

Effect of Borate and Boric Acid on Brightness Reversion of Lignin Containing Pulps

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Advances in thermomechanical and chemithermomechanical pulping and in bleaching provide the means of manufacturing high-yield pulps with brightness values above 80%. If it were not for the tendency of these pulps to yellow on use, they would be suitable for use in most printing grades. However, on exposure to light or heat, the lignin within the pulp forms highly colored structures or chromophores. Considerable research has been devoted to the development of processes or additives that will inhibit the formation of these chromophores. To date, no commercially viable solutions have been identified. This research presents data that show the use of low-cost combinations of sodium borate and boric acids can reduce photoyellowing of high yield pulps. The use of these compounds to reduce photoyellowing was suggested by their application in preventing wood discoloration and their use as free radical scavengers in fire retarding cellulose. The pulps employed in this study were commercial high-yield SW (black spruce) and IW (aspen) chemithermomechanical. Using standard TAPPI procedures, handsheet were produced from these pulps and treated with combinations of sodium borate, boric acid and ascorbic acid. After accelerated photoaging, the handsheet brightness was measured at 457-nm and brightness reversion determined using the post color number. The results from these experiments show that the combination of boric acid and sodium borate can reduce photoyellowing by as much as 30%. Continuing research with these agents should result in more effective applications and should provide a unique approach to reducing the yellowing of high yield pulps.

INTRODUCTION

Pulp yields of 80 percent or more can be obtained with chemithermomechanical or thermomechanical pulping. With two-stage bleaching sequences, (either two peroxide stages or a hydrogen peroxide stage followed by a sodium hydrosulfite stage), these lignin containing pulps can be bleached to TAPPI brightness values greater than 80 percent.

The major markets for these pulps are short life products such as newsprint, advertising inserts and catalogues. The brightness and strength properties of these pulps are sufficient for their use as furnish components for most publication grades. However, because of their lignin content, these pulps experience rapid yellowing on exposure to light.

Techniques that have been investigated to reduce brightness reversion include modification of the lignin structure by alkylation or acylation, application of UV adsorbing compounds, and the use of free radical scavengers. Although some of these techniques have shown considerable promise in reducing

photoyellowing, as reviewed by Heitner (1), they are too expensive for commercial application. The most successful methods for inhibiting light-induced yellowing of lignin containing papers are those that scavenge free radicals.

This paper presents the results of a study of the effect of boric acid and sodium borate on light induced yellowing of lignin containing pulps. Although, no use of either sodium borate or boric acid for reducing light induced yellowing of mechanical pulps was found in the literature, these compounds do have properties that may support their use as brightness reversion inhibitors. For example, Domburg, *et al.* (2) in a review of the reactions of borate derived chemicals with wood and cellulose during pyrolysis noted that boric acid suppresses both the dehydration reaction during the early stage of pyrolysis and the free radical induced degradation reaction during thermal decomposition. Chow (3) found that boric acid suppressed the thermal induced yellowing of polyethylene-wood based molding compounds during the molding process. Boric acid and sodium borate were also found to reduce the undesirable odor associated with the molding process.

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Photoyellowing

In his review of brightness reversion, Heitner (1) states that on exposure to light the brightness of high lignin pulps can be reduced by as much as 30 points in 6-8 months of normal use. This compares to a corresponding brightness reduction of 3 points in kraft pulps exposed to similar conditions. Photoyellowing is normally assessed as a loss in brightness based on reflectance at a given wavelength, usually at 457 nm. Since the chromophore concentration is not a linear function of brightness, the use of such brightness measurements to indicate photoyellowing can be misleading. Because of this difficulty, Giertz (4) proposed the use of P. C. (post color) number as an indicator of chromophore concentration. The P. C. number is related to the ratio of the specific absorption (k) to specific scattering (s) before and after aging as shown in Eqn (1).

$$P.C. Number = 100 \left[\left(\frac{k}{s_{aa}} \right) - \left(\frac{k}{s_{ba}} \right) \right] \quad (1)$$

The ratio k/s is defined by Kubelka-Munk equation (1) as shown below as Eqn (2).

$$k/s = (1 - R_{\infty})^2 / 2 R_{\infty} \quad (2)$$

One assumption of the Kubelka-Munk equations is that the chromophores are uniformly distributed throughout the sample. Since this is unlikely to be the case with a photoyellowed paper, the use of the P.C. number provides only an approximation to chromophore levels.

