Using dyes for improving the optical properties of high yield pulps

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Abstract: High yield pulps (HYP) have found increased use in many paper grades, including printing and writing, coated and uncoated wood-free papers. The residual lignin and other color- or substances cause the yellowish tint of HYP. To improve the pulp quality, dyes may be used to minimize or even eliminate the yellowish hue. In this paper we determined the effectiveness of using a basic dye to shade the yellowish hue of the HYP, and the results were compared to those obtained from a hardwood bleached kraft pulp (HBKP). The results showed that the basic dye can effectively increase the whiteness and decrease the yellowish color of the HYP, while the brightness decreased slightly. With a small amount of dye the HYP can get CIE whiteness and b* similar to those of a market HBKP. pH is an important parameter in determining the dye effectiveness and the acidic paper-making conditions was found to have a small negative effect on HYP shading. Contact time had a significant impact on the HYP shading process, and the CIE whiteness increased and b* decreased with increasing the contact time until a plateau was reached. In contrast, the shading process for the HBKP was extremely fast. Our results also showed that the basic dye had a strong affinity with the HYP under the typical conditions of stock refining, and the loss of dyes from the HYP under such conditions is negligible.

In recent years, the high-brightness High Yield Pulps (HYPs) have found increasing applications as a substitution for hardwood kraft pulp in many paper grades, including LWC, wood-free printing and writing [1]. However, the HYP has a typical yellowish hue because of the presence of lignin and other colored substances, which may affect negatively its further application in high-quality paper grades. Dyes are widely used in paper mills to shade the yellowish color and improve the appearance of the final products. Therefore, they may be used to offset the yellowish hue of the HYP.

In the paper mills, the function of dyeing includes coloring and tinting. For the coloring purposes, the dye dosage is usually very high, while for tinting, the dosage is usually low. The dyes used in the pulp and paper industry can be divided into 3 groups: basic dyes, direct dyes and pigment dyes. Generally speaking, the basic dyes are used to suppress the yellow hue of mechanical pulps in applications such as the production of newsprint and light weight coated papers [2]. The direct dyes find uses, e.g., in napkins, sanitary papers, and wood-free writing papers. Most direct dyes have a natural affinity for wood cellulose fibers [3,4]. The pigment dyes are suitable for dyeing and shading via coating and have been mainly applied to paper products requiring good lightfastness, such as laminated or decorating papers or book covers [4, 5].

The effect of adding dyes on paper optical properties has been well studied [6,7,8], however, the results available in the literature were mainly obtained from chemical pulps, while those on HYP were rather limited. Basic dyes, particularly the cationic basic dyes can be used in lignin-containing pulp furnish. The optical properties of the pulp are affected by the amount of dyes retained, which is, in turn, determined by the dyes-to-pulp interactions. The latter depends on the characteristics of the dyes and pulp fibers, as well as the chemical environment and the operating conditions, such as pH, temperature, contact time and water hardness etc [4].

Recently we started a project to improve the optical properties/appearance of the HYP. In the first phase, we focused on using OBAs for this purpose [14,15,16]. In the second phase, we have been studying the use of dyes. In this paper, we reported the results on the effect of using dyes in HYP fibers on the optical properties, in particular, CIE whiteness and b*. Also included in the study were those from a Hardwood Bleached Kraft Pulp (HBKP).

EXPERIMENTAL

Materials

The aspen HYP (325/85) used in this study was obtained from Tembec Inc., and was used as received. A hardwood eucalyptus kraft pulp was refined to 400 CSF in a PFI mill before use. Table I lists the optical properties of pulp samples. The basic dyes used were cationic violet dyes from BASF.

Handsheet Preparation

To prepare the dye-added handsheets, a 1% pulp slurry was made. The pH of the pulp slurry was adjusted to the desired level if needed. The dye was then added into the pulp slurry, which was stirred slowly for two hours by a magnetic stirrer, unless otherwise specified. The handsheets were subsequently prepared by following the Tappi Standard method T272 sp-02.

Optical Properties of Sheets

The optical properties were determined after
reconditioning the handsheets at 25°C and 50% humidity overnight. They were measured with a Technidyne Micro TB-1C reflectometer.

RESULTS AND DISCUSSION

The effect of adding dye to the HYP on the brightness, CIE whiteness and b* are shown in Table II. One can find that a small amount of dye can effectively increase the whiteness, and decrease the b*. For example, at a 4 ppm dye dosage (based on pulp), the whiteness increased from 65.9% to 80.6%, and the b* value decreased from 6.0 to 1.1. These results are compared to a whiteness of 75-80%, and a b* value of 3.5-4.5 for a typical bleached hardwood pulp.

Table II also shows that the addition of dye to the HYP slightly decreased the pulp brightness. For example, at a 4 ppm dye dosage, the brightness loss was 0.5 unit. This is because the addition of dye increased light absorbance in the visible wavelength range, thus decreasing the reflectance at 457 nm. A slight brightness decrease has also been observed when dye was added to a bleached chemical pulp [8].

