly pine to cyclic compression, nearly all the compressive strain and viscoelastic energy absorption occurs in the earlywood portion of the annual growth ring (Figure 1).<sup>13</sup> This result was largely anticipated since the elastic modulus of the earlywood (in tension parallel to the grain) is known to be about one third to one quarter of the modulus of the latewood.<sup>14,15,16</sup> These results indicate that earlywood is much more intensively stressed under the refining conditions than is the latewood. The implication of this is that earlywood will disintegrate faster and suffer more fiber damage than latewood in mechanical pulping processes. This has been confirmed by analyzing chlorite holopulped fibers from the various particle sizes produced after very low energy pressurized refining.<sup>17</sup> In this research, the smaller particles, those retained on the 20 and 100 mesh

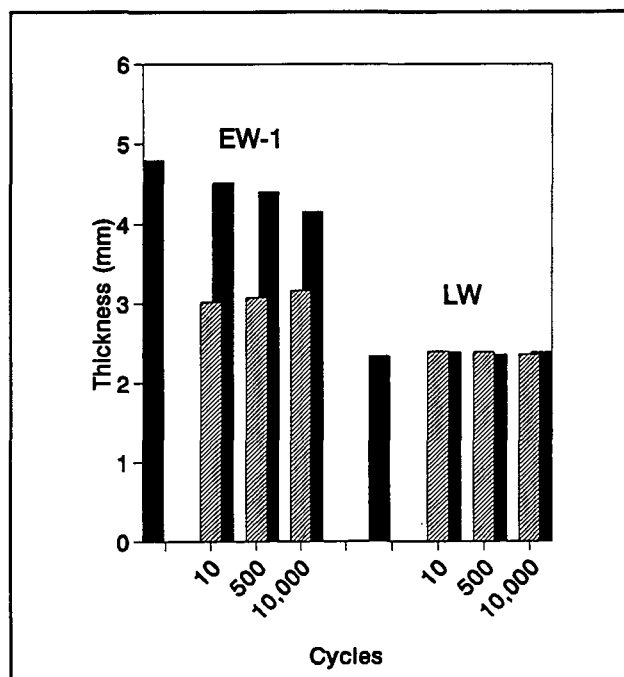
screens, had a lower fiber coarseness and more earlywood fibers than the fibers in the particles retained on the 4 and 8 mesh screens (Table 1). In addition, the smaller particle size fractions contained fewer whole fibers and there was a lower percentage of whole earlywood fibers than whole latewood fibers in all the size fractions (Table 1).

**Table 1** Fiber coarseness and fiber length of various particle size fractions after low energy refining.

Mesh Size	Coarseness mg/M	Fiber Length mm	% Whole Fiber	
			EW	LW
4	0.22	3.21	37	59
8	0.21	2.41	18	35
20	0.17	2.62	1	23
100	0.18	1.21	0	3
EW	0.16	2.80		
LW	0.38	3.26		

The uneven energy absorption in the early stages of disk refining fragments the earlywood fibers and leaves them less able to contribute to the strength of the product. This results in both wasted energy and a weaker paper. Because Douglas fir and the southern yellow pines contain large amounts of latewood, and the difference between the specific gravity, elastic modulus and tensile strength of the earlywood and latewood is very large,<sup>14,15,16</sup> these species suffer acutely from the concentration of refining energy in the earlywood and produce low strength mechanical pulps.<sup>18,19</sup> (Table 2)

The concentration of refining energy in the earlywood of the southern pines may explain an anomaly in the strength, specific refining energy relationship found for softwoods. Generally, the lower density northern softwoods such as spruce and fir give superior paper and fiberboard strength. If one assumes that this is due to wood density (or probably more accurately, the ratio of average fiber surface area to average fiber mass)<sup>1b</sup> one would conclude that juvenile southern pines should give stronger pulps (or have lower energy requirements) than mature



**Figure 1.** Compression of loblolly pine at 100° C and 1 Hz. Solid bars are the starting thickness and recovered thickness after compression. Patterned bars are the compressed thickness.

trees. For fiberboard pulps this is true,<sup>20,21</sup> but for paper pulps the opposite is true. Juvenile southern pines require more refining energy and/or give weaker pulp than TMP prepared from mature trees.<sup>22,23</sup> Although the juvenile wood generally has less latewood and should distribute the refining energy over a larger number of earlywood fibers, if the impact per bar crossing still exceeds the strength of an earlywood fiber, the earlywood fibers will break and pulp strength will have to be developed from the latewood fibers that remain. If this hypothesis is correct, improving the strength/specific refining energy relationship in southern pines using existing equipment will require trees where the latewood content is extremely small, or where the difference in perpendicular to the grain elastic modulus between the earlywood and latewood fibers is smaller so that refining energy will not be concentrated as strongly in the earlywood fibers.

