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Part 4: A Study on the Action of Thiols and Disulfides on Hardwood BCTMP

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# **BRIGHTNESS REVERSION OF MECHANICAL PULPS PART 4: A STUDY ON THE ACTION OF THIOLS AND DISULFIDES ON HARDWOOD BCTMP**

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## **Abstract**

Stabilization against thermal and photo-induced brightness reversion of high-brightness BCTMP (bleached chemithermomechanical pulp) by various sulfur compounds was investigated. Ethylene glycol bithioglycolate and 3-mercapto-1,2-propanediol were the most effective additives that provided bleaching action and prevented thermal and light-induced brightness reversion. The stabilizing activity of thiols is detrimentally influenced by long-term storage, particularly for the mercapto-carboxylic acids. However, the photostabilization effect of disulfides was moderate and can be retained during storage. In addition, the results of sulfur analysis for treated BCTMP handsheets support the occurrence of the Michael-type addition of thiols for photostabilizing mechanical pulps.

## **Keywords**

Mechanical pulps, Brightness, Thermal reversion, Photoyellowing, Stabilization, Thiols, Disulfides, Michael type addition

## **Introduction**

The major obstacle to the wide use of mechanical pulps is their tendency to yellow, called brightness reversion. Early studies by Kringstad demonstrated that the lignin present in mechanical pulps is the principal component contributing to this phenomenon [1]. Brightness reversion may occur through thermal discoloration upon long-term storage at ambient temperature and by photo-induced yellowing upon exposure to daylight. The latter mechanism frequently results in

much larger brightness losses [2]. Much progress has been made in elucidating reaction pathways involved in the photoyellowing [2]. It is generally accepted that the basic mechanism of photoyellowing involves a variety of pathways including:

1. direct absorption of UV light by conjugated phenolic groups to form phenoxy radicals;
2. abstraction of phenolic hydroxyl hydrogen by aromatic carbonyl triplets;
3. cleavage of non-phenolic phenacyl- $\alpha$ -O-arylethers to phenacyl-phenoxy free radical pairs.

Based on the proposed mechanisms, a potential means of inhibiting brightness reversion is the addition of hydrogen donors (radical scavenging antioxidants) that may compete with free phenolic units in the lignin, thereby preventing the formation of highly reactive phenoxy radicals. Mercaptans are efficient hydrogen donors and various sulfur-containing compounds act as antioxidants for synthetic polymers [3]. When applied to a variety of mechanical pulps, sulfur-containing compounds have been found to possess bleaching and/or photostabilization effects [4-8]. To explain these effects, Cole and Sarkanen [5] proposed that bleaching is likely the result of a Michael-type addition to  $\alpha,\beta$ -unsaturated carbonyl and quinoid structures, while stabilization may result both from addition reactions and from hydrogen donation to reactive intermediates.

The objective of the present study is three-fold: to evaluate the effectiveness of several well-known sulfur photostabilizing additives for retarding the brightness reversion of a high-brightness hardwood BCTMP (Tappi brightness values > 83); to examine the impact of prolonged storage on the performance of these additives for photostabilizing BCTMP; and to determine the role of the Michael-type addition of thiols in photostabilization.

Handsheets prepared from hardwood BCTMP were treated with solutions containing the additives and subsequently irradiated with artificial daylight lamps. These samples were analyzed by measuring the brightness before and after treatment, and at specific intervals during irradiation. Meanwhile, the additive-impregnated handsheets were stored for different time periods before being subjected to irradiation. This provided an approach to investigate whether extended storage can affect the photostabilization effect of various mercaptan additives. Furthermore, treated and irradiated handsheets were analyzed by measuring sulfur contents after exhaustive extraction with organic solvents. Sulfur present in the extracted handsheets could be considered to be chemically bonded and/or strongly attached to the fibres. This provides support for the occurrence of a Michael-type addition.

## Materials and Methods

### Sample preparation

A commercial hardwood BCTMP pulp, made from aspen using sodium sulfite for chemical pretreatment and hydrogen peroxide for bleaching, was used without further modification. Handsheets were prepared according to standard Tappi procedure T-218. The handsheets were then air-dried in a darkroom at constant temperature (22.0 +/-2.0 °C) and relative humidity (50 +/-2.0%). Methanol was used as solvent for additives. All handsheets, including the controls, were pre-washed with methanol to remove readily extractable material. Previous studies [9] have demonstrated that this mild extraction procedure was necessary to insure accurate determination of additive application levels and does not influence the overall brightness reversion properties of the handsheets. After air-drying, the handsheets were soaked in 0.1 M additive solution in methanol for 15 min. The handsheets were again air-dried and re-equilibrated at ambient temperature and humidity. The addition percentages (2 - 5 %) were calculated from weight differences before and after impregnation with additives. The value of each additive was an average of triplicate tests (error range: <10 %).