EXPERIMENTAL

Types of Paper Studied

The hardwood (aspen) and softwood (spruce) chemithermomechanical pulps used in this study were obtained from a Canadian pulp mill. These commercial pulps were produced using sulfite pretreatment followed by mechanical defibrillation and bleached using a two stage peroxide process to a TAPPI brightness of 80 to 85.

After refining this commercial pulp in the PFI mill, handsheets were made following TAPPI method T-205. It is well known that if tap water is used for handsheet production, the iron content of tap water may sufficiently reduce the brightness. Heitner (1) notes that the ferric ion (Fe^{3+}) could only cause an immediate decrease in pulp brightness but also accelerates brightness reversion. Gupta (5) found that as little as 10 ppm to 20 ppm of ferric can result in an increase of 5 pts. in the P. C. number. Because of the possibility of dissolved metals in the tap water, distilled water was used for the production of all handsheets production. The pulp itself may contain metal ions that can adversely affect brightness. Since the objective of this study was to determine the affect of boron compounds on commercial CTMP, no attempt was made to remove the residual metal ions from the pulp.

Methods

The handsheets described above were treated with various levels of the chemicals being studied. The principal boron chemicals used were sodium metaborate and boric acid. Since ascorbic acid is a recognized photoyellowing inhibitor and its effects have been accurately documented, it was used as a reference inhibitor. The effect of ascorbic acid was first described by Kringstad (6) and this compound continues to be studied. Recent work with ascorbic acid includes that of Schmidt and Heitner (7), and Pan *et al.* (8). These studies show that the addition of 1 to 5 % ascorbic acid by weight can reduce brightness reversion by as much as 25%.

In addition to studying these individual compounds, the interactions of boric acid with borate and ascorbic acid was also investigated. The compounds being studied were dissolved in water and sprayed onto the dried handsheets. TAPPI brightness – Method 452 – was measured before and after treatment of the handsheets.

A Sun-Test CPS "Fad-O-Meter", set at an intensity of 500 watts/m², was used for the accelerated aging. This unit was chosen since it provides a wavelength very close to that of natural sunlight. Artificial wavelengths for the accelerated aging were rejected, since there is no single standard. The Sun-Test unit provides an energy output such that one hour in the test chamber equals 12 hours outside sunlight intensity in June. In earlier research, Bailey *et al.* (9) found that 12 hours in an artificial aging system of similar design is equivalent to 6 months of normal light induced aging.

Experimental Design

The initial experiments were designed to determine the primary effects of sodium borate (borax), boric acid and ascorbic acid, as well as their interactions on reducing photoyellowing. The experiments reported here focused on effect of these compounds in treating softwood (black spruce). In later experiments, the effect of these compounds on hardwood pulps was also investigated.

During the accelerated aging of the paper, the apparatus was at a humidity of 50 % R.H. and 23 °C. Because of the heat from the high intensity light source, the samples were maintained at 35 °C. The experimental design consists of 64 cells with 32 distinct chemical addition levels and is shown in Table 1. The numbers in the table are the order in which the experiments were conducted. During the aging experiments, half of the cells were exposed to light, while the other half was exposed to the same temperature (35 °C) and but not light.

Table 1: Experimental Design

		<i>Exposed to Light</i>				<i>NOT Exposed to Light</i>				
		Boric Acid (%)				Boric Acid (%)				
		0	1	2	4	0	1	2	4	
Sodium Borate (%)	0	1	9	17	25	0	5	13	21	29
	1	2	10	18	26	1	6	14	22	30
	2	3	11	19	27	2	7	15	23	31
	4	4	12	20	28	4	8	16	24	32
Ascorbic Acid (%)	0	33	41	49	57	0	37	45	53	61
	1	34	42	50	58	1	38	46	54	62
	2	35	43	51	59	2	39	47	55	63
	4	36	44	52	60	4	40	48	56	64

To provide statistical data on the reproducibility of the experimental results duplicate experiments were conducted. The base line duplicate experiments with handsheets with no treatments and 4% boric acid addition are shown in Figure 1.

