

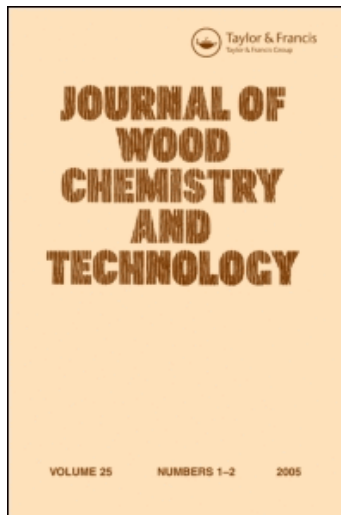
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Dye Stability in the Presence of Hydrogen Peroxide and Its Implication for Using Dye in the HYP Manufacturing Process

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Abstract: Dye can be used to improve the optical properties of high-brightness market high yield pulp (HYP). In this study, we aimed to develop a practical method of using dye for this purpose. The dye performance in the presence of residual hydrogen peroxide at different pH levels was determined. At a pH of 7.5, the dye performance was not affected by the presence of hydrogen peroxide; at a pH of 8.5, the dye performance decreased slightly; at a pH of 9.5 or higher, the dye effectiveness decreased significantly. Based on these results, a method of using dye to decrease the yellowish hue of the HYP in its manufacturing process is proposed.

Keywords: b*, CIE whiteness, dye, high yield pulp, HYP manufacturing process, hydrogen peroxide, optical properties

INTRODUCTION

HYP has been gaining wide applications in many paper grades with its unique properties.^[1–3] Generally, HYP was used as a substitution for hardwood bleached kraft pulp (HWBKP). Depending on the specific paper grades, the HYP substitution rate can be in the range of 0–40%.^[1]

Although the HYP can be bleached economically to 80–85% ISO brightness, it still looks more yellowish than the HWBKP in its appearance because of the high lignin content and some other color materials. For example, an aspen HYP (Freeness/brightness, 325/85 grade) has a brightness of 85% ISO, but its CIE whiteness of 64.8 is lower than that of HWBKP (76.0); and the b*

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values are 6.2 and 4.0 for the same aspen HYP and HWBKP pulp, respectively. In many applications, the yellowish color of the HYP is undesirable because it brings about some potential negative effects on the final products.

Most recently, we started a project aiming to improve the optical properties of HYP by using Optical Brightening Agents (OBA).^[4–6] Dyes are also widely used in the papermaking process for the appropriate control of shade/color of the paper sheets. There are different kinds of dye available (e.g., basic dyes, direct dyes, and pigment dyes). For the control of shade or tinting of paper, usually a very small amount of dye is needed. We used a cationic basic dye (Violet 57L NA) in this study. It was well documented^[7] that blue/violet dyes can mask a yellowish shade, which is responsible for the high b^* value and low whiteness of the HYP. Basic dyes have a strong affinity toward pulp fibers, and can attach to pulp fibers without any fixatives.^[7] They are widely used to suppress the yellow hue of unbleached and mechanical pulp fibers in the production of newsprint, telephone directories, and light weight coated papers.^[8] When a dye was added to the paper, it filtered off some shades that otherwise would have been reflected.^[7] For this reason, although the CIE whiteness and b^* value are improved by using blue/violet dyes, the brightness would always decrease to some extent, depending on the amount of dye added. This is in contrast to the effect of using OBA, which can convert absorbed UV light into visible blue light, thus increasing the brightness. Some of our early results^[9,10] have indicated that the addition of a small amount of dyes to HYP and HYP-containing paper sheets can effectively improve the whiteness and b^* of the products, and that dyes can be complementary to OBA and peroxide bleaching to improve the optical properties of HYP. In this project, we explored the potential of using dye in the HYP manufacturing process to improve the optical properties of the market HYP. This was done by adding dye at the completion of the peroxide bleaching process.

EXPERIMENTAL

Materials

An aspen HYP pulp, which was sampled at the exit of the bleaching tower, was received from a mill in Canada. The pulp slurry contained about 3.7 g/L residual peroxide; its consistency was 30.3%, and its pH was 6.5. They were stored in a cold room until use. A cationic basic dye (Violet 57L NA) was from BASF. Other chemicals used in this study were purchased from Fisher Scientific.

UV-VIS Spectra of Dye Solutions

The dye stability was determined by following the absorption on a UV-vis spectrophotometer as functions of pH and the H_2O_2 concentration. The initial

dye concentration was 3 mg/L. The UV-VIS spectra were recorded using a Milton Roy Spectronic 1001 + spectrophotometer. The cuvette width was 1 cm.