### Additives

All chemicals were purchased commercially and used without purification:

- I. mercaptoacetic acid  $\text{HSCH}_2\text{CO}_2\text{H}$ ;
- II. 3-mercaptopropionic acid  $\text{HSCH}_2\text{CH}_2\text{CO}_2\text{H}$ ;
- III. ethylene glycol bithioglycolate  $(\text{HSCH}_2\text{CO}_2\text{CH}_2)_2$ ;
- IV. 1-dodecanethiol  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ ;
- V. 3-mercapto-1,2-propanediol  $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{SH}$ ;
- VI. mercaptosuccinic acid  $\text{HO}_2\text{CCH}_2\text{CH}(\text{SH})\text{CO}_2\text{H}$ ;
- VII. *trans*-1,2-dithiane-4,5-diol  $\text{SCH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{S}$ ;
- VIII. 3,3'-dithiodipropionic acid  $\text{S}_2(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})_2$ .

### Brightness measurement and accelerated yellowing

The brightness values of the handsheets were measured following standard Tappi procedures T-452.

For the thermal reversion study, the handsheets were stored in the dark at room temperature (22.0 +/-2.0 °C) for certain time periods.

The accelerated photoyellowing studies were conducted with an Oriel 1000 W 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 [10] recommends the use of xenon-arc lamp systems. The lamp and samples were located in a fumehood which provided 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. Error range for triplicate tests is below 3 %.

#### Determination of sulfur content

Another commercial hardwood BCTMP pulp, made from aspen using hydrogen peroxide for both chemical pretreatment and bleaching, was employed in this portion of the research. Preliminary photoyellowing studies demonstrated that this pulp and the sulfonated BCTMP pulp exhibited comparable brightness reversion properties. After impregnation with thiols and irradiation, the handsheets were subjected to an exhaustive soxhlet extraction, successively, with methylene chloride, ethyl acetate and chloroform each for 24 hours. The measurement of sulfur in the extracted handsheets was performed by Galbraith Laboratories Inc., Knoxville, Tennessee.

## **Results and Discussion**

#### Bleaching action of thiols and disulfides

To assess the brightness reversion properties of mercaptan-treated BCTMP pulp we prepared a series of test sheets, as summarized in Table 1. Figure 1 shows the average value of brightness gain after impregnation by various sulfur-containing additives. Generally, the addition of the sulfur compounds, except 1-dodecanethiol and mercaptosuccinic acid, resulted in a brightness gain of around 0.7 percentage point for BCTMP. The bleaching effect of sulfur-containing compounds has previously been observed for unbleached and bleached mechanical pulps [4,5]. Our results indicate that the thiols and disulfides also provided a minor brightening effect for the high-brightness BCTMP. However, 1-dodecanethiol and mercaptosuccinic acid caused darkening of the pulp. Opposite results were obtained by Daneault et al [8], who found that 1-dodecanethiol, among the mercaptans employed, had the greatest bleaching and stabilization effects for mechanical pulps with brightness levels below 70% ISO. Although this discrepancy can not be readily explained, it is possible that 1-dodecanethiol is an ineffective bleaching agent for pulps of higher brightness levels.

### Brightness reversion through long-term storage

It is expected that photostabilization reagents applied to mechanical pulps should be thermally stable and not accelerate thermal discoloration. Figure 2 illustrates the brightness losses of untreated and impregnated BCTMP handsheets over a storage period of 3 months. Comparison of the brightness losses of the control and treated handsheets indicates that ethylene glycol bithioglycolate and 3-mercapto-1,2-propanediol retarded thermal discoloration during storage. The other additives provided no brightness stabilization and even increased thermal reversion. Particularly, mercaptoacetic acid and 3-mercaptopropionic acid appeared to possess poor thermal stability and, to a substantial extent, increased brightness loss on storage.

