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Brightness Reversion of Mechanical Pulps Part VI:
Cooperative Photostabilization Approaches for High-Yield Pulps

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Cooperative Photostabilization Approaches
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ABSTRACT

The effectiveness of combinations of additives as brightness stabilizers for hardwood and softwood BCTMP (bleached chemithermomechanical pulp) was examined. Certain additive combinations exhibit a synergistic interaction effect that provides a substantial brightness stabilization activity. Experimental results suggest that designing specific additive combinations is an effective approach to improve the brightness stability of mechanical pulps and to lower the overall charge of additives.

KEYWORDS

Mechanical pulp, brightness, photoyellowing, stabilization, thiol, disulphide, ascorbic acid, diene, UV absorber

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 photooxidation 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 has 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 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-faceted mechanism. Based on literature review [17] and our own research experiences, we believe that the necessary components required to photostabilize mechanical pulps include: an 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]. Castellán 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 bithioglycolate, 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-equilibrate 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 bithioglycolate (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 bithioglycolate 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-dihydroxybenzophenone. 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-dihydroxybenzophenone [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 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-dihydroxybenzophenone 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-dihydroxybenzophenone 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/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 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 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 test sheets 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 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 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-dihydroxybenzophenone 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.

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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.

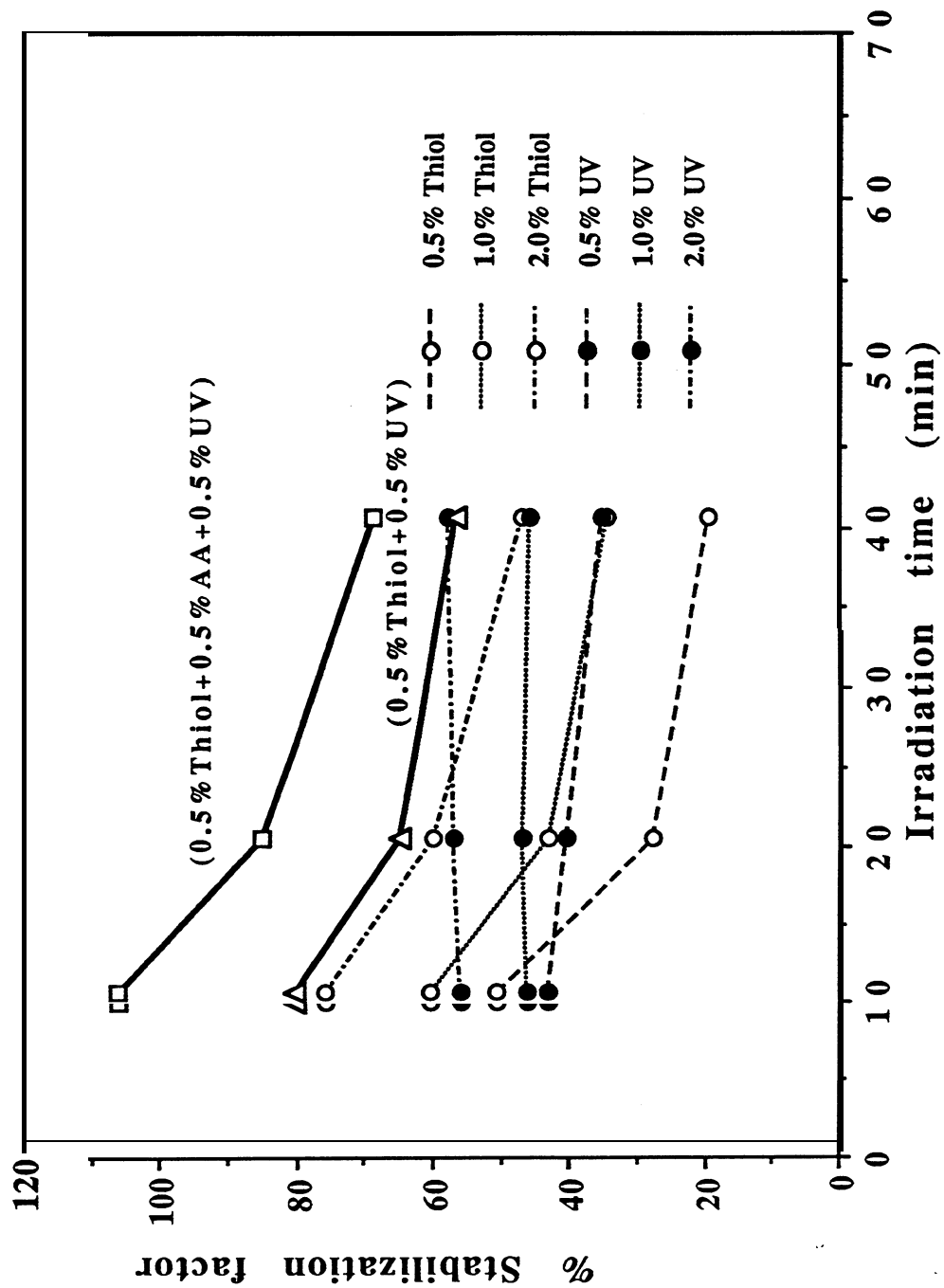


Figure 2. Brightness stabilization factors of combinations of varying application levels for softwood BCTMP as a function of irradiation time; UV: 2,4-dihydroxybenzophenone.