**Table 2.<sup>24</sup>** Specific energy requirements and strength of spruce and loblolly pine stone groundwood and TMP.

	Spruce		Loblolly Pine	
	SGW	TMP	SGW	TMP
Energy Kwh/Ton	1460	1900	1750	2500
Freeness	88	120	60	100
Breaking Length km	2.7	4.8	2.1	3.3
Tear Index, mN*m <sup>2</sup> /g	4.5	9.3	3.1	7.3

## PROPOSAL:

The proposed research will evaluate the sequential breakdown of southern pine wood chips into fibers in disk refining. The wood particles and fibers will be analyzed for particle size distribution and the particle surfaces analyzed as to earlywood and latewood composition and fraction of broken fibers. The samples will then be chlorite holopulped and the resulting fiber tested for fiber length, coarseness, earlywood and latewood content and the frequency of earlywood and latewood fiber cleavage. Three wood samples will be evaluated, a black spruce to be used as a control (black spruce should provide a near optimum pattern of wood chip breakdown into fiber), a mature loblolly pine with narrow growth rings and above average density, and a juvenile loblolly pine with large growth rings and below average density.

Two methods are being considered for obtaining representative samples of wood particles and fiber during the early stages of refining. One method involves stopping the refiner while still under load. With the plates held in position and trapping the fibers, the refiner casing will be flooded with either rice (starch) glue, or gelatin/agar to fix the particle positions. Once the refiner has cooled, the casing can be opened and the wood particles and fiber recovered and indexed relative to plate position. The second technique under consideration involves

progressively grinding away the perimeter bar sections of one refiner plate, a technique used previously by Attack and May on black spruce.<sup>24</sup>

The preferred methods of applying the matrix material (Glue/gelatin) is to stop the refiner, block the discharge opening and add the hot glue/gelatin solution to flood the casing. An alternate method is to add the glue/gelatin to the feed wood chips just before stopping the refiner. This technique will be required if it becomes impossible to flood the gap between the disks using the first procedure. It suffers the disadvantage of requiring the addition of extra water and a foreign material, both of which may alter the refining behavior. In either case, both gelatin and starch glue can be washed from the wood and flushed from the refiner with steam and hot water. Pulp trapped on the perimeter of the stationary disk and in the casing can be compared against the discharge pulp to determine if the matrix forming methods have changed the radial distribution of the wood particles and fiber in any way. In addition, when the refiner is opened to be cleaned after a normal refining experiment, some fiber usually adheres to the disks. Fiber collected in this manner can also be used to validate the glue/gel matrix technique. Because the matrix method involves adding a contaminant to the refiner, it is not considered suitable for scale up to larger refiners until we have confirmed the ability to steam clean the refiner using the IPST 12" Sprout Waldron refiner. Samples will be collected at two different plate gap settings and from three regions of the disk, giving a total number of samples to be analyzed of 24.

Besides the analysis indicated above, the trapped wood particles and fiber can be analyzed for particle orientation and axial distribution. This should give a static image of the fiber orientation between the disks.

The second technique under consideration involves progressively grinding away the perimeter bar sections of one refiner plate. This approach will likely require cooperation with a refiner or refiner plate manufacturer but is suitable for using a larger scale or commercial size refiner. Since the proportion of specific energy applied in each part of the refiner disks can only be estimated, a series of samples will be collected at different plate gaps/motor loads to provide samples representative of the specific energy/plate gap distribution for the reduced diameter plates. Four pulp samples will be collected at different specific energies for each wood supply/plate diameter. Three or four plate diameters will be evaluated to obtain pulps from whole plates and with one quarter, half and three quarters of the original bar sections remaining. The total number of samples to be evaluated using this method will be 36 to 48.

The results from this study will be used to develop rate estimates for earlywood and latewood fiber liberation and fiber cleavage relative to the specific energy application. Comparison of the three wood supplies will help determine how wood growth parameters influence the distribution of energy in refining and the sequence in which wood chips break down into fiber and fiber fragments. In particular, the results will determine the extent earlywood fibers are preferentially broken in the early stages of refining and whether this pattern holds for both spruce and loblolly pine.