### Photostabilization by thiols and disulfides

To evaluate the efficiency of the sulfur-containing additives in retarding brightness reversion, photostabilization factors were calculated by the equation shown below and the results are reported in Table 2.

$$\text{Photostabilization factor} = \frac{100 \times (\Delta \text{ Brightness of control} - \Delta \text{ Brightness of treated})}{\Delta \text{ Brightness of control}}$$

The sulfur-containing compounds investigated in this work, except 1-dodecanethiol, exhibit a stabilizing action on BCTMP against photo-induced yellowing. Comparison of the data in Table 2 indicates that when the impregnated handsheets were subjected to simulated light exposure immediately after application of the additives, the thiols were more effective in retarding brightness reversion than the disulfides. It is evident that 3,3'-dithiodipropionic acid provided a moderate degree of stabilization. This result is interesting since Cole and Sarkanen previously demonstrated that several disulfides were ineffective photostabilization agents for bleached cottonwood chemimechanical pulps [5]. Presumably these differences in photostabilization effect may be due to the chemical nature of the additives and the type of pulps employed.

In addition to exhibiting a darkening action, as mentioned above, 1-dodecanethiol had little photostabilization effect and slightly promoted discoloration. Our results differ from those of Daneault et al [8]. To verify our results and to rule out differences in experimental conditions, we treated BCTMP pulps following their procedure: 12% additive based on dry pulp, 4% consistency and room temperature. Neither bleaching action nor brightness stabilization was

observed. The differences between our results and those of Daneault et al are difficult to explain; although undoubtedly differences in the type of mechanical pulps, i.e. TMP vs CTMP, and wood source, i.e. softwood vs hardwood, influenced our observations.

Practical considerations require that any additive applied to mechanical pulps must fulfill several other criteria, including thermal stability and the retention of photostabilization activity over extended periods of storage. To date, no studies have been done to examine the photostabilization effect of sulfur-containing compounds on mechanical pulps after prolonged storage. Furthermore, it is frequently assumed that any additive that provides effective photostabilization of mechanical pulps will not detrimentally affect the thermal discoloration of mechanical pulps. This assumption has been found to be incorrect. For example, regardless of its well-known photostabilization effect, ascorbic acid promoted thermal discoloration of BCTMP [11]. Similarly, some of the additives used here had a detrimental impact on the stabilization of BCTMP against thermal reversion. Therefore, this paper evaluates the effect of prolonged storage on the efficiency of photostabilization by various sulfur-containing additives.

From Table 2, it can be observed that the photostabilization effect of the mercapto-carboxylic acids, mercaptoacetic acid, 3-mercaptopropionic acid and mercaptosuccinic acid, diminished substantially as a function of storage time. The mechanism responsible for the reduced brightness stabilization is not yet well understood. However, the reduction in photostabilization effect was at least, in part, due to the fact that mercaptoacetic acid and 3-mercaptopropionic acid accelerated thermal reversion and mercaptosuccinic acid caused darkening. On the other hand, the ability of the thiols, ethylene glycol bithioglycolate and 3-mercapto-1,2-propanediol, to retard photo-induced brightness reversion was also moderately diminished upon storage; while that of the disulfides, *trans*-1,2-dithiane-4,5-diol and 3,3'-dithiodipropionic acid, remained unchanged. As discussed above, these two thiols were effective in preventing thermal reversion. The reduced rate of thermal reversion was tentatively attributed to their radical scavenging ability. The mercaptans may react with oxygen and radicals generated by lignin autoxidation reactions, and the amounts of the thiol additives present on the surface of the handsheets could thus be reduced on long-term storage. In contrast, the disulfides were relatively stable towards storage; therefore their photostabilization activity remained unaltered during storage.

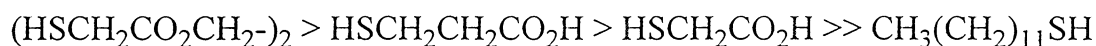
### Relationship between brightness stabilization and sulfur content of impregnated BCTMP handsheets

It is commonly speculated that thiols brighten and photostabilize mechanical pulps in part through the Michael-type addition to eliminate chromophores such as  $\alpha,\beta$ -unsaturated carbonyl and quinoid structures [4,5]. However, no direct evidence has been obtained to confirm that mercaptans are chemically bonded to the lignin moiety. In this work, we investigated the practical implication of this hypothesis. Assuming that exhaustive extraction with organic solvents is able to remove all thiols adsorbed onto handsheets, the detection of sulfur in the handsheets after such an extraction can be considered to be due to strongly attached and/or chemically bonded mercapto-lignin structures. The amounts of sulfur may reflect the extent of the occurrence of the Michael addition which results in bleaching and photostabilization. To this end, a sulfur-free bleached mechanical pulp was employed; and extraction was conducted successively with methylene chloride, ethyl acetate and chloroform to maximize the removal of unbound sulfur. The sulfur contents of a series of handsheet samples are reported in Table 3.

