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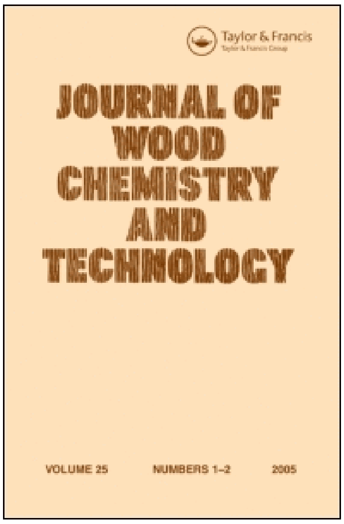

Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
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To cite this Article Cook, C. M. , Pan, X. and Ragauskas, A. J.(1996) 'Brightness Reversion of Mechanical Pulps VII: Photostabilization Studies of Thiol Additives for Ligniocellulosic Materials', Journal of Wood Chemistry and Technology, 16: 3, 327 — 345

To link to this Article: DOI: 10.1080/02773819608545812

URL: http://dx.doi.org/10.1080/02773819608545812

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 16(3), 327-345 (1996)

BRIGHTNESS REVERSION OF MECHANICAL PULPS VII: PHOTOSTABILIZATION STUDIES OF THIOL ADDITIVES FOR LIGNIOCELLULOSIC MATERIALS

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ABSTRACT

The chemical mechanisms contributing to the photostabilization properties of 1-thioglycerol and 2-mercaptoethyl ether for lignocellulosic materials was studied. The thio-additives were impregnated onto wood-based fibers, photolyzed, extracted, and characterized spectroscopically. Both thio-additives were shown to yield the corresponding disulfide when the photolysis experiments were performed on bleached chemithermomechanical pulp (BCTMP). Irradiation of BCTMP fibers impregnated with 2-mercaptoethyl ether under an argon atmosphere yielded only starting material indicating that the thio-additive scavenges radicals generated after the initial photochemical reactions that contribute to the photo-discoloration of wood-based materials.

INTRODUCTION

The production of high quality paper frequently employs high brightness, lignin free, cellulosic fibers. The use of wood pulps, containing near equal proportions of cellulose, hemicellulose, and lignin provides a

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valuable alternative manufacturing technology for the production of paper. Wood containing pulps, also referred to as mechanical pulps, provide several distinct manufacturing benefits including high utilization of wood, reduced waste products, and favorable paper making properties.[1] Unfortunately, commercial use of these pulps is limited due to their well know yellowing properties. Although mechanical pulp undergoes a slow thermal yellowing process, frequently referred to as thermal reversion,[2] the photoyellowing process, is more severe and is the limiting factor for many applications.[3]

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Research efforts over the last few decades have extensively characterized the photoaging process for mechanical pulps. It is now well established that the photoyellowing of mechanical pulps is initiated by near-UV light (λ 300-400 nm) and requires the presence of oxygen.[4] A variety of lignin functional groups are believed to contribute to the overall photoaging process including α-carbonyl-β-O-aryl ether groups, diguaiacyl stilbenes, coniferyl alcohol units, substituted biphenyl units, and quinoid-like lignin fragments. As our understanding of the mechanisms of photoyellowing has increased, research efforts have begun to focus on developing photostabilization technologies for mechanical pulp. Although no commercially viable technologies have, as of yet, been developed to photostabilize mechanical pulps several chemical additives have shown promise at inhibiting the photoaging process. UV absorbers such as 2-hydroxybenzophenone or 2-(2-hydroxyphenyl)benzotriazole have been examined extensively, but to-date, the application levels needed to substantially retard the photoyellowing properties of mechanical pulps has precluded their commercial use.[5] Radical scavenging agents such as ascorbic acid, thiol derivatives, thioethers, and formates have also been shown to retard the overall rates of the photoyellowing but unfortunately, these additives have not fulfilled all of the requirements needed for practical applications.[6] Recent studies by Castellan[7] and Ragauskas[8] have noted improved additive photostabilization effects by applying combinations of UV-absorbers and radical scavengers impregnated onto mechanical pulps.

