ANNUAL PROGRAM REVIEW

MECHANICAL PULPING AND BLEACHING PROJECT ADVISORY COMMITTEE

March 24, 1995

MECHANICAL PULPING AND BLEACHING

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FUNDAMENTALS OF BRIGHTNESS STABILITY

PROJECT F014

ANNUAL RESEARCH REVIEW

March 24, 1995

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TECHNICAL PROGRAM REVIEW

Project Title:	FUNDAMENTALS OF BRIGHTNESS STABILITY
Project Code:	BRITE
Project Number:	F014
Division:	Chemical and Biological Sciences
Project Staff:	A. Ragauskas
FY 94-95 Budget:	$ 89,000

Program Objective:

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

IPST Goal:

Increase the usefulness of high-yield fibers.

Summary of Results Since Last Report:

Previous Results:

Research efforts in this project have become increasingly focused on screening, designing, and defining the mechanisms by which chemical additives can retard and/or halt brightness reversion. Our investigative studies have examined the use of novel UV-absorbers/quenchers, radical scavengers, and other photostabilization technologies for retarding brightness reversion. Past research efforts demonstrated that several UV absorbers, such as substituted hydroxylphenyl benzotriazole, benzophenones, and 1,3-diketones, could retard brightness reversion. To date, the % stabilization effects we have observed are not sufficiently effective as to justify commercial applications. Nonetheless, we are continuing to improve these technologies and believe that in the near future successful additive technologies will be developed to photostabilize mechanical pulps.

Previous studies have demonstrated that long term storage of photostabilization agents such as ascorbic acid or thiol derivatives may cause a deterioration in their photostabilization effects. Indeed, for ascorbic acid treated mechanical pulp testsheets, we demonstrated that this additive accelerated thermal reversion properties, despite its well-known photostabilization properties. The long-term photostabilization effects of thiol-derivatives were shown to be highly dependent upon the structure of the additive and compounds; for example ethylene glycol bisthioglycolate was shown to have excellent short-term and long-term photostabilization properties. Interestingly, we have also shown that many disulfide derivatives actually exhibit improved photostabilization properties after prolonged periods of storage in the absence of light.

The identification of several new and promising thiol-additives that substantially retard brightness reversion has lead to investigations directed at incorporating these additives into polymeric derivatives. The use of thiol-polymers to stabilize mechanical pulp was initiated on the assumption that these high-weight additives would not have any malodorous properties while retaining the photostabilization effects of the low molecular weight additives. To this end, we prepared a series of polymers which contained thiol derivatives incorporated into the back-bone of the polymer. These preliminary studies confirmed our hypothesis that the use of polymeric thiol-derivatives could remove the malodorous properties of low molecular weight compounds while retaining the photoreversion properties of the mercapto-group. Unfortunately, we have also discovered that a variety of secondary issues, such as physical compatibility with mechanical pulp and effective surface concentration of the additive on the pulp fiber, play an important role in influencing the photostabilization properties of these additives. The results of these studies will require further investigative studies to develop effective photostabilization techniques for mechanical pulps.

Current Results:

To date, no one additive has met all of the commercial requirements needed to photostabilize mechanical pulps. One of the most critical considerations in the design of photostabilization technologies for mechanical pulp is the requirement that the technology remain cost-competitive. Many photostabilization additives developed for mechanical pulps require high levels of additive application so as to achieve significant reductions in photoyellowing. The effectiveness of combinations of various additives as brightness stabilizers for hardwood and softwood BCTMP (bleached chemithermomechanical pulp) was examined during this years research program. Certain additive combinations exhibited synergistic interactions that provided a substantial level of brightness stability. Experimental results suggest that designing specific additive combinations is an effective approach to improving the brightness stability of mechanical pulps and to lowering the overall charge of additives.

Goals for FY 1995-1996:

Additives for Photostabilization (Ragauskas):

Future research studies will continue to examine the use of additive mixtures for the photostabilization of mechanical pulps. Specifically, we propose to study the use of benzotriazole derivatives in conjugation with a mixture of antioxidants applied onto mechanical pulps. Research plans will also determine if the application levels of well-known photostabilization polymer additives, such as polyethylene glycol, can be reduced when they are applied onto handsheets in the presence of several other additives.

Research efforts will also be directed toward determining the optimal type structural features needed for UV absorbers to effectively coat the surface of pulp fibers. Finally, the fundamental chemical properties influenced by the presence of additive mixtures during brightness reversion will be examined.

INTRODUCTION

Technological advances in mechanical pulping and bleaching have made it possible to manufacture mechanical pulps that have a Tappi brightness of above 80 %. The major obstacle to the use of mechanical pulps in high grade paper products is their tendency to photoyellow. This yellowing phenomenon, also known as brightness reversion, occurs primarily as a result of exposure to light and is attributable to photoxidation of lignin [1]. It is generally accepted that the basic mechanism of photoyellowing involves a variety of pathways including: direct absorption of near-UV light by conjugated phenolic groups to form phenoxy radicals; abstraction of phenolic hydroxyl hydrogen by aromatic carbonyl triplet excited state; cleavage of phenacyl-O-aryl ethers to phenacyl-phenoxy radical pairs; and breakdown of arylglycerol-β-O-aryl ethers to phenoxy radical and ketone [2].

Attempts to inhibit the photoyellowing of mechanical pulps are based upon our current understanding of the brightness reversion mechanism. One potential approach is to chemically modify the lignin in mechanical pulps so as to halt the initiation and subsequent radical-based reactions leading to the formation of chromophoric compounds. Although a variety of such preventative measures have been tried, including reduction with borohydride, methylation, acetylation, and hydrogenation, none have been fully effective [2].

On the other hand, the use of additives to inhibit the photoyellowing of mechanical pulps continues to provide encouraging results. A wide variety of potential brightness stabilizers has been studied to date. The application of UV-absorbers onto the surface of mechanical pulp has been shown by several researchers to be an effective method of retarding the overall rates of

photoyellowing [3 - 6]. As stated above, all the proposed reaction pathways of photoyellowing involve a series of radical reactions leading to a phenoxy radical, which is a key intermediate to the formation of colored chromophores. Accordingly, radical scavenging antioxidants have been one of the most successful means of photostabilizing mechanical pulps via hydrogen donation to quench reactive intermediates, such as phenoxy radicals. Ascorbic acid is a well-known radical scavenger and reported to be capable of photostabilizing mechanical pulps to a certain extent [7, 8]. Sulphur-containing compounds have been shown to be effective in retarding light-induced yellowing [6, 7, 9 - 12]. Recently, diene-type compounds have also been investigated as antioxidants for photostabilizing hardwood mechanical pulps [13]. The photostabilizing activities of diene-type structures, such as 1,4-pentadien-3-ol and *trans,trans*-2,4-hexadien-1-ol, are believed to be due in part to radical trapping properties of these unsaturated structures [14]. In addition, conjugated diene structures, such as 2,4-hexadien-1-ol and 2,4-hexadienoic acid, have been shown to quench the excited state of lignin-like model compounds [15]. Ragauskas et al. have extended these studies onto mechanical pulp and suggested that one of the molecular pathways by which 2,4-hexadien-1-ol photostabilizes mechanical pulps is by quenching the excited state of lignin chromophores [16].

To date, no one additive has met all of the commercial requirements needed to photostabilize mechanical pulps. One of the most critical considerations in the design of photostabilization technologies for mechanical pulps is the requirement that the technology remain cost-competitive. Many photostabilization additives developed for mechanical pulps require high levels of additive application to achieve significant reductions in photoyellowing. To date, these difficulties have hindered the commercial development of a variety of photostabilization technologies. Furthermore, from a hypothetical view the development of a single additive which will substantially retard or halt photoyellowing of mechanical pulps is highly improbable since photoyellowing

of mechanical pulps is a multi-facetted mechanism. Based on literature review [17] and our own research experiences, we believe that the necessary components required to photostabilize mechanical pulps include: UV-absorber, an excited state quencher, and a radical scavenger. By employing these three types of additives the amount of near-UV light which interacts with the fibers will be reduced, the presence of an excited state quencher will deactivate some of the lignin chromophores which absorb light, and the radical scavengers will retard the overall rates of lignin oxidation.

Until recently this field of research has been largely unexplored. Agnemo's ascorbic acid/sulphite patented photostabilization mixture (i.e., sulphite acts solely as a preservative for ascorbic acid) was one of the first successful additive blends for mechanical pulps [18]. Castellan and co-workers have also begun to be active in this field of research and recently patented a mixture of 2,4-dihydroxybenzophenone (i.e., UV absorber) and methylenebisthiopropionate (i.e., radical scavenger) as an effective photostabilization blend for mechanical pulps [19]. In this paper we wish to report our preliminary studies directed at evaluating the effectiveness of combinations of various additives including radical scavengers and UV absorber.

MATERIALS AND METHODS

All chemicals, ethylene glycol bisthioglycolate, 3,3'-dithiodipropionic acid ascorbic acid, 5-phenylpenta-2,4-dienoic acid, and 2,4-dihydroxybenzophenone, are commercial products and were employed as received. Commercial hardwood BCTMP and softwood BCTMP pulps, made from aspen and black spruce, respectively, using sodium sulphite for chemical pretreatment and hydrogen peroxide for bleaching, were used without modification.

Handsheets were prepared according to standard TAPPI procedure T-218. The handsheets were then air-dried at constant temperature (22.0 +/-2.0 °C) and relative humidity (50 +/-2.0 %). Weighed amounts of various additives were dissolved in approximately 10 ml of methanol and sprayed onto handsheets. The handsheets were again air-dried and re-equilibrated at ambient temperature and humidity. For thermal reversion study, the handsheets were stored in the dark at room temperature for five months.

The accelerated photoyellowing studies were conducted with an Oriel 1000W solar simulator which uses a xenon-arc lamp and is fitted with an air-mass 1.5 global filter to model the average wavelength distribution of solar irradiation in the continental United States. Although several light sources have been employed for accelerated brightness reversion studies, a recent report recommends the use of xenon-arc lamp systems [20]. The lamp and samples were located in a fumehood which provides sufficient air circulation to minimize heating of the samples. Untreated handsheets were used as controls and all experiments were carried out in triplicate. After irradiation, the handsheets were allowed to re-equilibrated at controlled temperature and humidity as described above prior to brightness measurements.

The brightness values of the handsheets were measured following standard TAPPI procedure T-452. Light absorption and scattering coefficients were measured according to TAPPI procedures T 220-om 88 and T 425 om 91.

RESULTS AND DISCUSSION

1. Additives

To explore the effects of additive combinations on the photoyellowing process we selected several representative agents. Three radical scavengers were studied: ethylene glycol bisthioglycolate (thiol), 3,3'-dithiodipropionic acid (disulphide), ascorbic acid, and two UV absorbers: 5-phenylpenta-2,4-dienoic acid (diene), and 2,4-dihydroxybenzophenone. Our recent research has demonstrated that ethylene glycol bisthioglycolate is an effective thiol additive that provides bleaching action and prevents thermal and light-induced brightness reversion [12]. Disulphide is an alternative mercaptan for photostabilizing mechanical pulps. The stabilization effect of 3,3'-dithiodipropionic acid, although moderate, can be retained upon long-term storage [12]. Both of the UV agents absorb in the near-UV and therefore when applied onto handsheets these additives can reduce the intensity of 300 - 400 nm light that pulp is exposed to.

Ascorbic acid is a well-known radical scavenger and reported to retard the photoyellowing of mechanical pulps [7, 8]. On the other hand, the ascorbic acid-impregnated mechanical pulp handsheets have a high tendency to yellow upon long-term storage at ambient temperature [21]. This phenomenon limits the application of ascorbic acid as brightness stabilizer. To explore potential methods of preventing ascorbic acid accelerated thermal reversion, we examined the application of thiol and disulphide as co-additives for ascorbic acid and these results are summarized in Table I.

It can be observed that ascorbic acid considerably reduces the rate of brightness reversion shortly after its application onto handsheets. The incorporation of ascorbic acid with thiol is shown to further photostabilize the

pulp; but the addition of disulphide provides little improvement in brightness stabilization activity. However, after five month storage, there is a brightness loss of 44 percent points for the ascorbic acid-impregnated handsheets, whereas, only 3 points for the control. Interestingly, the presence of thiol successfully prevents yellowing caused by ascorbic acid; furthermore, the photostabilization activity of ascorbic acid can be retained. It was also shown that disulphide has no preventative effect on the thermal reversion of ascorbic acid. Our results demonstrate that a thiol/ascorbic acid mixture provides an effective alternative to Agnemo's ascorbic acid/sulphite patent. The thiol additive presumably acts as hydrogen donor (or radical scavenger) to quench reactive radical intermediates which contribute to an autoxidation of ascorbic acid to yellowed products.

2. Brightness stabilization

To assess the effects of various brightness stabilizers on mechanical pulps, we prepared a series of hardwood BCTMP handsheets impregnated by either one individual additive or a mixture of two different additives at varying charge levels, as summarized in Table II.

Generally, the addition of the reagents onto BCTMP handsheets resulted in brightness gains of one to two points, with the exception of 2,4-dihydroxy-benzophenone. Presumably, for the radical scavenging agents, such as ascorbic acid, this brightening effect can be attributed to the donation of hydrogen to certain unsaturated structures in lignin, which are known to discolor mechanical pulps, and thereby reducing colored species in the pulp. The bleaching effect observed for the thiol has been suggested to be due to thiol Michael-type additions to α-β-unsaturated carbonyl and quinoid structures [10, 12]. The slight loss in brightness for the benzophenone treated handsheets is due to the well known UV/Vis absorption at λ_{max} 322 nm for 2,4-dihydroxybenzophenone which tails into the visible range. Studies summarized

in Table II also demonstrate that 5-phenylpenta-2,4-dienoic acid is an efficient brightness stabilization agent comparable in activity to well known 2,4-dihydroxy-benzophenone [5, 6].