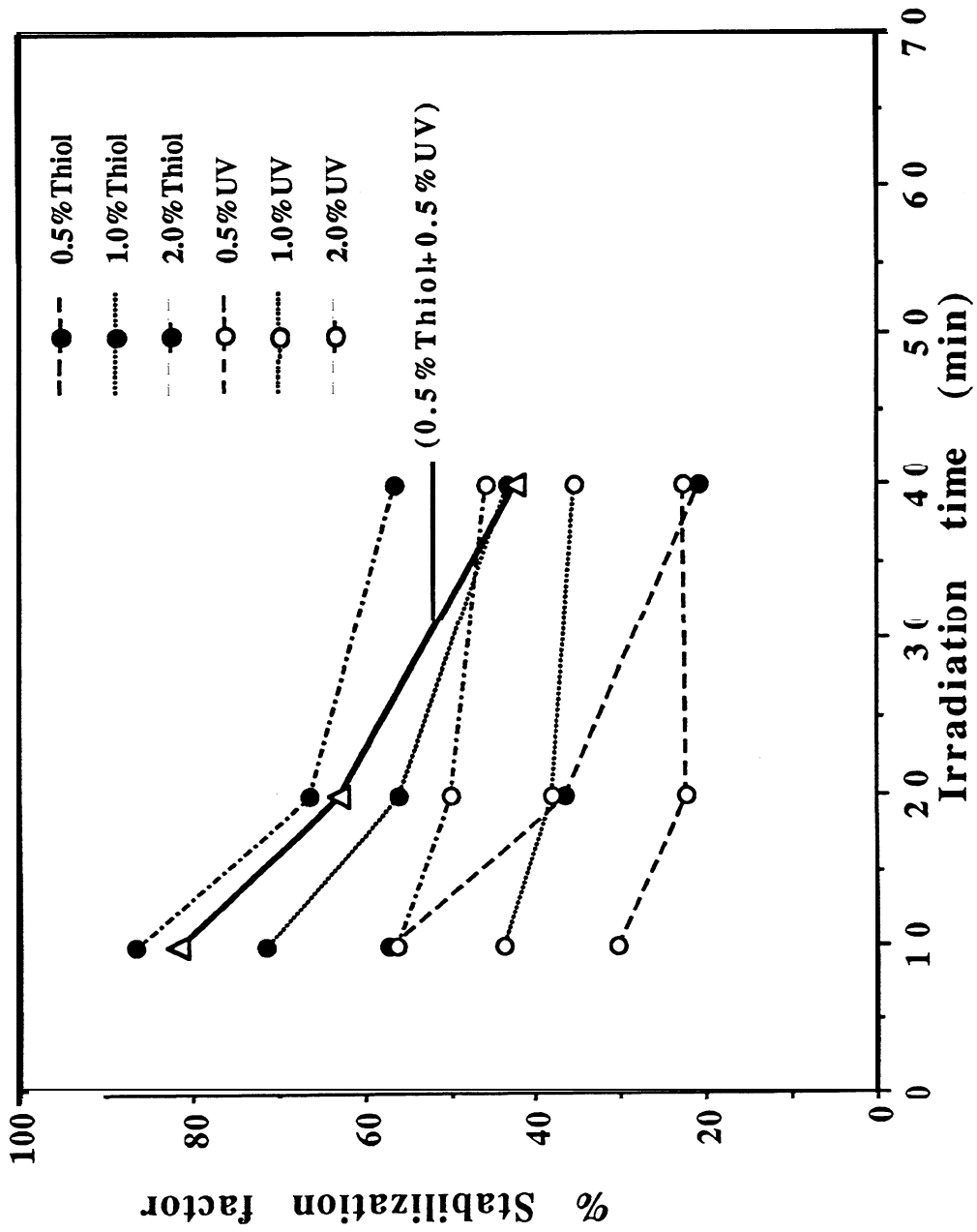


Table I. TAPPI brightness values of hardwood BCTMP handsheets before and after addition of additives and after storage and solar simulator irradiation.

Additive ^a	Initial	TAPPI Brightness				
		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	-	-	-

^a5% (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

to be continued next page

Table II continued

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

^awt of additive/wt of od paper;

^bBenzophenone 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

^awt of additive/wt of od paper; ^bBenzophenone: 2,4-dihydroxybenzophenone

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			Irradiation/min		
		Initial	Post Addition		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 coefficient	Application level ^a	Absorption coefficient ^b			Scattering		
		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

^awt of additive/wt of od paper;

^bI₀:before irradiation; I₁₀:10 min irradiation; I₄₀:40 min irradiation;

^cBenzophenone referres to 2,4-dihydroxybenzophenone.

