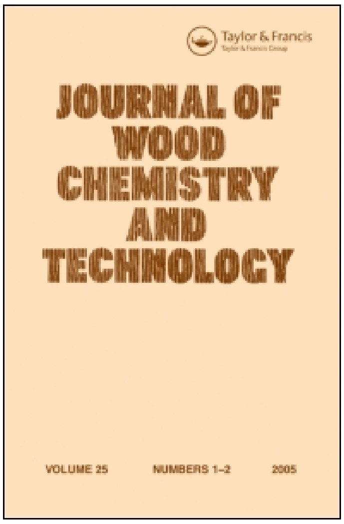

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Comparison of Dye Behavior from Aspen HYP: Dyes Added in the HYP Manufacturing Process Versus Dyes Added at the Papermaking Wet End

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Abstract: The yellowish color of High Yield Pulp (HYP) gives some psychological obstacles and limits its application in some paper grades. Dyes are widely used in the papermaking process to shade the yellowish color of the paper products. We proposed to add dyes into the HYP manufacturing process to minimize the yellowish hue. In this work, we substituted the dye-added HYP (dyes added in the HYP manufacturing process) for hardwood kraft pulp in the production of fine paper grades, and compared the results from those by adding dyes into the papermaking wet end. A higher dye effectiveness was obtained when we used the dye-added HYP. Also, the dye-added HYP gave more effective performance of Precipitated Calcium Carbonate (PCC) fillers and Optical Brightening Agents (OBA) in terms of CIE whiteness and b*. In addition, the dye-added HYP showed less negative effect on brightness and better compatibility with other dyes. The underlying mechanism for the above experimental observation was proposed.

Keywords: Dyes, High Yield Pulp, optical properties, papermaking, peroxide bleaching

INTRODUCTION

High Yield Pulp (HYP) has been widely used in many paper grades.[1–3] Some functional advantages can be gained when using HYP as a substitution for a hardwood kraft pulp in addition to cost savings.[2–7] In particular, aspen HYP,

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has been gaining much interest due to its high brightness, high bulk, and strength properties.[2,4,8] Although the aspen HYP can be bleached economically to 85% ISO brightness, it still has some yellowish color because of the high lignin content and some other colored materials. Thus, it has lower CIE whiteness and higher b* than the typical hardwood kraft pulp.[9,10]

As we reported earlier,[11–13] dyes can be used for improving the whiteness and decreasing the yellowish color of HYP. The yellowish color can be minimized or even eliminated by adding a very small amount of dyes (i.e., 4 ppm). We proposed a process to add dyes in the HYP manufacturing process.[13] The appearance of the dye-added HYP improved greatly. Generally, dyes are added into the papermaking wet end. In this work, we compared the dye performance of the two methods: adding dyes in the HYP manufacturing process, and adding dyes to the mixed furnish containing HYP at the papermaking wet end. Finally, we proposed the mechanism which explains the advantage of using dye-added HYP.

EXPERIMENTAL

Pulp Samples and Chemicals

A softwood (mainly spruce) bleached kraft pulp (SBKP) and a hardwood (eucalyptus) bleached kraft pulp (HBKP) were refined in a PFI mill to 470 and 400 ml CSF freeness, respectively. An aspen HYP (freeness/brightness of: 325/85) was obtained from a Canadian mill. The optical properties of these three pulps are listed in Table 1. PCC filler was from Specialty Mineral. Four types of dyes were received from BASF: Violet 57L NA (cationic basic dye), Violet 92L NA (cationic direct dye), Blue 31L NA (anionic direct dye), and Blue 07L (pigment dye). The optical brightening agent used (Tinopal UP) was obtained from Ciba, and a cationic polyacrylamide (Percol 182) from Hydrocol.