To evaluate the efficiency of the additives in retarding photo-induced yellowing, brightness stabilization factors were calculated by the equation shown below and the results are reported in Table III.

$$\text{Brightness Stabilization Factor (BSF)} = \frac{100 \times (\text{Brightness loss of control} - \text{Brightness loss of sample})}{\text{Brightness loss of control}}$$

Individually, both the thiol and 2,4-dihydroxybenzophenone appear to be effective brightness stabilization reagents for the test pulp. The three other additives provide moderate photostabilization effects. Clearly the thiol is more efficient than 2,4-dihydroxybenzophenone for retarding the early phase of photoyellowing. However, the stabilizing activity of the thiol is substantially decreased by extended light exposure. This result suggests that the consumption of the additive is significant as a function of irradiation time. It is known that thiols are easily oxidized and can scavenge radicals by acting as hydrogen donors. There are at least two following ways in which the thiol is possibly being consumed while acting as brightness stabilizers: 1) reaction with carbonyl chromophores and quinones to provide both bleaching action and brightness stabilization effect, 2) scavenging free radicals to inhibit the formation of colored species. On the other hand, the 2,4-dihydroxybenzophenone absorber seems to have a good stability probably due to its mechanism involved in inhibition of photoyellowing. Therefore, this additive remains effective over a long period of time.

As can be seen from Table III, the brightness stabilization factors are not linearly proportional to the additive application levels employed in this study. These results suggest that the addition of high amounts of additives is an inefficient means of photostabilizing mechanical pulps. Interestingly, several of the multi-additive combinations were found to reduce relative rates of photoyellowing far more effectively than a treatment with a single additive. For example, the brightness stabilization factors (BSF) for thiol and 2,4-dihydroxy-benzophenone treated handsheets, at 0.5% application levels were shown to be 50.5% and 43.2% after 10 min. irradiation with the solar simulator. In comparison, a handsheet treated with 0.5% thiol and 0.5% 2,4-dihydroxy-benzophenone exhibited a BSF of 80.2% after a comparable 10 min. period of irradiation. To achieve similar levels of photostabilization with only one additive would have required in excess of 2% thiol or 2,4-dihydroxybenzophenone.

Several other additive mixtures, including thiol/2,4-dihydroxy-benzophenone, thiol/ascorbic acid, and thiol/5-phenylpentadienoic acid also exhibited substantially improved photostabilization properties over single additive applications. Although, to some extent, it was anticipated that the use of a UV-absorber in conjugation with a radical scavenging agent would provide improved photostabilization effects the photoaging properties observed for the thiol/ascorbic acid treatment were unexpected. Since both of these latter reagents are antioxidants, it was anticipated that the use of this mixture would not exhibit substantially improved photoaging performance when applied as a mixture. Inspection of the reversion data in Tables II and III indicates that the use of 0.5% ascorbic acid and 0.5% thiol application on hardwood BCTMP retards the photoyellowing process to such an extent that comparable photostabilization effects by a single additive would require greater than 2% application levels. These results suggest that the photostabilization mechanisms of ascorbic acid and thiol operate, at least in part, on different components of the overall brightness reversion process.

Our results also indicate that not all additive mixtures result in a beneficial cooperative photostabilization effect for BCTMP testsheets. For example, the use of disulphide/ascorbic acid or ascorbic acid/diene provide no net benefit from applying the additives as a mixture onto mechanical pulp handsheets. Indeed, the mixture of ascorbic acid and 5-phenylpentadienoic acid appeared to contribute to the reversion phenomena.

Among the brightness stabilizers investigated in this study the thiol/2,4-dihydroxybenzophenone absorber is the best additive combination for the hardwood BCTMP. Figure 1 shows that the brightness stabilization effects by these additives are shown to be of the following order, namely, (0.5 % thiol + 0.5 % ascorbic acid + 0.5 % 2,4-dihydroxybenzophenone) > (0.5 % thiol + 0.5 % 2,4-dihydroxybenzophenone) > 2 % 2,4-dihydroxybenzophenone > 2 % thiol. The implication of this observation is significant. In order to achieve a given brightness stabilization level, designing specific additive combinations will be more beneficial than using a single additive and could provide an effective approach to photostabilizing mechanical pulps.

To further examine the effectiveness of the additives in photostabilizing mechanical pulps, we prepared a series of softwood BCTMP test sheets. Here, only the thiol and 2,4-dihydroxybenzophenone absorber were elected for investigation, since they were shown to have the greatest brightness stabilizing activity for the hardwood BCTMP, as discussed above. The brightness data and BSF are reported, respectively, in Table IV and Figure 2.

Generally, the overall trend of brightness change appears similar to the case of hardwood BCTMP. However, the thiol additive was found to be more effective than 2,4-dihydroxybenzophenone in preventing brightness reversion for softwood BCTMP. It was also observed that the softwood BCTMP pulps exhibit a greater sensitivity to the additive applications levels. Compared to hardwood

BCTMP, softwood BCTMP can be photostabilized more efficiently by employing higher additive charges. These differences in sensitivity to additive application levels are presumably due to differences in lignin content and the nature of lignin found in softwood and hardwood BCTMP.

3. Absorption and Scattering Coefficients

In addition to the regular brightness measurements, we have measured absorption and scattering coefficients for hardwood BCTMP handsheets impregnated with the thiol and 2,4-dihydroxybenzophenone to obtain more information about color formation during brightness reversion. Table V shows that for the BCTMP handsheets studied nearly all testsheets exhibited identical scattering coefficients which are not altered by both the addition of reagents and irradiation. It is also seen that both the thiol and 2,4-dihydroxybenzophenone absorber can reduce the absorption coefficient upon irradiation indicating that the formation of color can be retarded. The thiol seems to be more efficient than the 2,4-dihydroxybenzophenone absorber in preventing the early phase of yellowing, which is in agreement with the brightness changes observed beforehand.

CONCLUSIONS

The results presented here indicate that certain additive combinations provide cooperative interactions, which can substantially retard the rate of brightness reversion for mechanical pulps. In general, it is more beneficial to design specific additive combinations than to employ one single agent for maximizing brightness stabilization.

Hardwood and softwood BCTMP pulps respond differently to the stabilizing action of the various additives. For the hardwood BCTMP, there is a lower additive requirement. To obtain a high degree of brightness stabilization, combining two additives is more efficient than using one single additive at higher application levels. However, the addition of relatively high amounts of additives can more efficiently photostabilize softwood BCTMP.

In summary, the combination of thiol/ascorbic acid/2,4-dihydroxy-benzophenone is an effective brightness stabilizer mixture. The thiol/ascorbic acid is a representative example of the cooperative effect of two additives for photostabilizing mechanical pulps. The interaction of thiol and ascorbic acid, although both acting as radical scavenging antioxidant, not only prevents the thermal reversion caused by ascorbic acid but also retains the brightness stabilization activity of ascorbic acid upon a long-term storage.

ACKNOWLEDGEMENTS

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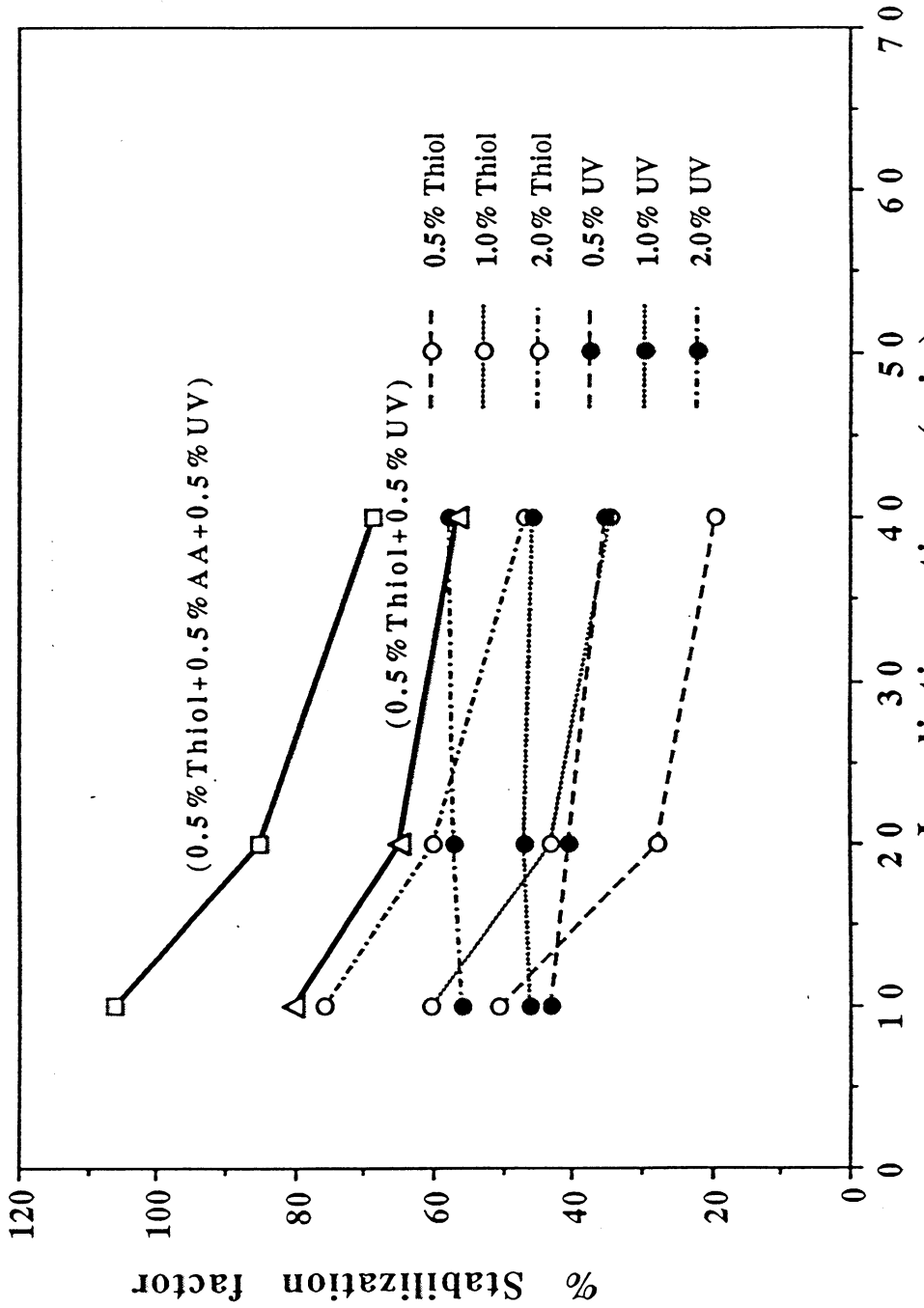

Figure 1. Brightness stabilization factors of combinations of varying application levels for hardwood BCTMP as a function of irradiation time; AA: ascorbic acid; UV: 2,4-dihydroxybenzophenone.

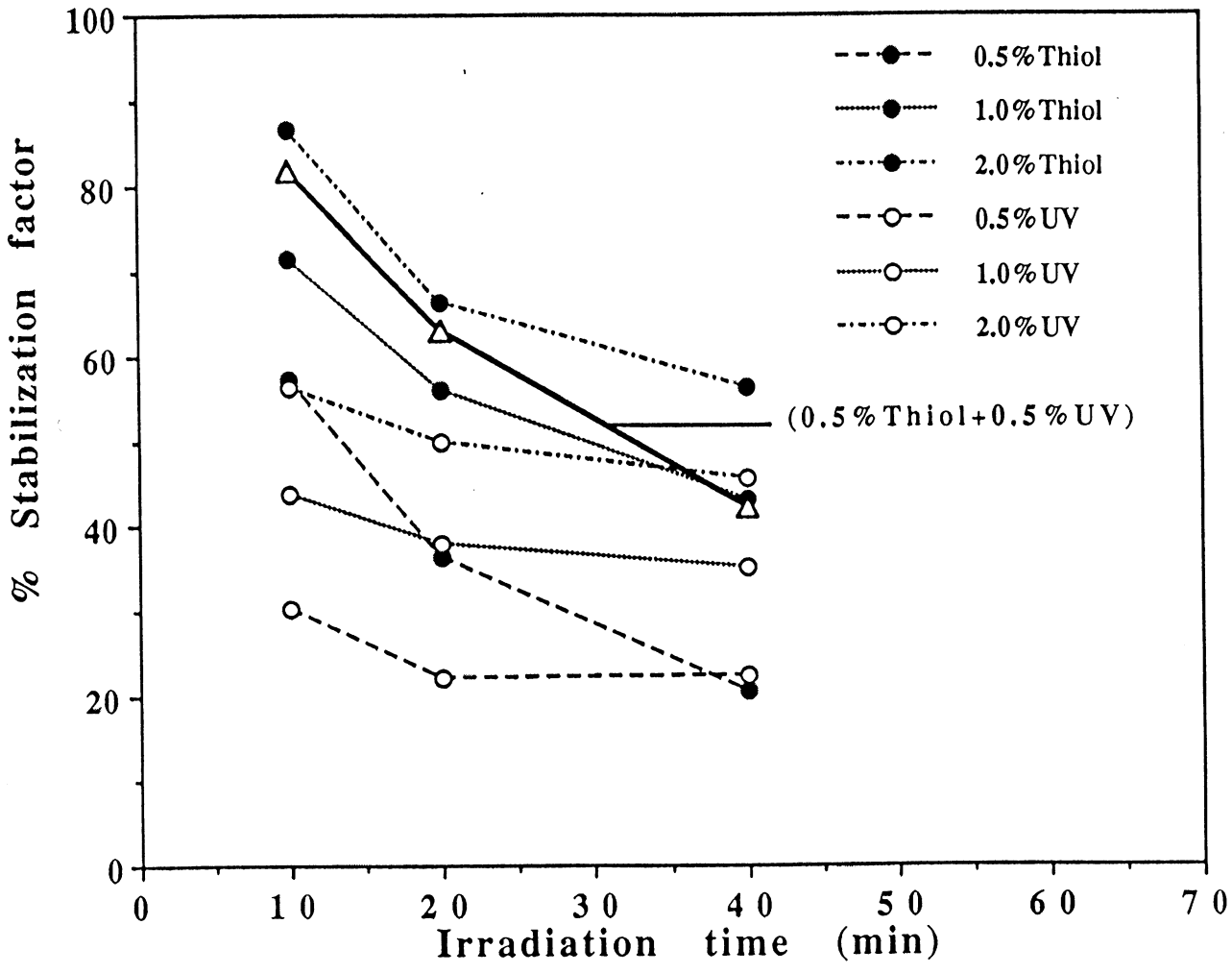

Figure 2. Brightness stabilization factors of combinations of varying application levels for softwood BCTMP as a function of irradiation time; UV: 2,4-dihydroxybenzophenone.