Dyeing Process

The dyeing process was performed in plastic bags under the following conditions: 10% pulp consistency, 80°C and 20 min. The desired amounts of H₂O₂ were added into the plastic bags and mixed with the pulp thoroughly. A sodium hydroxide solution (1N) was used to produce a desired initial pH. The pulp slurry was pre-heated for 5 min to get the target temperature (80°C). The dye was added into the pulp slurry and then mixed with the pulp. At the completion of required time, the pulp suspension was cooled down immediately and then filtered using a Büchner funnel with a 200-mesh polymer screen. The pulp cake was diluted and acidified to pH 5 with sulfuric acid, then made into hand-sheets by following the TAPPI method. The optical properties of the resultant handsheets were determined on a Technibrite TB-1C brightness tester.

RESULTS AND DISCUSSION

Dye-H₂O₂ System in the Absence of Pulp Fibers

The maximum absorbance of this cationic violet basic dye was at 590 nm, which was used to determine the dye concentration in solutions. Figure 1 shows the

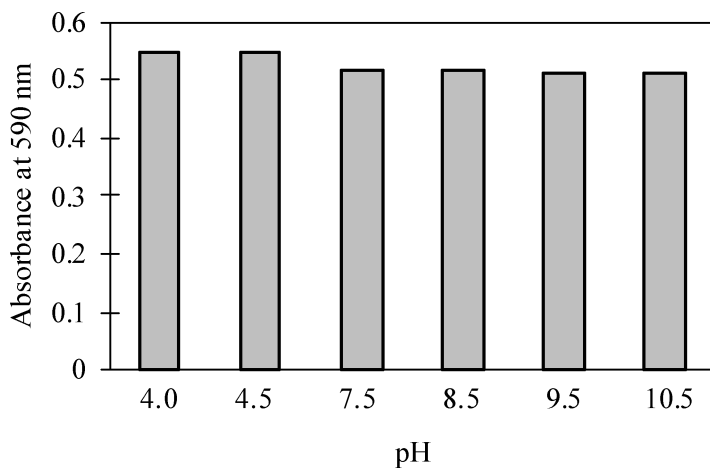


Figure 1. Dye stability at different pH levels (absorbance was measured 20 min after the solution was prepared at room temperature, with 3.0 ppm dye but no hydrogen peroxide). The dye concentration was based on pulp assuming that the solution was equivalent to the liquid phase of a pulp suspension of 10% pulp consistency.

Table 1. Dye stability in the presence of hydrogen peroxide at different pH (no pulp addition)

Peroxide concentration (% on pulp*)	Absorbance at 590 nm at different pH					
	4.0	4.5	7.5	8.5	9.5	10.5
0	0.547	0.531	0.516	0.513	0.483	0.457
0.5	0.546	0.532	0.384	0	0	0
1	0.546	0.520	0.361	0	0	0
2	0.548	0.502	0.191	0	0	0
4	0.546	0.428	0.132	0	0	0

Conditions: 3 ppm dye, 20 min, room temperature.

*Peroxide and dye concentrations were based on pulp, assuming that the solution was equivalent to the liquid phase of a pulp suspension of 10% pulp consistency.

dye stability as a function of pH. One can find that the absorbance decrease was small, indicating that the cationic dye tested is stable under the conditions studied.

The effect of the hydrogen peroxide concentration on the dye stability is shown in Table 1. At pH 4.0, the dye solution was stable. However, when the pH increased, some of the dye reacted. At pH of 8.5 or above, the dye studied was destroyed completely by the alkaline peroxide solution.

Based on the aforementioned results, one can conclude that in the absence of pulp fibers, the dye solution was stable in the H₂O₂-containing system when its pH was 4 or less; however, as the pH increased, the dye stability decreased. At pH of 8.5 or higher, the dye reacted very quickly with hydrogen peroxide.

Dye-H₂O₂ System in the Presence of Fibers

Again we studied two systems: (1) in the absence of hydrogen peroxide at different pH levels and (2) in the presence of hydrogen peroxide at different pH levels. As an indicator for the dye stability, we determined the dye performance in terms of increasing the CIE whiteness and decreasing the b* value.