The data of Table 3 show that most of the mercaptans impregnated into the handsheets can be removed by an exhaustive extraction. Assuming this removable portion is free mercaptans, the rest might be strongly attached and/or chemically bonded to fibres of the handsheets. The mechanism involved in the attachment is most likely a Michael-type addition of thiols to  $\alpha,\beta$ -unsaturated carbonyl structures and quinones present in the lignin. The sulfur content of the impregnated/extracted handsheets is quite low in all cases, which is in agreement with the previous finding that the mercaptans used here only provided a minor bleaching effect on the BCTMP handsheets.

On the other hand, the irradiation appeared to substantially change the nature of sulfur present in the handsheets. As can be seen in Table 3, the impregnated handsheets before (A) and after ( $A/h\nu$  15) irradiation had comparable amounts of sulfur. However, the irradiation substantially increased the amount of unextractable sulfur in the handsheets. The occurrence of a Michael addition of the thiols to the lignin during irradiation is the most probable explanation of the increase in unextractable sulfur, which led to brightness stabilization of the BCTMP handsheets. In a model compound study, Lee and Sumimoto isolated Michael addition products from 3,4-dimethoxystilbene-p-quinone irradiated in the presence of thioglycerol [12].

It is interesting to note that the degree of photostabilization observed for the thiols and the amount of thiols attached to the handsheets follow the same order, namely:



Very little 1-dodecanethiol was attached to fibres of the handsheets upon irradiation, and thus it is ineffective in retarding brightness reversion. To our knowledge, this is the first experimental result that correlates the amount of sulfur present in handsheets with the effectiveness of mercaptans as a brightness stabilizer for mechanical pulps. Our work also supports the speculation that stabilizing mechanical pulps by thiols partially results from a Michael addition mechanism.

### Conclusions

This report examines the effectiveness of thiols and disulfides as agents for improving the brightness stability of a high-brightness BCTMP against long-term storage and irradiation. Most of the additives provided a minor bleaching action. 1-dodecanethiol was found to be ineffective in both bleaching and photostabilizing the pulp. Ethylene glycol bithioglycolate and 3-mercapto-1,2-propanediol were the only additives that reduced the rate of thermal discoloration, while mercaptoacetic acid and 3-mercaptopropionic acid had poor thermal stability, which promoted thermal discoloration. Generally, the thiols were more effective brightness stabilizers than the disulfides. Unfortunately, the stabilizing effect of the thiols was reduced on storage, particularly for the mercapto-carboxylic acids. The photostabilization effect of the disulfides, although moderate, can be retained during storage. Combining both the beneficial and adverse effects of these sulfur-containing additives, we conclude that ethylene glycol bithioglycolate and 3-mercapto-1,2-propanediol are the most effective additives, since they provide some bleaching action and also prevent thermal and light-induced brightness reversion.

Sulfur analysis of treated handsheets established a correlation between the degree of photostabilization and the amount of sulfur strongly attached to the irradiated handsheets. This would suggest that a Michael-type addition of thiols is involved in photostabilizing mechanical pulps.

To date, we remain uncertain as to the exact mechanism(s) contributing to these observed reversion tendencies and research activities in our laboratories are

directed at investigating these issues. Nonetheless, these results demonstrate the need to determine photostabilization effects of additives over a prolonged period of time.