Table I: TAPPI brightness values of hardwood BCTMP handsheets before and after addition of additives and after storage and solar simulator irradiation.

Additive[a]	TAPPI Brightness				
	Initial	Post Addition	Post Storage	Irradiation/min 15	30	60
Control	84.7	-	-	67.9	61.9	55.5
Ascorbic Acid	84.4	83.7	-	75.1	71.1	63.3
Thiol/Ascorbic Acid	84.8	86.3	-	83.3	80.4	78.5
Disulphide/Ascorbic Acid	84.2	85.6	-	78.0	73.8	62.9
		Five Months Dark Storage				
Control	86.8	-	83.6	50.3	64.5	58.9
Ascorbic Acid	86.2	84.1	41.9	-	-	-
Thiol/Ascorbic Acid	86.4	87.7	87.7	85.2	83.8	81.0
Disulphide/Ascorbic Acid	83.8	85.3	42.7	-	-	-

[a]5% (wt of additive/wt of od paper %) per additive application levels were incorporated onto each testsheet.

Table II: TAPPI brightness values of hardwood BCTMP handsheets before and after addition of additives and after solar simulator irradiation.

Additive	Application level[a]	TAPPI Brightness Initial	Post Addition	Irradiation/min 10	20	40
Control	-	80.2	-	68.8	64.1	59.4
Thiol	0.5	82.7	84.7	76.1	69.7	64.9
	1.0	81.6	83.4	77.2	72.2	67.9
	2.0	81.5	84.2	78.9	75.0	70.5
Disulphide	0.5	79.9	81.9	71.7	67.1	62.4
	1.0	79.5	81.8	72.9	68.1	63.3
	2.0	79.8	81.2	73.3	68.5	64.1
Ascorbic Acid	0.5	81.1	83.1	74.3	68.9	63.5
	1.0	80.7	81.4	73.8	68.5	63.3
	2.1	81.0	82.4	75.9	70.2	65.0
Diene	0.5	80.5	82.1	73.3	68.5	63.6
	1.0	79.6	81.5	73.4	68.8	63.9
	2.0	80.7	82.0	74.4	70.5	65.1
Benzophenone[b]	0.5	81.6	81.9	75.3	71.8	68.1
	1.0	80.4	80.3	75.6	72.8	70.3
	2.0	80.5	80.2	76.7	74.5	72.8

(Note: Table 2 continued next page)

Table II continued:

Additive	Application level[a]	TAPPI Brightness Initial	Post Addition	Irradiation/min 10	20	40
Thiol/Disulphide	0.5/0.5	80.4	84.6	77.6	71.8	66.2
Thiol/Ascorbic acid	0.5/0.5	80.9	86.0	78.9	73.8	67.9
Thiol/Diene	0.5/0.5	80.2	84.2	78.1	73.0	66.8
Thiol/Benzophenone	0.5/0.5	81.6	83.2	79.5	75.8	72.5
Disulphide/Diene	0.5/0.5	82.4	83.8	75.3	70.9	65.4
Disulphide/ Benzophenone	0.5/0.5	79.5	81.2	75.8	73.1	69.6
Ascorbic acid/Diene	0.5/0.5	82.6	77.4	70.4	65.2	61.0
Ascorbic acid/ Benzophenone	0.5/0.5	80.7	81.8	77.1	73.6	69.9
Diene/Benzophenone	0.5/0.5	79.2	81.3	74.8	71.8	67.7
Thiol/Ascorbic acid /Benzophenone	0.5/0.5/0.5	80.4	84.1	81.1	78.0	73.9

[a] wt of additive/wt of od paper; [b]Benzophenone referres to 2,4-dihydroxybenzophenone.

Table III. Brightness Stabilization Factors of Various Additives Applied to Hardwood BCTMP Handsheets.

Additive type	Addition[a] %	Irradiation (min) 10	20	40
Thiol	0.5	50.5	27.9	19.6
	1.0	60.4	43.0	34.4
	2.0	75.7	60.0	46.9
Disulphide	0.5	38.5	20.0	16.7
	1.0	43.6	28.7	22.9
	2.0	44.5	29.4	25.2
Ascorbic acid	0.5	41.9	23.7	16.2
	1.0	41.0	23.7	17.1
	2.0	56.4	32.5	23.8
Diene	0.5	38.5	25.0	19.5
	1.0	47.0	32.5	25.2
	2.0	46.2	36.2	25.7
Benzophenone[b]	0.5	43.2	40.6	35.4
	1.0	46.0	46.7	45.9
	2.0	55.9	57.0	57.9
Thiol/Disulphide	0.5/0.5	75.4	46.6	31.4
Thiol/Ascorbic acid	0.5/0.5	82.5	55.9	37.2
Thiol/Diene	0.5/0.5	81.6	55.3	35.3
Thiol/Benzophenone	0.5/0.5	80.2	64.8	56.5
Disulphide/Diene	0.5/0.5	39.3	28.1	19.0
Disulphide/Benzophenone	0.5/0.5	68.4	60.0	52.9
Ascorbic acid/Diene	0.5/0.5	-4.3	-8.8	-2.9
Ascorbic acid/Benzophenone	0.5/0.5	67.5	55.6	48.6
Diene/Benzophenone	0.5/0.5	62.4	53.7	45.2
Thiol/Ascorbic acid /Benzophenone	0.5/0.5/0.5	106.0	85.1	68.6

[a]wt of additive/wt of od paper; [b]Benzophenone referres to 2,4 dihydroxy-benzophenone.

Table IV: TAPPI brightness values of softwood BCTMP handsheets before and after addition of additives and solar simulator irradiation.

Additive	Application level[a]	TAPPI Brightness Initial	Post Addition	Irradiation/min 10	20	40
Control	-	77.5	-	67.0	63.0	57.6
Thiol	0.5	77.6	80.7	73.1	68.4	61.8
	1.0	77.7	80.7	74.7	71.3	66.4
	2.0	77.1	80.4	75.7	72.2	68.4
Benzophenone[b]	0.5	77.5	78.0	70.2	66.2	62.1
	1.0	77.1	77.4	71.2	68.1	64.2
	2.0	77.7	78.2	73.1	70.4	66.9
Thiol/Benzophenone	0.5/0.5	77.5	80.2	75.6	72.1	66.0

[a] wt of additive/wt of od paper; [b]Benzophenone referres to 2,4-dihydroxybenzophenone.

Table V: Absorption and scattering coefficients of hardwood BCTMP handsheets treated with thiol and 2,4-dihydroxybenzophenone before and after irradiation with the solar simulator.

Additive	Application level[a]	Absorption coefficient[b]			Scattering coefficient		
		I_0	I_{10}	I_{40}	I_0	I_{10}	I_{40}
Control	-	0.2	0.45	0.86	34	33	33
Thiol	0.5	0.19	0.31	0.77	34	35	34
	1.0	0.16	0.25	0.59	35	35	34
	2.0	0.17	0.22	0.46	34	34	33
Benzophenone[c]	0.5	0.21	0.36	0.69	34	34	33
	1.0	0.22	0.36	0.57	35	35	33
	2.0	0.22	0.32	0.53	35	35	33
Thiol/Benzophenone	0.5/0.5	0.16	0.24	0.62	34	35	34

[a]wt of additive/wt of od paper; [b]I_0:before irradiation;I_{10}:10 min irradiation;I_{40}:40 min irradiation; [c]Benzophenone referres to 2,4-dihydroxybenzophenone.

SOUTHERN PINE MECHANICAL PULP

PROJECT F012

ANNUAL RESEARCH REVIEW

March 24, 1995

Alan W. Rudie

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TECHNICAL PROGRAM REVIEW

Project Title:	SOUTHERN PINE MECHANICAL PULP
Project Code:	SPMP
Project Number:	F012
Division:	Chemical and Biological Sciences
Project Staff:	A. Rudie, B. Carter, A. Shakhet
FY 94-95 Budget:	$150,000

Program Objective:

Improve the performance of mechanical pulping processes.

SUMMARY OF RESULTS:

Previous Results:

None, new project in FY 94-95.

Current Results:

The current research will evaluate the sequential breakdown of southern pine wood chips into fiber in a disk refiner. The project briefly evaluated a method of obtaining fibers from the breaker bar and intermediate bar zones of a refiner plate by stalling out the refiner under load and filling in the plates with gelatin to fix wood particles in position. Particles were then recovered from the refiner plates and the gelatin removed by washing with hot water. Although the technique was successful, it has not been pursued because the results obtained from the small lab scale refiners may not be applicable to commercial refining and the technique could not be used effectively on larger scale equipment. A larger scale trial has been set up with the Andritz Sprout-Bauer pilot plant in Ohio to prepare TMP using plates with portions of the refiner bars removed. This trial will take place this June.

TENTATIVE GOALS FOR FY 1995-1996:

Influence of Species on Rate of Wood Disintegration (Rudie):

1. Rate for average wood particle size reduction vs SEC and radial position. (Target 9/95).

2. Rate of earlywood and latewood fiber liberation vs SEC and radial position. (Target, 11/95: Evidence of selectivity of energy absorption in the initial stages of refining.)

3. Rate of earlywood and latewood fiber cleavage relative to SEC and radial position. (Target, 1/96: Evidence of the distribution of energy between earlywood and latewood after fiber liberation.)

4. Analysis of earlywood and latewood content of wood particles by size and radial position. (Target 2/96: Evidence of selective energy absorption in initial stages of refining.)

5. SEM analysis of exposed particle surfaces (Target, 6/96).

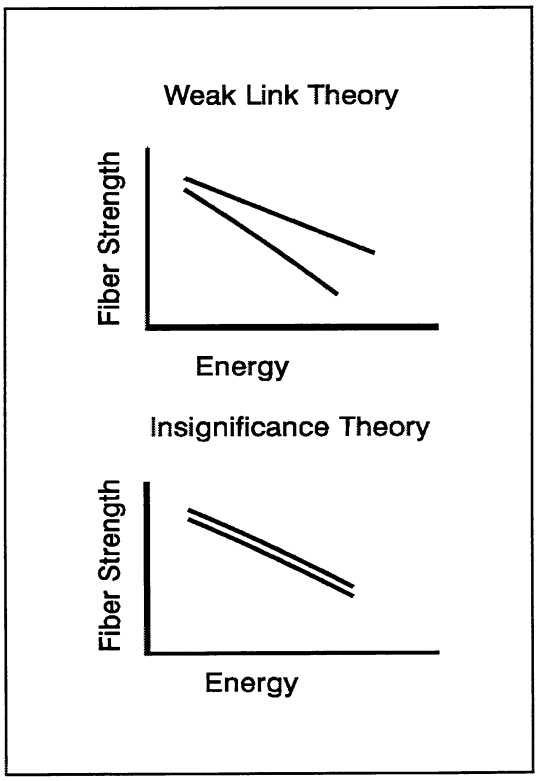
6. Task completion: 9/96.

STATUS REPORT:

Introduction

Papers made from mechanical pulp are generally a fiber bonding limited structure.[1] In an ideal bond limited paper, fibers pull out of the sheet at failure and relatively few fibers break. Tensile and tear strength depend only on surface area and bond shear strength. However, for sulfite chemithermomechanical pulp[2] (CTMP), alkaline peroxide chemimechanical pulps[3] (APMP), and low freeness thermomechanical pulps (TMP),[4] tear index goes through a maximum with increasing specific energy and begins to decline with additional refining. These pulps reach the point where bond strength exceeds fiber strength and the paper will benefit from improved processing to preserve the native strength of the wood fibers.

To avoid fiber strength losses in high yield pulping, it is important to consider fiber damage that occurs early in the process. Fiber damage in chipping, chip handling, chip compression in the plug screw feeders, and in the initial size reduction in the first stage refiner, may increase the susceptibility of the fiber to cleavage later in the process. The result would be a magnification of damage throughout the process. If this occurs, the gap between the fiber strength resulting from good processing and poor processing will expand with increasing energy. This situation is depicted in figure 1 labeled as the weak link theory.



It is also possible that early fiber damage becomes lost in the damage induced in the later stages of mechanical pulping. This possibility is shown (Fig. 1) as two parallel lines for fiber strength with the additional strength loss from poor processing before refining making just a small contribution to lower fiber strength in the final pulp. It is referred to as the insignificant loss theory.

