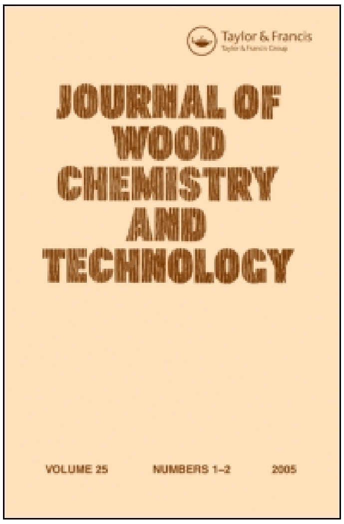

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Cang Li[a]; Charles M. Cook[a]; Arthur J. Ragauskas[a]
[a] Chemical and Biological Sciences Division, The Institute of Paper Science and Technology, Atlanta, Georgia

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BRIGHTNESS REVERSION OF MECHANICAL PULPS XI: PHOTOSTABILIZATION OF HIGH-YIELD PULPS BY THIOSULFINATES

Cang Li, Charles M. Cook, and Arthur J. Ragauskas*
Chemical and Biological Sciences Division
The Institute of Paper Science and Technology
Atlanta, Georgia 30318

ABSTRACT

A series of eleven cyclic and acyclic thiosulfinates was synthesized and applied onto hardwood BCTMP (bleached chemithermomechanical pulp) testsheets. Treated and untreated testsheets were photoaged and their optical property were monitored. The results of these photoaging experiments indicated that cyclic thiosulfinates were relatively ineffective at retarding brightness reversion, whereas most acyclic additives were effective photostabilization agents for BCTMP. The use of acyclic thiosulfinates in combination with UV absorbers provided a very effective means of retarding the photoaging process of mechanical pulps.

INTRODUCTION

In general, sulfur-based antioxidants have been shown to be one of the most effective classes of photostabilization additives for mechanical pulp.[1-10] The application of thiol additives to mechanical pulp has been shown to bleach lignin chromophores in high-yield mechanical pulps and also trap reactive photochemically generated radical intermediates. It is currently believed that both

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of these mechanisms contribute to the reported photostabilization effects of thio-additives.[11] Unfortunately, the odoriferous properties of thiols and their propensity to undergo autooxidation upon storage when deposited on mechanical pulp have hindered commercial application.[12] Recently, we reported[4] that thiosulfinates exhibit photostabilization properties equivalent to those of thiol derivatives and yet this new class of photostabilization additives for high-yield pulps does not have the malodorous properties associated with mercapto-additives. The mechanism of photostabilization by thiosulfinates is undoubtedly due to the strong reducing properties of these additives as the corresponding disulfide and thiosulfonate derivatives do not exhibit effective photoprotection of high-yield pulps. The antioxidant properties of thiosulfinates have been utilized to retard aging effects for synthetic polymers[13]. Thiosulfinates have been proposed to trap oxygen radicals indirectly or decompose to sulfenic acids that are active radical scavenging agents (see Scheme 1).

This study examines the structural requirements of thiosulfinate additives needed for effective photostabilization of mechanical pulps and their synergistic interactions with UV absorbers.

EXPERIMENTAL

Materials

All chemicals, including methyl disulfide, *t*-butyl disulfide, phenyl disulfide, *p*-tolyl disulfide, and 4,4′-dichlorodiphenyl disulfide, were

$$2\,RS(O)SR + H_2O \rightarrow RSO_2H + RSSR + RSOH$$

$$RSOH + R'OO^{\bullet} \rightarrow R'OOH + RSO^{\bullet}$$

$$2RSO^{\bullet} \rightarrow \text{inactive products}$$

Scheme 1

commercially purchased and used as received. Commercial hardwood BCTMP (93% yield) prepared from aspen using hydrogen peroxide for both the chemical pretreatment and bleaching stages was employed for all studies in this report.

