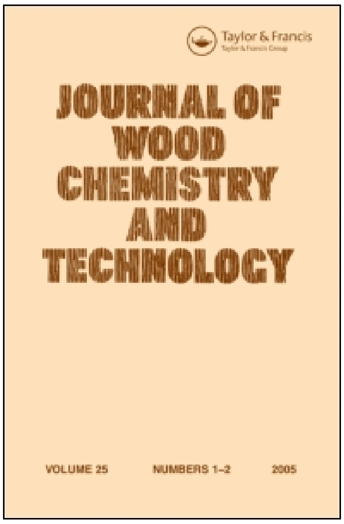

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Brightness Reversion of Mechanical Pulps. III. Mechanistic Studies of Mercapto-Stabilizers for High Brightness Mechanical Pulps

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BRIGHTNESS REVERSION OF MECHANICAL PULPS PART 3: MECHANISTIC STUDIES OF MERCAPTO-STABILIZERS FOR HIGH BRIGHTNESS MECHANICAL PULPS

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ABSTRACT

The photo and thermal stabilizing effects of 2,2'-thiodiethanol (**1**), 2,2'-dithiodiethanol (**2**), and 2,2'-oxydiethanethiol (**3**) were investigated for high brightness bleached chemithermomechanical pulps (BCTMP). The dithiol additive **3** was shown to be the most effective photostabilizing reagent for freshly impregnated handsheets. Mechanistic studies suggest that dithiol additives photostabilize BCTMP pulps no more effectively than monothiol additives. Long-term thermal reversion studies indicated that 2,2'-oxydiethanethiol also stabilized BCTMP handsheets against thermal yellowing. Photolysis of the aged handsheets indicated that the photostabilizing efficiency of additive **3** was detrimentally impacted upon by long term storage prior to photolysis.

INTRODUCTION

Recent advances in mechanical pulping and bleaching technology have yielded BCTMP with final brightness values in excess of 85% TAPPI brightness.[1] These grades of mechanical pulp could be employed for a variety of high quality paper products were it not for their well-known 1 photoyellowing properties.[2] Research efforts directed at investigating the mechanisms of brightness reversion have significantly advanced our knowledge of the general photochemical reaction pathways involved.[3] These results have provided a theoretical basis upon which brightness stabilization methods can be developed and investigated.

Although no reagent has been shown to be commercially successful at photo-stabilizing high-yield pulps, substantial progress has been made in this area. Early research efforts by Nolan[4] demonstrated that the addition of near-UV absorbing compounds such as dihydroxy or tetrahydroxy-benzophenone could photostabilize mechanical pulp. The application of sulfur-containing compounds for retarding brightness reversion of groundwood paper was initially examined by Kringstad.[5] Subsequent screening studies by Cole and Sarkanen[6] identified 1-thiogylcerol and glycol dimercaptoacetate as particularly promising reagents for moderately bright chemimechanical pulp (CMP, ISO brightness of 75-79). Castellan[7] has also examined the use of thiols to retard brightness reversion for bleached stoneground-wood pulp (SGW, ISO brightness values of 70-75). Their studies demonstrated that n-butylthioglycollic acid had comparable stabilization effects to thiogylcerol. A recent study by Daneault et al.[8] has indicated that 1-dodecanethiol provides greater photoprotection for TMP testsheets than 1-thioglycerol.

The focus of the aforementioned studies has been directed at retarding the photo-yellowing process for moderately bright mechanical pulps. In this report we describe the results of our initial studies directed at employing mercapto-additives with high-brightness BCTMP pulps (ISO brightness values of 80-87). Specifically, we examined the antioxidant effects of 2,2'-thiodiethanol, 2,2'-dithiodiethanol, and 2,2'-oxydiethanethiol when applied to hardwood and softwood BCTMP pulps. The effects of these additives were evaluated by monitoring the rates of photo and thermal reversion over an extended time period. To date, most photo-reversion studies have examined the brightness stabilization effects of additives shortly after application. Although these results are informative, they neglect the potential impact that storage may have on the impregnated handsheets prior to exposure to sunlight. This paper provides some of the first experimental results, which demonstrate that prolonged storage of BCTMP handsheets impregnated with mercapto-additives can detrimentally impact photo-stabilization properties.