The conventional method of evaluating damage that occurs early in the refining process is to complete the refining under controlled conditions and pass judgement on the merit of the chip treatments and early stage refining by the effects observed on final pulp quality. Overall, this is not a bad concept, final pulp quality is the issue of real commercial interest and both the weak link theory and insignificant loss theory suggest that under controlled conditions, the damage from early stage processing would be observable in the final pulp. Unfortunately, the concept of control in refining is as much a goal as a reality and the remaining uncontrolled process instability limits the sensitivity for detecting change. In addition, without a detailed analysis, it is impossible to determine from a refining

study whether the process change has preserved the native fiber strength or increased the interfiber bonding strength. This knowledge is useful for fully exploiting a new process and understanding it's applications and limits.

Ideally, to understand the process, it is vital to separate paper strength into it's component parts, fiber strength, surface area, relative bonded area and specific bond strength and to be able to evaluate the progress in developing each of these component throughout the chip treatment and refining process. This project has evaluated a chemical delignification method for measuring fiber strength throughout the refining process. The technique was then used successfully to evaluate pulp strength problems at the MacMillan Bloedel TMP mills in British Columbia, and the Bowater TMP mill in Calhoun Tennessee.

Chlorite holopulping and handsheet testing were selected for evaluation in this project. Chlorite holopulping provides a means to selectively delignify wood at any point in the wood handling and pulping process.[5,6] Handsheet testing has the advantage of using a fully representative sample of the wood or pulp. Although fiber bond strength, fiber strength and the presence of handsheet defects all influence handsheet strength, these problem can be minimized by relying on zero span[7] tensile testing and both the tensile and tear indices[8,9] as a measure of fiber strength. Handsheet defects such as shives and variations in basis weight will increase the standard deviation in the handsheet testing. These can be controlled by proper preparation of the pulp for sheet forming.

REVIEW OF PAST PROJECT ACTIVITIES:

Chlorite Holopulping

A room temperature acetate buffered chlorite technique and a 60° C buffered chlorite technique were evaluated for preparing the pulp. The principle advantage offered by the high temperature procedure is in faster sample handling. At 60° C each chlorite treatment was complete in about 24 hours. This allowed the samples to be treated with five chlorite treatments (and 4 alkaline extractions) in about 15 days. The room temperature procedure required five days for each chlorite treatment and 8 weeks to completely delignify wood chips. In both cases, pulps were evaluated for Kajaani fiber length and handsheet testing of zero-span tensile index, tensile index and tear index. The hot chlorite techniques showed lower fiber length, tear strength and scattering coefficient than the pulps prepared with the room temperature procedure (Table 1). The room temperature method was used in all subsequent experiments.

Several changes were required in the standard literature holopulping procedures to make them suitable for this project. It was not acceptable to grind or slice wood chips prior to delignification since this introduces unwanted chip and fiber damage. This makes it difficult if not impossible to solvent extract the wood or pulp prior to the chlorite treatment. The solvent usual extraction step was eliminated[10] but to improve the removal of soluble lignin fragments and saponify and remove extractives, the chlorite delignification was separated into several steps and the partially delignified wood extracted with dilute sodium hydroxide between the chlorite treatments. Long treatment times and additional treatment stages were required to fully delignify

the wood chips. Vacuum impregnation of the chlorite solution was used on the first two treatment stages to assist penetration of the chemicals into the wood chips[10] and wood chips were screened on a Williams Classifier and the retained 1 inch fraction was replaced with an equal weight of pass 1" retained 3/4" chips. After the wood is broken up in the British Disintegrator, a gel like precipitate forms during the alkali extraction steps. This plugs filter papers and makes fiber recovery more difficult. To avoid this problem, filtration was carried out on a 150 mesh wire screen. It was assumed this would increase the loss of fines and hemicellulose but these were judged to make a minimal contribution to the testing and the use of the wire screen improved handling substantially.

In the initial evaluation (Table 1), two chip sources were evaluated with replicate samples treated by the room temperature procedure to provide additional information on test reproducibility. Chip source 1 had been destructured by compression at room temperature to 28% of its initial volume. Chip source 2 had also been to 28% of it's initial volume, but after atmospheric presteaming for 30 minutes.

Table 1: Replicate chip crushing and holopulping experiments.

Run #	Tensile Index N·m/g	Tear Index mN·m²/g	Z-Span Tensile N·m/g	Fiber Length mm	Scattering Coefficient m²/kg	Chlorite Yield %
1a	60.8	12.1	142.7	3.64	20.0	53
1b	65.0	13.5	120.2	3.44	20.4	50
$1_{60°}$	59.9	9.1	147.6	3.36	18.1	55
2a	55.1	11.7	139.6	3.40	18.9	71
2b	73.1	13.9	144.5	3.40	21.4	67
2c	69.6	14.0	123.3	3.56	21.5	72
$2_{60°}$	78.7	10.2	130.6	3.29	18.1	46

Run $1_{60°}$ is the same chip source as runs 1a and 1b but with the chlorite delignification conducted at 60° C. Run $2_{60°}$ is the same chip source as runs 2a, b and c but with the chlorite delignification carried out at 60° C.

A high level of variability was observed in this initial evaluation. This made it impossible to observe differences in fiber quality caused by the two wood chip compression methods. The room temperature compression procedure does appear to have a significant influence on the yield after chlorite treatment. Presumably, this is due to a larger percentage of fines generated in the room temperature compression procedure and liberated by the holopulping.

Evaluation of Fiber Damage in Plug Screw Feeders

Although the precision of the chlorite procedure was still in doubt, the project needed information on the magnitude of fiber damage from commercial processes to know what level

of precision was needed and whether the chlorite delignification procedure could be useful. For an initial test, samples were collected from the feed and discharge of two Impressafiners® in the MacMillan Bloedel British Columbia TMP mills. The impregnation stage in mill A was thought to be operating well, but the impregnation stage in mill B was thought to suffer from steam channelling problems. The four samples were holopulped in duplicate. After completing the holopulping, the samples were screened on an 0.008" slot Valley Flat Screen before making the hand sheets for testing. This removed the remaining shives that were not completely delignified and it was hoped would improve the reproducibility between duplicate samples. The averages are reported in table 2 with the variation between duplicates indicated in brackets.

For these samples, the average values show a strength loss in the chips exiting both Impressafiners®. In mill A the strength losses range from 1% in Tear Index to 9% in Tensile Index. Mill B shows a loss ranging from 7% in Tear Index to 19% in Number Average Fiber Length. The average loss for all tests is 4.5% in mill A and 12% in mill B.

The agreement between duplicates is quite good and the results clearly indicate that there is measurably greater fiber damage occurring in the Impressafiner® in mill B.

Table 2: Holopulping results from the feed and discharge of two impressafiners®.

Sample	Zero Span Tensile N•m/g	Tensile Index N•m/g	Tear Index $mN•m^2/g$	Fiber Length (Number Average) mm
Mill A				
Feed (chips)	148(4)	103(1)	8.4(.3)	1.76(0)
Discharge	145(5)	94(9)	8.3(.2)	1.65(.06)
% Retention	98	91	99	94
Mill B				
Feed (chips)	148(2)	104(3)	8.2(.2)	1.81(.05)
Discharge	135(6)	90(3)	7.6(.1)	1.47(.08)
% Retention	91	86	93	81

Each value is the average of duplicate experiments, the number in brackets is range ÷ 2

RECENT RESULTS:

Influence of Holopulping Parameters on Handsheet Strength

The initial project demonstrated that chlorite holopulping and handsheet testing could be used to detect relatively small changes in fiber strength in wood chip handling and treatment prior to

refining. For a second trial, it was decided to test the process throughout a refiner line where large changes in fiber strength, fiber surface area, and fiber length could be expected. In this task, the project encountered several more issues with the chlorite holopulping technique that had not been faced previously and needed to be addressed.

1. The different wood particle sizes delignify at vastly different rates. Typically, the refiner discharge samples appear to be fully delignified and fiberized while the wood chips still have hard centers.

2. The time spans between sample periods requires a comparison of results from one series of chlorite delignification experiments to another. This introduces more opportunities for differences in sample treatment that could reduce the precision of the testing.

3. After completing a series of samples, it was discovered that there was considerable variation in holopulping yield and final pulp brightness between samples (table 3).

The first problem was handled by treating all the samples with 5 chlorite stages. Thompson indicated the chlorite treatment was mild enough that the differences in rate of delignification would not seriously influence the results.[11] The second question was evaluated by repeating the chlorite treatment and pulp testing of a chip sample after several months had elapsed. The yield variation was thought to be due to the more rapid delignification of TMP fiber than wood chips, and loss of fines when the pulps were filtered and washed. The fines loss was not considered to be a problem since the intent was to measure the fiber strength. The influence of yield on final strength needed to be addressed. Because of the concern over yield, it was deemed necessary to improve the reliability of the final pulp weight measurement. This was a difficult measurement since the high hemicellulose content of the pulps and the need to make quantitative transfers when handling the samples. This usually resulted in samples with about a 6% consistency, where it is difficult to collect a representative subsample. It was decided to air dry samples before determining final mass and preparing handsheets for testing.

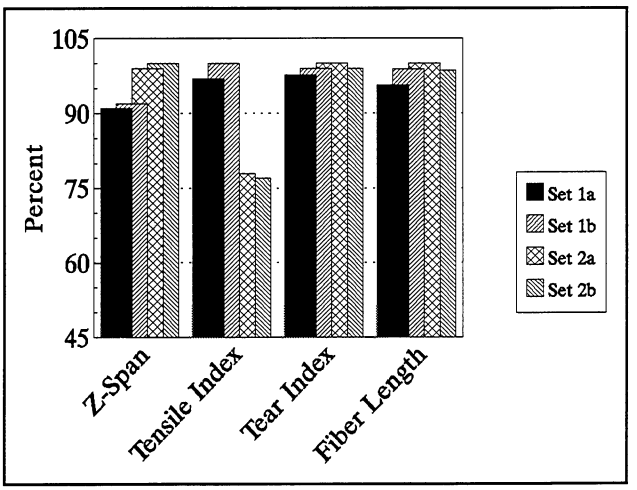


Figure 2. Normal mill production wood chip samples. Set 1 a & b are winter chip data. Set 2 a & b are winter chips processed with the spring samples.

As a check on the effect of air drying pulps on sheet strength, and of the test precision over time, the two samples of wood chips from the initial series of tests were holopulped and tested a second time. This data is listed in table 3 for one set of wood chips and is graphed as a percent of maximum bar chart in figure 2 for the other. In figure 2, the first two bars in each group are the duplicate samples for the initial test made from slush pulps. The third and fourth bars are the same chips pulped about three months later and tested as once dried pulp. The zero

span tensile index, tear index and fiber length show a reproducibility between periods of 90% or better, in spite of the air drying procedure. However, the tensile index is 25% lower for the chips treated with the spring samples. This low tensile index is observed in all the samples that were air dried before making the handsheets.

Table 3: Yield, Brightness, Zero Span Tensile Index and Tensile Index .

Sample	Yield	Brightness	Z-Span	Tensile Index
Chips	60.23	77.95	134.41	58.15
	58.33	76.42	136.30	59.52
Chips (AD)	61.40	81.85	141.10	43.80
	62.20	82.52	138.00	42.80
Primary	53.70	81.29	138.96	75.22
	53.10	81.98	135.84	75.30
Secondary	47.40	80.67	142.11	80.51
	49.90	81.57	151.82	80.33
Latency	48.41	77.10	139.03	71.17
	48.10	76.89	135.36	77.15

To answer the remaining questions, an extended series of tests was carried out on a sample of wood chips supplied by the Bowater mill. Twenty two 30 OD gram samples were delignified with sodium chlorite as indicated in the experimental section. 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 beaten in a PFI mill to 0, 2300, 4000, 6500, and 9000 revolutions giving freeness levels ranging from 760 to 355. Half the sample at each freeness level was air dried. TAPPI handsheets were then made from each sample giving sets for two yield levels, 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 of The Beater Run Testing:

The number of chlorite treatment stages and the air drying process proved to have a significant effect (95% confidence level) 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 3 for the wood samples treated with four and five stages of sodium chlorite delignification. The four stage data are shown as trend lines since this data gave a good fit to a linear regression. The line for the air dried pulp sample 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 (8.6%). The data for the five chlorite stage case are plotted as data points for comparison to the trend lines for the four stage case. Although these data 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 (3.7%) for the fifth stage of chlorite treatment.

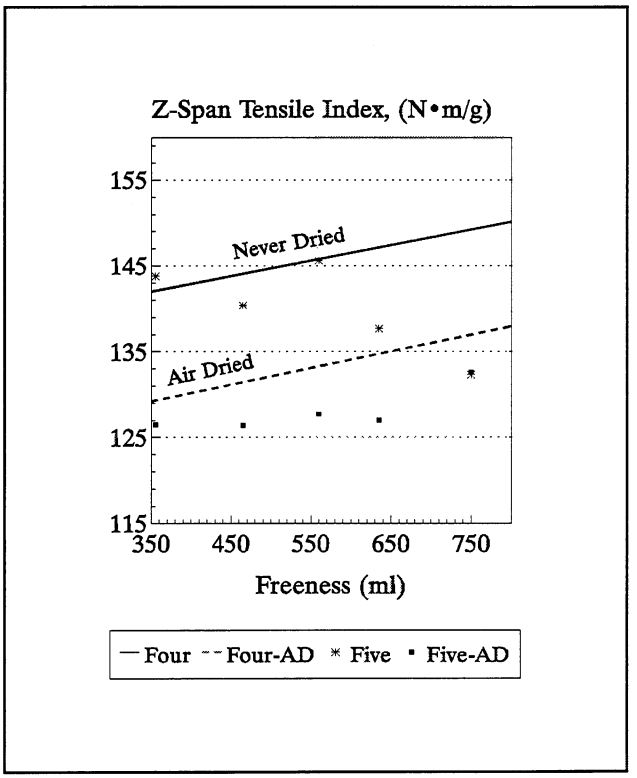


Figure 3. Zero Span Tensile Index for the beater run samples.