**Milestones (Relative to a starting date of July 1st):**

1. Initial evaluation of the matrix technique. (September 1)
2. Preliminary discussions with refiner manufacturers for project support including plates and large scale refiner trials. (September 1)
3. Finalize methods (Fall PAC).
4. Collect and prepare wood for refining. (November, 94)
5. Carry out the refining trials. (March 95)
6. Complete the fractionation and holopulping of the coarse wood pulps and particles. (May, 95)
7. Complete the microscopic analysis for earlywood and latewood content of the fractions, and % broken earlywood and % broken latewood fibers in each fraction. (July, 95)

#### **Limitations:**

The two techniques considered for obtaining the partially refined wood have different advantages and limitations. The gelatin technique is untried and may require considerable preliminary work to develop and validate the technique. The initial work on applying the matrix material and collecting the samples is not time consuming and will be evaluated before the Fall PAC meeting to help in selecting a final approach. Minimal pulp analysis will be carried out since the full testing and evaluation proposed is quite extensive and time consuming. The disadvantages of this technique are:

- ◆ The amount of pulp obtained in each experiment is small and it may require several refiner runs to obtain sufficient sample for analysis.
- ◆ The particle size distribution and position may be affected when the refiner slows to a stop.
- ◆ Particles may drift as the gel solution is added and flows between the plates.
- ◆ The technique involves contaminating a refiner and it will have to be thoroughly tested on the IPST 12" refiner before it can be taken to larger equipment.

The particle distribution in the gels and a comparison of the fiber obtained from the discharge of the refiner to the fiber on the perimeter of the plates will provide some evidence for the ability of the gelatin to permeate the refiner without significantly changing the distribution of particles between the plates. A Bauer McNett will be carried out on the initial samples, prior to the Fall PAC meeting to help in making the decision on how to proceed.

Grinding away the bars on a stationary refiner disk will provide much larger samples and can

be carried out on large scale refiners but has other limitations:

- As the perimeter sections of the refiner plates are opened up, steam velocity will increase and the amount of back flow steam will decrease. The wood will move through the refiner faster and suffer fewer bar impacts than normal. (This is probably not a significant problem with samples collected at the breaker bars and initial bar segment, and in fact may help in avoiding confusion from particles transferred back into the breaker bars by back-flow steam.)
- The increased steam velocity will be accompanied by a lower steam pressure and temperature between the refiner plates.
- The cut away plates will make the refiner difficult to operate. The refiner will not develop the levels of axial thrust and the discharge steam volume of normal operation. These problems will have to be addressed by running the refiner at static plate gaps rather than a motor load target, and by adding additional steam to the refiner casing to help discharge the pulp.
- Additional problems may be encountered from the coarse wood particles plugging the blow line and this may prevent an analysis of the earliest stages in the wood disintegration, or restrict the evaluation to an atmospheric refiner.

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**Project F014**  
**Fundamentals of Brightness Stability**

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September 28, 1994

**PROJECT TITLE:** FUNDAMENTALS OF BRIGHTNESS STABILITY

**PROJECT CODE:** BRITE

**PROJECT NUMBER:** F014

**DIVISION:** CHEMICAL AND BIOLOGICAL SCIENCES

**PROJECT STAFF:** RAGAUSKAS, A.J. and PAN, X.

**FY 94-95 BUDGET:** \$100,000

**OBJECTIVE:** Research objectives are directed at investigating the fundamental chemical reactions which are initiated when high-yield pulps are photolyzed. As our knowledge of the photooxidation of mechanical pulp increases, methods to eliminate and/or significantly retard the yellowing process will be pursued.

**IPST GOAL:** Increase the usefulness of high-yield fibers.

#### **OVERVIEW OF RECENT RESEARCH ACTIVITIES & RELATED ACCOMPLISHMENTS:**

1. The National Science Foundation proposal titled "Stabilization of Mechanical Pulp Against Color Reversion" was successfully reviewed and we have secured substantial funding in this area for the next two years. The thrust of these future studies will be directed toward examining the fundamental chemical pathways by which, sulfur-based additives retard brightness reversion of mechanical pulps. The results of these studies will strengthen our applied research studies in project F 014. The overall direction of the NSF project will be reviewed at the upcoming fall PAC meeting.

2. The manufacturing of high-yield pulps has advanced substantially over the last few decades. Modern mechanical pulping technology provides furnishes with brightness values greater than 85% which can be readily incorporated into a variety of paper products. The principal obstacle for increased use of these grades of pulp is their well known tendency to undergo photoyellowing.<sup>1</sup> The photochemical mechanisms contributing to brightness reversion have been extensively studied<sup>2</sup> and this knowledge is being applied to develop new stabilization technologies. In general, three alternative technologies are available to reduce brightness reversion properties of mechanical pulps:

- Application of UV absorbers to reduce the amount of near UV-light arriving onto the pulp fibers;

- Incorporation of radical trapping agents to retard autoxidation pathways leading to brightness reversion;
- Chemical modification of mechanical pulp fibers to remove photo-yellowing agents.