Despite these advances in photostabilization technology, our understanding of the chemical mechanisms that contribute to these effects remain poorly defined. This report summarizes the results of our initial investigations into the chemical mechanisms that contribute to the overall photostabilization properties for mercapto-additives. Cole and Sarkanen[9] suggested that thiol additives photostabilize mechanical pulp, in part, by scavenging reactive lignin radicals that are involved in the photoaging process (see Fig. 1, eq. 1).[10] Davidson et al. speculated that the products from the initial radical scavenging reactions would lead to the formation of disulfides and these products could trap additional radicals yielding the thiosulfinate (see Fig.1, eq. 3).[11]

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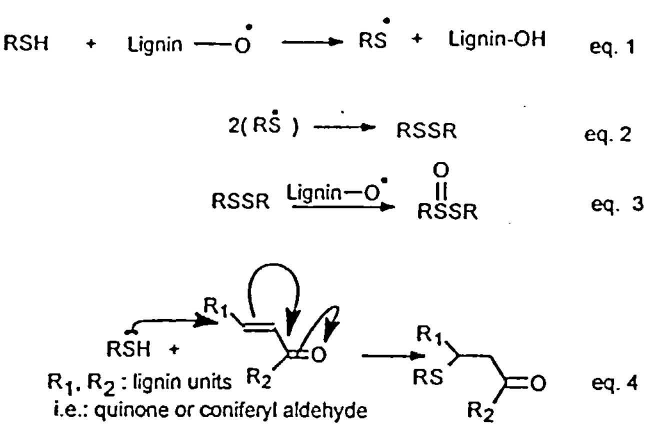

$$\mathrm{RSH} + \mathrm{Lignin{-}\dot{O}} \longrightarrow \mathrm{R\dot{S}} + \mathrm{Lignin{-}OH} \qquad \text{eq. 1}$$

$$2(\mathrm{R\dot{S}}) \longrightarrow \mathrm{RSSR} \qquad \text{eq. 2}$$

$$\mathrm{RSSR} \xrightarrow{\mathrm{Lignin{-}\dot{O}}} \mathrm{R\overset{\overset{\displaystyle O}{\|}}{S}SR} \qquad \text{eq. 3}$$

FIGURE 1: Proposed mechanisms for thio-photostabilization of mechanical pulp.

The second commonly proposed thio-photostabilization mechanism relies upon the nucleophilic properties of thiol additives[12] and proposes that these reagents undergo Michael additions to unsaturated lignin chromophores (see Fig.1, eq. 4) such as coniferyl aldehyde units, stilbene derivatives, and *ortho-* and *para-* quinoid structures formed during the photoaging process and thereby removing lignin chromophores.[9]

Model studies by Gellerstedt[13] and Lee[14] have shown that 1-thiogylcerol will rapidly add to lignin-like stilbene structures under brightness reversion conditions. Hirashima[15] and Pan[16] have recently extended these studies to pulp and demonstrated that near-UV irradiation of mercapto-treated BCTMP testsheets resulted in sulfur incorporation into the pulp. Furthermore, Pan[16] demonstrated that the more effective the additive was at retarding photoyellowing the more sulfur compound was incorporated into the pulp. These results were interpreted as supporting evidence for the proposed Michael addition mechanism for photostabilizing pulps.

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The emerging picture to develop from these experiments is that thiol additives photostabilize mechanical pulps, in part, by removing lignin chromophores during the photoaging process. Unfortunately, the exact role played by thiol additives as radical scavenging agents has remained poorly defined. To explore the thio-based radical trapping mechanisms that contribute to the photostabilization effects of mercapto compounds we have examined the fate of 1-thioglycerol and 2-mercaptoethyl ether when applied onto hardwood mechanical pulp and irradiated with near UV light. The result of these studies provide some of the first experimental evidence that mercapto-additives act as radical scavenging agents during photolysis of mechanical pulps.