Instrumentation

A Perkin-Elmer 320 UV/VIS spectrometer was used routinely to measure UV-visible absorption spectra and to characterize the compounds. All ^{1}H NMR spectra were recorded on a 400 MHz Bruker DMX spectrometer at ambient temperature. A VG 70SE high-resolution mass spectrometer was used to measure the mass spectra of all synthesized thiosulfinates. A Brightimeter Micro S-5 (Technidyne Corporation) was used to measure the brightness according to TAPPI standard procedure T 452 om-92.[14]

Procedures

Synthesis of thiosulfinates (equation 1). Several disulfides were oxidized by 3-chloroperoxybenzoic acid (*m*-CPBA) as previously described.[15-16]

$$\text{R-S-S-R} + \text{3-Cl-}C_6H_4CO_3H \rightarrow \text{R-S(O)-S-R} + \text{3-Cl-}C_6H_4CO_2H \qquad (1)$$

In brief, 3-chloroperoxybenzoic acid (0.015 mol), dissolved in 300 mL of chloroform, was added dropwise with stirring to a chloroform (300 mL) disulfide (0.015 mol) solution, cooled to 0°C. Upon completion of the addition of 3-chloroperoxybenzoic acid, the reaction mixture was stirred for an additional 5 minutes and the mixture was then washed with a cold aqueous 5% sodium carbonate solution (63 mL) followed by a second wash with aqueous 2% sodium carbonate solution (100 mL) and finally with water (100 mL). The water wash was re-extracted with chloroform and the combined organic phases were dried over sodium sulfate, filtered, and distilled under reduced pressure to remove the solvent. The thiosulfinate esters were purified by medium-pressure liquid chromatography with 3:1 petroleum ether/ethyl acetate as eluent. The thiosulfinates prepared (see Figure 1) in this manner were characterized by ^{1}H NMR and mass spectroscopy and these results agreed with reported values.[15, 17]

Preparation of handsheets. BCTMP fibers were Soxhlet-extracted with acetone for 24 h and air-dried prior to handsheet formation. The removal of extractives facilitated accurate measurements of the amounts of additives applied onto handsheets. We have previously demonstrated that the removal of extractives does not alter the fundamental photoreversion properties of mechanical pulp.[18] BCTMP handsheets (3 g) were prepared following TAPPI standard procedure T 218 om-91[14] and air-dried at constant temperature (22.0 ± 2.0°C) and relative humidity (50 ± 2.0%). Initial TAPPI brightness was measured to be 83%.

Handsheets treated with additives. In a typical experiment, a BCTMP handsheet was sprayed with a methanol solution (10 mL) of the thiosulfinate (0.015 mol, ca 1 wt.%) and then allowed to air-dry overnight in the absence of light. Control handsheets were prepared in an analogous manner except that the thiosulfinate was omitted from the methanol solution.

Handsheets containing a mixture of the thiosulfinate (**3** or **7**) and UV-absorber (**12** or **13**) were prepared in an analogous manner except that the methanol solution contained (a) 2,2'-dithio-2-oxodiethanol **3** (0.5% wt/wt basis) and 0.5% 2,4-dihydroxybenzophenone **12**, (b) 0.5% thiosulfinate **3** and 0.5% 3-(2H-benzotriazole-2-yl)-5-(*t*-butyl)-4-hydroxybenzene-propanoic acid, methyl ester **13**, (c) 0.5% phenyl thiosulfinate **7** and 0.5% UV absorber **12**, and (d) 0.5% thiosulfinate **7** and 0.5% UV absorber **13**.