EXPERIMENTAL

Chemicals

All solvents and reagents employed were commercial products and were used as received.

Pulps and Preparation of Handsheets

BCTMP hardwood and softwood pulp samples were obtained from a commercial source and used without further modification. BCTMP handsheets were prepared according to standard TAPPI procedures T-218 and T-205.[9] After air drying the handsheets in a darkroom at constant temperature (22.0° C ± 2.0°) and relative humidity (50% ± 2.0%), the handsheets were washed in methanol to remove extractives. Removal of the extractives was required to allow for determination of the amounts of additive applied onto the handsheets (± 10%). Literature results[10] indicate that extractives do not contribute to photoyellowing of mechanical pulp and their removal does not influence the overall rate of brightness reversion.

The brightness values for the dried handsheets were measured following standard Tappi procedures T-452 and/or T-534.[9] The handsheets were then soaked in a methanolic solution of the additive for 15 min and vacuum dried. After drying, the handsheets were re-equilibrated with room humidity prior to the brightness measurements. The amount of the additive impregnated onto the handsheets was determined by weighing the handsheets before addition to the methanolic solution and after re-equilibrating the impregnated handsheets with room humidity. Reference handsheets were prepared in a similar manner with the exception that they were not treated with the additive.

Accelerated Yellowing Studies

The accelerated photoaging studies were conducted with an Oriel 1000 Watt Solar Simulator. The Solar Simulator uses a xenon-arc lamp and was fitted with an air-mass 1.5 global filter to model the average wavelength distribution of solar irradiation in the continental United States. The lamp and pulp samples were located within a fumehood which provided sufficient air circulation to minimize heating of the sample. Three impregnated handsheets and three reference brightness pads were placed 10.5" from the lens of the lamp and irradiated simultaneously. Immediately after photolysis, the handsheets were stored in the controlled paper testing laboratory for 4 hours prior to determining TAPPI brightness values.

Long-Term Thermal Reversion Studies

Thermal reversion studies were accomplished at RT (25° C $\pm$ 2.0°) with the samples stored in sealed plastic containers and stored in a darkroom. Testsheets were periodically removed and TAPPI brightness values recorded.

RESULTS AND DISCUSSION

Photo Reversion Studies

Hardwood and softwood BCTMP handsheets prepared from commercial pulp samples were impregnated with methanolic solutions of compounds **1**, **2**, and **3** and then air dried overnight. The effectiveness of the proposed stabilization reagents was then evaluated by irradiating the handsheets with a xenon-arc lamp. The brightness changes were monitored at specific intervals during irradiation by measuring the percent light reflectance at 457 nm according to standard literature procedures.[9] These results are summarized in Table 1. The differences in rates of photoyellowing for the treated and untreated handsheets can be expressed in terms of a stabilization effect which we calculate employing equation 1.[11]

eq. 1) % Stabilization Effect (SE) =

$$\frac{100 \times [(\Delta \text{ Brightness of reference}) - (\Delta \text{ Brightness of treated})]}{(\Delta \text{ Brightness of reference})}$$

Figure 1 summarizes the results of the accelerated photoyellowing studies for 2,2'-thiodiethanol, 2,2'-dithiodiethanol, and 2,2'-oxydiethanethiol applied onto hardwood and softwood BCTMP handsheets. As expected, the di-thiol additive **3** was the most effective stabilizer for both softwood and hardwood BCTMP pulps. Of greater interest was the observed photostabilization effects for 2,2'-dithiodiethanol. Although the disulfide additive **2** was not as effective as the di-thiol additive at retarding brightness reversion of BCTMP handsheets, these beneficial effects have not been previously observed for lower brightness pulps.