EXPERIMENTAL

All chemicals were purchased from Aldrich Chemical Co., Milwaukee, WI. and used as received. A commercial BCTMP pulp was employed for the studies described in this report. The pulp was manufactured from aspen[17] employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. The pulp was shown to be free of sulfur by elemental analysis. All pulp samples were disintegrated using only glass or Teflon labware to prevent metal contamination. After disintegration, the pulps were soxhlet extracted with acetone for 24 h and allowed to air dry for 24 h in a controlled 50% humidity environment. Previous studies have demonstrated that this mild extraction procedure does not influence the brightness reversion properties of mechanical pulp but does simplify post-photolysis additive studies.[18]

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General Photolysis Procedure For Mercapto Treated Mechanical Pulp

In a typical experiment, 80 g of BCTMP pulp was treated with a solution of 4 g of thiol (1-thioglycerol or 2-mercaptoethyl ether) in 700 ml methanol and the resulting slurry was stirred under nitrogen. After 1h, the methanol was removed using a rotary evaporator and the resulting 5 % w/w thiol/pulp mixture was photolyzed in a Rayonet Photochemical Reactor (Model Number: RPR-100) equipped with eight RPR 3500 A lamps and a cooling fan. During irradiation, the pulp fluff was vigorously stirred with a teflon stirrer for 12 - 60 h. Upon completion of the photolysis experiments, the thiol treated pulp was washed with methylene chloride (3 x 350 ml), the extracts were combined, and the solvent removed using a rotary evaporator to leave a yellow oil. This yellow oil was weighed and then analyzed using GC, GC/MS, ^{1}H, and ^{13}C NMR. Pulp samples submitted for elemental analysis were subjected to a prolonged (24 h) methylene chloride soxhlet extraction to remove all unbound sulfur from the pulp.

NMR analysis of the extracts from the 24 h photolysis of 1-thioglycerol treated pulps (94.0 - 95.5% yield) indicated the presence of starting thiol and corresponding disulfide in a 1.94:1 ratio. NMR analysis of the extracts from the 2-mercaptoethyl ether treated pulps (94.0% yield) indicated the presence of starting and two additional products (**1** & **2**) in a 1.5:1:2 ratio. MPLC chromatography (95:5 hexane:ethyl ether) afforded a 33% yield of 1,4,5-oxadithiepane (**1**) : ^{1}H-NMR ($CDCl_3$): 4.10 ppm (t, J=2.0 Hz, 4H) (O-CH_2-); 3.00 ppm (t, J=2.0 Hz, 4H) (-CH_2-S-); ^{13}C-NMR ($CDCl_3$): 72.58, 40.46 ppm; LRMS *m/e*: 136.0, 108.0, 88.9, 77.9, 60.0, 43.0

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Extensive washing (99:1 hexane:ethyl ether) of the photolysis mixture also afforded an analytical of **2**. Gel permeation chromatography, employing a 4mg/mL THF solution on a American Polymer 500A column, eluted at a rate of 1.0 ml/min, indicated that sample **2** was a polymeric material with a M_n of 7,660 and polydispersity of 2.39. Spectroscopic characterization of **2** gave: ^{1}H-NMR ($CDCl_3$): 3.58 ppm (t, J=4.0 Hz, 4H) (O-CH_2 -); 2.84 ppm (t, J=4.0 Hz, 4H) (-CH_2 -S-); ^{13}C-NMR ($CDCl_3$): 69.17, 38.72 ppm; LRMS *m/e*: 272.1, 213.1, 168.0, 136.0, 91.9, 77.9, 61.0, 43.0 ppm.