UV photolysis and brightness of handsheets. Four BCTMP handsheets were attached to a "merry-go-round" and photolyzed in a Rayonet RPR-100

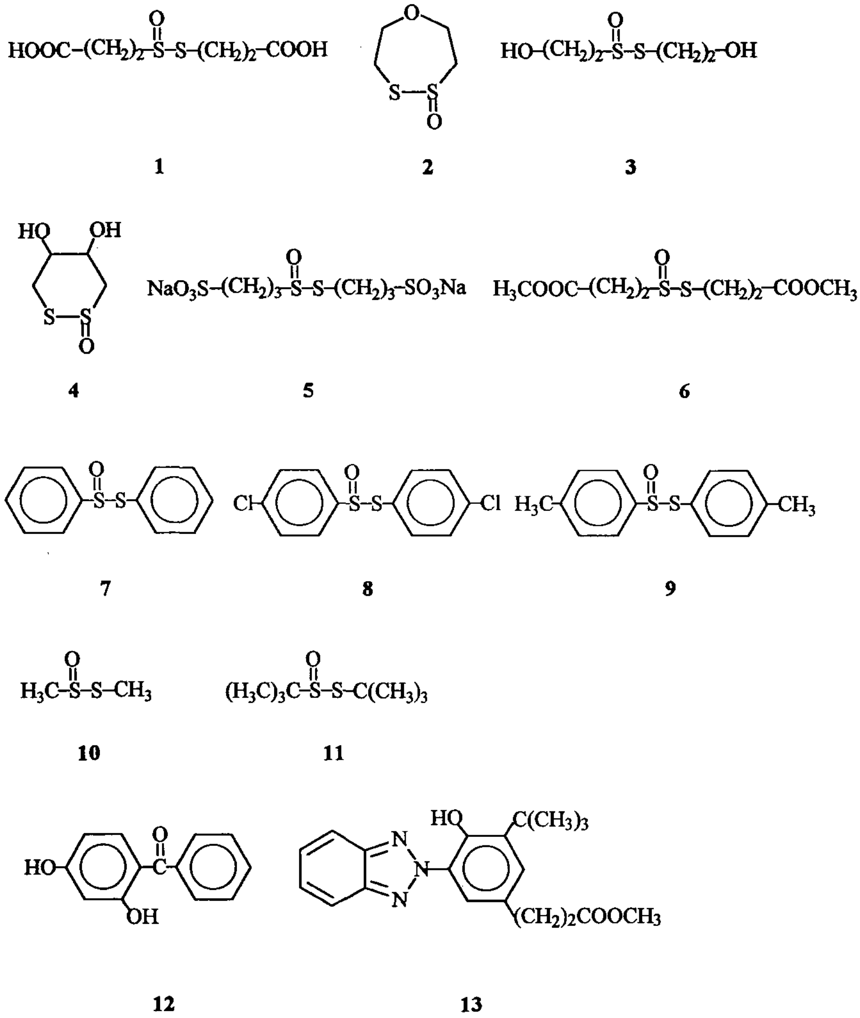

FIGURE 1. *Structures of thiosulfinates and UV absorbers.*

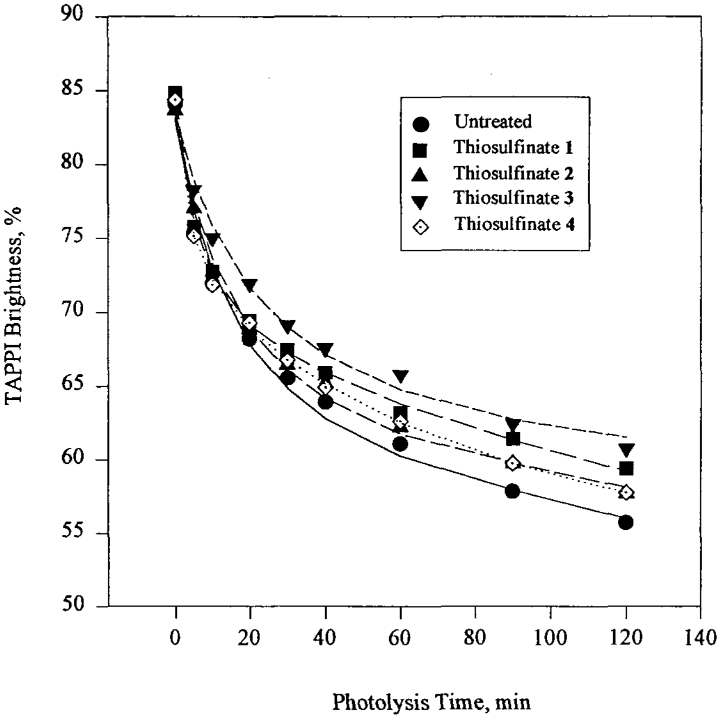

FIGURE 2. TAPPI Brightness of testsheets treated with 0.015 mole of thiosulfinates **1-4** as a function of photolysis time.

photochemical reactor with 16 black lamps at ~ 30°C. At selected time periods, the handsheets were removed from the reactor and kept in the dark for 4 h to equilibrate to constant temperature (22.0 ± 2.0°C) and relative humidity (50 ± 2.0%). TAPPI brightness values[14] were then determined and the handsheets were further photolyzed. The tests were run three times. Each curve in the plots was an average of three TAPPI brightness readings with ±2% of error.

RESULTS AND DISCUSSION

Structure-activity effects. As a preliminary investigation of the structural components contributing to the photostabilization effects of thiosulfinates, we