Figure 1 shows the light reflectance of the HYP handsheets with or without dyes. One can find that the reflectance of wavelengths decreased, particularly at 590 nm, which is the peak absorbance of this basic dye. The yellowish hue is lowered due to the absorbance of violet color. The reflectance of 457 nm decreased slightly, as shown in Figure 1. This is consistent with the slight brightness loss after dyes added into the pulp, as shown in Table II.

Effect of Process Variables

The shading process has a number of variables, including pH, temperature, the fiber-dye contact time, and the water hardness [4,7]. We studied these process variables and determined the effectiveness of the dye for HYP by measuring the CIE whiteness and b* of the handsheets.

pH

The pH of the paper machine’s water system can exercise a significant influence on the shade of dyestuffs and on dyestuff retention [4,9]. Figure 2 shows the whiteness and b* of the HYP and HBKP dyed with the basic dyes as a function of pH of the pulp slurry. For the HYP, the basic dye had a good performance in the pH range of 5.5-7.5, with a constantly high CIE whiteness and low b*, however, the CIE whiteness decreased and b* increased at more alkaline (pH 8.5 and 9.5) conditions. For the HBKP pulp, there was a gradual decrease in the CIE whiteness and an increase in the b* when the pH increased, although the changes were more dramatic at pH higher than 8.0. These results were in agreement with those reported in literature that for basic dyes the pH significantly influences the absorptivity and stability of the dyes [10,11]. The basic dyes have a higher stability under acidic conditions, which can lead to better effectiveness (higher CIE whiteness and lower b*). On the other hand, under more alkaline conditions they were less stable, causing decreased CIE whiteness and increased b*. Another factor, which may be of importance, in particular for the HYP, is the alkaline darkening effect. It must also be responsible for part of the decreased CIE whiteness and increased b* when pH was higher than 8.0, as shown in Figure 2.

Temperature

Figure 3 shows that the effect of the temperature in the range we studied had a negligible effect on the shading process for the HYP, as the whiteness and b* of the HYP decreased only slightly when the temperature increased from 20 to 50°C. This may be partially explained by the thermal yellowing effect as the temperature increased. For the HBKP, Figure 3 shows that the best shading results can be obtained at 30°C. The possible reason may be that the increased temperature decreases the energy barrier between the dyes and fibers, so that more dyes will be effectively absorbed on the fiber surface, however, as the temperature further increases, the dye stability is negatively affected. Our results in Table III showed that the dyes can be destroyed by the increased temperature.

Contact time

The effect of contact time had a very significant effect on the dyeing performance for the HYP, as shown in Figure 4. The CIE whiteness continued to increase during the first 30 min, then increased slowly.
and reached a plateau. In contrast, Figure 4 shows that for the HBKP pulp the contact time had no effect on the CIE whiteness and $b^*$. The cationic basic dyes can form hydrogen bonds, Van der Waals’ and hydrophobic interactions with cellulose fibers [12], and they can readily diffuse into fiber structure via the pore openings. The fast adsorption of dyes into HBKP fibers indicated that the dye to pulp fiber interaction is very rapid; so is the diffusion of dyes into fiber structures. However, due to the smaller pores and overall lower porosity, the diffusion and absorption of dyes into the HYP fibers are much slower.

**Ca²⁺ Concentration**

The effect of calcium concentration in the process water on the dye performance was presented in Figure 5. Metal ions, such as calcium, can compress the electrical double layers of the pulp fibers, thus improving the retention of dyes. One can find that at 0-100 ppm the increased calcium addition had a positive effect on the results for both HBKP and HYP. However, as the calcium concentration further increased to 200 ppm for both HYP and HBKP, it had a negative effect on both CIE whiteness and $b^*$. A very high calcium concentration may displace some dyes in pulp fibers [13].

**Affinity of Dyes on HYP and HBKP**

Once added, the affinity of dyes onto pulp fibers is of practical importance, and this may be particularly true for market HYP. This is because paper mills usually repulp/refine market pulp in the papermaking process. To simulate such operations, we determined the performance of dyes on HYP after mechanical treatments (in a standard disintegrator, or a PFI mill) and hot water treatment. The results on HBKP were included as a comparison. Dyeing HYP and HBKP was performed under the following conditions: 1% pulp consistency, 8 ppm and 4 ppm basic dyes for HYP and HBKP, respectively, pH of 7.0, 2hrs contact time and room temperature. Once the dyed pulp was air-dried, it was subjected to the post-treatment in a standard disintegrator or PFI mill, or with hot water.

Figure 6 shows that with up to 20,000 revolutions in a standard disintegrator, the CIE whiteness and $b^*$ of the dyed pulp remained the same, and this is true for both HYP and HBKP samples, indicating that the basic dyes have a strong affinity to pulp fibers. Others reported that some other basic dyes had poor affinity to the bleached pulp [10,12]. Such discrepancies may be explained by the different dyes used.

