

Photoyellowing of mechanical pulp

Part 1: Inhibition of brightness reversion by unsaturated compounds

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ABSTRACT: *The stabilization of bleached chemithermomechanical hardwood pulp against photoyellowing was studied. Impregnation of cyclic and acyclic diene compounds was shown to retard relative rates of brightness reversion. Experimental results demonstrated that the efficiency of stabilization is dependent upon the structure of the diene. Accelerated photo-aging studies suggest that trans,trans-2,4-hexadien-1-ol is as efficient as ascorbic acid at stabilizing mechanical pulp with respect to brightness reversion.*

KEYWORDS: *Antioxidants, color reversion, inhibition, mechanical pulps, yellowing.*

Advances in mechanical pulping and bleaching have provided the means of manufacturing ultra-high-yield pulps that have a TAPPI brightness above 80%. At these levels of brightness, mechanical pulps could potentially be employed in high value paper products such as business forms, reprographic papers, and writing papers. However, the rapid light-induced yellowing of these brightened pulps restricts their use to short-life, low-value paper products. It has been suggested by Cockram that, if the relative rate of light-induced yellowing could be reduced from 3 months to 36 months, the potential market for bleached CTMP would increase four-fold (1).

The use of additives to retard brightness reversion of mechanical pulp has seen increasing attention.

Early research efforts by Nolan and co-workers (2) demonstrated that the addition of near-UV-absorbing compounds such as dihydroxy or tetrahydroxybenzophenone could photostabilize mechanical pulp. Alternatively, the research efforts of Janson and Forsskahl (3) demonstrated the efficiency of several mercaptans to retard brightness reversion of high-yield pulps. These observations were further pursued by Sarkanen (4) and Daneault *et al.* (5). The use of ascorbic acid as an inhibitor of light reversion has also been explored. The effectiveness of this reagent and the proposed mechanism of photostabilization have been investigated by Heitner and others (6). To date, no one additive has met all of the market requirements needed to photostabilize mechanical pulp for commercial applications.

Based upon these photostabilization studies and others, we have initiated a survey study to identify novel methods of retarding brightness reversion. The principal focus of our studies has been the use of unsaturated cyclic and acyclic structures as antioxidants for high-yield mechanical pulps. The chemical literature suggests that unsaturated systems could stabilize mechanical pulp with respect to brightness reversion by several potential chemical mechanisms. In principle, olefinic additives could act as radical traps for hydroxy and phenoxy radicals believed to be generated during photoyellowing of mechanical pulp (7). Furthermore, photolysis studies by Schmidt *et al.* (8) have demonstrated that conjugated dienes can act as triplet quenchers for the excited state of α -guaiacoxycetoveratrone and other lignin-like structures in protic solvents. These and other considerations suggest that the impregnation of mechanical pulp with olefinic additives could yield a novel method of photostabilizing mechanical pulp.

Results and Discussion

The effectiveness of the proposed stabilization reagents was evaluated by impregnating mechanical pulp handsheets with the additive and irradiating with a xenon arc lamp. All irradiation experiments were carried out in triplicate, in the presence of three untreated handsheets. The brightness changes were monitored at specific intervals during irradiation. The stabilization effect of a given reagent on

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retarding brightness reversion of mechanical pulp was monitored by employing the percent stabilization concept developed by Bailey and Lamont (9):

$$\% \text{ Stabilization} = 100 \times [(\Delta \text{Brightness of reference sample} - \Delta \text{Brightness of treated sample}) / \Delta \text{Brightness of reference sample}] \quad (1)$$

Our initial attempts at photostabilization of mechanical pulp employed 1-methoxy-1,3-cyclohexadiene (1,3-CHD), 1-methoxy-1,4-cyclohexadiene (1,4-CHD), and 1,2,4,5-tetramethyl-1,4-cyclohexadiene (TMCHD) impregnants for TMP handsheets. Preliminary studies with 1-methoxy-1,4-cyclohexadiene indicated that the % stabilization effect was dependent upon the solvent the additive was dissolved in. A series of experiments established that methanol was the optimal solvent for impregnating handsheets with these dienes. The stabilization effect for 1-methoxy-1,4-cyclohexadiene was also shown to be dependent upon the application time and based strictly upon experimental convenience, all handsheets were treated with methanolic solutions for 15 min.