Dyeing Process

For the preparation of the dye-added HYP, the dyeing process was conducted in plastic bags using the following conditions (simulating the addition of dyes

Table 1. Optical properties of the pulp samples

Pulp samples	Brightness (%)	CIE whiteness	L*	a*	b*
SWBKP	87.6	73.6	97.4	–0.6	4.4
HWBKP	88.7	76.0	97.6	–0.5	4.0
HYP Aspen (325/85)	85.0	64.8	97.1	–1.4	6.2

at the completion of the peroxide bleaching process[13]): 10% pulp consistency, 4 ppm dyes, pH 6.0, at room temperature for 20 min. Another sample was also treated with the same procedure under the same conditions except for no dye addition. Mixing was provided by hand kneading. Subsequently, a Büchner funnel was used to filter the pulp, the filtrate was recycled once to improve the fines retention and dye retention. The pulp cake was separated into small pieces and air-dried. To simulate the addition of dyes at the papermaking wet end, we added dyes into the mixed furnish (softwood BKP, hardwood BKP and dye-free HYP), the dye dosage was 4 ppm (based on the HYP). The conditions of the stock preparation were: 0.5% consistency, pH of 7.0, room temperature, 5 min. In all the experiments, the softwood BKP was fixed at 30%, the hardwood BKP varied from 40 to 70% while the HYP varied from 0 to 30%. If needed, PCC was added after the dye addition followed by the addition of 0.05% cationic polyacrylamide (Percol 292 from Hydrocol) before handsheet preparation.

Handsheets were made from the stock according to TAPPI methods, and the optical properties of the resultant handsheets were tested at C/2° conditions on a Technibrite Micro TB-1C tester with d/0° geometry. The PCC contents in the handsheets were tested according to a method reported earlier,[14]and the retention of PCC was found to be within 80–85% in all cases.

RESULTS AND DISCUSSION

Effect of HYP Substitution

In Figure 1, dyes were added into the HYP by two different addition methods: adding dyes to the pulp furnish containing HYP at the papermaking wet end (HYP) and adding dyes in the HYP manufacturing process (dye-added HYP). The CIE whiteness increased with the increase of the HYP substitution because of the increased dye addition, while b* decreased with the increasing of the HYP substitution rate, suggesting that the yellowish color of the HYP can be decreased with the addition of a small amount of dyes.

Figure 1 also shows that adding dyes in the HYP manufacturing process is advantageous compared to adding dyes to the mixed furnish at the papermaking wet end. The former resulted in a higher CIE whiteness and lower b* value constantly. For example, at 4 ppm dye dosage (based on HYP for both) and 20% HYP substitution, the CIE whiteness was 77.7% for the dye-added HYP and 76.6% for HYP, b* was 2.9 and 3.3, respectively.

Figure 2 shows that the two different addition methods gave similar brightness under otherwise the same conditions. The brightness decreased with the increase of the HYP substitution, which was caused by the presence of more HYP (because HYP has a lower brightness than KP) and also, by the dye addition.