As seen in Figure 1, the experimental results in this study are highly reproducible. In the chemical addition replication, there is an additional error introduced with level of chemical addition. This is especially apparent at the lower addition levels and slightly increases the experimental error.

RESULTS AND DISCUSSION

Table 2 contains a summary of the experimental results obtained in this study. The cells in this table correspond to those shown in Table 1 and contain brightness values before and after 12 hours of aging. The first value in each cell is the brightness after chemical treatment but before aging and the second value is the brightness after 12 hours of aging. The two columns of data are samples that were exposed to light and samples under the same conditions but shielded from the light. As shown in Table 2, the samples not exposed to light showed no reduction in brightness.

Initial Beaching with Inhibitor Addition

The addition of either ascorbic acid or boric acid to the handsheets resulted in a slight initial increase in TAPPI brightness, usually less than one-half of a point. This increase in brightness has been attributed by the donation of hydrogen to unsaturated lignin structures. In contrast to the initial increase in brightness with these acids, the addition of the more alkaline sodium borate decreased the brightness by 1 to 2 points. This reduction in brightness with the sodium borate may be a result of alkali induced darkening of the paper.

Ascorbic Acid: The effect of ascorbic acid addition on brightness stabilization is shown in Figure 2. In these experiments, four-percent addition of ascorbic acid decreases photoyellowing by approximately 25 percent. This result is consistent with the previous studies (6-8) with respect to the ability of ascorbic acid to reduce photoyellowing. This consistency adds confidence in the experimental and analyses employed in this study.

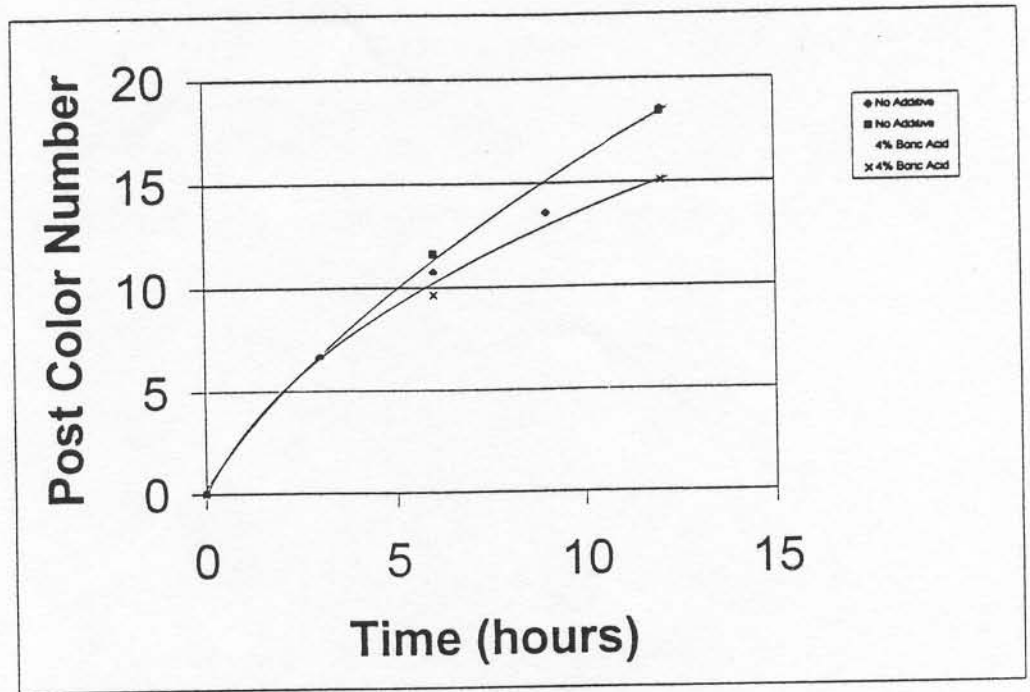


Figure 1, Duplicate Photoyellowing Experiments

Table 2, Summary of TAPPI Brightness before and after Twelve Hours of Accelerated Aging