Upon completing these preliminary experiments, research efforts were focused on determining the efficiency of photostabilizing TMP handsheets with the three cyclohexadienes. The results of these studies are summarized in Table I, and the data clearly indicate that 1-methoxy-1,3-cyclohexadiene and 1-methoxy-1,4-cyclohexadiene can reduce the rate of brightness reversion. These studies were then repeated employing bleached chemithermomechanical (BCTMP) hardwood pulp handsheets which had initial TAPPI brightness values above 80%. The results of the photostabilization studies, tabulated in Table I, demonstrate that the use of the methoxycyclohexadienes can moderate the relative rate of brightness reversion for low- and high-brightness pulps.

Although these results were encouraging, the methoxycyclohexadienes were difficult to study due to the vola-

I. Photostabilization effects for mechanical pulp handsheets treated with methanolic solutions of cyclohexadienes.

Irradiation time, h	% Stabilization ^a					
	1,3-CHD ^b		1,4-CHD ^c		TMCHD ^d	
	TMP	BCTMP	TMP	BCTMP	TMP	BCTMP
1	32	24	35	31	5	3
2	20	22	18	28	-5	2
4	3	7	-2	16	-3	2

^aInitial brightness value for TMP treated handsheets was 58.6 ± 1.8 (ISO) and for the BCTMP treated handsheets it was 86.0 ± 1.81 (TAPPI).
^b1-methoxy-1,3-cyclohexadiene applied at 0.05 and 0.04 g/g of TMP and BCTMP handsheet, respectively
^c1-methoxy-1,4-cyclohexadiene applied at 0.05 and 0.04 g/g of TMP and BCTMP handsheet, respectively
^d1,2,4,5-tetra-methyl-1,4-cyclohexadiene applied at 0.06 and 0.02 g/g of TMP and BCTMP handsheet, respectively.

II. Photostabilization effects for BCTMP handsheets treated with methanolic solutions of unsaturated acids.

Additive	Application level, g/g handsheet	Period of irradiation, h	Stabilization ^a %
1,4-Dihydro-2-methylbenzoic acid	0.02	1	27
	2	25	
	4	23	
1,4-Dihydro-2-methylbenzoic acid	0.17	1	57
	2	58	
	4	58	
2,4-Hexadienoic acid	0.16	1	40
	2	42	
	4	44	
2,4-Hexadienoic acid Sodium salt	0.04	1	0
	2	-1	
	4	9	
2,4-Hexadienedioic acid	0.03	1	20
	2	14	
	4	11	
2,5-dimethyl-2,4-hexadiene-dioic acid	0.06	1	8
	2	11	
	4	14	

^aInitial TAPPI brightness for treated handsheets was 86.3 ± 1.1 .

III. Photostabilization effects for BCTMP handsheets treated with methanolic solutions of *trans,trans*-2,4-hexadien-1-ol and ascorbic acid.

Additive	Application level, g/g handsheet	Period of irradiation, handsheet h	Stabilization ^a %
2,4-Hexadien-1-ol	0.03	1	56
		2	51
		4	49
2,4-Hexadien-1-ol	0.05	1	88
		2	78
		4	75
Ascorbic acid	0.03	1	56
		2	52
		4	49
Ascorbic acid & 2,4-Hexadien-1-ol ^b	0.06	1	74
		2	74
		4	72

^aInitial TAPPI brightness for treated handsheets was 87.0 ± 0.7 .
^bHandsheets were soaked in a 0.01 M methanolic solution of *trans,trans*-2,4-hexadien-1-ol and ascorbic acid.