The stabilization effects of the handsheets impregnated with 2,2'-oxydiethanethiol were of interest since di-thiol structures are known to be strong reducing agents yielding the corresponding di-sulfide upon oxidation.[13] To determine if the observed stabilization effects for 2,2'-

Table 1
Changes in TAPPI Brightness for Irradiated Mercapto-Impregnated and Control BCTMP Handsheets

	TAPPI Brightness Period of Irradiation/h					
Hardwood BCTMP[a]	0	1	2	4	6	12
1.5%[b] $(HSCH_2CH_2)_2O$	87.6	86.1	84.3	80.9	78.8	71.2
Control	87.3	82.3	78.5	73.6	70.6	63.5
1.8%[b] $(HOCH_2CH_2)_2S_2$	87.4	82.6	80.6	77.4	74.5	69.4
Control	87.6	79.2	77.2	73.3	70.3	63.0
1.6%[b] $(HOCH_2CH_2)_2S$	87.7	83.8	80.2	75.6	72.6	65.7
Control	87.4	82.2	78.5	73.4	70.4	63.3
Softwood BCTMP[a]						
1.7%[b] $(HSCH_2CH_2)_2O$	79.9	77.5	76.3	74.6	72.5	64.7
Control	80.1	73.6	70.8	65.6	64.3	57.0
2.8%[b] $(HOCH_2CH_2)_2S_2$	80.3	75.9	73.9	70.6	68.4	63.5
Control	80.5	73.4	70.7	66.0	64.4	57.1
2.4%[b] $(HOCH_2CH_2)_2S$	80.1	74.0	71.7	67.7	66.0	59.4
Control	80.0	73.2	70.9	66.4	64.5	56.4

[a]treated and control handsheets were photolyzed simultaneously; [b](g additive applied/g handsheet)%.

oxydiethanethiol could be attributed to the unique reductive capabilities of the di-thiol structure, we studied the photostabilization effects for 2,2'-oxydiethanethiol and 1-mercapto-2-propanol (**4**) impregnated onto hardwood BCTMP testsheets at various application levels. The changes in brightness for treated and untreated handsheets were measured after six hours of irradiation with the xenon-arc lamp and these data are summarized in Figure 2. Analysis of these results suggests that additive **3** is as effective as compound **4** at retarding brightness reversion on a gram per gram

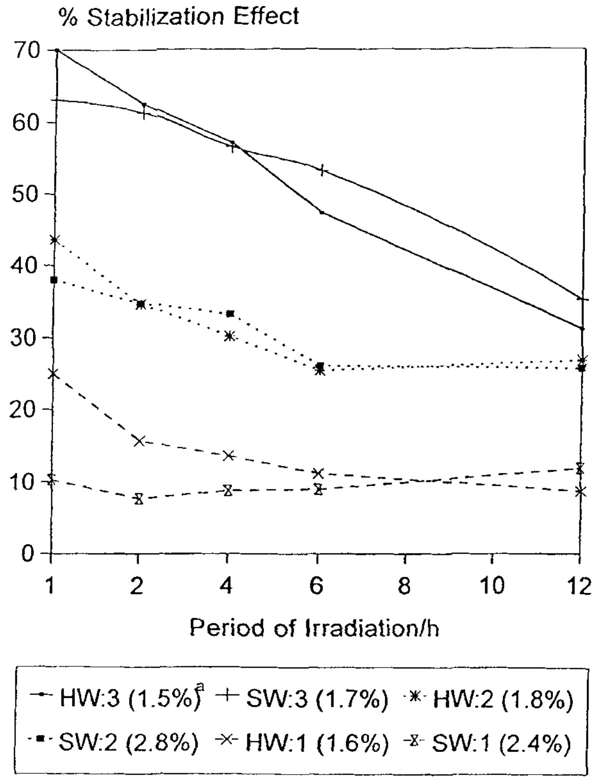


Figure 1 Brightness stabilization effects for hardwood (HW) and softwood (SW) BCTMP handsheets[b] impregnated with additives **1**, **2**, and **3**.