To-date, some of the most promising technologies used to hinder brightness reversion have employed the use of either UV absorbing agents or radical trapping additives. Interestingly, few studies have examined the possibility of employing mixtures of additives to determine if combinations of stabilizers could express a synergistic action, which could result in more effective stabilization strategies. Over the past six month period, we have begun to examine this research issue.

Our research efforts have examined the photo-stabilization properties of several UV-absorbers, including 2,4-dihydroxybenzophenone and 5-phenylpenta-2,4-dienoic acid combined with radical trapping agents, such as ascorbic acid, ethylene glycol bithioglycolate, and 3,3'dithiopropionic acid. Employing our routine experimental procedure these additives were impregnated onto BCTMP mechanical pulp handsheets and irradiated with the solar simulator. Brightness measurements were determined before and after selected periods of irradiations. The impact of any given additive is then determined by comparing the relative rates of brightness reversion for the treated and untreated handsheets.

As anticipated, several additive combinations expressed substantial synergistic interactions; representative photo-aging data is summarized in Table 1. The results of these studies indicate that one means of lowering the overall charge/cost of applying chemical additives to mechanical pulps will be accomplished by designing specific additive mixtures which are more effective than a single photo-stabilizing agent. The implications of these studies and further experimental details will be reviewed in the upcoming Fall PAC review.

3. The final area of research under study in this program has been directed at optimizing the brightness reversion properties of mercapto-compounds while at the same time removing the unfavorable malodorous properties of these compounds. The overall thrust of these studies was reviewed in detail in the last PAC report. In general, our studies are aimed at incorporating sulfur compounds into a flexible polymer backbone. Unfortunately, due to support staffing issues, we have not been able to advance this portion of the program in the last six months.

**Table 1. Brightness Reversion Properties for Hardwood BCTMP handsheets Treated with Ascorbic Acid, Ethylene Glycol biththioglycolate, and 2,4-Dihydroxybenzophenoneone.**

<u>Additive</u>	<u>Charge(%)</u>	<u>TAPPI Brightness</u>			
		Period of Irradiation (min)			
		0	10	20	40
Control	-	80.2	68.8	64.4	59.7
Ascorbic Acid (I)	0.5	83.1	74.3	68.9	63.5
	1.0	81.4	73.8	68.5	63.3
	2.1	82.4	75.9	70.2	65.0
Ethylene Glycol bisthioglycolate (II)	0.6	84.7	76.1	69.7	64.9
	1.2	83.4	77.2	72.2	67.9
	1.9	84.2	78.9	75.0	70.5
2,4-Dihydroxy benzophenoneone(III)	0.5	81.9	75.3	71.8	68.1
	1.0	80.3	75.6	72.8	70.3
	2.0	80.2	76.7	74.5	72.8
I + II	I (0.5)				
	II (1.0)	84.8	79.1	75.3	70.3
I + III	I (0.5)				
	III (0.5)	81.8	77.1	73.6	69.9
II + III	II (0.7)				
	III (0.5)	83.2	79.5	75.8	72.5

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**Evaluation of Strain in Earlywood and Latewood of  
Loblolly Pine in Cyclic Compression**

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August 1994

## THESIS OBJECTIVES

The goal of this research is to investigate the distribution of strain between earlywood and latewood in fiber aggregates subjected to cyclic loads to simulate a disk refiner. The working hypothesis is that the earlywood fibers will be preferentially strained and have a larger temperature increase than the latewood fibers.

## INTRODUCTION

Mechanical pulping is a process which uses mechanical energy to grind or refine logs or wood chips into papermaking fibers. Although the refining process has been around for many years, no one knows exactly how it is accomplished. Research is being done to increase the information base on various topics from raw materials to energy usage. It is hoped that by characterizing the fundamental processes, industry practices will improve leading to improved fibers, decreased energy consumption, and promotion of this environmentally-friendly process (1).

Many mechanical and chemimechanical processes have evolved from the initial refiner method. The most common process used in industry today is thermomechanical pulping (TMP). TMP produces a pulp with many of the qualities needed for the newsprint and printing papers industry: a reasonable fines content for smoothness and opacity, a large amount of long fibers for strength, and a high yield resulting in lower production costs. Because TMP uses electrical energy to produce the mechanical energy needed to refine the chips into pulp, there is concern over the energy requirements and cost of electricity. This is especially of concern in the Southern United States where southern yellow pines are used. These pines have the highest energy requirements and produce the poorest quality pulp of all softwood species used routinely for the production of newsprint (2).