		<i>Exposed to Light</i>				<i>NOT Exposed to Light</i>			
		Boric Acid (%)				Boric Acid (%)			
		0	1	2	4	0	1	2	4
Sodium Borate (%)	Initial	80.8	81.6	81.4	81.4	80.9	80.6	81.9	81.9
	After	53.0	53.2	55.5	56.0	81.0	81.3	82.1	81.9
	Initial	79.6	80.7	82.0	82.5	79.5	80.9	81.3	81.9
	After	52.0	53.7	56.3	56.7	79.2	81.0	81.6	81.8
Ascorbic Acid (%)	Initial	78.9	80.3	81.7	81.8	78.6	80.3	81.6	81.7
	After	52.1	53.9	56.8	58.0	78.5	80.0	81.7	82.0
	Initial	78.8	79.4	80.5	81.9	78.8	78.4	81.1	81.8
	After	52.3	53.8	56.5	58.2	78.1	79.0	82.1	81.7
Sodium Borate (%)	Initial	81.1	81.2	81.6	81.7	80.9	81.7	81.7	81.6
	After	53.2	52.7	53.8	56.1	81.0	81.5	81.6	81.8
	Initial	81.6	81.7	81.1	82.1	81.1	81.6	81.1	81.3
	After	53.9	54.7	56.2	58.2	81.3	81.6	81.1	81.4
Ascorbic Acid (%)	Initial	81.9	81.5	82.1	81.8	81.6	81.9	81.9	81.3
	After	55.0	55.1	57.7	59.4	81.3	81.6	81.7	81.7
	Initial	81.9	82.0	82.2	83.1	81.9	81.9	82.1	81.5
	After	56.7	56.6	58.2	60.1	81.4	81.5	81.9	82.0

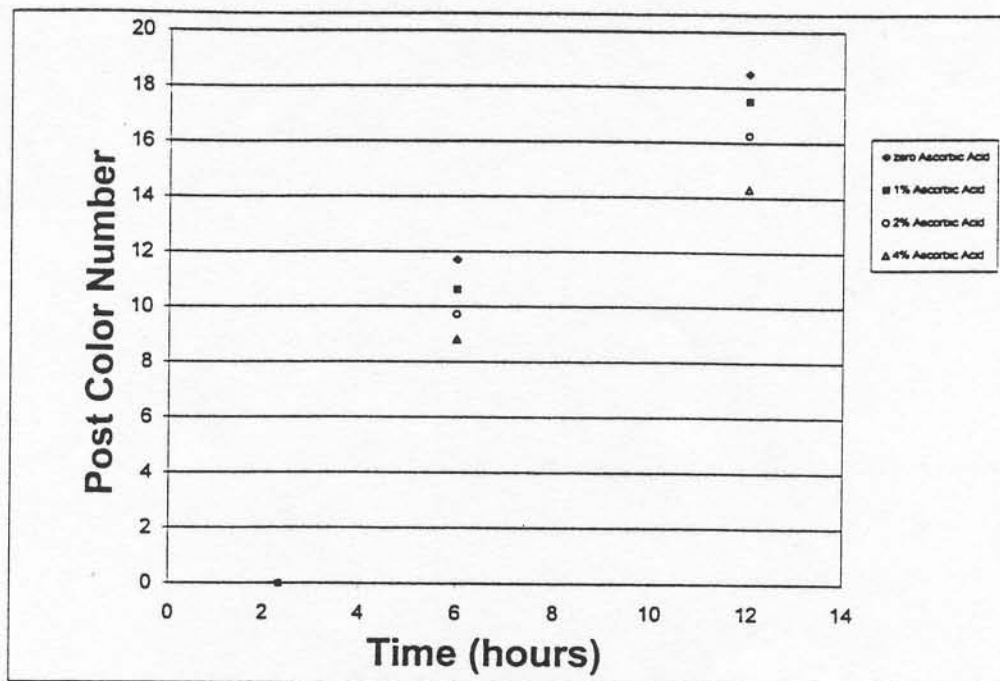


Figure 2, Effect of Ascorbic Acid on Photo-Induced Brightness Reversion

Effect of Sodium Metaborate Plus Boric Acid on Photoyellowing

The focus of this study was the effects of borate and/or boric acid on photoyellowing. In situations where these compounds are used as fire retardant, they may be used individually or in combination. Their effects, when used in combination, are sufficiently different from their individual effects. Therefore, this work examined both individual and combinations of these compounds.