[a]% additive (g/g) applied onto handsheet; [b]initial TAPPI brightness values averaged 87.8 ± 1.0 for hardwood samples and 80.6 ± 0.3 for the softwood samples.

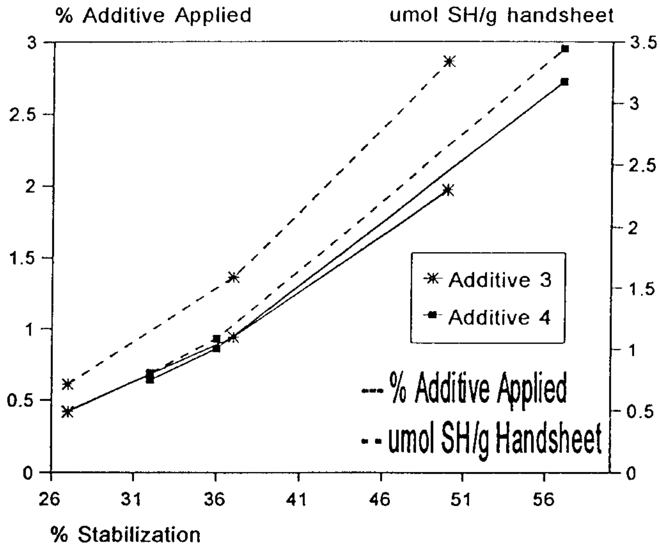


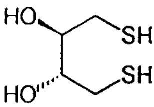
Figure 2 Dose response[a] for softwood BCTMP handsheets impregnated with 2,2'-oxydiethanethiol and 1-mercapto-2-propanol.

[a]handsheets were photolyzed for 6 hours following standard photolysis procedures, initial TAPPI brightness values averaged 88.4 ± 0.3.

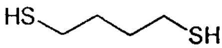
application basis. But when the % stabilization effects are plotted against moles of "free thiol" applied/gram of handsheet it is apperent that compound **4** is actually more effective photo-stabilizing the BCTMP testsheets than **3**.

To further explore the apparent lack of correlation between reducing abilities of the di-thiol compound and its photostabilization effects, we impregnated a host of structurally related di-thiol compounds onto hardwood BCTMP handsheets. The additives, along with their formal electrochemical half-cell potentials [ϵ_0(V)] are summarized in Figure 3.[14] The results of the accelerated photo-aging studies are summarized in Table

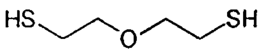
Additive — Electrochemical Half-Cell Potential



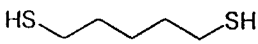
5 — -0.327



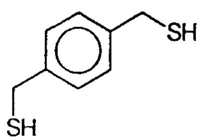
6 — -0.316



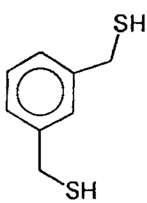
3 — -0.284



7 — -0.277



8 — -0.276



9 — -0.275

Figure 3. Di-Thiol Additives Employed For Photo-Stabilizing Hardwood BCTMP

2. Since photostabilization effects are sensitive to the amounts of additive applied onto the handsheet, the calculated percent stabilization effects were normalized (see below) to take into account the varying molar amounts of additive applied.

eq.2) Normalized % Stabilization Effect (NSE) =

% Stabilization Effect/[10^{-4} mol of additive/gr of handsheet]

Although several methods of calculating a percent stabilization effect for mechanical pulp additives have been developed,[8] none of these relationships takes into *direct* account the differences in application levels. The relationship shown in equation 2 is our initial attempt at developing a method of evaluating percent stabilization effects which would take into account these differences.