Figure 7 shows that the CIE whiteness and $b^*$ of the dyed HYP and HBKP did not change with the PFI treatment of up
to 5,000 revolutions. These results again support the conclusion that once added onto the pulp, dyes bound tightly with pulp fibers, and that typical mechanical treatments, such as those encountered in industrial refiners, will not be able to remove dyes from pulp fibers.

A typical process water in a paper mill is in the range of 40 to 50 °C. We determined the dyeing performance of both HYP and HBKP at different temperatures. Table IV shows that for both HYP and dyed HYP, the whiteness decreased only slightly, while b* increased slightly, suggesting that the loss of dyes during hot water treatment was minimum. For the HBKP pulp, there was no change in the whiteness and b*.

### CONCLUSIONS

The yellowish color of the HYP can be minimized or eliminated by the addition of dyes. The dyes can improve the CIE whiteness and decrease the b* of the pulp dramatically at a very small amount of dosage, for example, 4 ppm (based on the pulp). Therefore, the additional cost associated with the addition of dye for this purpose may be very small. The shading performance when using a basic dye is similar between a HYP and a HBKP.

Under the laboratory conditions, we found that for the HYP the dye performance is good in a wide pH range, 5.5-7.5. Increasing the temperature up to 30°C can improve the dyeing efficiency for the HBKP pulp, however its effect is negligible for the HYP. A longer contact time increased the dye retention for the HYP, on the other hand, the maximum dyeing performance can be reached rapidly for the HBKP. The presence of some salts, such as calcium (up to 100 ppm), is beneficial to the shading process for both the HYP and HBKP. The basic dyes had good affinity on the HYP and HBKP fibers and the loss of dyes under typical conditions of stock refining is negligible.

The practical implication from this research is that market HYP with similar whiteness and b* to those of bleached KP can be produced by the addition of a small amount of dyes.

### LITERATURE

4. Holmberg, M., Chapter 14, Dyes and fluorescent whitening agents, Papermaking Chemistry, Neimo, L. (book editor), Finnish Paper Engineers’ Association

| Table IV. Effect of hot water post-treatment on optical properties of HYP and HBKP with or without dyes. |
|-----------------|-----------------|-----------------|
|                 | Control         | 40°C            | 60°C            |
| CIE whiteness   |                 |                 |
| HYP             | 65.3            | 65.2            | 64.7            |
| Dyed HYP        | 82.3            | 81.6            | 81.0            |
| HBKP            | 78.2            | 78.0            | 78.3            |
| Dyed HBKP       | 90.8            | 90.5            | 91.1            |
| b*              |                 |                 |
| HYP             | 6.1             | 6.0             | 6.1             |
| Dyed HYP        | 0.6             | 0.8             | 0.9             |
| HBKP            | 3.7             | 3.6             | 3.5             |
| Dyed HBKP       | -1.0            | -0.9            | -0.8            |

Treatment conditions: pulp consistency: 1%, time: 1 hr.


Résumé: Les pâtes à haut rendement (PHR) sont de plus en plus utilisées dans bon nombre de catégories de papiers, notamment les papier impression et écriture, et les papiers couchés et non couchés sans bois. La lignine résiduelle et les autres substances colorées peuvent jaunir ces types de pâtes. Pour améliorer la qualité de la pâte, on peut utiliser des colorants pour réduire ou même éliminer le teint jaune. Dans la présente communication, nous avons déterminé l’efficacité d’un colorant basique pour atténuer le ton jaunâtre de la PHR, et nous avons comparé les résultats aux résultats obtenus avec une pâte kraft blanche de feuillus (PKBF). Les résultats indiquent que le colorant basique peut efficacement accroître la blancheur et atténuer la couleur jaunâtre des PHR, bien que le degré de blancheur diminue légèrement. Avec une petite quantité de PHR, nous pouvons obtenir un degré de blancheur CIE et de b* similaires à ceux d’une pâte PKBF commerciale. Le pH est un paramètre important lors de la détermination de l’efficacité du colorant, et un état acide lors de la fabrication du papier a eu un léger effet négatif sur la teinte des PHR. Le temps de contact a eu un effet important sur le processus d’atténuation du jaunissement, et le degré de blancheur CIE s’est accru et le b* a diminué lorsque le temps de contact s’accroissait jusqu’à un certain plateau. Par contre, le processus d’atténuation de la PKBF a été extrêmement rapide. Nos résultats indiquent aussi que le colorant basique présentait une forte affinité avec les PHR dans les conditions typiques du raffinage de la pâte, et la perte de colorants des PHR dans de telles conditions est négligeable.


Keywords: DYES, OPTICAL PROPERTIES, HIGH YIELD PULPS, YELLOWING, BRIGHTNESS.