General Photolysis Procedure Of Mercapto-treated Mechanical Pulp Testsheets

Mechanical pulp testsheets, prepared according to a standardized TAPPI testing protocols[19] (test method T 218) were sprayed with 20 ml of methanol containing 1 - 5 % w/w (based on BCTMP testsheet weight) thiol additive and air dried for 4 h. The testsheets attached to a merry-go-round and photolyzed in a Rayonet Photochemical Reactor (Model Number: RPR-100) equipped with eight RPR 3500 A lamps. At specified amounts of time the testsheets were removed from the photochemical reactor and TAPPI brightness values were recorded (test method T 452).[19]

Treatment Of Cellulose With Thiols

The treatment of cellulose with thiols was carried out exactly as the thiol treatment of BCTMP pulp with the exception that the cellulosic fibers, derived cotton linters, were not soxhlet extracted before use.

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Photolysis Of Pulp Under Argon

A sample of extractives free BCTMP (30 g) was purged under argon for 24 h.. A solution of oxygen-free methanol and 1.50 g 2-mercaptoethyl ether was added to the purged pulp and this slurry was further purged (with stirring) under argon for 24 h. The methanol was removed under vacuum without heat and the remaining pulp/thiol mixture was photolyzed for 24 h with a Rayonet Photochemical Reactor (Model Number: RPR-100) equipped with eight RPR 3500 A lamps. A wash of 1 L methylene chloride (first purged with argon for 24 h) was cannulated into the pulp/thiol mixture, stirred for 4 h, and removed under argon. This wash was reduced in volume to 1.40 g of clear colorless oil that was analyzed by NMR and GC. The clear oil proved to be the starting material, 2-mercaptoethyl ether. Optical reflectance values were determined following TAPPI test method T-452 for the starting BCTMP pulp and the photolyzed pulp.

Synthesis Of 1,4,5-Oxadithiepane (Cyclic Disulfide Of 2-Mercaptoethyl ether)

A solution of 700 ml chloroform and 20.24 g (0.20 mole) triethylamine was prepared and stirred at RT. To this stirring solution, 13.82 g (0.10 mol) of 2-mercaptoethyl ether in 250 ml chloroform and 13.82 g (0.10 mol) iodine in 1100 ml chloroform was added dropwise simultaneously, at such a rate that a slight yellow iodine color persisted. The iodine and mercaptan addition required 8 h. The resulting slightly yellow reaction solution was washed with 0.1 % sodium thiosulfate (2 x 500 ml), 0.1 N HCl (2 x 500 ml), and finally with water (2 x 500 ml), saving the organic phase. The chloroform mixture was then dried over Na_2SO_4 and filtered. The filtrate was reduced in volume to 20 ml of a viscous yellow oil on a rotary evaporator. This yellow oil was vacuum distilled (bp^{20} 67 - 73° C, 5 mm) to yield 9.93 g (0.073 mol, 73.3 % yield) of 1,4,5-oxadithiepane. Spectral characterization (^1H NMR, ^{13}C NMR, LRMS, elemental analysis) agreed with the results acquired from samples of **1** isolated from photolyzed pulp experiments.

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Synthesis Of 3,3'-Dithiobis-1,2-propanediol (Disulfide Of 1-Thioglycerol)

A solution of 70 ml of DMSO, 10.0 g of 1-thioglycerol, and one drop of H_2SO_4 was heated at 100° C for 48 h. After 48 h, the reaction tested negative to Ellman's reagent and was poured into 100 ml of chloroform and a white solid precipitated from the solution. The white powder was removed by vacuum filtration and the filtrate was put in the freezer (-10° C) for 24 h. A second crop of white powder was collected, combined with the first crop and dried under vacuum for 48 h. A total of 9.91 g of 3,3'- dithiobis-1,2-propanediol, m.p. 67 - 70 ° C was obtained: ^1H-NMR (CD_3OD): 3.86 ppm (m, 1H) (-S-CH_2-CH*OH-CH_2OH); 3.57 ppm (m, 2H) (-S-CH_2-CHOH-

CH^*_2OH); 2.95 ppm (dd, 1H) (-S-CH^*_2-CHOH-CH_2OH); ppm (m, 1H) (-S-CH^*_2-CHOH-CH_2OH); ^{13}C-NMR (CD_3OD): 70.67, 64.64, 42.28 ppm

RESULTS AND DISCUSSION

Previous studies by Cole and Sarkanen[9] had demonstrated the photostabilization benefits of 1-thioglycerol. We have noted comparable effects for 2-mercaptoethyl ether.[10] Figure 2 summarizes the photostabilization effects that can be accomplished with these two mercapto-additives with BCTMP pulps. The photostabilization effects of 2-mercaptoethyl ether appear to be very similar to that of 1-thioglycerol when applied onto testsheets on a per weight application basis.