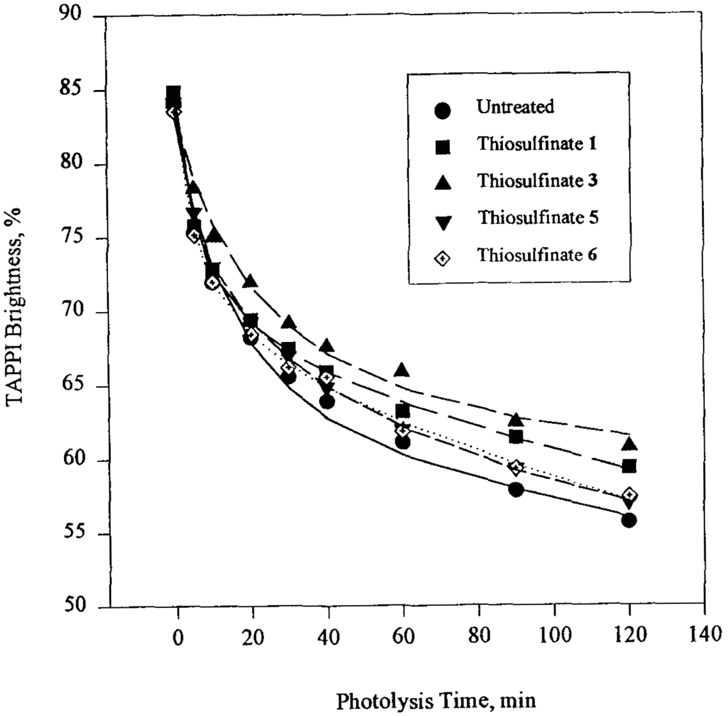

FIGURE 3. TAPPI Brightness of testsheets treated with 0.015 mole of thiosulfinates **1**, **3**, **5**, and **6** as a function of photolysis time.

prepared a series of acyclic and cyclic thiosulfinates (see Fig. 1). The reactivity of acyclic and cyclic thiosulfinates with radicals is know to differ[13, 19] and we had hypothesized that these differences could influence their photostabilization effects for mechanical pulp. These additives were conveniently prepared from the corresponding disulfides by *m*-CPBA oxidation. Cyclic additives examined included *trans*-1,2-dithiane-1-oxo-4,5-diol **4** and 1-oxo-1,2-dithiane-4-oxepane **2**. Acyclic derivatives included 3,3'-dithio-3-oxo-propinate **1**, 3,3'-dithio-3-oxo-dipropionate acid, methyl ester **6**, 3,3'-dithio-3-oxo-dipropanesulfonic acid, sodium salt **5**, and 2,2'-dithio-2-oxo-diethanol **3**.