With chemical pulps, zero-span tensile strength usually increases with beating, rising to a maximum or broad plateau around 600 ml CSF.[12] In the freeness range of these experiments the zero span tensile should be nearly independent of freeness. In a multiple regression analysis of the zero span data, the air drying process and the number of chlorite stages were significant, but pulp freeness was not significant at the 95% confidence level.

The influence of the three pulp variables on tensile index is shown in figure 4. The air drying process reduces the tensile index by about 20 N·m/g (25%) 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 (4.4%). The graph for tear index relative to never-dried freeness is shown in figure 5. The fifth chlorite stage reduces the tear index by about 0.45 mN·m^2/g (4.7%) and the air drying process increases the tear index by about the same amount.

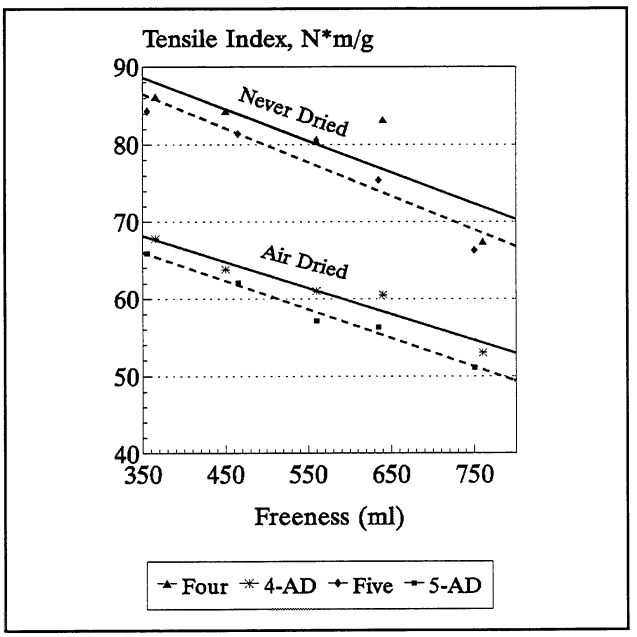


Figure 4 Tensile strength data.

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 6. 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.

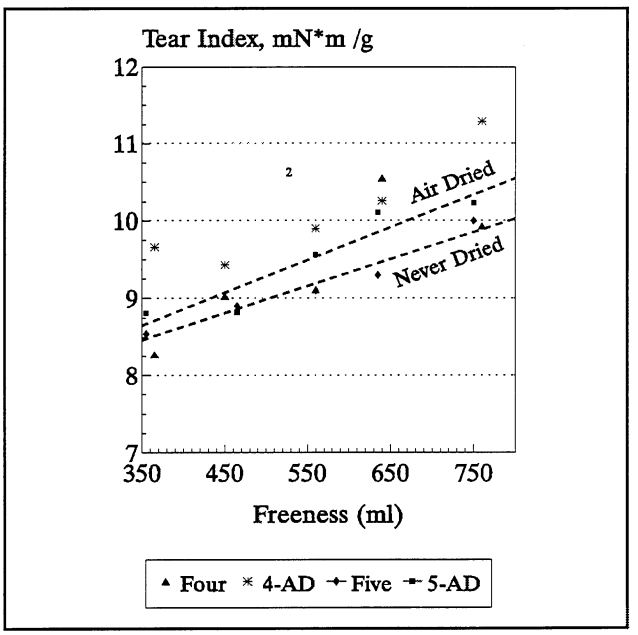


Figure 5. Tear index data.

Seasonal Strength at Bowater Calhoun

In January 93, the project began an evaluation of a seasonal strength loss in the Bowater southern pine TMP mills. The Bowater mills had observed a regular loss in pulp strength during the winter months. The Bowater Mercy mill in Liverpool Nova Scotia recently reported a similar problem and provided evidence that the winter strength loss was related to seasonal changes in the chip size distribution.[13]

Arrangements were made to test samples from the Bowater Calhoun, Tennessee TMP mill during the January, March/April, June/July, and October/November time periods. The final sample was postponed in favor of collecting a second set of samples during the seasonal low strength period. When the mill did not experience a definite loss in strength the second winter, a control sample was sent and used for the PFI beater runs reported above.

For each season, the mill supplied samples of wood chips from the chip washer and fiber from the discharge of the primary refiner, the discharge of the secondary refiner, and the latency chest. Samples were collected twice during the sample period. One set of samples was taken under conditions as closely controlled as possible. The second set of samples was representative of the normal mill operation at the time. Wood chip samples were screened on a Williams Classifier to determine if there was a significant change in chip size distribution between the seasons. Each sample was pulped and analyzed in duplicate. All samples were holopulped and tested as before. A complete table of results is given in the Appendix.

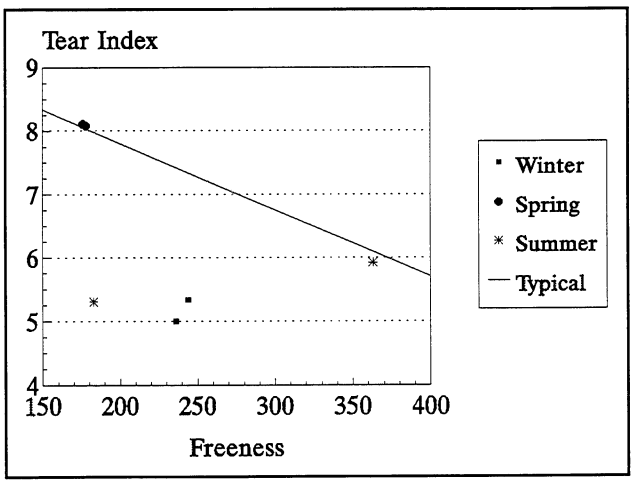


Figure 6. Tear Index plotted against freeness for the latency chest samples (mill data). The response line is generated using Pilot Plant data.

Results and Discussion

The mill operating data and secondary refiner pulp test results for the controlled production samples are listed in the appendix.

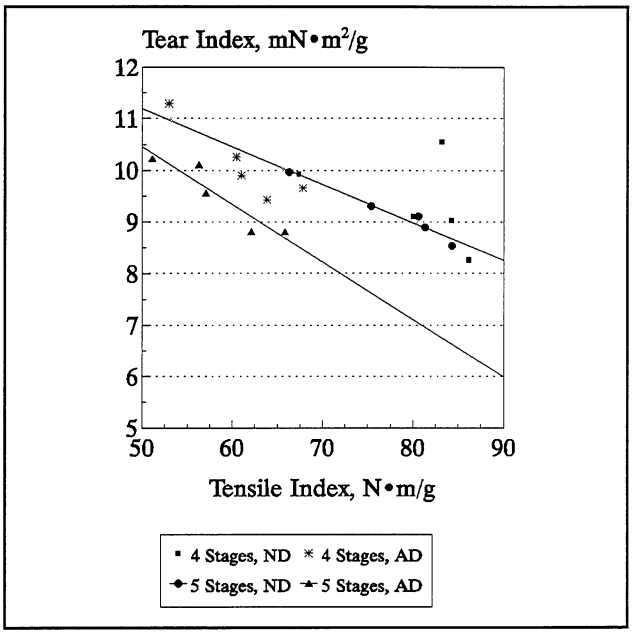


Figure 7 Tear vs Tensile.

TMP strength was low for the winter sample period, when the mill was experiencing an extended period of low pulp strength. However, it was also low during the summer sample period which was not expected. Specific energy (estimated from total motor load divided by rpm) was highest in spring and lowest in winter, correlating with tensile strength. Tear Index is plotted against freeness in Figure 7. A linear regression line using pilot plant data from the Andritz Sprout-Bauer laboratory in Springfield has been added as a typical response curve. The two samples from the winter collection period confirm the low strengths reported by the mill. The low freeness sample from the summer collection period also shows a low tear strength relative to the expected response line.

Table 4: Student *t* values for pooled Zero-Span Tensile Index data.

	Winter		Spring		Summer	
	Normal	Control	Normal	Control	Normal	Control
Z-Span $N \cdot m^2/g$	139	139	150	152	142	144
WinNorm	0	-0.218	**3.230**	**3.668**	0.621	1.627
WinCont	-0.218	0	**3.693**	**4.130**	0.912	**2.059**
SprNorm	**3.230**	**3.693**	0	0.526	**-2.706**	**-1.918**
SprCont	**3.668**	**4.130**	0.526	0	**-3.169**	**-2.425**
SumNorm	0.621	0.912	**-2.716**	**-3.169**	0	0.994
SumCont	1.627	**2.059**	**-1.918**	**-2.425**	0.994	0

Entrees in bold print are significantly different. $t_{crit.}$ = 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.

Since freeness was not a significant variable for zero span tensile testing of the chlorite pulps, the data from the three seasonal test periods was pooled and tested for significant differences.

The average zero-span data and results of the *t* tests are summarized in table 4. 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-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.

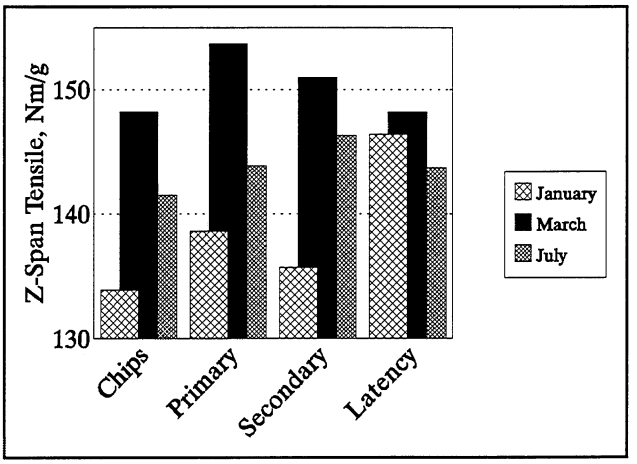


Figure 8. The zero span tensile data for the normal mill pulps from the three sample periods.

It was expected that holopulps produced from wood chips would give the highest zero span tensile index since these are the strongest fibers available to the process. As seen in figure 8, this is not the case. There appears to be an improvement in zero span tensile index from the refining, probably from increased bonded area. Typically, the range of zero span tensiles for the four samples in each set was less than 8%, confirming the relative insensitivity of the test to beating and largely justifying the pooling of this data.

The tear/tensile data for the three sample periods and four sample locations are graphed in figure 9 as a bar chart showing percent Tear Index relative to the control five stage PFI data (see the appendix). For this graph, the tear index and tensile index data of the standard production and control samples were averaged, and the average Tear Index compared to the estimated tear index of the appropriate control sample. For the winter samples, the control sample is the five stage never dried PFI beater run data, for the spring and summer samples the control is the five stage air dried beater run data. Each bar represents four holopulping and handsheet testing replicates.At all four positions the spring samples give the highest tear index (at constant tensile). For the wood chips, primary refiner discharge and secondary refiner discharge, the winter samples have a higher tear index than the summer samples. At the latency chest, the relative tear index of

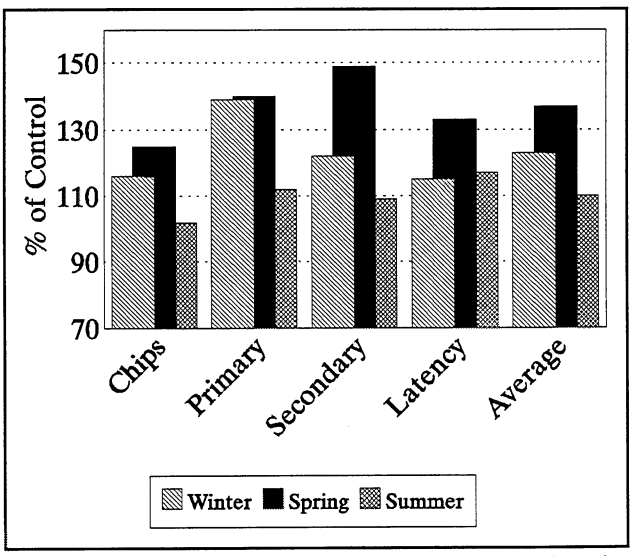


Figure 9. Sample tear index divided by the estimated control tear index at the sample tensile index, expressed as a %.

the summer samples exceeds the tear index of the winter samples. The average % Tear Index relative to the controls is shown in the last cluster of bars. The spring samples show the highest overall average test followed by the winter and summer samples in that order.

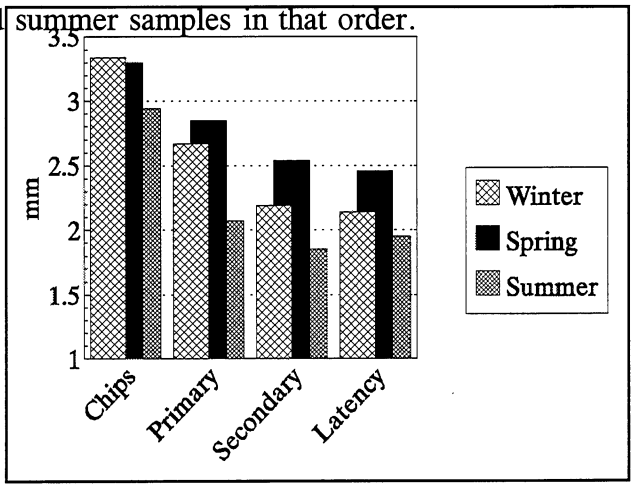


Figure 10. The chlorite holopulp fiber lengths for the controlled refining conditions.