Many research projects are presently being conducted to characterize the mechanisms underlying the refiner mechanical pulping process. These projects are essential to the continued use of mechanical pulping, considering the projected increases in fuel costs (3). It is hoped that improved understanding will lead to methods allowing more efficient use of energy at each stage in the refining process. In addition to decreasing the energy usage in this process, if specific morphological properties could be identified for preferred mechanical pulping traits, these variants could be chosen for the tree plantations. This would then lead to better fibers to make paper.

This proposal develops a method to discern what is happening to the wood fibers due to compressive forces in the coarse and fine bar sections of the refiner, specific to the dense pines found in the Southern United States. Information will be gained on the theory of whether earlywood continues to preferentially absorb energy in the later stages of refining. Such information is important because it is theorized that the earlywood fibers are absorbing the energy and may become over refined, leading to a loss of pulp quality (4). The studies on refining intensity demonstrate how this could happen. To refine the stiffer, thick-walled latewood fibers, refining intensity was increased leading to a degradation of the earlywood fibers, as can be seen in an increase in fines content (earlywood) (5,6).

An experiment has been proposed to simulate the coarse and fine bar section of a disk refiner, to determine whether there continues to be preferential energy absorption by the earlywood fibers. This will be done by separating the earlywood from the latewood and then individually refining to separate the fibers from one another. This will be followed by selective staining of the fibers, followed by recombining the fibers into a fiber aggregate with the same earlywood and latewood proportions as the tree. The fiber bundle will then be put into a device to selectively apply a cyclic compression force from 10 Hz to 10,000 Hz, or as high of a frequency as is possible. High speed video will be used to record each experiment. After the compression procedure, infrared thermography will be used to record the temperature differences of the fibers within the device.

Fatigue is thought to be one of the processes that occurs within a refiner to aid fiber separation and improve fiber flexibility. It is theorized to be caused by the repeated cyclic compression of fibers by impacts between opposing bars on the refiner plates. Studies

show correspondence between fatigue measurements and refining results; therefore, it is believed that analogies may be drawn between fatigue of wood during cyclic loading and refining (7).

The difference between the mechanical properties of the two types of fibers within the wood block can probably be best understood when viewed as a composite material. The processes that occur when composite materials are exposed to cyclic loading have been defined by Hull (13). If a composite consisting of elastic fibers in a viscoelastic matrix (wood) is loaded in a direction perpendicular to the fiber axis, strain is intensified. Delamination at the fiber-matrix interface and severing of the matrix by cleavage or molecular flow may begin at stress and strain levels beneath those at which final failure of the material occurs. During conditions of cyclic (fatigue) loading, delamination and matrix severing will occur at even lower stress levels. The system and speed of crack propagation will depend on the viscoelastic attributes of the matrix substance. The defibration and refining of wood chips is believed to be an example of a fracture mechanism, with the fracture occurring on several levels due to division of the fibers at or near the middle lamella to fracture between and within the various elements of the fiber at the microfibrillar position (14).

When wood is mechanically deformed, energy is consumed in the process (8). It has been calculated that the amount of energy required to separate wood chips into fiber is around 300 kWh/ton. In contrast, the industry requires 2000 kWh/ton for TMP (9). Extra energy is needed due to the viscoelastic nature of wet wood which causes the wood to absorb energy and release it as heat. Salmen et al. (10) has found, with fatigue testing of wood, that structural breakdown is favored by an increase in temperature. But, separation of fibers with good bonding ability may be favored by temperatures slightly below the softening temperature of the wood. Optimal fiber separation and flexibilization cannot be performed at the same temperature. Instead, fiber separation should be performed at a lower temperature than that which promotes flexibilization of the fibers. In other papers (7,9,11), Salmen voices the opinion that energy could be conserved by refining at lower frequencies with increased temperatures, leading to more flexible fibers. This can be demonstrated with Figure 1, a graph showing greater fatigue at lower frequencies. Figure 1 is a "master curve" constructed from Figure 2 by shifting the curves horizontally with respect to frequency until they overlap (12). Normally these "master curves" are only constructed for an amorphous polymer above its glass transition temperature, but Salmen has found that water saturated wood follows the general laws for simple synthetic polymers (12). These curves are an attempt to correlate low frequency testing with actual refiner frequencies. This is needed because Salmen's work was performed at 20 Hz, while refiners reach frequencies between 1000 and 10,000 Hz in the fine bar section.

Hickey (4) has shown that cyclic loading of wood blocks causes the temperature of the specimen to increase, and that the temperature increase is not the same for both earlywood and latewood (Fig. 3). The temperature of the blocks compressed at 15 and 30 Hz rose dramatically during the experiments, some with a 15° C difference between the warmer earlywood and cooler latewood portions of the blocks. This seems to suggest that the majority of the energy applied in the earliest stages of disk refining is absorbed by the earlywood (4). This work also demonstrated that the amount of strain is different for earlywood and latewood fibers after cyclic compression. Earlywood consistently demonstrated the effects of compression by mechanical deformation of the thickness of the growth ring. Latewood showed very little change after the compression test (Fig. 4).