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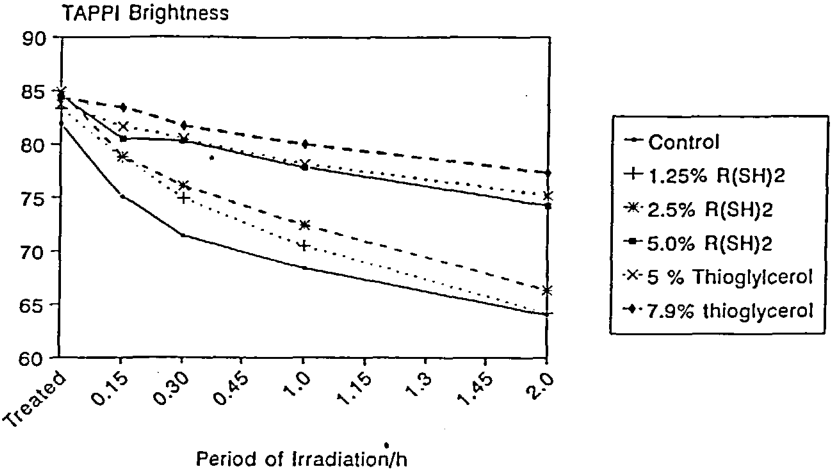

$R(SH)_2$: 2-mercaptoethyl ether

FIGURE 2: Photoyellowing properties for BCTMP testsheets treated with 1-glycerol and 2-mercaptoethyl ether.

However, when testsheets of BCTMP were impregnated with equal molar amounts of thiol (see Fig. 2, 5.0% of 2-mercaptoethyl ether and 7.9% 1-thioglycerol) the photostabilization effects for 1-thioglycerol were slightly more pronounced. To study the fundamental chemical mechanisms that contribute to the photostabilization effect of these additives, we examined the photolysis products formed when 1-thioglycerol and 2-mercaptoethyl ether were irradiated on BCTMP.

BCTMP pulp impregnated with 5% 2-mercaptoethyl ether (wt/wt basis) was irradiated with a phosphor black light source (λ_{max} :350 nm) lamps for 24 h. Soxhlet extraction (under nitrogen) of the photolyzed 1-thioglycerol treated pulp yielded a 1.9:1.0 mixture of starting material and a second component which by NMR was shown to be the symmetric disulfide of thiogylcerol, 3,3'-dithiobis-1,2-propanediol (93.4 % material recovery). Extended photolysis of 1-thioglycerol treated pulp for 60 hours yielded a 1.5:1 ratio of starting material and the disulfide dimer of thioglycerol (91 % material recovery). Control experiments demonstrated that impregnation of 1-thioglycerol onto BCTMP pulp and subsequent extraction did not yield the disulfide dimer of thioglycerol.

Although these results suggested that conversion of 1-thioglycerol to the disulfide was a result of the photoyellowing process, additional photolysis experiments on cellulose also yielded 3,3'-dithiobis-1,2-propanediol. For example, 24 hour irradiation of 1-thioglycerol impregnated on cellulose following the same procedure as described above, yielded a 32% conversion of 1-thiolglycerol to 3,3'-dithiobis-1,2-propanediol (99% recovery). Careful monitoring of the cellulose and mechanical pulp samples during photolysis indicated that the temperature of the pulp was

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warmed to 38° C. Immersion of BCTMP pulp treated with 1-thiogylcerol in a water bath set at 38° C, in the dark, resulted in a 30% formation of disulfide after 24 h. In conclusion, these preliminary studies suggested a slight enhancement of 3,3'-dithiobis-1,2-propanediol formation when 1-thiolgylcerol is photolyzed on BCTMP which may be due to brightness reversion associated reactions. Nonetheless, the major reaction pathway is simple autoxidation of thiol and this represents a significant loss of additive to nonproductive photostabilization pathways.