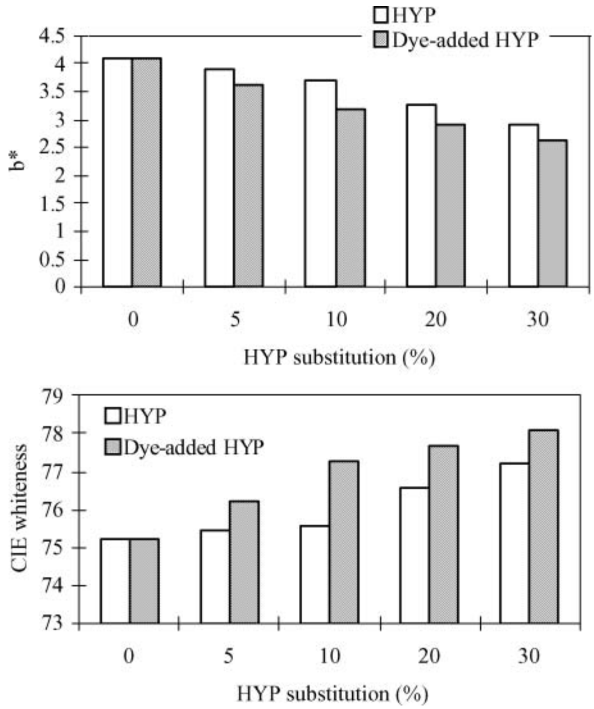

Figure 1. Effect of HYP substitution rate on CIE whiteness and b* (conditions: dye dosage: 4 ppm (based on HYP), pH: 7.0, room temperature).

The L* value is an important parameter for the assessment of the paper visual appearance.[15,16]The plot of L* versus b* is of practical interest; at the same b* value, a lower L* means "duller paper." In Figure 3, one can find that at a given b* value, adding dyes in the HYP manufacturing process gave a higher L*, which is an indicator of better paper appearance, than adding dyes at the papermaking wet end.

Effect of PCC Filler

Figure 4 shows the effect of PCC filler on these two addition methods. It is evident that the dye-added HYP always had higher CIE whiteness and lower b* value, regardless of the PCC load. It is well known that PCC has large specific surface area and some crevices, which will absorb dyes and decrease the dye effectiveness at the papermaking wet end.[12,17,18] When dyes are added in the HYP manufacturing process, they bind tightly with pulp fibers and are well distributed into the fiber network. Our earlier results showed that dyes added to

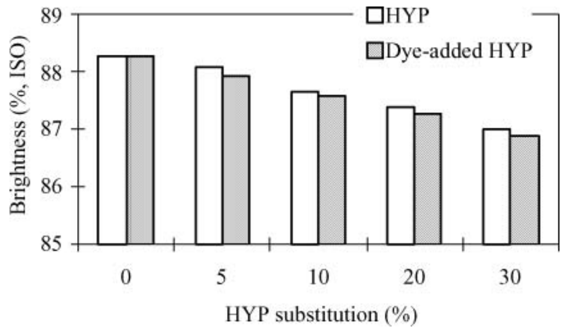

Figure 2. Effect of HYP substitution rate on the brightness (conditions: dye dosage: 4 ppm (based on HYP), pH: 7.0, room temperature).

the HYP manufacturing process had excellent affinity under typical conditions of stock refining when contacting with white water.[13] When PCC fillers are added into the wet end, dyes bind so tightly with pulp fibers that very little may be available for PCC. While adding dyes to the mixed pulp furnish at the papermaking wet end, some of the dyes may be adsorbed onto PCC and therefore less dyes would be available for the HYP.

The original brightness of the dye-added HYP was lower than the HYP with dyes added at the wet end, as shown in Figure 5. However, one can also find from Figure 5 that the dye-added HYP had higher brightness than HYP with dyes added at the wet end after PCC filler addition. Dyes can decrease the brightness of paper because of the absorbance of visible light.[18] The higher brightness after PCC addition for the dye-added HYP can be explained by the interaction of dyes with PCC fillers. In the case of the dye-added HYP, the dyes

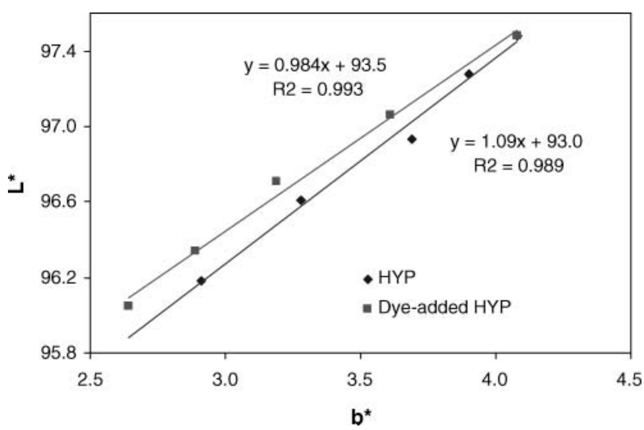

Figure 3. Comparison of the relationship of L* and b* for the two dye addition methods.