### Acknowledgements

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Table 1. TAPPI brightness values of hardwood BCTMP sheets before and after addition of various sulfur-containing compounds and after long-term storage and irradiation.

|   | Initial | After    | Addition % | After   | 15   | Irradiation (min) |      |      |
|---|---------|----------|------------|---------|------|-------------------|------|------|
|   |         | addition |            | storage |      | 30                | 60   | 90   |
| Control   | 85.9    |          |            |         |      |                   |      |      |
| HSCH <sub>2</sub> CO <sub>2</sub> H   | 84.6    | 85.1     | 2.1        | 66.4    | 59.9 | 54.0              | 49.6 |      |
| HSCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H                             | 85.5    | 86.4     | 2.5        | 76.1    | 71.1 | 63.4              | 58.7 |      |
| (HSCH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> -) <sub>2</sub>              | 85.6    | 86.2     | 4.2        | 77.8    | 73.2 | 66.2              | 61.7 |      |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> SH                             | 85.5    | 84.1     | 4.6        | 80.8    | 76.8 | 70.1              | 64.4 |      |
| CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> SH                                    | 84.3    | 85.3     | 2.6        | 65.5    | 59.7 | 53.1              | 49.1 |      |
| HO <sub>2</sub> CCH <sub>2</sub> CH(SH)CO <sub>2</sub> H                        | 84.7    | 84.1     | 2.6        | 75.7    | 70.9 | 63.6              | 59.0 |      |
| SCH <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> S                                  | 84.4    | 84.9     | 3.1        | 74.8    | 68.8 | 61.1              | 55.1 |      |
| S <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H) <sub>2</sub> | 85.7    | 85.9     | 3.5        | 72.8    | 66.4 | 57.6              | 52.3 |      |
|   |         |          |            | 74.1    | 67.8 | 61.5              | 56.7 |      |
| 1 month storage   |         |          |            |         |      |                   |      |      |
| Control   | 86.0    |          |            | 84.9    | 65.7 | 60.9              | 53.7 | 50.1 |
| HSCH <sub>2</sub> CO <sub>2</sub> H   | 86.1    | 86.6     | 2.1        | 86.2    | 75.5 | 69.5              | 61.1 | 55.6 |
| HSCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H                             | 85.5    | 86.1     | 2.4        | 85.2    | 76.5 | 72.6              | 66.2 | 61.1 |
| (HSCH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> -) <sub>2</sub>              | 84.7    | 86.0     | 4.6        | 85.7    | 77.9 | 73.0              | 65.5 | 60.2 |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> SH                             | 85.1    | 83.8     | 5.0        | 82.2    | 65.5 | 59.9              | 54.3 | 50.3 |
| CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> SH                                    | 84.6    | 85.0     | 2.3        | 84.5    | 75.0 | 69.5              | 63.2 | 58.1 |
| HO <sub>2</sub> CCH <sub>2</sub> CH(SH)CO <sub>2</sub> H                        | 83.3    | 80.0     | 2.4        | 80.5    | 69.6 | 63.7              | 56.5 | 51.9 |
| SCH <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> S                                  | 85.1    | 85.7     | 2.4        | 84.5    | 74.4 | 68.1              | 59.8 | 54.3 |

S<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub> 84.4 84.6 3.0 83.3 73.7 69.2 63.0 58.4

2 months storage

Control 85.1 83.6 65.4 60.0 53.7 50.1  
 HSCH<sub>2</sub>CO<sub>2</sub>H 84.6 85.3 2.0 83.6 71.8 66.2 59.0 54.2  
 HSCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H 85.6 86.4 2.3 84.7 76.2 72.0 65.4 60.8  
 (HSCH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> 85.0 86.1 4.8 85.6 77.6 72.3 65.6 60.2  
 CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH 84.8 83.0 4.9 82.5 66.6 61.0 54.7 50.8  
 CH<sub>2</sub>(OH)CH(OH)CH<sub>2</sub>SH 85.1 86.1 2.6 86.0 75.8 70.6 63.8 58.4  
 HO<sub>2</sub>CCH<sub>2</sub>CH(SH)CO<sub>2</sub>H 85.6 84.1 2.2 82.7 71.3 65.6 58.3 53.6  
 SCH<sub>2</sub>CH(OH)CH(OH)CH<sub>2</sub>S 85.0 85.7 2.8 84.3 74.7 68.8 60.9 55.8  
 S<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub> 86.0 86.0 3.1 84.5 75.0 69.7 63.0 58.1