The fiber length for the three sample periods is shown in figure 10. Fiber length gives a clear indication of fiber damage in the refiners. The fiber lengths reported in this study are Kajaani weight weighted averages and are carried out on latency relieved holopulped samples. The latency treatment reduces the fiber curl that develops in refining and the extended chlorite holopulping process. For the testing in this study, the winter and spring wood chips have slightly longer average fiber length than the summer samples. The fiber length decreases substantially between the wood chips and primary refiners in both the winter and summer samples, confirming the fiber shortening expected in high yield refining. Unfortunately, there is little information of what was causing the fiber shortening in these samples. Primary refiner plate gap, motor load (divided by RPM) and plug wiper flow were all in the normal range for both periods. The closing pressure was higher on the primary refiner for both the winter and summer samples and was quite high for the normal mill samples collected in summer. This is probably representative of the higher plate hours on the refiner when these samples were taken. Chip compression damage from chipping frozen wood in winter, and dry wood in summer is a possible source of the problems and needs to be evaluated more fully. The loss in fiber length with refining may simply reflect the native fiber strength of the wood in the spring samples relative to winter and summer. Net fiber length retention from the wood chips to the secondary refiner is 77% in spring, 65% in winter and 63% in summer for the controlled production samples. The standard production samples had similar losses in fiber length in winter and spring, but the summer sample retained only 48% of the native wood fiber length through the refiners.

Wood Chip Analysis

The chip size distribution changed only slightly during the sample period, with the spring period having the largest retained 1/2 and 1/4 inch fractions. (figure 11) There did not appear to be a significant change in the pass 1/4 inch fraction but there were considerably more chips retained on the 1 inch screen for both winter and summer samples. If the Bowater Mersey data is equally applicable to southern pine, this change in chip size distribution is sufficient to cause a 7 to 10% loss in burst strength.[13] This however, is an unlikely source for the low pulp strength. Larger chips can produce low strength pulps because they may not have adequate time for the cores to attain the desired process temperature and the large chips can reduce bulk density of the chips and disrupt the flow of material to the refiner. They should not have an impact on native fiber strength, the fiber strength of the unrefined wood chips.

The mill TMP pulp test data shows a seasonal loss in both tensile index and tear index for the low strength periods. In contrast, carefully controlled studies of chip size confirm the loss in tensile strength but show relatively little change in tear index when increasing the larger chip content.[14,15] This inconsistency suggests that chip size may not be the source of the reduced pulp strength and may instead be caused the changes in the wood supply responsible for the low pulp strength.

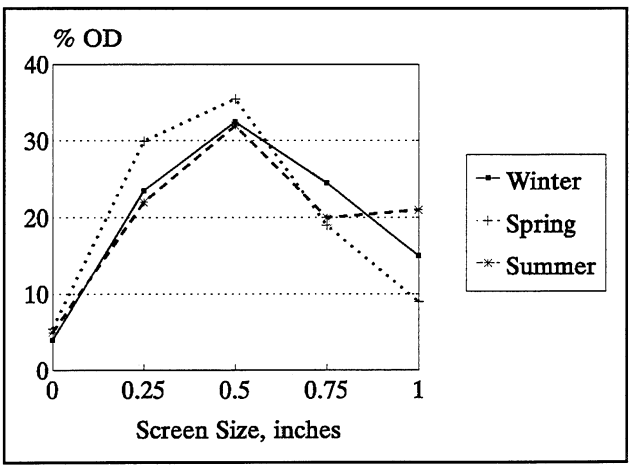


Figure 11. Chip size distribution for the Winter, Spring and Summer samples.

The reason for the broader chip size distribution in winter is presumably chipping of frozen wood.[16] The reason for the broader chip size distribution in summer may have been worn chipper knives or dryer wood. Whereas the winter chips were received at a moisture content of 120% (moisture on dry wood basis, 45% consistency) and the spring wood chips at 109% (48% consistency), the summer wood chips were received at just 84% moisture content (54% consistency). Further analysis of these 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 5.

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. The growth ring widths are also quite similar at 3 to 4 mm and 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.

Table 5: Wood chip density and average growth increment.

	Density g/cc	Growth Increment, mm				
		3/4" Average	RMSD	1/2 "Average	RMSD	% ≥6mm
Control	0.433	4.15	1.72	4.09	1.48	19
Winter	0.437	3.77	1.01	3.70	1.48	12
Spring	0.446	3.71	1.50	3.36	1.47	10
Summer	0.443	3.93	1.76	3.17	0.994	12

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. When the wood density is plotted against average zero span tensile index, a straight line relationship is obtained with an R^2 of 0.94 (figure 12). Based on the results of a 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 observed in the Bowater wood chips should change burst by 10 to 15% and Tear by about 5%.[17] These changes are within the range observed in the Bowater samples.

Conclusions:

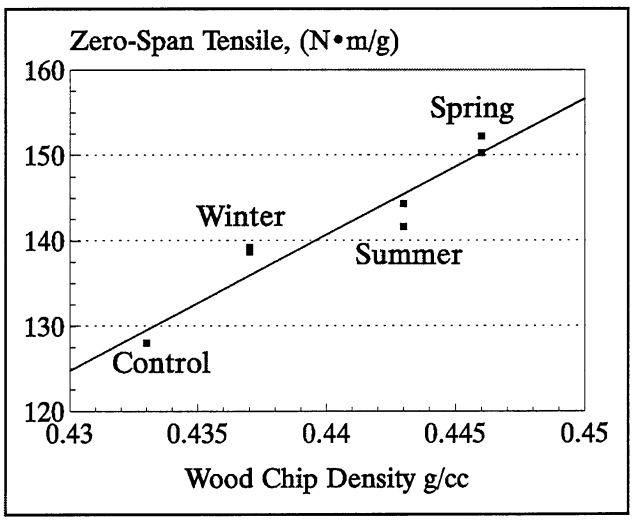


Figure 12. Average wood chip density influences chlorite holopulp fiber strength. R^2 = 0.94.

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 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. 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 the 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. It needs to be emphasised that the fiber strengths observed in the TMP holopulps greatly exceeds the strength obtained in mill TMP. The mill paper strength is still bond strength limited in these samples, and an appropriate choice of refining conditions may provide the bond strength and paper strength desired.

This project has provided an excellent test of the chlorite holopulping technique and it's 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.

FUTURE ACTIVITIES:

The proposed research will evaluate the sequential breakdown of southern pine wood chips into fiber in a disk refiner. The wood particles and fiber will be evaluated for earlywood and latewood composition, fiber length (broken fibers) and exposed surface. The initial work will focus on analyzing the particle size distribution and fiber quality as wood moves radially across the disks from the chip breaker to the discharge of the refiner.

The technique proposed to obtain samples involves grinding away the perimeter bar sections of the refiner plates. This approached will 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 plate diameters will be evaluated to obtain pulps from whole plates, plates with the fine bar section removed, and plates with the fine bar and 2/3rds of the intermediate bar section removed.

Each sample will be analyzed for particle size distribution and fiber length, coarseness, earlywood/latewood content and the frequency of earlywood and latewood fiber cleavage relative to the radial position and particle size. A higher density, mature loblolly pine wood sample and a lower density juvenile loblolly pine wood sample will be evaluated to determine how wood growth influences the wood disintegration. The loblolly pine results will be compared to the behavior of black spruce refined under similar conditions.

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.

Specific Objectives and Deliverables:

Listed objectives are for all three wood sources. And Target dates are contigent on obtaining an Industrial Partner and completing the refining work by June 15th. The task objectives are:

- Determine if the rates of earlywood fiber liberation and cleavage are similar among the three wood supplies, juvenile pine, mature pine and northern spruce.

- Determine whether preferential cleavage of earlywood fibers is unique to the pines or is

as prevalent in spruce

- Determine whether preferential cleavage of earlywood extends beyond the fiber liberation point.

Specific Data milestones are:

1. Rate for average wood particle size reduction vs SEC and radial position. (Target 9/95).

2. Rate of earlywood and latewood fiber liberation vs SEC and radial position. (Target, 11/95: Evidence of selectivity of energy absorption in the initial stages of refining.)

3. Rate of earlywood and latewood fiber cleavage relative to SEC and radial position. (Target, 1/96: Evidence of the distribution of energy between earlywood and latewood after fiber liberation).

4. Analysis of earlywood and latewood content of wood particles by size and radial position. (Target 2/96: Evidence of selective energy absorption in initial stages of refining.).

5. SEM analysis of exposed particle surfaces (Target, 6/96).

6. Task completion: 9/96.

Acknowledgement:

John Griffey from the Bowater Calhoun mill has coordinated all the sample and mill data collection, and IPST technicians Blair Carter and Alex Shakhet performed all the laboratory work on this project. These three are co-authors of the final report. We would like to express our thanks to Bob Harley of Bowater Corporation, and the Bowater Southern mill in Calhoun Tennessee for providing an interesting problem and the samples to study it. We thank the TMP mill operators and staff for their effort to reproduce the controlled refining conditions on a periodic basis and Melanie Gray and Shawn Wendell who collected all the samples and mill data to support the project. Thanks also to Jim Turnbull and Peter Joyce of MacMillan Bloedel Ltd. for providing the impregnator samples and background information. Finally, we thank the members of the Mechanical Pulping Project Advisory Committee for their advice and support of the project and for the member companies of the Institute of Paper Science and Technology who provided the financial support for the project.

Experimental Procedures:

Chlorite Holopulping:

A stock buffered chlorite solution is prepared as follows: To a 1 liter volumetric flask, add approximately 500 ml of distilled water, 60 g (0.66 moles) of reagent grade sodium chlorite and 60 g (0.72 moles) of reagent grade sodium acetate. Dilute to the mark with distilled water.

This reagent is photosensitive but is otherwise stable and can be stored for several months if kept in the dark.

To delignify wood chips, place 50 g (OD basis) wood chips in a 500 ml Erlenmeyer flask. Add 300 ml of buffered sodium chlorite solution and 20 ml of reagent grade glacial acetic acid. Attach the flask to a vacuum source and evacuate for five minutes (make sure the vacuum has a trap to prevent water vapor and ClO_2 from contaminating the pump oil). Turn off the vacuum source and slowly allow air into the flask. Place the flask under vacuum for another five minutes and release the vacuum to air again. Stopper the flask and place in a dark cabinet underneath a fume hood. After 30 minute to 1 hour, a distinct yellow green color should be observed indicating that chlorine dioxide is forming in the flask. At room temperature the wood chips will take 4 to 5 days to consume the majority of the chlorite. The sodium acetate buffer will maintain the pH around 4 for the during the reaction. Once the majority of the sodium chlorite/chlorine dioxide is consumed, filter the wood chips and wash once with distilled water. Transfer the chips back into the Erlenmeyer flask and add sufficient distilled water to cover the chips. Let the wood soak in the distilled water over night and filter again or decant the wash water. Add 200 ml of 0.15 N NaOH, cover the Erlenmeyer flask and let the wood soak for 24 hours. Filter or decant the alkaline solution and check the pH. If below 9.0 repeat the caustic extraction by adding another 200 ml of 0.15 N NaOH and letting the chips soak another 12 to 24 hours. Filter and wash the chips thoroughly. Place them back into the Erlenmeyer flask and repeat the chlorite procedure as described above with the exception of using 200 ml of chlorite stock solution and 20 ml of acetic acid.

The second chlorite procedure is followed by a second wash and caustic extraction. At this point the chips are broken up in the British Disintegrator (3000 revolutions). A third chlorite treatment is performed using 200 ml of stock chlorite solution and 20 ml of acetic acid. Since the wood/fiber is saturated, the vacuum step is ineffective and can be skipped. Follow the third chlorite treatment with another caustic extraction. Wash and disintegrate for 3000 revolutions in the British Disintegrator. This will render most of the remaining chips to shives and fiber. Once the chips are broken into fibers, the filtrates tend to plug filter paper and a 150 mesh wire screen is substituted for filter paper in the Büchner funnel. A fourth chlorite stage, extraction and a final chlorite treatment are required to complete the pulping process. The pulp is then washed thoroughly and disintegrated another 3000 revolutions.

During this project period, a hot chlorite delignification procedure exploded in the Research Services Division and it was decided to perform an additional safety check on this procedure. Blank chlorite samples were prepared substituting dilution water for the mass of the wood chips. The samples were otherwise handled in the same manner as the normal chlorite delignification procedure and were checked daily for the chlorine dioxide concentration. Under these conditions, the chlorine dioxide concentration never exceeded 0.6 gpl which is considered well below the limit at which ClO_2 can form an explosive atmosphere at room temperature.[18] It was concluded that the procedure was safe and we have continued using it with only slight modification.

Fiber length was determine using the Kajaani FS-100 optical fiber length analyzer. Samples were screened on a 0.008" Valley slot screen prior to making handheets. Handsheets were

prepared (TAPPI T-205) and tested for tensile index, tear index, scattering coefficient and absorption coefficient according to TAPPI 220. Zero span tensile index was carried out according to TAPPI T-231.