Normalized percent stabilization effects for additives **3** and **5** - **10** are summarized in Table 2. This data indicates that for a series of structurally similar compounds, such as 1,4-butanedithiol, and 1,5-propadithiol or ortho-, and para-xylene-α,α-dithiol there appears to be a correlation between the reduction potential and the normalized percent stabilization effects during the first few hours of irradiation. Nonetheless, there appears to be no global relationship between the normalized percent stabilization effects of the di-thiol additives and reported half-cell reduction potentials for these additives. The absence of a strong relationship between these two parameters could be due to several competing factors, such as autoxidation of the di-thiols by oxygen. Alternatively, if as previously suggested by Sarkanen,[6] the principal brightness stabilization mechanism for the thiol additives is a Michael type addition to unsaturated lignin structures, then we would not expect a direct correlation with reducing potentials. Clearly, additional studies will be needed to establish the preferred pathways by which thiol additives photo-stabilize mechanical pulps, and our research efforts are ongoing in this field.

Table 2
Normalized Photostabilization Effects for Di-thiol Additives Applied onto Hardwood BCTMP Handsheets

Additive	Initial TAPPI Brightness[a]	% Appl.[b]	Period of Irradiation/h	1	2	4
3	87.6	1.5	SE[c]:	70	62	51
			NSE[d]:	64	57	47
5	87.6	1.5	SE:	70	62	57
			NSE:	57	50	46
6	88.9	1.7	SE:	47	44	36
			NSE:	33	32	26
7	89.1	2.7	SE:	49	46	35
			NSE:	25	23	18
8	88.8	1.5	SE:	50	44	28
			NSE:	56	50	32
9	88.1	3.0	SE:	62	58	41
			NSE:	35	33	23

[a]TAPPI brightness number after impregnation with additive; brightness values prior to impregnation (average 87.5 ± 1.0); [b](g of the additive)/(g of handsheet); [c]% stabilization effect (see text); [d]normalized % stabilization effect (see text).

Long-term Thermal and Photo Reversion Studies

Practical considerations require that any photo-stabilization additive applied onto mechanical pulps must fulfill several other criteria including thermal stability. To date, there have been no studies directed at evaluating the photo-stabilization effects of mercapto-additives after prolonged storage on mechanical pulp handsheets. Furthermore, it is frequently assumed that any reagent that yields effective photo-stabilization of mechanical pulp will not detrimentally impact upon their thermal reversion properties. This latter assumption has been shown to be incorrect for ascorbic acid impregnated BCTMP handsheets, which suffer from accelerated thermal reversion properties despite the well-known photo-stabilization effects of this reagent.[15]

To investigate the impact that long term storage could have on the performance of mercapto-additives we monitored the thermal reversion properties of BCTMP handsheets impregnated with additives **1**, **2** and **3** over a period of 4 months. The rates of thermal yellowing for treated and untreated BCTMP softwood and hardwood handsheets are summarized in Figures 4 and 5. Impregnation of the additives onto the handsheets was accompanied by a brightness gain for additives **2** and **3**. Comparable thiol-bleaching effects have been reported for TMP pulps and it is interesting to note that these effects also occur with the high-brightness BCTMP pulps.[12] A comparison of the relative rates of thermal reversion for the control and treated BCTMP handsheets indicates that testsheets treated with 2,2'-oxydiethanethiol exhibited the least amount of thermal reversion. Indeed, after nearly four months in storage handsheets treated with di-thiol additive **3** had brightness values greater than its pre-impregnation values. These brightness gains are due in part to the initial bleaching effect of the di-thiol additive and also due to reduced rates of thermal reversion. The reduced rates of thermal reversion were tentatively attributed to the radical scavenging abilities of the 2,2'-oxydiethanethiol interrupting autoxidation reactions which would normally contribute to thermal reversion.[17]

After 125 days in storage the handsheets were photolyzed with the xenon-arc lamp and the results of these studies are summarized in Figure 6. This data indicates that the photo-protection effects of 2,2'-oxydiethanethiol have been substantially decreased from the effects observed in Figure 1. In contrast, the photo-stabilization effects of 2,2'-