tility of these structures. A carboxylic acid functional group should prevent volatilization of the inhibitor and enhance binding to the fibers; therefore handsheets of BCTMP were impregnated with 1,4-dihydro-2-methylbenzoic acid and photolysis studies were conducted (Table II). The data indicate that this diene is a moderately effective stabilizing reagent. As anticipated, the efficiency of photostabilization was shown to be charge dependent. Furthermore, the % stabilization effect was found to be relatively stable over the 4 h of photolysis, unlike the methoxycyclohexadienes. The differences in stabilization after 4 h of irradiation were tentatively attributed to the differences in volatility of the compounds. Several other unsaturated cyclic systems were examined, such as 1,3-cycloheptadiene, 1,3,5,7-cyclooctatetraene, 2-furoic acid, and furfuryl alcohol, but all of these compounds failed to retard relative rates of brightness reversion.

Research efforts were then focused on studying the photostabilization effects of acyclic unsaturated compounds. The initial additive examined was 2,4-

hexadienoic acid. This compound was of interest since Robinson *et al.* (10) had reported it possessed mild antioxidant properties for mechanical pulp during bleaching and sheet drying. Accelerated photo-aging studies suggested that the photostabilization effect for 2,4-hexadienoic acid was approximately 40% over a period of 4 h, as summarized in Table II. A comparison of these results with those noted for 1,4-dihydro-2-methylbenzoic acid suggests that both additives provide comparable reductions in the relative rate of brightness reversion.

The photostabilization effect of 2,4-hexadienoic acid promoted our interest, and we initiated a study to determine if structural modification of this acid could enhance the observed effect. Preliminary studies indicated that the sodium salt of 2,4-hexadienoic acid actually accelerated brightness reversion. Furthermore, impregnation of 2,4-hexadienedioic acid or 2,5-dimethyl-2,4-hexadienedioic acid onto BCTMP handsheets failed to significantly retard the relative rates of brightness reversion. Table II summarizes these results.

In contrast to these results, the application of *trans,trans*-2,4-hexadien-1-ol onto BCTMP handsheets was shown to be very effective at retarding brightness reversion, as reported in Table III. Accelerated photo-aging studies demonstrated that a 5% application of the dienol on BCTMP handsheets afforded a % stabilization effect in excess of 80% after 1 h of irradiation. Continued irradiation reduced the % stabilization effect to 75% after 4 h, nonetheless this value was significantly larger than that noted for any other unsaturated systems studied. The photostabilization efficiency of *trans,trans*-2,4-hexadien-1-ol was evaluated by repeating the accelerated photo-aging experiments in the presence ascorbic acid impregnated BCTMP brightness pads as reference handsheets. A comparison of the % stabilization effect for *trans,trans*-2,4-hexadien-1-ol and ascorbic acid indicated that both reagents were nearly equally effective in their ability to retard photoyellowing, as summarized in Fig. 1. The application of both ascorbic acid and 2,4-hexadien-1-ol onto a BCTMP handsheet yielded handsheets which maintained a stabilization effect of approximately 73% throughout the 4 h of irradiation in the solar simulator.

The successful commercial implementation of a photostabilization reagent for BCTMP and other ultra-high-yield mechanical pulps is dependent upon several issues, including thermal stability of the additive. The latter condition has imposed a serious challenge to the application of *trans,trans*-2,4-hexadien-1-ol for retardation of photoyellowing. A series of long-term experiments indicated that the unsaturated alcohol impregnated onto BCTMP accelerates thermal reversion (see Table IV). The use of the mixture of ascorbic acid and *trans,trans*-2,4-hexadien-1-ol also exhibited accelerated long-term thermal reversion properties. Current research efforts are directed at understanding the important chemical mechanisms by which *trans,trans*-2,4-hexadien-1-ol contributes to accelerated thermal

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yellowing and photostabilization of mechanical pulp samples.

Conclusion

The results of these studies indicate that certain diene systems can retard the relative rates of brightness reversion for BCTMP hardwood pulps. The reduction in brightness reversion is dependent upon the chemical and physical properties of the additive. The most effective unsaturated system found to retard photoyellowing of BCTMP hardwood samples was *trans,trans*-2,4-hexadien-1-ol. Accelerated photo-aging experiments suggest that this additive is as efficient as ascorbic acid in photostabilizing BCTMP handsheets. The value of the dienes as a commercial photostabilizer is questionable because the material appears to contribute to thermal reversion, nonetheless these results have suggested alternative methods of photostabilizing mechanical pulp and we are currently pursuing these avenues of research.