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To explore the generality of this thio chemistry we impregnated BCTMP pulp with 2-mercaptoethyl ether and irradiated for 24 h. Methylene chloride extraction of the photolyzed pulp afforded a 94% material recovery which, by NMR analysis, was free of lignin fragments. GC and NMR analysis indicated that pulp extracts contained 44% starting material and two new components, compound **1** (33 %) and **2** (23 %). The major new component was readily identified as the cyclic dimer of 2-mercaptoethyl ether, 1,4,5-oxadithiepane as shown in Figure 3.

Independent synthesis of **1** was accomplished by oxidizing 2-mercaptoethyl ether with iodine in chloroform employing high dilution conditions. The use of dilute oxidative conditions was required to minimize the oxidative polymerization of the starting material.

Chromatography of the photolysis product mixture ultimately yielded an analytically pure sample of compound **2**. GC/MS, NMR and gel permeation molecular weight determination clearly indicated that the second product was a mixture of low molecular weight disulfide oligomers with a M_n of 7,660 and a polydispersity of 2.39. Presumably, under the

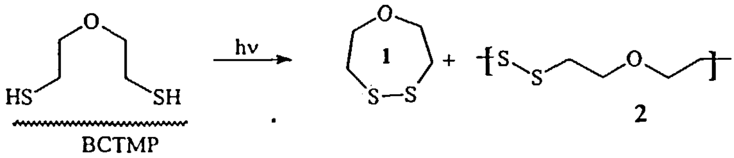

FIGURE 3: Photolysis of 2-mercaptoethyl ether impregnated on BCTMP.

oxidative conditions of photoaging, 2-mercaptoethyl ether undergoes a slow polymerization process along with the formation of **1**.

To further explore the mechanisms contributing to the oxidative formation of **1** and **2**, we photolyzed samples of 2-mercaptoethyl ether on cellulose for 12 h. Extraction and product analysis indicated a 37.5% conversion of 2-mercaptoethyl ether to compounds **1** and **2** in a 2:1 ratio. Prolonged photolysis for 60 hours afforded an 10:1 mixture of compounds **1** and **2**. Careful monitoring of the reaction temperature indicated that the temperature of the BCTMP and cellulose photolysis experiments was raised to 38° C. Control experiments with 2-mercaptoethyl ether adsorbed on either mechanical or cellulose fluff and warmed to 38° C for 60 hours, in the dark, resulted in starting material and the formation of **1** and **2** in 83% yield in a 1:1:10 ratio.

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The results of all of these investigations suggest that the formation of **1** and **2** comes about due to a variety of radical scavenging mechanisms but the dominant product pathway is autoxidation by air, as previously observed with 1-thioglycerol. Unfortunately, these autoxidation reactions result in the consumption of the thiol additive prior and during photolysis. We have previously noted that thiol treated BCTMP testsheets stored for prolonged periods of time prior to photolysis exhibited reduced photostabilization effects in comparison to testsheets freshly prepared and irradiated.[21] The chemical reactions noted in this report provided a first principle explanation of these observations. In more general terms, these results are reminiscent of the difficulties encountered with the use of ascorbic acid as a photostabilization agent for mechanical pulps[22] as it was found that ascorbic acid underwent an oxidative decomposition upon long term storage.