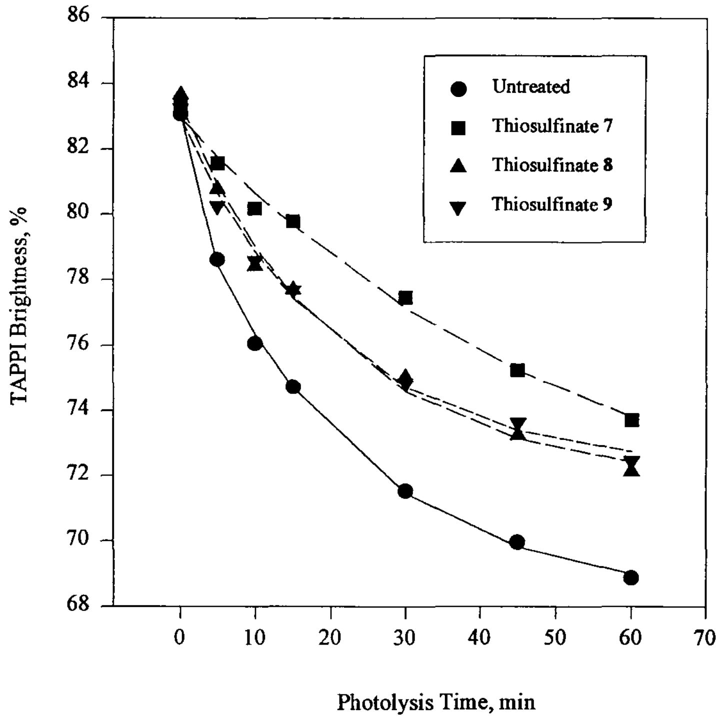

FIGURE 4. TAPPI Brightness of testsheets treated with 0.015 mole of thiosulfinates **7**-**9** as a function of photolysis time (6 black lamps were used).

The photostabilization effects of these additives were examined by treating BCTMP testsheets with 0.015 mole of the additive and irradiating the treated and untreated handsheets with black lamps ($\lambda_{max} \approx 350$ nm) for selected time periods. The relative changes in brightness were then monitored following standard TAPPI testing methods. In summary, the results demonstrate that the thiosulfinates are effective photostabilization agents but this property is governed by the alkyl substituents attached to the thiosulfinate group. In Figure 2, a comparison of the reversion properties of testsheets treated with thiosulfinate **3** or its cyclic analogue **4** clearly shows that the acyclic additive is more effective (Figure 2). Likewise, the photostabilization resulting from **2** is as effective as that produced by **4**.