Work has been done on a type of single fiber cyclic loading. Instead of compression the fibers are bent cyclically. These studies have demonstrated that it is possible to weaken the structure of fibers by subjecting them to either a small number of loading cycles at high stresses, or to a large number of loading cycles at lower stresses (15). The problem with this work is that the fibers selected for stressing are those which are free from physical defects such as kinks. This gives an unrealistic behavior of the

fibers from chip refining and also does not address how individual fibers behave in a fiber aggregate as they are found in refiners.

Recently, work has started on the effects of compression of fiber aggregates. Shakhmet has separated, refined, and stained earlywood and latewood fibers to determine if earlywood fibers are preferentially strained under static compression conditions (16). Fiber bundles were photographed and then compressed between two microscope slides, and then the same fibers were photographed again. The after compression photo was made into a transparency and was laid over the non-compressed fiber photo. The middles of the matching fibers were mated together, followed by the measurement of deflection of the ends of the fibers. This data supports Hickey's work, in that the earlywood fibers were found to change curvature more than did the latewood fibers. The t test seen on Table 1 was performed on a fiber bundle where the earlywood and latewood fibers were stained different colors. Using this method, both types of fibers were capable of being differentiated and they were stressed the same amount. The t test on Table 2 includes the deflection data on multiple samples where only a portion of either the earlywood and latewood were stained plus those of the previous data set. The data of Table 2 is not as reliable as Table 1, since it was impossible in these experiments to gauge whether the same amount of stress was applied to each sample, but still confirms the hypothesis that earlywood and latewood fibers are stressed differently within the refiner.

Table 1. Deflection data and t tests on Shakhet's work on compression of fiber bundles after second compression (16).

EW (cm)	LW (cm)	t-Test: Two-Sample Assuming Unequal Variances		
0	0		EW	LW
0.4	0.0	Mean	0.22	0.05
0.6	0.0	Variance	0.09	0.02
1.0	0.0	Observations	20	20
0.0	0.0	Pooled Variance	3.50	
0.5	0.0	df	26.99	
0.0	0.6	t	2.22	
0.0	0.0	P(T<=t) one-tail	0.02	
0.0	0.2	t Critical one-tail	1.71	
0.2	0.05	P(T<=t) two-tail	0.04	
0.2	0.0	t Critical two-tail	2.06	
0.6	0.1			
0.1	0.0			
0.0	0.0			
0.6	0.0			
0.0	0.1			
0.0	0.0			
0.0	0.0			
0.0	0.0			
0.1	0.0			

Table 2. T tests on pooled data from compression testing of fiber bundles (16).

t-Test: Two-Sample Assuming Unequal Variances (cm)		
	EW	LW
Mean	0.26	0.14
Variance	0.14	0.03
Observations	52	45
Pooled Variance	3.50	
df	75.41	
t	1.96	
P(T<=t) one-tail	0.03	
t Critical one-tail	1.67	
P(T<=t) two-tail	0.05	
t Critical two-tail	1.99	

## EXPERIMENTAL

### Experimental Plan

1. Development of an apparatus to induce and record high frequency cyclic compression.
2. This apparatus will be used to perform experiments to measure the strain distribution between earlywood and latewood fibers subjected to cyclic compression. The change in fiber curl index, will be determined and used as a measure of strain.
3. Temperature differences between earlywood and latewood fibers will be measured using infrared thermography to confirm that the distribution of strain is indicative of the distribution in energy.
4. Analysis of the strain distribution and temperature gradients will determine whether differences in energy absorption between the earlywood and latewood fibers exist and their frequency dependence.

### Experimental Progress to Date

#### Equipment

The cyclic compression device will be adapted from components of other systems. The major components will be a wave generator, an amplifier, an electromagnetic vibration generator (shaker), a spectrophotometric cell, a piston assembly, and an enclosure. The wave generator will be set to produce a sine wave pattern. An MTS servo-hydraulic tester will be used as the wave generator, amplifier and shaker for the lower frequency experiments.

The design of the sample chamber, holder, and camera frame for use with the MTS is finished (Fig.). This equipment has been manufactured and has been tested in practice runs. A narrow table was attached to the MTS and a linear slide with two platforms on top of the table. The platforms are attached to each other by a metal plate thereby moving together. A microscope and CCD color video camera are connected to the metal plate and focus is achieved by rolling the platforms forward and back.