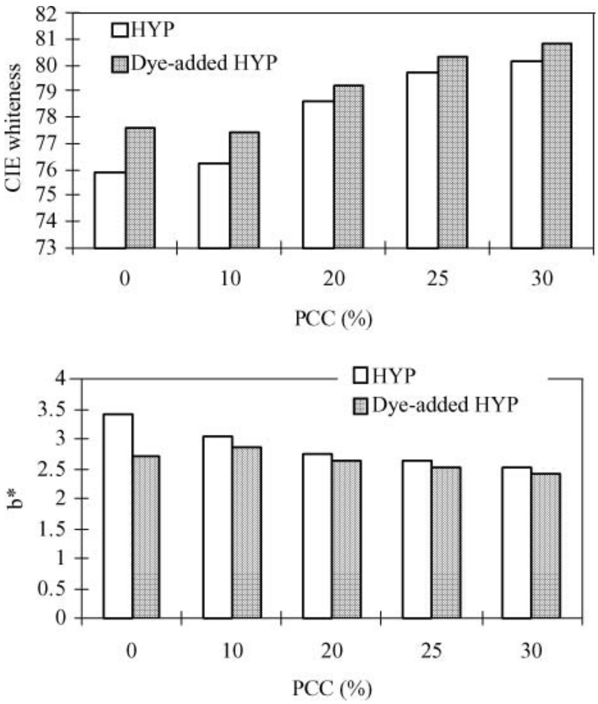

Figure 4. Effect of PCC load on the CIE whiteness and b* (conditions: HYP substitution: 20%, dye dosage: 4 ppm (based on HYP), CPAM: 0.05%, pH: 7.0, room temperature).

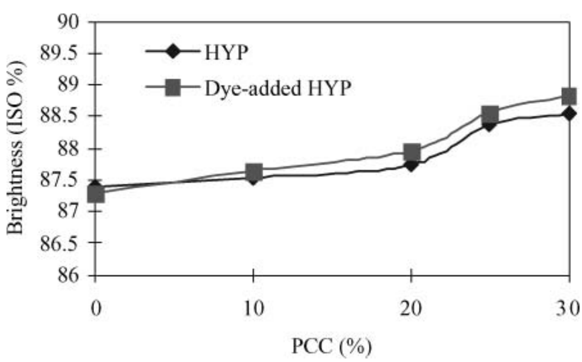

Figure 5. Effect of PCC on the brightness (conditions: HYP substitution: 20%, dye dosage: 4 ppm (based on HYP), CPAM: 0.05%, pH: 7.0, room temperature).

have been fixed on the HYP fibers, and there is no potential negative effect of dyes on the PCC filler. Consequently, the positive contribution of PCC filler to the brightness will not be affected by dyes. On the other hand, some of the dyes can be absorbed by the PCC filler when dyes are added at wet end, resulting in the decreased brightening effect of PCC.

OBA Effect

Optical Brightening Agents (OBA) are widely used in the papermaking process to improve the brightness and whiteness of the final products. The results of the effect of adding OBA on the CIE whiteness gain from OBA and b* for the two methods are shown in Figure 6. It can be seen that the dye-added HYP had higher CIE whiteness gain and lower b* value than the other method of adding dyes at the wet end. The higher original whiteness and lower b* of