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Appendix

Mill Operating Conditions and IPST Pulp Test Results

	Standard				Controlled			
Primary	Jan.	April	July	Feb. 94	Jan.	April	July	Feb. 94
Days High ° C	12	28	37	12	12	28	37	12
Days Low ° C	-2	15	22	-3	-2	15	22	-3
Plate Hours	275	21	445	130	279	22	447	133
Production (RPM)	51	41	45	43	51	42	51	43.1
Load (MW)	7.1	6.6	6.1	7.7	7.2	6.8	7.5	7.5
Gap (mm)	6.68	5.51	7.92	6.07	6.73	5.56	7.32	6.07
Closing Pressure (kPa)	4300	3600	6200	4100	4300	4000	5000	4200
Freeness (ml)	707	636	742	-	665	621	750	-
Secondary								
Load (MW)	5.4	5.7	5.8	6.0	5.7	5.9	6.5	5.8
Gap (mm)	5.05	5.10	7.29	5.76	5.16	5.18	7.26	5.76
Closing Pressure (kPa)	2300	2100	3800	1900	2900	2100	7400	2200
Freeness (ml)	236	178	183	-	244	176	363	-
Tensile Index N·m/g	15.1	22.2	17.5	25.2*	14.9	21.0	16.7	27.4*
Tear Index mN·m^2/g	4.47	7.16	4.71	7.77*	4.97	6.74	5.12	7.56*
Burst Index kPa·m^2/g	0.71	1.05	0.75	1.30*	0.75	0.95	0.66	1.31*
Brightness	56.0	58.9	55.8	57.5*	54.7	59.3	55.3	57.5*

* Mill test data.

Student Work

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

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A490

Chemical & Biological Sciences Division

Institute of Paper Science and Technology
Atlanta, GA

March 1995

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 that simulate a disk refiner. The working hypothesis is that the earlywood fibers will be preferentially strained and have a larger viscoelastic 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, the exact mechanisms of how wood is reduced to fiber are poorly understood. It is hoped that by better characterizing the fundamental processes, industry practices can be improved leading to improved fibers, decreased energy consumption, and promotion of this environmentally-friendly process (1). 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.

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 the southern yellow pines are used. These species have the highest energy requirements and produce the poorest quality pulp of all softwood species used routinely for the production of newsprint (2).

This proposal develops a method to discern what is happening to the wood fibers due to the compressive forces in the coarse and fine bar sections of the refiner. Such information is important because it is theorized that the earlywood fibers are preferentially absorbing energy and may become over refined, leading to a loss of pulp quality (3). Studies on refining intensity demonstrate how this could happen. To refine the stiff, thick-walled latewood fibers, refining intensity needs to be increased leading to extensive degradation of earlywood fibers (4,5).

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 the 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 (6).

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 to produce TMP (7). Extra energy is needed due to the viscoelastic nature of wet wood which causes the wood to absorb mechanical energy and release it as heat. Salmen et al. (8) 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 (6,7,9,10), Salmen voices the opinion that energy could be conserved by refining at lower frequencies and higher amplitudes with increased temperatures, leading to more flexible fibers. This can be demonstrated with Figure 1, a graph showing greater fatigue at lower frequencies. This curve is 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 (3) 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. 2). 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 (3). This work also demonstrated that the amount of strain is different for earlywood and latewood growth zones. The thickness of the earlywood growth zone was markedly decreased while little change was seen in the thickness of the latewood growth zone (Fig. 3).

St. Laurent, Rudie, and Shakhet have also done experiments which show preferential earlywood degradation with low energy refining (5). The low energy refining was done to simulate early stage TMP pulping. After the low energy refining, the fibers were screened and the 4, 8, 20, and 100 mesh fractions from a Bauer-McNett fiber classifier were collected. The fibers were then holopulped and both fiber length and coarseness were measured. These measurements were them compared with similarly treated pure earlywood and latewood fibers. One can see evidence of earlywood enrichment in the smaller particle sized samples (Table 1). Microscopic examination further revealed this trend with one exception. One hundred fibers were viewed under magnification and were classified as either earlywood or latewood by the thickness of their fiber wall thickness. These 100 fibers were then examined to see if they were whole fibers (unbroken ends). Earlywood consistently revealed more broken fibers than latewood under the same refining conditions.

Table 1. Results from low energy refining (5).

Pure Earlywood or Latewood					
Wood		Coarseness (mg/m)		Fiber length (mm)	
Earlywood		0.14		3.08	
Latewood		0.37		3.32	
TMP Fractions					
Mesh Size	Coarseness	Fiber length	% Earlywood	Number of whole fibers	
				Earlywood	Latewood
4	0.22	3.21	46	37	59
8	0.21	2.41	49	18	35
20	0.17	2.62	53	1	23
100	0.18	1.21	43	0	3

Recently, work has started on the effects of compression of fiber aggregates. Shakhet has separated, refined, and stained earlywood and latewood fibers to determine if earlywood fibers are preferentially strained under static compression conditions (11). 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 2 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 in Table 3 includes the deflection data on multiple samples where only a portion of either the earlywood or latewood were stained, plus those of the previous data set. The data of Table 3 is not as reliable as Table 2, since it was impossible in these experiments to gauge whether the same amount of stress was applied to each sample. It still confirms the hypothesis that earlywood and latewood fibers absorb stress differently.

Table 2. Deflection data and t tests on Shakhet's work on compression of fiber aggregates after second compression (11).

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			
0.5	0.0			
0.0	0.6	Pooled Variance	3.50	
0.0	0.0	df	26.99	
0.0	0.2	t	2.22	
0.2	0.05	P(T<=t) one-tail	0.02	
0.2	0.0	t Critical one-tail	1.71	
0.6	0.1	P(T<=t) two-tail	0.04	
0.1	0.0	t Critical two-tail	2.06	
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 3. T tests on pooled data from compression testing of fiber aggregates (11).

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

An experiment has been proposed to simulate the coarse and fine bar section of a disk refiner and determine whether preferential energy absorption by the earlywood fibers continues beyond fiber separation. 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 subjected to cyclic compression at frequencies ranging from 10 Hz to as high of a frequency as is mechanically possible. High speed video will be used to record each experiment. After the compression procedure, infrared imaging will be used to measure the temperature differences of the fibers within the device.

Experimental Plan

1. Development of an apparatus to induce and record high frequency cyclic compression.

2. 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 imaging 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 major components of the cyclic compression device are a wave generator, an amplifier, an electromagnetic vibration generator (shaker), a spectrophotometric cell, a piston assembly, and an enclosure. An MTS servo-hydraulic tester will replace the wave generator, amplifier and shaker for the low frequency experiments.

The design of the sample chamber, holder, and camera frame for use with the MTS is finished (Fig. 4). This equipment has been manufactured and has been tested in practice runs. A narrow table was attached to the MTS and a linear slide platform set on top of the table. A microscope and CCD color video camera are connected to the platform and focus is achieved by rolling the platform as needed.

An infrared thermal imaging system will be borrowed from Georgia Tech Research Institution. For the infrared measurements, the spectrophotometric cell must be replaced with an infrared transparent material. 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. A sapphire window is recessed into the block in front of the notch with a cover plate to hold it in place. An adapter has been designed and produced to attach a 15X microscopic lens to the IR dewar.

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 was provided by the Bowater Inc., Southern Division mill in Calhoun, Tennessee. The log was cut into disks, and the disks cut 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 were prepared. The fibers were then fractionated in a Bauer-McNett, and placed into sealable Kapak bags and 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. 5)(12) and has a high repeatability for a single pulp (13).

The fiber aggregate will have a density of 0.083 g/cm^3. This density was determined by opening a fully loaded refiner during the second pass and extracting five bundles from the intermediate bars. The bundles were measured for length, width, and thickness and then oven dried to determine mass. The test chamber for this work has a volume of 0.5 cm^3. An aggregate will be placed in the chamber of the appropriate mass. This aggregate will be fifty percent earlywood/latewood by mass. Five percent of the mass, either earlywood or latewood, will be differentially stained. The stain of choice at the moment is Luecophor B-302 from Sandoz. This stain fluoresces blue white when excited by ultra-violet light. The aggregate is video taped during compression and the IR images taken at the end. The video will then be analyzed by image analysis for curl index.

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FIGURES

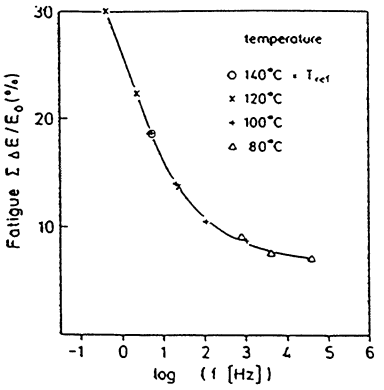

Figure 1. "Master curve" for fatigue of wood across the grain at an energy absorption level of 1000 cycles at 2kJ/m^3 per cycle (10).

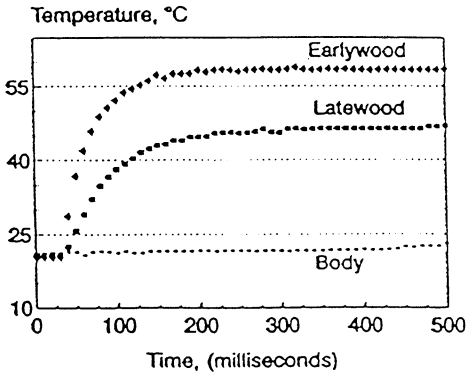

Figure 2. Temperature record of the sample tested at room temperature and 15 Hz (3).

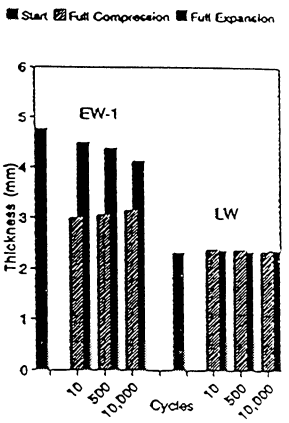

Figure 3. Earlywood and latewood - the effects of cyclic loading (3).

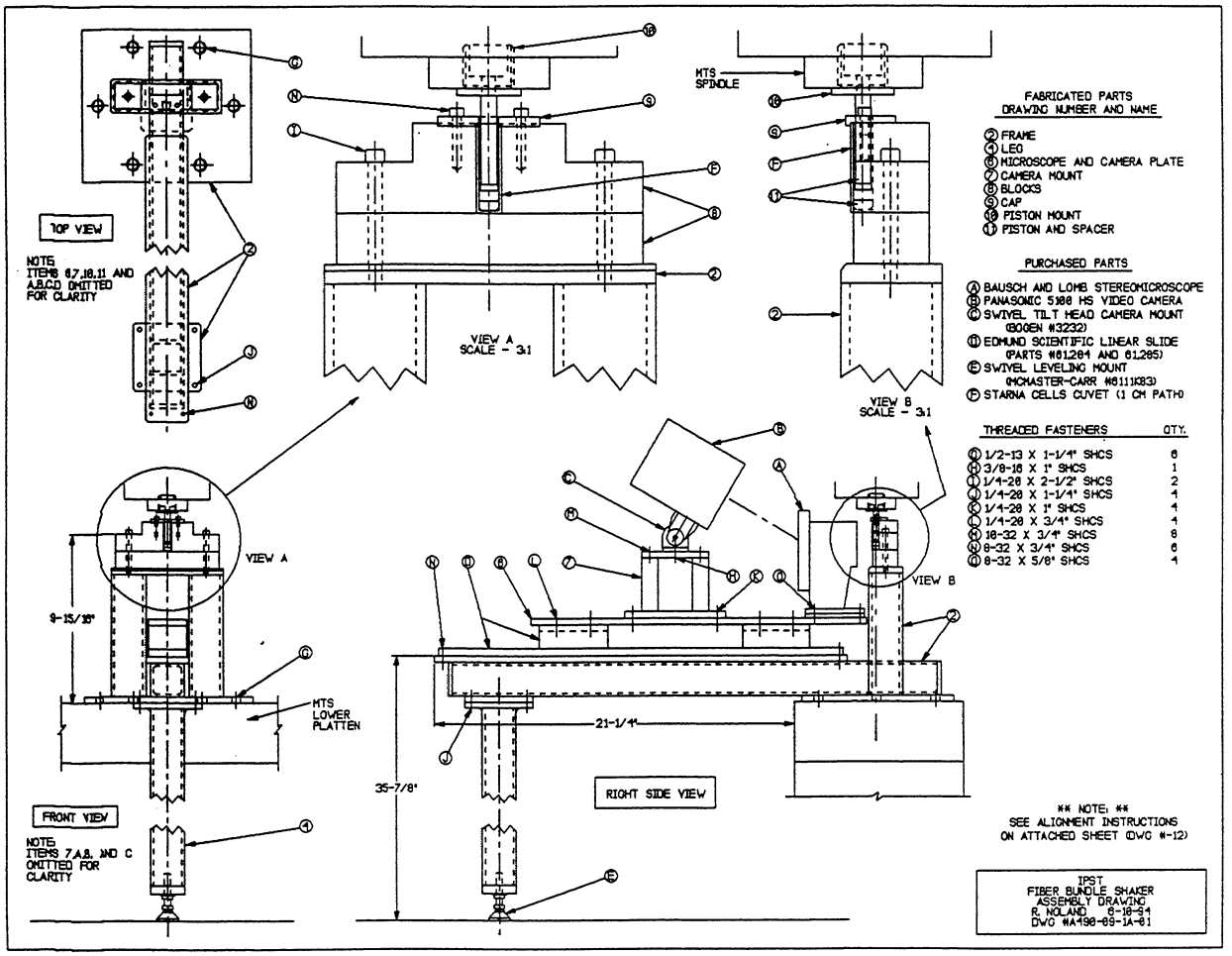

Figure 4. Design of sample chamber, holder, and camera/microscope frame for the MTS.