Figure 2 shows that the dye performance in terms of increasing the CIE whiteness and decreasing b* was negatively affected somewhat as the pH was increased from 7.5 to 10.5. It is noted that in the absence of dye, the CIE whiteness also decreased somewhat while the b* increased, as the pH increased, and it can be explained by the alkaline darkening effect. Therefore, part of the CIE loss at a pH of 10.5 when 4 ppm dye was added (in comparison with that of pH 7.5), is due to the alkaline darkening effect, however, the CIE whiteness decrease of the dye-added pulp at pH 10.5 was still higher than that of the dye-free pulp.

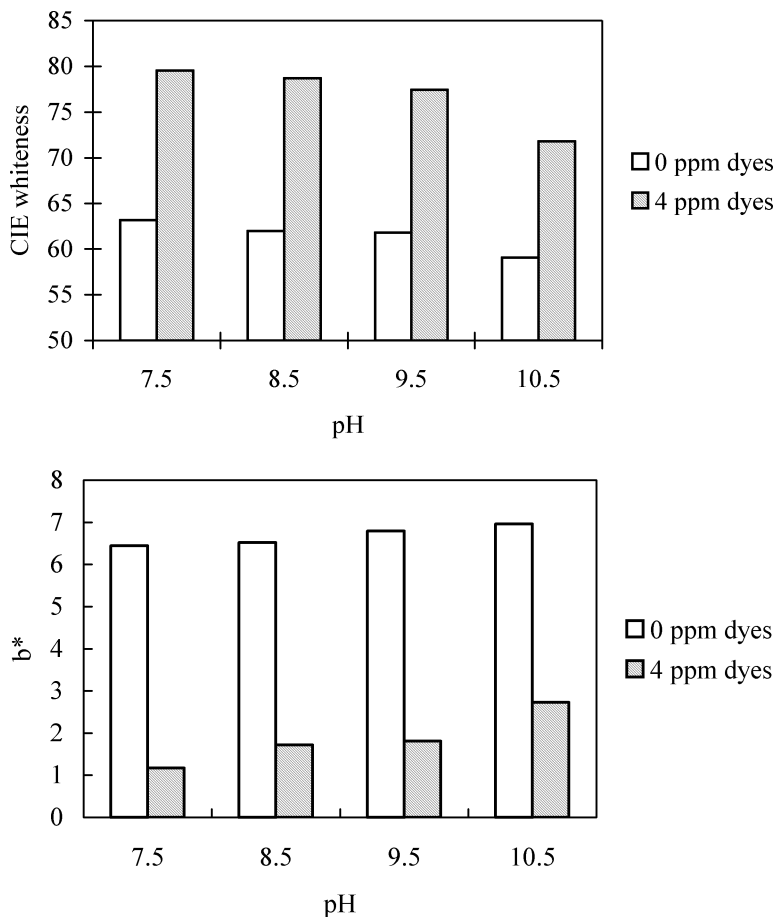


Figure 2. Effect of dyeing pH on the CIE whiteness and b* of dyed pulp (no peroxide, 20 min, 80°C, the dye concentration was based on pulp).

Figure 3 shows the results obtained in the presence of hydrogen peroxide and 4 ppm dye. At a pH of 7.5, the dye performance was not affected by the presence of hydrogen peroxide. At a pH of 8.5, the dye performance decreased only slightly. At a pH of 9.5 and higher, the dye performance started to deteriorate, with a more pronounced effect at a higher hydrogen peroxide charge. These results are different from those obtained in the absence of pulp fibers. Evidently, the presence of pulp fibers increased the dye stability in the alkaline peroxide system. This can be explained as follows: it is well known that basic dyes have good affinity to pulp fibers, and dye molecules are both on the fiber surface and inside the fiber structures through diffusion.^[11] Stable dye-pulps complexes can be formed.^[7,12] The formation of these complexes