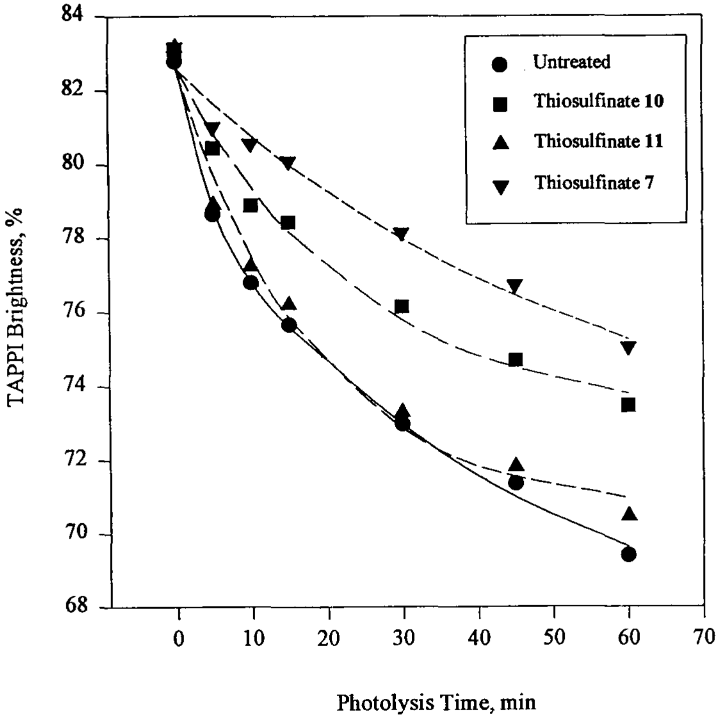

FIGURE 5. TAPPI Brightness of testsheets treated with 0.015 mole of thiosulfinates **7**, **10**, and **11** as a function of photolysis time (6 black lamps were used).

Although the exact factors contributing to this difference in reactivity between acyclic and cyclic thiosulfinates are unknown for mechanical pulps, it has been shown that acyclic thiosulfinates are unstable under ambient condition and are able to undergo the radical scavenging reactions[13, 19] but some cyclic thiosulfinates have been found to be stable for several weeks in the presence of oxygen, light, and air.[20] These factors presumably contribute to the observed photostabilization effects observed in Figure 2. The differences in photostabilization effects observed between **1** and **6** can be tentatively attributed

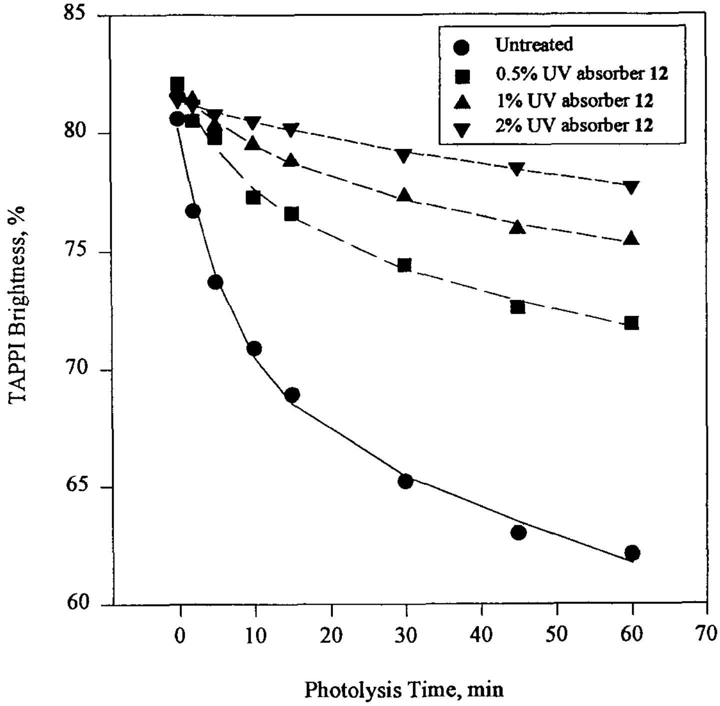

FIGURE 6. TAPPI Brightness of testsheets treated with UV absorber **12** as a function of photolysis time and absorber charge.

to an improved compatibility of the former with the lignocellulosic fibers. Nonetheless, additives **1**, **5**, and **6** were all less effective than **3** (Figure 3).

The effects of electron-donating and electron-withdrawing groups on the photostabilization properties of thiosulfinates were further examined with additives **7**, **8**, and **9** as summarized in Figure 4. Interestingly, additive **7** was found to be a very effective photostabilization agent but placement of either chloro or methyl on the *para*-position substantially reduced this photostabilization effect. These results demonstrate that the photostabilization effect of thiosulfinates is independent upon the availability of an α-hydrogen but is