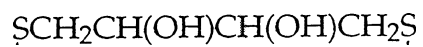
3 months storage

Control 83.9 82.8 65.5 59.4 53.0 49.6  
 HSCH<sub>2</sub>CO<sub>2</sub>H 85.6 86.0 2.2 81.2 72.4 65.5 59.2 55.0  
 HSCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H 85.4 86.4 2.3 83.3 74.6 68.5 62.6 58.7  
 (HSCH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>)<sub>2</sub> 82.5 82.7 4.8 82.5 75.8 69.2 63.5 59.2  
 CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>SH 84.3 82.7 5.0 81.6 64.4 59.9 55.6 51.7  
 CH<sub>2</sub>(OH)CH(OH)CH<sub>2</sub>SH 85.3 86.5 2.6 86.3 75.1 69.6 64.3 59.9  
 HO<sub>2</sub>CCH<sub>2</sub>CH(SH)CO<sub>2</sub>H 84.8 83.7 2.4 81.8 69.9 63.1 57.7 53.8  
 SCH<sub>2</sub>CH(OH)CH(OH)CH<sub>2</sub>S 85.6 86.5 3.0 84.2 75.5 67.9 62.6 57.6  
 S<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub> 84.4 85.3 2.6 83.8 73.9 67.4 62.4 58.2

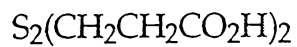
Table 2. Photostabilization factor of thiols and disulfides applied to aspen BCTMP handsheets.

| Storage time<br>( Months )                                       | Irradiation time |         |         |         |
|--|------------------|---------|---------|---------|
|  | 15 min.          | 30 min. | 60 min. | 90 min. |
| $\text{HSCH}_2\text{CO}_2\text{H}$                               |                  |         |         |         |
| 0  | 56.4             | 48.1    | 33.5    | 29.2    |
| 1  | 47.8             | 33.9    | 22.6    | 15.0    |
| 2  | 35.0             | 26.7    | 18.5    | 13.1    |
| 3  | 28.3             | 18.0    | 14.6    | 10.8    |
| $\text{HSCH}_2\text{CH}_2\text{CO}_2\text{H}$                    |                  |         |         |         |
| 0  | 60.5             | 52.7    | 39.5    | 34.4    |
| 1  | 55.7             | 48.6    | 40.2    | 32.0    |
| 2  | 52.3             | 45.8    | 35.7    | 29.1    |
| 3  | 41.3             | 31.0    | 26.2    | 22.2    |
| $(\text{HSCH}_2\text{CO}_2\text{CH}_2)_2$                        |                  |         |         |         |
| 0  | 72.3             | 63.8    | 49.5    | 40.4    |
| 1  | 66.5             | 53.4    | 40.6    | 31.8    |
| 2  | 62.4             | 49.4    | 38.2    | 29.1    |
| 3  | 63.6             | 45.7    | 38.5    | 32.1    |
| $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$                         |                  |         |         |         |
| 0  | -2.6             | 08      | -16     | -0.3    |
| 1  | 3.4              | -0.4    | 46      | 3.1     |
| 2  | 7.6              | 5.2     | 4.1     | 2.9     |
| 3  | -8.2             | -3.7    | 7.1     | 5.0     |
| $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{SH}$ |                  |         |         |         |
| 0  | 55.9             | 48.5    | 35.1    | 30.3    |
| 1  | 52.7             | 39.8    | 33.7    | 26.2    |
| 2  | 52.8             | 42.2    | 32.2    | 23.7    |
| 3  | 44.6             | 35.9    | 32.0    | 25.9    |
| $\text{HO}_2\text{CCH}_2\text{CH}(\text{SH})\text{CO}_2\text{H}$ |                  |         |         |         |
| 0  | 52.3             | 41.2    | 27.9    | 20.8    |
| 1  | 32.5             | 21.9    | 17.0    | 12.5    |

|   |      |      |      |      |
|---|------|------|------|------|
| 2 | 27.4 | 20.3 | 13.1 | 8.6  |
| 3 | 19.0 | 11.4 | 12.3 | 96 . |



|   |      |      |      |      |
|---|------|------|------|------|
| 0 | 38.0 | 28.8 | 14.4 | 10.9 |
| 1 | 47.3 | 32.3 | 21.7 | 14.2 |
| 2 | 47.7 | 35.5 | 23.2 | 16.6 |
| 3 | 45.1 | 27.8 | 25.6 | 18.4 |



|   |      |      |      |      |
|---|------|------|------|------|
| 0 | 39.5 | 30.4 | 23.5 | 20.2 |
| 1 | 47.3 | 39.4 | 33.7 | 27.6 |
| 2 | 44.2 | 35.1 | 26.8 | 20.3 |
| 3 | 42.9 | 30.6 | 28.8 | 23.6 |

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Table 3. Sulfur content ( S % ) of aspen BCTMP handsheets before and after addition of various thiols and after extraction and irradiation/extraction.