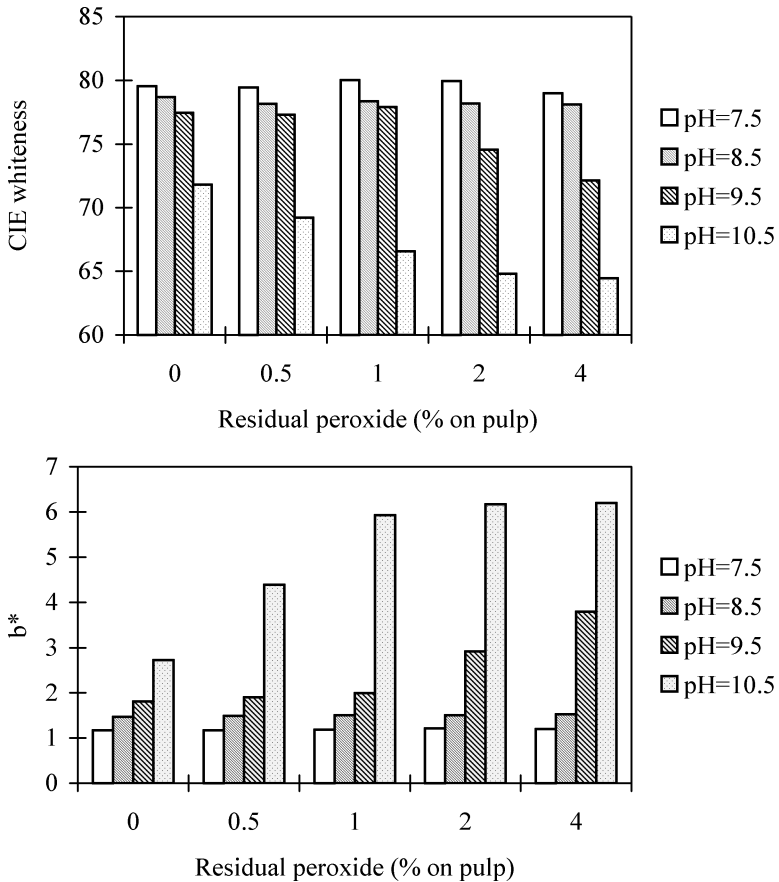


Figure 3. Effect of hydrogen peroxide on the CIE whiteness and b^* at different pH (Original HYP: 64.2 CIE whiteness, 6.4 b^* , 117 meq/kg DCS; dyeing conditions: 4 ppm dye based on pulp, 20 min, 80°C).

makes the dye relatively stable, particularly at a lower peroxide concentration and a lower pH. At the completion of an industrial peroxide stage for HYP/BCTMP manufacturing processes, the typical pH is about 7.5 to 8.5. There are two different practices at the end of bleaching: some acidify the bleached pulp using SO_2 , whereas others do not. Based on the results in Figure 3, one can conclude that with mills practicing SO_2 souring, dye may be added directly to the pulp slurry, and the best dye performance can be expected. With mills without practicing SO_2 souring, a slightly inferior dye performance is expected if dye is added directly to the pulp slurry after peroxide bleaching.

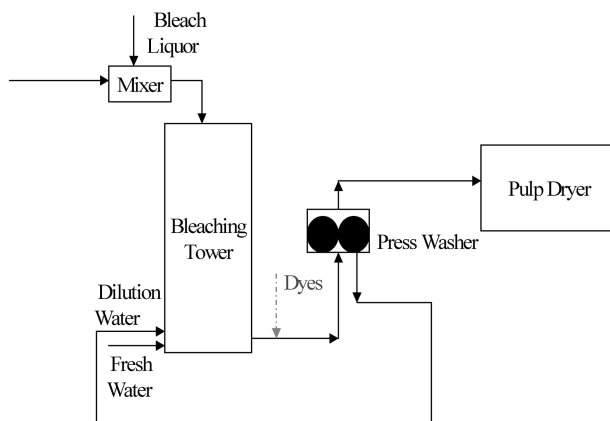


Figure 4. Proposed dye addition in the HYP manufacturing process.

Proposed Process Configuration

Based on our results presented in the previous sections, we proposed to add the dye to the pulp slurry at the completion of peroxide bleaching to improve the optical properties of high-brightness HYP, as shown in Figure 4. Dye may also be added with the fresh water and/or dilution water.

To simulate the proposed process in Figure 4, we conducted more experiments on a pulp slurry received from a market HYP mill, and the results are shown in Table 2. It should be pointed out that the pulp sample was used as received, which contained 0.85% residual H_2O_2 (based on pulp); a pH adjustment was carried out before the addition of dye. At a pH of 5.8 or lower, the dye performance was not affected by the pH level, at a dye dosage of 4 ppm, the b^* value was constantly at 1.2 and the CIE whiteness was 80.2–80.6. However, when the pH reached 7.5 and above, the dye started to lose its effectiveness. These results were different from those we obtained in the controlled peroxide-dye-fiber system, presented in the previous section. It is also noted that the pulp