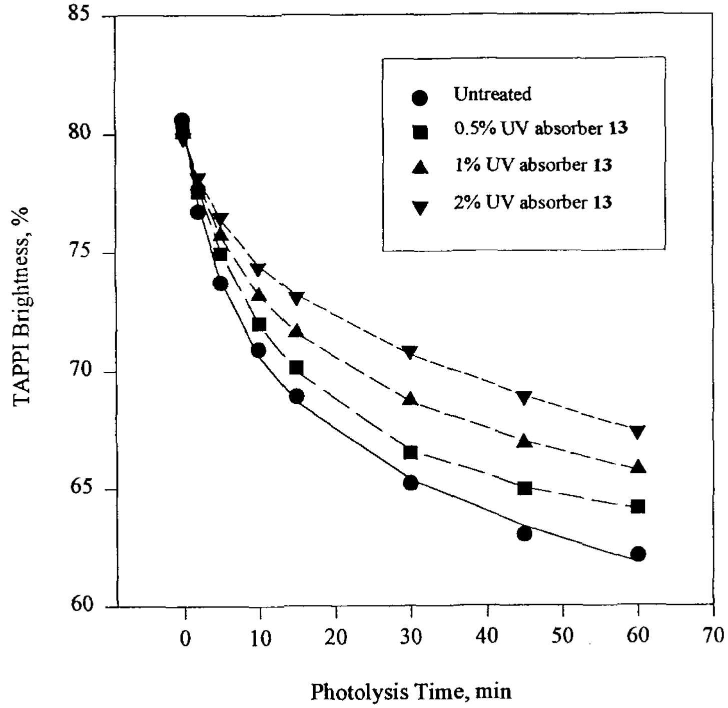

FIGURE 7. TAPPI Brightness of the testsheets treated with UV absorber **13** as a function of photolysis time and absorber charge.

sensitive to the structure of the alpha substituent. The sensitivity of the thiosulfinate photostabilization effect to the nature of the alkyl substituent is further exemplified by comparing the photoyellowing properties of handsheets treated with 2,2'-dithio-2-oxo-dimethane **10** and 2,2'-dithio-2-oxo-di-*t*-butane **11** (see Fig. 5). The poor photostabilization effect of **11** is most likely due to steric considerations.

Synergistic effects. Prior studies by Pan[6] have demonstrated that the use of antioxidants and UV absorbers can provide a very effective means of retarding

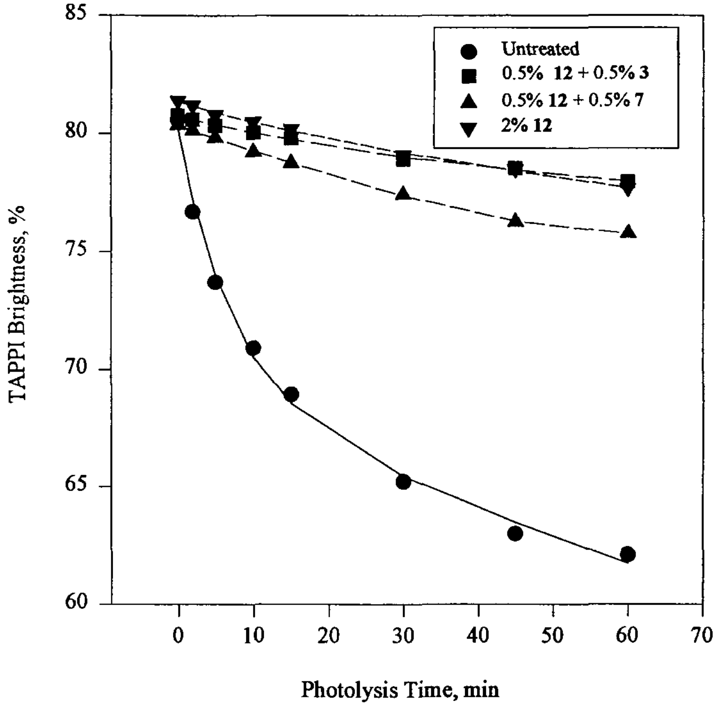

FIGURE 8. TAPPI Brightness of the testsheets treated with 0.5% (wt/wt basis) of UV absorber **12** and 0.5% of thiosulfinates **3** and **7** as a function of photolysis time.