Photolysis Of Thiol-Treated BCTMP Under Argon

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As previously discussed, the photoyellowing of lignocellulosic material occurs only in the presence of oxygen . This has been attributed to the *in-situ* formation of singlet oxygen by Gratzl[23] and others investigators, although recent studies by Forsskahl[24] have questioned the contribution of singlet oxygen to photoyellowing. Several researchers[25]· have also suggested that oxygen may be involved in post-photolysis reactions combining with reactive lignin radicals generated during photolysis and thereby yielding reactive peroxy and hydroxy radicals.

Despite these differences in proposed mechanisms, our interest in this field was to determine if wood pulps treated with 2-mercaptoethyl ether *would undergo oxidative coupling to the disulfide in absence of oxygen.* If this were to occur, it would suggest that the mercapto-additive was quenching either the excited state of lignin chromophores or reactive lignin radicals formed from the initial photolysis reactions (i.e., the reactive intermediates formed form the photolysis of α-carbonyl-β-O-aryl ether groups[26]). Both of these reactive lignin intermediates would occur either in the presence and absence of oxygen. To examine this issue, BCTMP pulp was purged with argon and then impregnated with 2-mercaptoethyl ether.

The treated pulp samples were then photolyzed for 24 hours under an argon atmosphere with phosphorous black lamps. Analysis of the pulp after photolysis indicated that the pulp had not undergone photoyellowing. Extraction of the pulp with methylene chloride yielded a 97.1% recovery of starting material and no other material was detected in the extracts. These results suggest that the formation of components **1** and **2** are dependent upon the presence of oxygen during the photoaging process. The absence of any new disulfide adduct from the argon experiment also suggests that 2-mercaptoethyl ether does not quench the excited state of lignin chromophores.

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Sulfur Incorporation During Photolysis

Due to oxidative formation of the disulfide dimers formed from 1-thioglycerol or 2-mercaptoethyl ether, it was of interest to determine if the additives employed in this study also underwent sulfur incorporation into the pulp during the photoaging process. As summarized in Table 1, BCTMP pulp treated with 5% of 2-mercaptoethyl ether was readily shown to contain 1% S by elemental analysis. Exhaustive methylene chloride extraction (24 h) removed almost all of the sulfur present on the pulp. The trace amounts of sulfur remaining on the pulp was attributed to mercapto Michael-addition reactions into unsaturated lignin chromophores, such as *ortho* and *para*-quinones which are known to be present in the starting pulp. Upon photolysis, the amounts of sulfur incorporated into the pulp increased the longer the pulp was photolyzed. The results summarized in Table 1 extend our previous observations[16] which noted that BCTMP pulp undergoes sulfur incorporation during brightness reversion conditions when treated with mercaptoacetic acid, 3-mercaptopropionic acid, ethylene glycol

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TABLE 1

Sulfur Incorporation for Mercapto-Treated BCTMP Pulp

Thiol Additive[a]	Irradiation Time/h	Elemental Analysis of Pulp		
		% C	% H	% S
Starting Pulp[b]	0 h	43.53	6.60	<0.05
5% thioglycerol/pulp[b]	24 h	43.60	6.35	0.16
“”	60 h	43.69	6.36	0.19
Starting Pulp	0 h	44.41	6.35	<0.05
Pulp impregnated with 2-mercaptoethyl ether		34.66	7.67	1.11
5% 2-mercaptoethyl ether/pulp[b]				
“ “	0 h	43.25	6.44	0.07
“ “	24 h	43.84	6.31	0.35
“ “	60 h	43.98	6.34	0.38

[a]% application reported in terms of g additive/g oven dry pulp %; [b]sulfur-free BCTMP impregnated with thio additive and extracted after x h photolysis.

bisthioglycolate, or 1-dodecanethiol. Presumably the thio-additives reported in this study also remove lignin chromophores by Michael-type reactions.

CONCLUSIONS

Studies presented in this paper are consistent with the proposed radical scavenging mechanisms for thiol photostabilization agents. Nonetheless, the dominant mechanism contributing to the formation of disulfides is autoxidation of the starting thiol by oxygen. This well known reaction undoubtedly contributes to the reduced photostabilization effect of thiol additives impregnated onto BCTMP pulp and stored for prolonged periods prior to photolysis. The results described in this paper serve to illustrate the technical challenges involved in developing an antioxidant system for mechanical pulp since the additive needs to be sufficiently reactive to quench lignin radicals and yet be resistant to atmospheric autoxidation reactions.