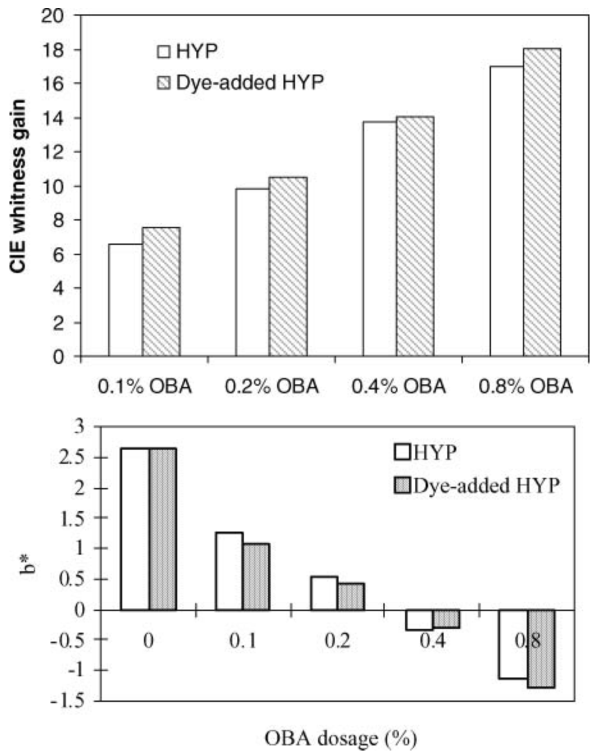

Figure 6. Effect of OBA on CIE whiteness and b* (conditions: HYP substitution: 20%, dye dosage: 4 ppm (based on HYP), PCC: 20%, CPAM: 0.05%, pH: 7.0, room temperature).

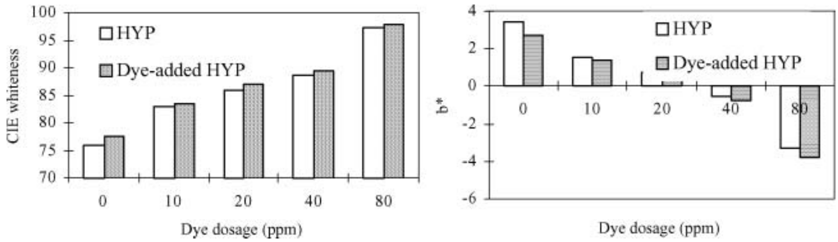

Figure 7. Effect of cationic direct dyes on the CIE whiteness and b* (conditions: HYP substitution: 20%, dye dosage: 4 ppm (based on HYP), PCC: 20%, CPAM: 0.05%, pH: 7.0, room temperature).

the dye-added HYP is responsible for the higher effectiveness of OBA.[19–21] When adding dyes at the wet end, a lower CIE whiteness and higher b* were obtained, which resulted in a lower OBA efficiency, thus a lower CIE whiteness gain and a lower brightness gain after the OBA addition.

Compatibility with Other Types of Dyes

In the papermaking process, there are several types of dyes that can be used to adjust the color match, such as cationic direct dyes, anionic direct dyes, and pigment dyes, or a combination of these dyes. In this study, we used three types of dyes: 92 L NA (cationic direct dye), 31L NA (anionic direct dye), and 07L (pigment dye). These three dyes were added at the wet end to simulate the papermaking process and to determine their shading compatibility for HYP. Figure 7 shows that the dye-added HYP had good compatibility with the cationic direct dye (92 L NA). HYP with dye added at the wet end was lower on the whiteness gain compared to the dye-added HYP. Similar conclusions can be drawn for the pigment dyes used, as shown in Figure 8. Again, the dye-added HYP showed better performance than the HYP with dye added at the wet end. For the anionic direct dyes, as shown in Figure 9, the dye-added HYP had a lower CIE whiteness and higher b* value than the HYP with dye added at the wet end, indicating that the anionic dyes had inferior compatibility with the dyes added in HYP. This can be explained by the interactions of the dyes;[17,22] when the cationic basic dyes are added and absorbed first, they can form salts with the subsequently added anionic direct dyes.