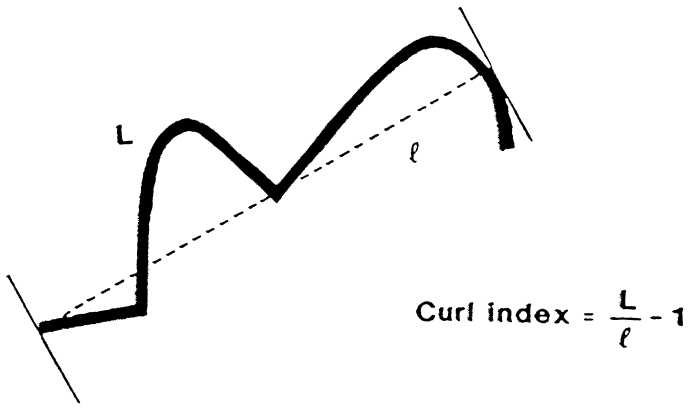

Figure 5. Curl index developed by Jordan and Page (12).

The Effects of *Ophiostoma piliferum*on Properties of Wood Pulp: Investigating the Impact of *Ophiostoma piliferum* on the Strength Properties of Handsheets

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SUMMARY
Effects of *Ophiostoma piliferum* (*O.p.*) treatment on strength properties of handsheets were studied by producing refiner mechanical pulps from chips treated with the fungus for varying time periods. *O. p.* treatment yielded handsheets with increased tear, tensile, and zero-span tensile strengths. Pulps produced from fungally treated chips also exhibited increased fiber length. Density, fines content, and scattering coefficients decreased with increasing fungal treatment periods.

INTRODUCTION

The fungus, *Ophiostoma piliferum*, marketed as Cartapip® (Cp) by Sandoz Chemicals Corporation is used to control pitch problems in paper production. Pitch consists of low-molecular-weight oleophilic materials extracted from wood chips in neutral, nonpolar, organic solvents. Pitch contains triglycerides, fatty acids, diterpenoid resin acids, sterols, waxes, and other compounds, some of which are not well characterized(1) . Cartapip is an albino strain of *O. p.* which does not stain wood, as do most blue stain fungi(2) .

In addition to controlling pitch problems and preventing blue stain, *O.p.* yields products with improved strength and runnability characteristics(3). This work documents strength increases in mechanical pulps produced from loblolly pine (*Pinus taeda*) chips treated with *O.p.*, and explores probable causes.

MATERIALS AND METHODS

Wood Source

Three half-sibling, loblolly pine trees were obtained from a Union Camp Corporation progeny test in Bellville, Georgia. Trees were cut into boards at a local saw mill. The boards were sawn into blocks, and then uniformly cut into chips with a band saw. To increase uniformity, care was taken to remove knots and associated compression wood. Chips were stored frozen until used. All experiments were conducted with random mixtures of chips taken from all three trees, including early wood, late wood, juvenile, and mature wood.

Innoculation and Fungal Growth Period

Frozen Cp master stocks, provided by Sandoz Chemicals Biotech Research Corp., were grown at IPST in shake flasks. Fungal suspensions were centrifuged after 36 hours. Pellets from centrifugation were homogenized and diluted before being pipetted into plastic bags containing about 1200 g. (wet weight) of wood. Chips were innoculated with 1.61×10^7 c.f.u.s for every 100 g. of chips, and incubated at 25 C for one, three, and five week periods. Non-treated controls were also incubated and aged for the same time periods.

Refining

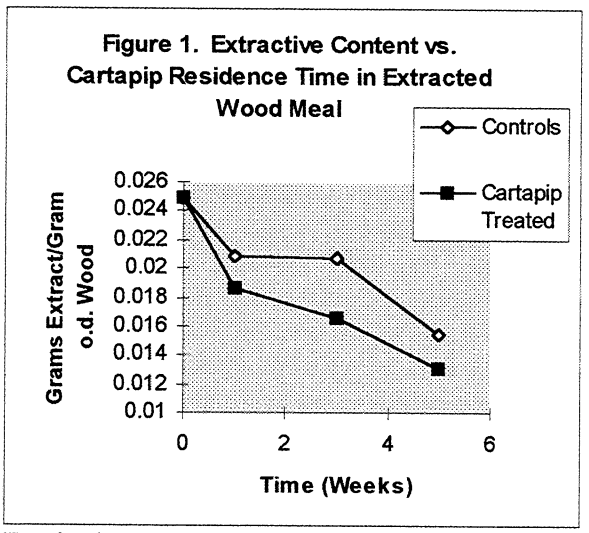
A Sprout-Waldron atmospheric refiner equipped with 12 inch, D2B505 patterned, 440C stainless steel plates was used to refine the fungally treated and non-treated chips. Chips were refined with periferal water flowing into the refiner casing. Consecutive passes were carried out at 30% consistency. Refining was executed in 5 to 7 refining passes. Pulp retained for latency removal, and handsheet production ranged in freeness from 250 to 30 mL CSF.

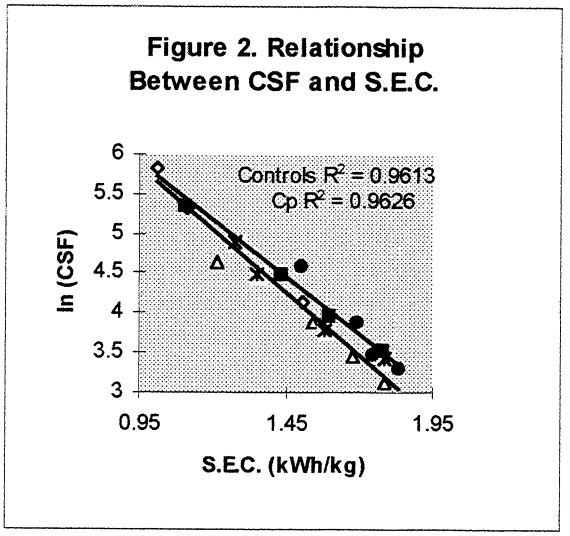
DCM Extractions and Handsheet Production

Wood meal samples from chips used for refining were extracted with dichloromethane according to Tappi Test Method T-204 after grinding to 10 mesh size in a Wiley mill. Freeness testing, handsheet production, physical and optical property testing were carried out according to Tappi Test Methods. Fines contents were determined and fiber lengths were estimated from Bauer-McNett classification. Statistical analyses of the data were performed using multiple regressions. In the multiple regressions, Cp treatment, incubation time, and specific energy consumption were independent variables, while freeness, fines content, tensile, density, tear, z-span, fiber length, and scattering coefficient were used as dependent variables.

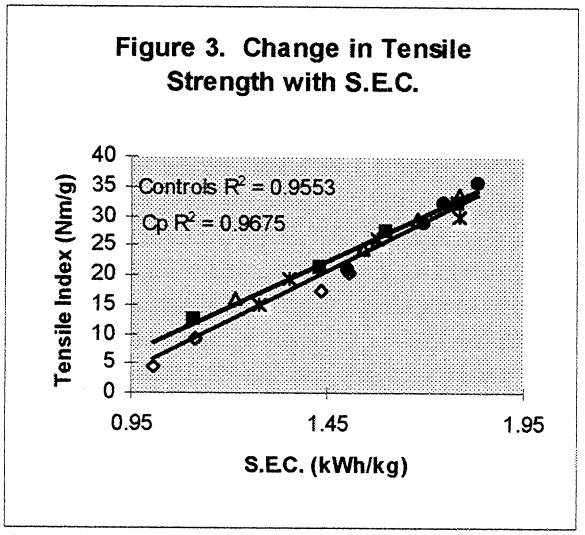
RESULTS AND DISCUSSION

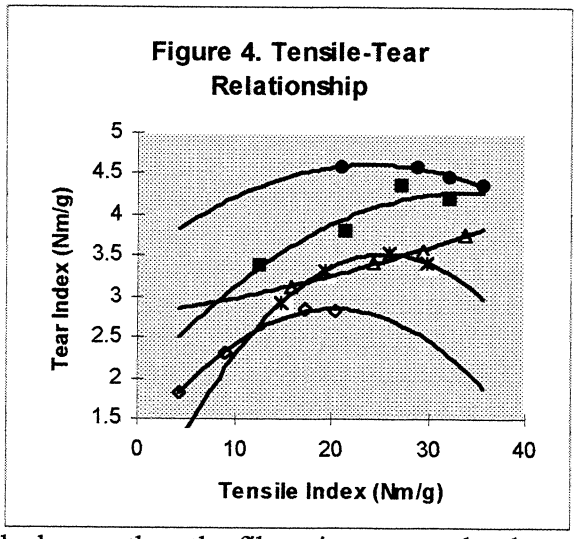
Cp treatment reduced extractive content as much as 16.5% more than wild-type fungi on non-treated, non-sterile wood chips aged for one, three, and five week time periods (Fig. 1). (Symbols in the figures are defined as follows: diamonds are non-sterile, time zero controls, triangles are non-sterile, controls aged three weeks, stars are non-sterile controls aged five weeks, squares are pulps produced from chips treated with Cartapip for three weeks, circles are pulps produced from chips treated with Cartapip for five weeks. Desciptors preceding the coefficients of determination descibe which data sets have been used to obtain the R^2.).



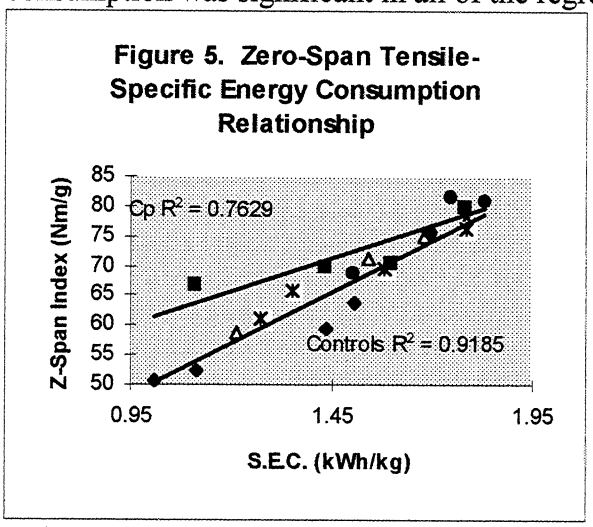


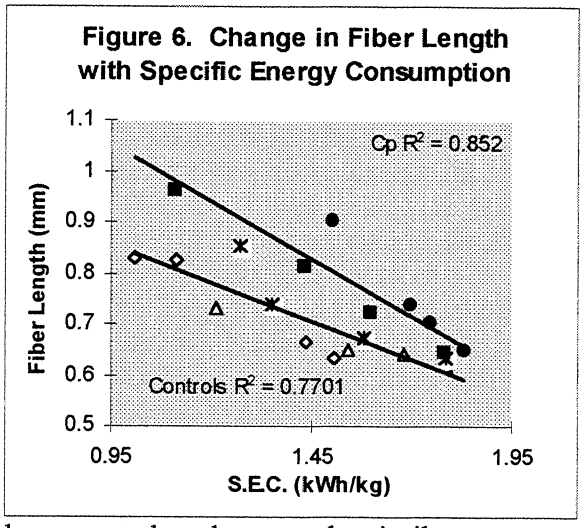
Equivalent refining energy input to treated and non-treated chips and resulting pulps did not produce pulps with different freeness levels (Fig. 2). Although fungal treatment did not appear to drastically reduce energy usage to produce these RMP pulps, the same amount of energy input in the fungally treated pulps produced greater tensile and tear strengths (Fig. 3,4). Tensile, tear, and zero-span tensile strengths all increased with *O.p.* treatment, but tear strength dramatically increased from 18 to 35% over aged three and five week control pulps respectively.





Fungal treatment yielded pulps with fiber lengths longer than the fibers in untreated pulps (Fig. 6). Cartapip treatment results in significant increases for C.S.F., fines content, density, tear, and zero-span tensile. Incubation time also yields significant increases in the cases of fines content, tensile, tear, z-span tensile, and scattering coefficient. Specific energy consumption was significant in all of the regressions.





Aging, in the presence of wild-type *O.p.* would be expected to show results similar to Cartapip's, because wild-type, blue-stain fungi generally grow during chip aging. Fungi present on the non-treated, aged control chips was 85% wild-type, blue-stain fungus. Fungi on the chips were analyed by Bob Blanchette at the University of Minnesota.

Table 1. Multiple Regression Equations and R^2 for Dependent Variables (Cartapip Significance = *, Incubation Time Significance = #)

Dependent Variable, y	Regression Equation, where:x_1=SEC, x_2=Incubation Time, x_3=Cartapip Presence	R^2
CSF	y=-2.986x1-.0149x2+.24x3+8.629	0.962*
Fines	y=21.85x1-1.212x2-3.527x3+16.827	0.9034*#
Tensile Index	y=31.54x1+.83x2+.419x3+26.147	0.969#
Density	y=161.15x1+.443x2-19.33x3+56.29	0.9226*
Tear Index	y=1.327x1+.1182x2+.7973x3+.8403	0.9214*#
Z-Span Tensile Index	y=26.87x1+.939x2+3.895x3+23.918	0.9179*#
Scattering Coefficient	y=.0143x1-.0012x2-.0012x3+.0383	0.4516*#

Examination of this data yields the conclusion that fungal treatment with *O.p.* brings about enhanced strength properties in addition to decreased extractive levels. The question remaining is; through what mechanism is the strength enhancement taking place? The increased fiber length may contribute to increased tear strength. The data also bear resemblances to the properties of pulps produced from chemically pretreated mechanical pulps[4], where tear and tensile strength increase while freeness does not change greatly. Increased fiber conformability could allow fibers to come through the refining process with greater length. A mechanism by which these strength properties may be improved will be provided in an upcoming publication.

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