Borate The addition of sodium borate to the handsheets resulted in an immediate one to two point reduction in brightness. Accelerated photoaging brightness measurements showed that the borate did not reduce photoyellowing. During these experiments, the brightness of the borate treated sheets remained approximately 1 to 2 brightness points lower than the control.

Boric Acid The effect of boric acid on photoyellowing was studied by treating the handsheets with boric acid (1 to 4% based on sheet weight) and subjecting the sheets to accelerated aging. The addition of boric acid immediately increased the brightness of the handsheet

by approximately one point. Figure 3 shows the ability of boric acid to reduce photoyellowing. After 12 hours of accelerated aging, the addition of boric acid reduced the post color number by about 20 percent.

Interaction of Brightness Reversion Inhibitors

Figure 4 shows the effect of combination of boric acid with borate and Figure 5 shows the effect of the combination of boric acid with ascorbic acid.

Figures 4 and 5 demonstrate that the combinations of boric acid and borate or boric acid and ascorbic acid reduce brightness reversion to a greater extent than is observed with the use of the individual additives.

The combination of boric acid with sodium borate has a synergistic effect on inhibiting brightness reversion. Without boric acid present, the use of borate results in a slight initial darkening of the paper, and does not reduce light induced yellowing. However, with boric acid, the addition of sodium borate increases the effectiveness of the boric acid. With ascorbic acid, the use of boric acid also increases the effectiveness of the treatment, but it is unclear if it is simply an additive or synergistic effect.