the overall rates of brightness reversion. Indeed, it was shown that the use of 0.5% charge of ethylene glycol bisthioglycolate (thiol) and 0.5% charge of 2,4-dihydroxybenzophenone **12** provided photostabilization effects greater than treating a handsheet with 2% ethylene glycol bisthioglycolate or 2% UV absorber **12** separately.[6] To study the potential benefits of using two additives to photostabilize high-yield pulps, we examined the relative rates of brightness reversion for BCTMP handsheets treated with thiosulfinate **7** or **3** combined with either UV absorber **12** or **13**. Figures 6 and 7 show that the brightness loss decreases when the charge of **12** or **13** increases.

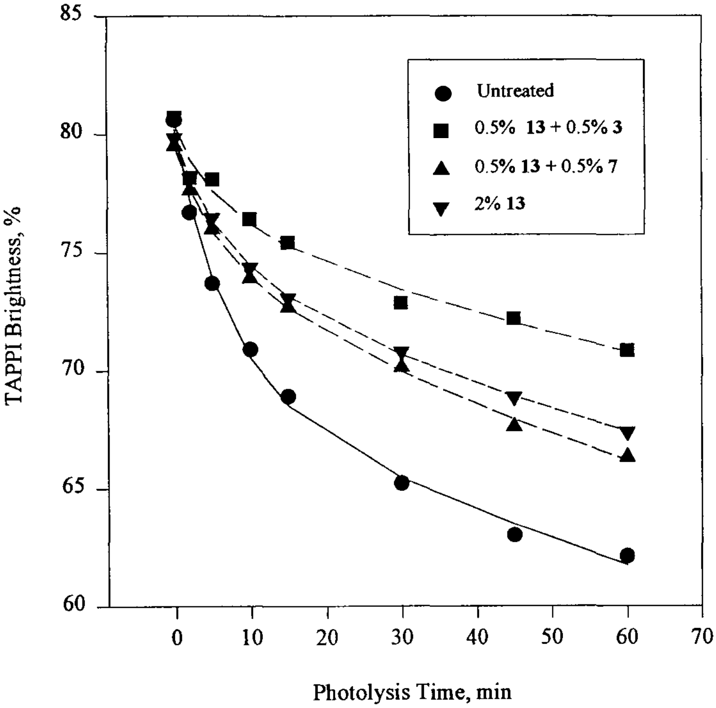

FIGURE 9. TAPPI Brightness of testsheets treated with 0.5% (wt/wt basis) of UV absorber **13** and 0.5% of thiosulfinates **3** and **7** as a function of photolysis time.

The addition of thiosulfinate **7** or **3** clearly enhances the photostabilization effect of the UV absorber, as shown in Figures 8 and 9. In general, the use of 0.5% **3** and UV absorber possesses a higher photostabilization property compared to 0.5% **7** and UV absorber. In each case the use of 0.5% charge of the thiosulfinate and a 0.5% charge of a UV absorber retards photodiscoloration more than can be achieved with at least a 1.5% singular charge of the UV absorber. The use of 0.5% **3** and **12** leads to the lowest brightness loss, indicating a very effective photostabilization agent.

CONCLUSIONS

This study further demonstrates the versatility and applicability of thiosulfinates in retarding the brightness reversion of mechanical pulps. The synergistic effect observed between thiosulfinates and UV absorbers is most likely due to a cooperative photostabilized mechanism in which the UV absorber reduces the light flux on the fiber and the thiosulfinate traps the photoinduced intermediates. The structure-activity investigations have highlighted some limitations in the use of thiosulfinates. Additional studies need to be performed before we completely understand the mechanisms of thiosulfinate photostabilization.

ACKNOWLEDGMENTS

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