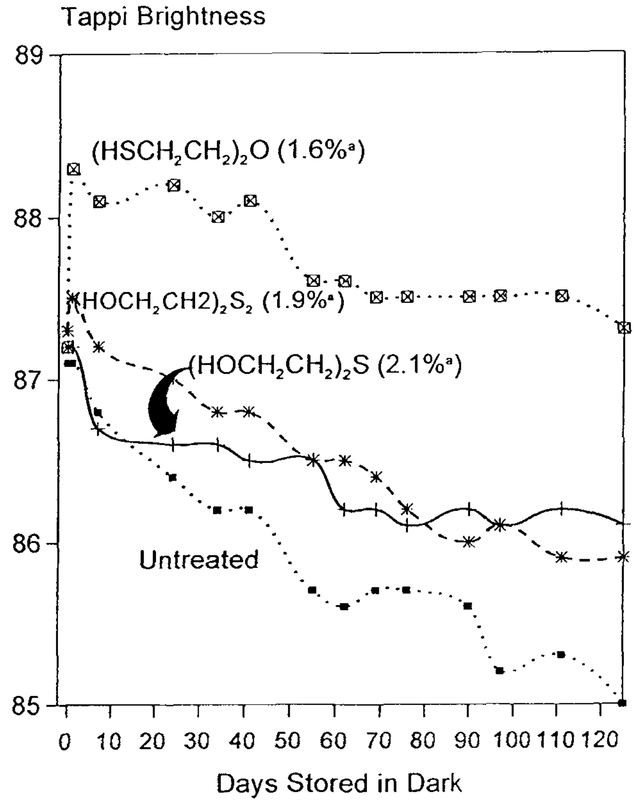


Figure 4 Long-term thermal reversion properties of hardwood BCTMP handsheets impregnated with 2,2'-thiodiethanol, 2,2'-dithioethanol, and 2,2'-oxydiethanethiol.

[a]% additive (g/g) applied onto handsheet.

dithiodiethanol have remained comparable to the percent stabilization effects observed for freshly prepared handsheets.

The reduced photo-stabilization effects of 2,2'-oxydiethanethiol impregnated handsheets were not completely unexpected since it is well known that thiols undergo autoxidation reactions.[17] In addition, the reduced rates of thermal reversion for the thiol-treated handsheets *suggest that*

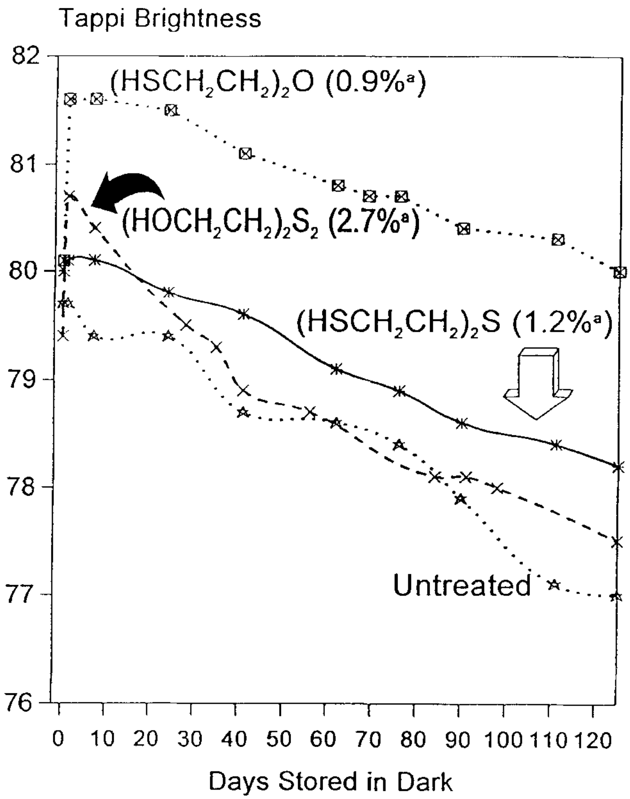


Figure 5 Long-term thermal reversion properties of softwood BCTMP handsheets impregnated with 2,2'-thiodiethanol, 2,2'-dithioethanol, and 2,2'-oxydiethanethiol.