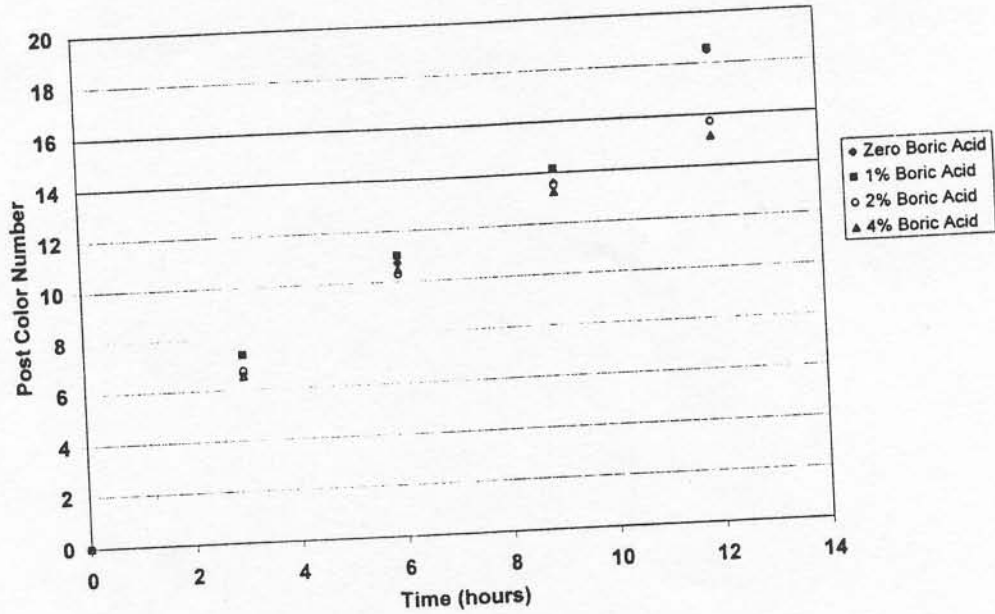


Figure 3, Effect of Boric Acid on Photo-Induced Brightness Reversion

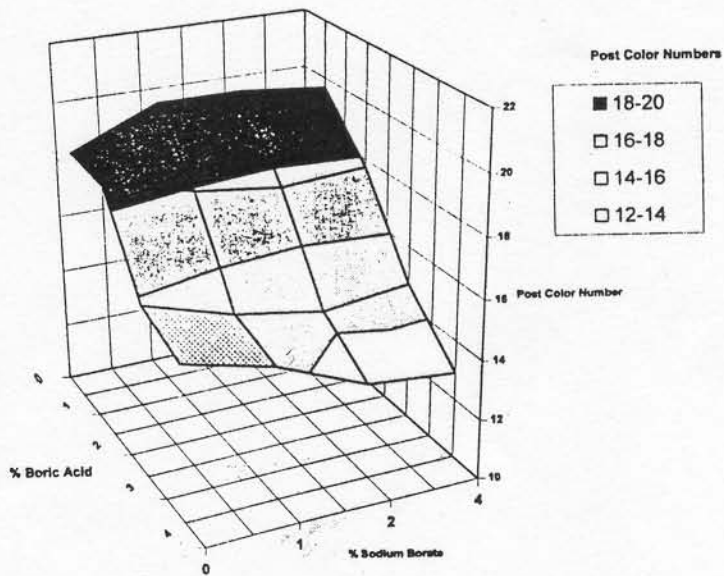


Figure 4, Effect of Sodium Metaborate Borate and Boric Acid on Photo-Induced Brightness Reversion

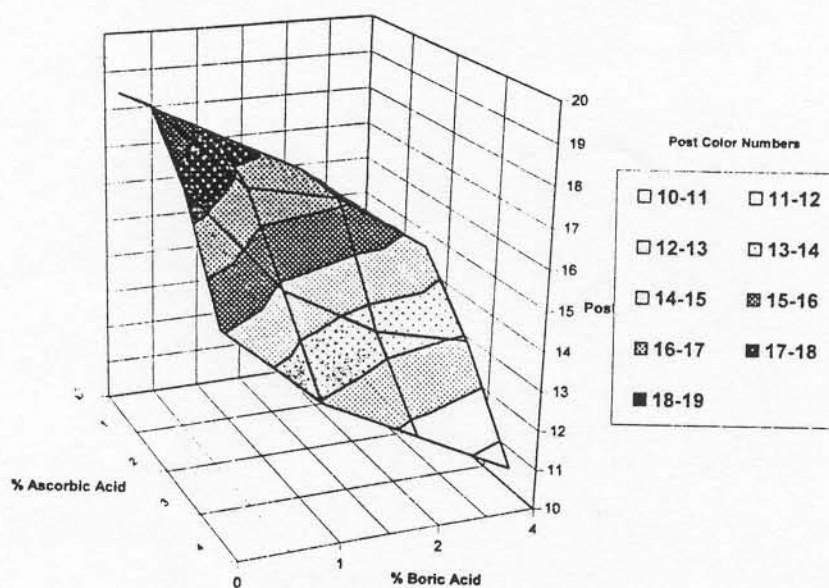


Figure 5, Effect of Ascorbic Acid and Boric Acid on Photo-Induced Brightness Reversion

Although boric acid and sodium borate are relatively inexpensive compared to additives such as ascorbic acid, the addition levels used in this study are likely too high to justify general commercial application. Some specialty applications may provide opportunities for the use of borate and boric acid. Possibilities may include the use of these materials in specialty coatings.

CONCLUSIONS

These results shown above demonstrate that boric acid used alone or in combination with sodium reduces photoyellowing of high yield mechanical pulps. The effectiveness of these compounds in reducing photoyellowing compares favorably to the effect of ascorbic acid.

The experimental approach used in this study produce results that were reproducible and consistent with the known effect of ascorbic acid. The initial results of the effect of boric acid and sodium borate are encouraging and continuing research in this project includes studies into the mechanism through which borate and boric acid reduce photoyellowing and optimization of the chemical combinations and addition process. A mechanistic understanding of the actions of boric acid

and sodium borate should provide insight into the more effective use of these compounds.

This work shows that boric acid by itself or in combination with sodium borate or ascorbic acid reduces light induced yellowing of lignin containing pulps. Although the effect achieved with these compounds at the addition levels used in this study compares favorably with that of other brightness reversion inhibitors, the levels required are likely too high for commercial applications. If the mechanism through these function is identified, it is likely that more effective application process can be develop. This may then result in commercially economic solutions to light induced brightness reversion of high lignin containing mechanical pulps.

NOTATION

- k specific adsorption
- s specific scattering
- ba before aging
- aa after aging
- R_{∞} reflectance value with multiple sheet backing

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