Experimental

Chemical

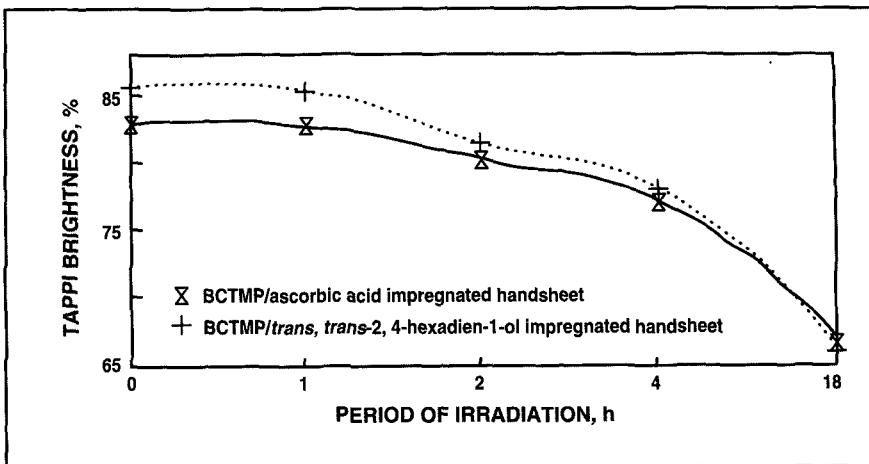
All solvents and reagents employed were commercial products and were used as received.

Pulp

Thermomechanical pulp was prepared by preheating juvenile southern pine chips for 10 min at 220 kPa saturated steam prior to refining in a two-stage Sunds Defibrator CD-300 pressurized first-stage refiner and a Defibrator ROP-20 atmospheric second-stage refiner.

BCTMP hardwood samples were obtained from a commercial source and used without further modification. Optical TMP and BCTMP handsheets were prepared according to TAPPI Test Methods T 218 om-83 and T 205 om-88. After being air-dried in the dark at room temperature (22°C and 50% RH), the handsheets were washed in

1. Comparison of the photostabilization effects for *trans,trans*-2,4-hexadien-1-ol and ascorbic acid impregnated BCTMP handsheets. Impregnated handsheets were photolyzed simultaneously; each handsheet had 0.03 g of additive/g of handsheet.



IV. Thermal reversion effects for treated and untreated BCTMP handsheets^a.

Days in darkroom	TAPPI brightness for BCTMP handsheets		
	Untreated	2,4-Hexadien-1-ol	2,4-Hexadien-1-ol & ascorbic acid
0	87	88	87
3	87	85	86
8	86	86	83
19	86	81	—
33	86	—	75
87	85	76	62

^aHandsheets were soaked in either a 0.09 M methanolic solution of *trans,trans*-2,4-hexadien-1-ol or a 0.09 M methanolic solution of *trans,trans*-2,4-hexadien-1-ol and ascorbic acid.

methanol to remove extractives. Removal of the extractives was required to allow for accurate determination of the amounts of additive applied onto the handsheets. Literature results (11) indicate that extractives do not contribute to photoyellowing of mechanical pulp, and their removal does not influence the overall rate of brightness reversion. After drying the handsheets under vacuum, brightness was measured according to TAPPI Test Method T 452 om-87 and/or T 534 om-86. 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 and brightness values were measured. 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 except that they were not treated with the additive.

Accelerated yellowing studies

The accelerated photo-aging 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. An exhaust fan

provided air circulation to minimize heating of the sample. Three impregnated handsheets and three reference brightness pads were placed 10.5 in. from the lens of the lamp and irradiated simultaneously. Immediately after photolysis the handsheets were stored in the dark until brightness values were recorded.

The long-term thermal reversion studies were accomplished at room temperature with the samples stored in a darkroom. **■**

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