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ACKNOWLEDGEMENTS

This investigation was made possible by the financial support provided by the National Science Foundation (Grant CTS-9414695) and the member companies of the Institute of Paper Science and Technology.

REFERENCES

1. K. L. Patrick, ed., Modern Mechanical Pulping in the Pulp and Paper Industry, Muller Freeman Publication, 1989.

2. C. Heitner, in Photochemistry of Lignocellulosic Materials, C. Heitner and Scaiano (eds), ACS, Washington D.C., 1, 3(1993).

3. R. A. Cockram, CTMP in Fine Papers, Proceedings of the 1989 International Mechanical Pulping Conference, Helsinki, June, (1989).

4. M. G. Nueman and A.E. Machado, J. Photochem. Photobiol.: Biology 3, 473, 1989.

5. R.S. Davidson, L. Dunn, A. Castellan, and A. Nourmamode, J. Photochem. Photobiol A: Chemistry, 86, 275, (1995).

6. C. Heitner, Photochemistry of Lignocellulosic Materials, eds C. Heitner and Scaiano, ACS, Washington D.C., 15, 192(1993).

7. A. Castellan, N. Colombo, H. Bous-Laurent, P. Fornier de Violet, and D. Lachenal, Methods for Improving the Lightfastness of Lignocelluolsic Materials, French Patent # 2,636,358, Application # 8812018, Sept. 9, 1988.

8. X. Pan, L. C. Harvey, and A. J. Ragauskas, J. Pulp Paper Sci., April 1996 (in press).

9. B. J. W. Cole, and K. J. Sarkanen, Tappi J., 70(11), 117, (1987).

10. J. B. Lombardini and T. P. Singer, J. Biol. Chem. , 244, 1172(1969).

11. K. S. Davidson, L. A. Dunn, A. Castellan, N. Colombo, A. Nourmamode, and J. H. Zhu, J. Wood Chem. Technol., 11(4), 419(1991).

12. G. W. Kutney, J. Pulp Paper Sci., 12(4), J129(1986).

13. L. Zhang, and G. Gellerstedt, Proc., 7th. Intl. Symp.on Wood and Pulping Chem., 1, 759(1993).

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14. D. Y. Lee, and M. Sumimoto, Holzforschung, 45 (suppl.), 15(1991).

15. H. Hirashima, and M. Sumimoto, Tappi J., 77(1), 146(1994).

16. X. Pan, and A. J. Ragauskas, J. Pulp and Paper Sci. and Technol., 21, J25(1995).

17. C. J. Biermann, ed., Chpt. 5, Pulp Bleaching in Essentials of Pulping and Papermaking, Academic Press (1993).

18. A. J. Ragauskas, Tappi J., 76(12), J184, (1993).

19. TAPPI Test Methods, 1991, TAPPI Press, Atlanta, GA (1990).

20. M. H. Goodrow and W. K. Musker, Synthesis, 457, (1981).

21. X. Pan and A.J. Ragauskas, J. Wood Chem. Technol., 15(1), 135(1995).

22. A. J. Ragauskas, Cellulose Chem. Technol., 28, 265(1994).

23. J. S. Gratzl, D. Papier, 39, v14(1985).

24. Forsskahl I., Olkkonen C., and Tylli H., J. Photochem. Photobiol., 49, 337(1989).

25. D.N.S. Hon, J. Wood Chem. Technol., 13(2), 179(1992).

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26. (a) R. Agnemo and R.C. Francis, 6th. Intl. Symp.on Wood and Pulping Chem., 1, 631(1991).

(b) K. Fischer, I. Schmidt, and H. Koch, 6th. Intl. Symp.on Wood and Pulping Chem., 1, 431(1991).

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