An infrared thermal imaging system will be borrowed from Georgia Tech Research Institution. It is an older system that may need a new lens manufactured for it to image a suitable quantity of fibers. The infrared fiber holder with a sapphire window has been designed and produced (Fig. 6). It is made out of acrylic and a rectangular notch has been drilled into the block with the same dimensions as the inner portion of the cuvet. The sapphire window is recessed into the block in front of the notch with a cover plate to hold it in place.

The higher frequency strain testing will need the use of high speed video equipment. This is available for use at Oak Ridge National Laboratories in Knoxville, Tennessee.

#### Materials

A Loblolly pine log has been obtained from the Bowater, Inc. mill in Calhoun, Tennessee. The log was cut into disks, and the disks into narrow wedges with a band saw. The wedges were then hand cut into chips of three types: earlywood, intermediate wood, and latewood. The earlywood and latewood chips were then refined in the Asplund Defibrator D to separate the fibers. A total of approximately 200 oven-dry grams of earlywood, and 400 oven-dry grams of latewood has been separated. The fibers were then fractionated in a Bauer-McNett, and placed into sealable Kapak bags with nitrogen gas blown into the bags to drive the oxygenated air out. The sealed bags were then placed into a 150°F water bath and pasteurized for 75 minutes to preserve the fibers from microbial damage.

### Methods

A method for measuring strain has been selected. Curl index can be measured using the Optimas image analysis system in the microscopy department at IPST. Curl index was developed by Jordan and Page (Fig. 7)(20) and has a high repeatability for a single pulp (21).

The quantity of fiber to be present in the cuvet for each test has been determined using the density of the fiber bundles taken from the inside of a Sprout Waldron refiner stopped in the middle of a pass.

Approximately 100 earlywood and latewood fibers will be measured for curl index. According to Jordan and Nguyen (21), the mean for a population of 100 fibers is repeatable to within 2 to 4%.

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FIGURES

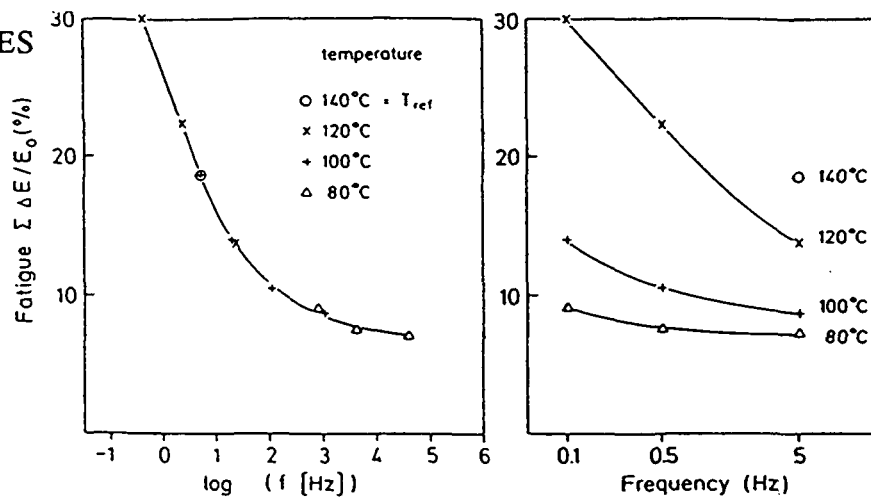


Figure 1 and 2. "Master curve" of fatigue of wood across the grain at an energy absorption level of 1000 cycles at  $2\text{kJ/m}^3$  per cycle. Fatigue of wood across the grain (12).

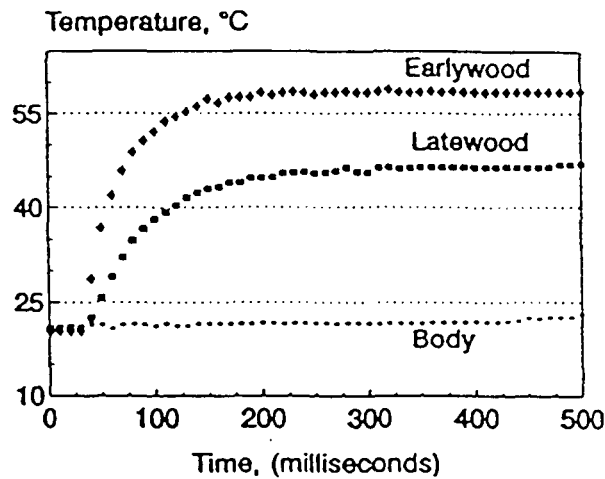


Figure 3. Temperature record of the sample tested at room temperature and 15 Hz (4).