Table 2. Effect of pH on the dye performance in the presence of residual peroxide and DCS (Original pulp: 85.4% ISO brightness, 65.0 CIE whiteness, 6.4 b^* , 84.8 meq/kg DCS, 0.85% residual H_2O_2)

pH	4.5	5.5	5.8	6.5	7.5	8.5	9.5	10.5
Brightness (% ISO)	84.8	85.0	84.9	85.0	85.0	85.1	85.3	85.8
CIE whiteness	80.2	80.6	80.6	78.2	76.5	72.2	68.3	66.9
b^*	1.2	1.2	1.2	1.8	2.4	3.8	5.2	5.7

Dyeing conditions: 10% pulp consistency, 20 min, 80°C, 4 ppm dye (based on pulp).

brightness showed a slight increase as the pH increased, which was due to the bleaching effect from the residual hydrogen peroxide.

A question arises as to why the results in Table 2 in the pH range of 6.5 to 10.5 are significantly inferior to those in Figure 3. The only difference between these two systems was the amount of DCS (dissolved and colloidal substances). In Figure 3 the amount of DCS of 11.7 meq/kg of pulp was much less than that of the system for Table 2 (84.8 meq/kg). To determine the DCS effect on the dyeing process, we designed more experiments to compare DCS-free and DCS-containing HYP pulps. The DCS-free pulp was prepared by following a procedure reported in the literature.^[13] We then mixed the DCS-free HYP with the regular HYP collected at the bottom of the bleaching tower (referred to as the “DCS-containing pulp”). Subsequently, the dyeing process was followed.

Table 3 shows that DCS had a negative effect on the dye performance, particularly at a higher pH. At a pH of 6.5, the CIE whiteness increased from 78.2 for the 100% DCS-containing pulp to 81.3 for the 100% DCS-free pulp, whereas the b^* decreased from 1.9 to 0.9. At a pH of 8.5, the difference was even more pronounced. These results can be explained by the negative effect from DCS, which was also reported on chemical pulp furnish.^[14] It was reported^[15] that in a pH range of 3.5–9, the cationic demand of DCS increases as the pH increases. The average diameter of the DCS particles from HYP is approximately 0.6 μm , suggesting that DCS particles have a larger specific surface area than pulp fibers and fines. The implication of the above is that the added dye is preferentially attached to DCS particles, rather than to pulp fibers and fines.

The practical implication of this research is that the addition of dye to the pulp slurry at the completion of the peroxide bleaching process can decrease

Table 3. Effect of DCS on the CIE whiteness and b^* at different pH

DCS-containing pulp/DCS-free pulp	Optical properties	pH		
		6.5	7.5	8.5
100/0	CIE whiteness	78.2	76.2	72.2
	b^*	1.9	3.0	3.9
75/25	CIE whiteness	79.2	76.4	72.4
	b^*	1.6	2.5	3.8
50/50	CIE whiteness	79.7	76.5	73.7
	b^*	1.5	2.4	3.4
25/75	CIE whiteness	80.2	79.0	75.2
	b^*	1.2	1.7	2.9
0/100	CIE whiteness	81.3	80.7	78.3
	b^*	0.9	1.1	1.5

Conditions: 10% pulp consistency, 4 ppm dye (based on pulp), 20 min, 80°C.

the yellowish hue of the market HYP. This can be complementary to the use of OBA and peroxide bleaching to improve the HYP optical properties. A small amount of dye, for example, 4 ppm (on pulp), is sufficient for serving this purpose. If the acid souring by using either SO_2 or sulfuric acid (to about a pH of 5 at the completion of peroxide bleaching) is practiced before the addition of dye, the best results can be obtained; however, if dye is directly added to pulp slurry without the SO_2 souring, one may consider adding dye after the press washer; by doing so, a significant improvement in the CIE whiteness and b^* can still be achieved.

CONCLUSIONS

The dye performance in terms of increasing the CIE whiteness and decreasing b^* was only slightly decreased at a pH of 8.5 or lower and the residual hydrogen peroxide of less than 1%. These results suggest that under such a condition, dye was stable. The good dye stability is due to the fact that dye interacts strongly with pulp fibers both on the fiber surface and inside the cell wall, thus decreasing its reaction with hydrogen peroxide. On the other hand, the presence of DCS in the pulp system negatively affects the dye performance.

To improve the optical properties of market HYP (increasing the CIE whiteness and decreasing b^*), we proposed adding a small amount of dye (e.g., 4 ppm based on pulp fibers) to the pulp slurry after the peroxide bleaching process. The best results can be obtained if, prior to the dye addition, the pulp slurry is SO_2 soured.

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