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|  |                   |       |
|--|-------------------|-------|
| Untreated pulp   |                   | <0.05 |
| HSCH <sub>2</sub> CO <sub>2</sub> H                                | A                 | 1.16  |
|  | A/E               | 0.13  |
|  | A/ <i>hν</i> 15/E | 0.35  |
| HSCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H                | A                 | 1.21  |
|  | A/E               | 0.08  |
|  | A/ <i>hν</i> 15/E | 0.44  |
| (HSCH <sub>2</sub> CO <sub>2</sub> CH <sub>2</sub> -) <sub>2</sub> | A                 | 2.03  |
|  | A/E               | 0.12  |
|  | A/ <i>hν</i> 15   | 1.86  |
|  | A/ <i>hν</i> 6/E  | 0.61  |
| CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> SH                | A/ <i>hν</i> 15/E | 0.76  |
|  | A                 | 0.60  |
|  | A/E               | <0.09 |
|  | A/ <i>hν</i> 15/E | 0.10  |

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A: addition of thiols; E: extraction with organic solvents; *hν* 6: irradiation 6 hours; *hν* 15: irradiation 15 hours.

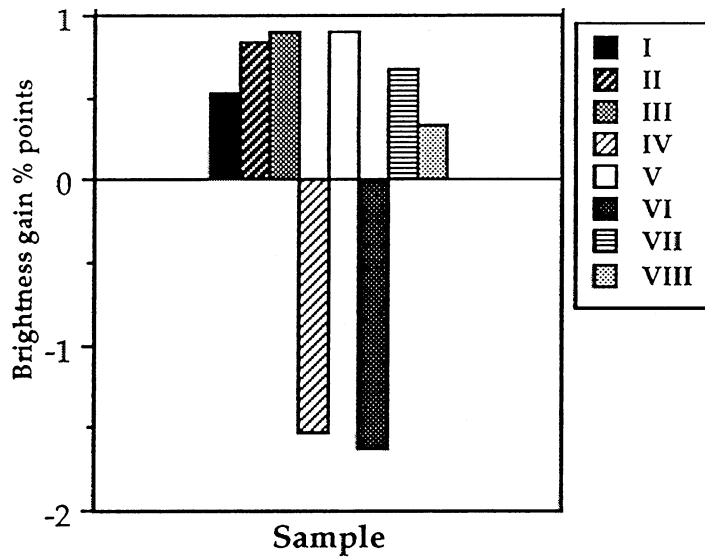


Figure 1. Average Values of Brightness Gain after Treatment of Hardwood BCTMP Handsheets by Sulfur Compounds I - VIII.

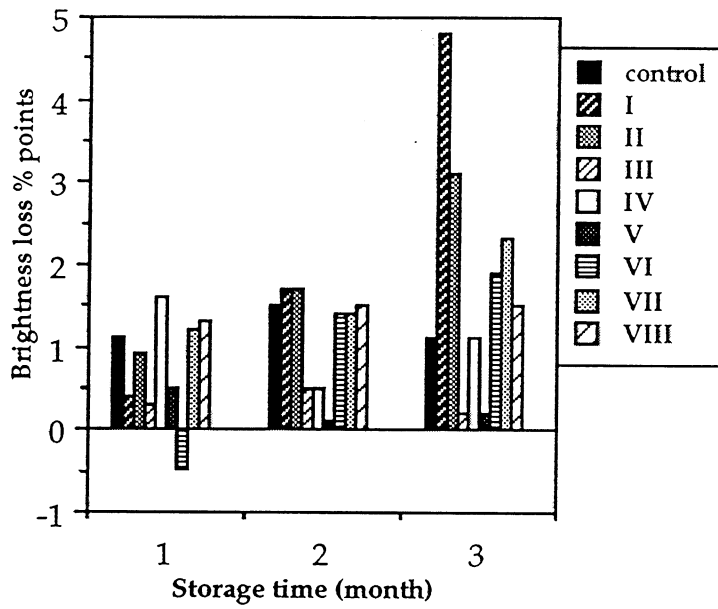


Figure 2. Brightness Loss of Hardwood BCTMP Handsheets Treated by Sulfur Compounds I - VIII as a Function of Storage Time.