[a]% additive (g/g) applied onto handsheet.

additive **3** is acting as a radical scavenger of thermally initiated autoxidation reactions in lignin. These thermal reversion reactions could therefore provide a second mechanism by which the amounts of the di-thiol additive present on the surface of the handsheet could be reduced during long-term storage. Alternatively, although we were unable to detect a loss of the additive after storage and photolysis, the precise relationship between the

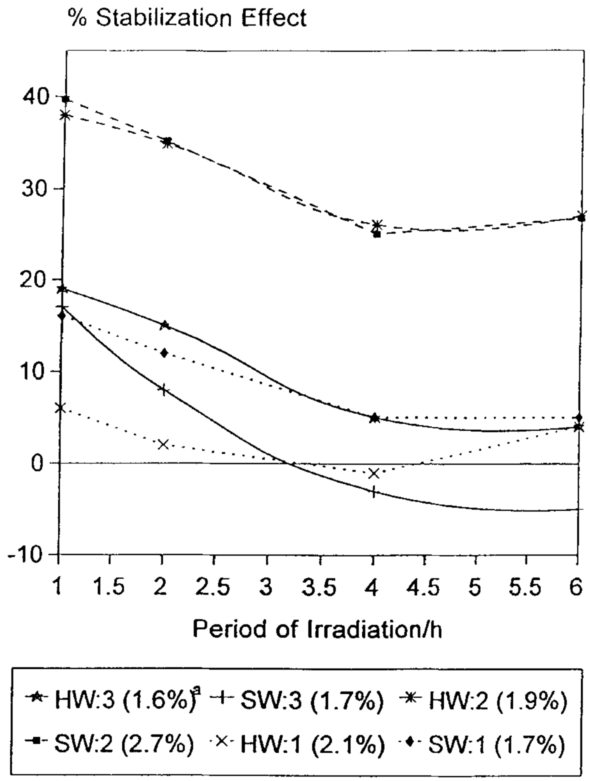


Figure 6 Brightness stabilization effects for aged hardwood (HW) and softwood (SW) BCTMP handsheets[b] impregnated with **1**, **2**, and **3**.

[a]% additive (g/g) applied onto handsheet; [b]handsheets were stored for 128 days and then photolyzed (see Figure 5 for initial TAPPI brightness values).

observed stabilization effects and the amount of additive applied onto the handsheets remains ill-defined. The observed changes in brightness stability could potentially be due to subtle changes in the effective concentration of the additive present at the surface of the pulp fibers due to either minor evaporational losses or to the molecular mobility of the additive. This latter phenomena has been shown to detrimentally impact on the performance of some low molecular weight additives incorporated into synthetic polymers.[18]

In contrast, prolonged storage of the 2,2'-dithiodiethanol impregnated handsheets appears to have little effect on the photo-stabilizing effects of this additive. A comparison of the percent stabilization effects for freshly prepared and aged handsheets indicates that the percent stabilization effects have not been dramatically altered. These latter results are presumably due to differences in the mechanisms of stabilaization and studies directed towards understanding this phenomena are ongoing.

CONCLUSIONS

In summary, the results of these studies have shown that although dithiol additives are particularly effective, photo and thermal stabilization reagents for BCTMP pulps the photo reversion properties are diminished upon storage. In contrast, handsheets impregnated with the disulfide additive **2** demonstrate no detrimental effects upon aging.

These results demonstrate the complex relationship that occurs between the stabilizing additive and mechanical pulp. As the design of brightness stabilization additives for mechanical pulps becomes more sophisticated, we believe that the interrelationships that occur between thermal and brightness stability will become increasingly important. Furthermore, these studies have highlighted the need for developing a standardized method of expressing brightness stabilization effects which takes into account not only the changes in brightness stabilization, but also the levels of additive application.

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