Proposed Explanations for the Advantages of Dye-Added HYP

The results from this work supported the notion that adding dyes to the HYP manufacturing process is advantageous compared to adding dyes to the mixed

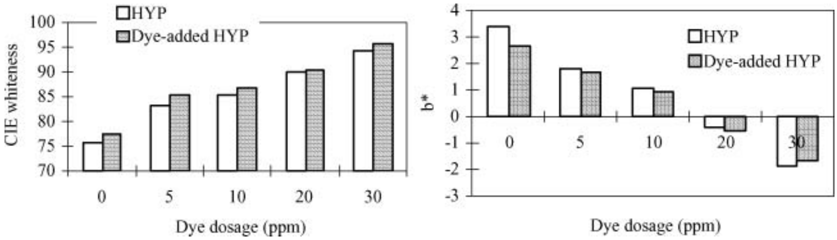

Figure 8. Effect of pigment dyes on the CIE whiteness and b* (conditions: HYP substitution: 20%, dye dosage: 4 ppm (based on HYP), PCC: 20%, CPAM: 0.05%, pH: 7.0, room temperature).

pulp furnish containing HYP in the papermaking wet end. We proposed the following to account for these results:

1) When adding dyes to the HYP manufacturing process, the basic dyes are strongly attached to HYP fibers,[13] consequently, when mixed with other pulp furnishes (softwood BKP and hardwood BKP), dye re-distribution is unlikely. This not only leads to higher dye effectiveness on HYP for improving the CIE whiteness and decreasing b*, but also minimizes the interference with other wet end additives, such as OBA;
2) When adding dyes to the mixed furnish containing HYP at the papermaking wet end, all pulp fibers (softwood KBP, hardwood BKP, and HYP) have an equal opportunity to interact with dyes, rather than specifically the HYP. For this reason, the effectiveness for increasing the CIE whiteness and decreasing b* is decreased. Also, when fillers, such as PCC, are present, dyes can interact with or be absorbed by PCC, further decreasing their effectiveness.

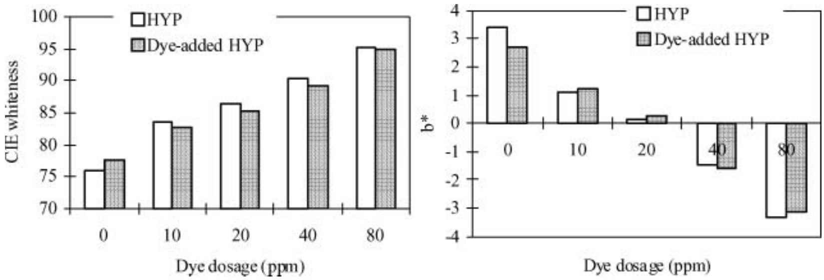

Figure 9. Effect of anionic direct dyes on the CIE whiteness (conditions: HYP substitution: 20%, dye dosage: 4 ppm (based on HYP), PCC: 20%, CPAM: 0.05%, pH: 7.0, room temperature).

CONCLUSIONS

Adding dyes in the high yield pulp (HYP) manufacturing process is an effective method to improve the optical properties (the CIE whiteness and b*) of market HYP. Such a technique is advantageous over the traditional method of using dyes (adding dyes to pulp furnish at the papermaking wet end). A higher dye effectiveness has been obtained when using the dye-added HYP as a substitution for hardwood kraft pulp in comparison with the addition of dye at the wet end. PCC had less negative effects on the dye performance for dye-added HYP than the method of adding dyes at the wet end. OBA showed higher effectiveness on brightness development with dye-added HYP. The compatibility of dye-added HYP was good for the cationic direct dyes and pigment dyes, which are widely used in the papermaking process of high quality paper grades. Anionic direct dyes had slightly negative compatibility with the dyes added into the HYP.

Our explanation for the improved performance of dye-added HYP is that dyes added in the HYP manufacturing process can bind tightly with pulp fibers; consequently, when mixed with other pulp furnishes, dye re-distribution is unlikely.

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