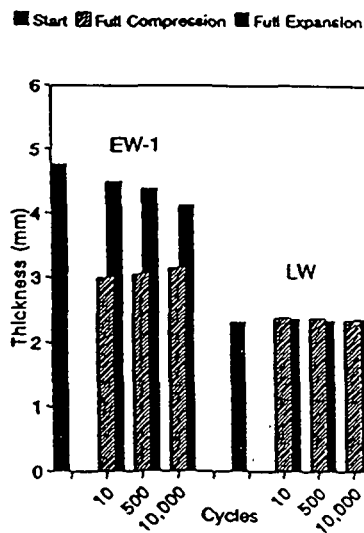


Figure 4. Earlywood and latewood - the effects of cyclic loading (4).

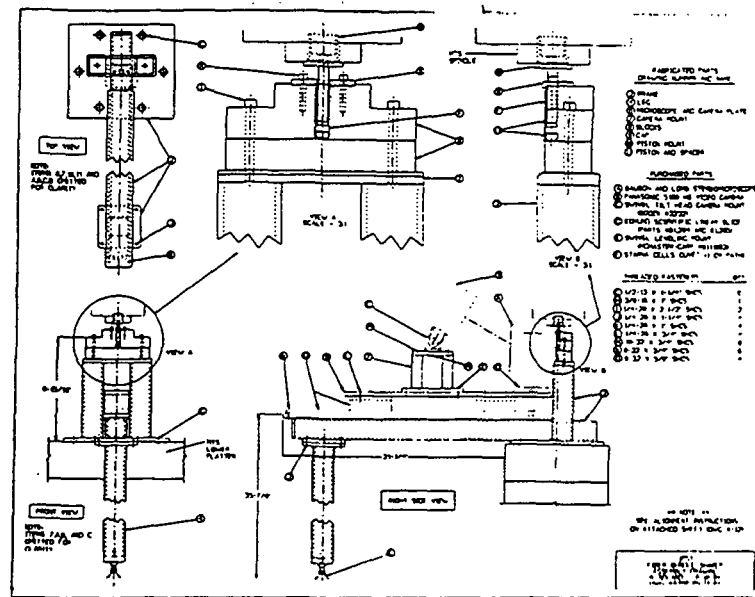


Figure 5. Design of sample chamber, holder, and camera/microscope frame for the MTS.

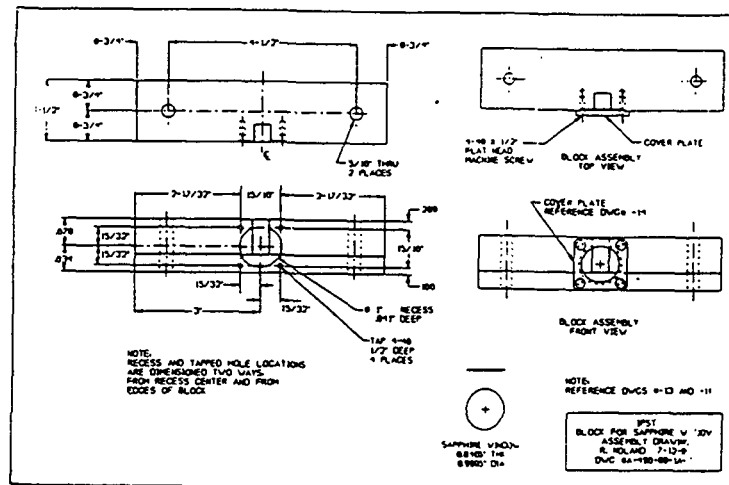


Figure 6. Design of infrared sample chamber.

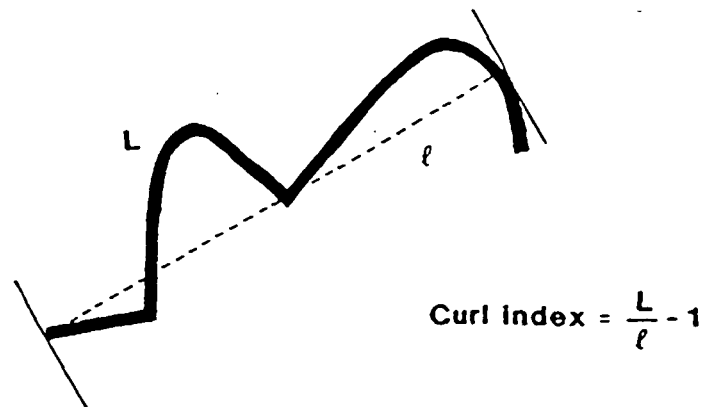


Figure 7. Curl index developed by Jordan and Page (17).