Thermal Yellowing of Hornbeam Chemi-mechanical Pulps Bleached with Hydrogen Peroxide and Sodium Dithionite

Ramin Vaysi,* and Seyed Eshagh Ebadi

The thermal yellowing of hornbeam chemi-mechanical pulps (CMP) after bleaching with hydrogen peroxide and sodium dithionite was investigated. The hornbeam chips were randomly chosen from Mazandaran wood and paper industries. The CMP pulps prepared with 85% yield were separately bleached with diethylenetriamine pentaacetic acid (DTPA), without DTPA, and hydrogen peroxide. Some pulps were bleached with sodium dithionite. The optical properties of prepared hand-sheets of 60 g/m² after spraying with 0.5% DTPA were measured using TAPPI standard methods. All prepared papers were thermally aged separately in an oven at 105 °C for 0, 10, 20, 30, and 40 h. The optical properties, such as brightness, yellowness, coefficient of absorption, k/s ratio, post color (PC) number, and a” factor, before and after thermal aging were measured. The results showed that from 0 to 40 h, the optical properties of paper increased except brightness and greenness. This increase was more extensive up to 15 h. Additionally, among the various treatments, DTPA treatment in long-term thermal aging and the use of sodium dithionite and hydrogen peroxide in the short-term aging had noticeable effects on brightness durability and decrease in the color reversion. Thus, there was an increase in the durability of the paper against thermal deterioration.

Keywords: Hornbeam wood; Color change; Optical properties; Chemi-mechanical pulps; Thermal aging

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INTRODUCTION

Pulp yellowing commonly includes either light- and heat-induced color reversion or yellowing. Certain papermaking pulps easily become yellow when exposed to daylight, indoor illumination, or high temperatures. Natural yellowing of pulp and paper is slow at ambient temperature but is accelerated with increasing temperature. In thermal yellowing, both radical and ionic reactions occur. The important chemical reactions that influence the optical properties involve hydrolysis (often autocatalytic), depolymerization, rearrangement reactions, and transformation to low-molecular products, hornification, and macromolecular reorganization with a change in scattering (Carter 1996; Forsskahl et al. 2000). For chemical pulps, heat-induced yellowing is the main form of brightness reversion. Lignin residues, carbonyl groups, xylan, hexenuronic acid (HexA) groups, and transition metal ions are involved in the yellowing reactions (Borrega et al. 2013).

The thermal yellowing of chemical pulps has been reported to be influenced by the chemical composition of the pulp, i.e., the contents of lignin, hemicellulose, metal ions, and carbonyl and carboxyl groups (Rapson and Spinner 1999). High temperature, low pH, and high humidity accelerate the yellowing (Granström et al. 2001). Recently, thermal yellowing has been related to the content of hexenuronic acid (HexA) (Vuorinen et al. 2013).
1999; Tenkanen et al. 2002), and pulps with a high HexA content were less stable to heat treatment.

Residual lignin, the thermal decay products of polysaccharide chain, and xylan contents are the main (although debatable) causes for heat-induced yellowing of chemical pulps (Loureiro et al. 2013). Although the initiation reactions are different, the photochemical induced color reversions are also possible for the thermal counterpart. Radicals are thermally formed by the cleavage of a peroxidic bond or other weak chemical bonds. Moreover, the radicals are also formed in oxygenation reactions in which oxygen and oxygen-containing radicals participate. Hydroperoxides are often formed as intermediate products. Eventually, the reactions of the radicals lead to the formation of colored products. Acid-catalyzed depolymerization or saccharification of cellulose introduces a random cleavage of the glucosidic linkages, and D-glucose is formed in high yield. The rate of cleavage of cellulose depends strongly on the pH and the rate of reaction is slower than that of smaller glycosides but may be appreciable already below 100 °C (Theander and Nelson 1987; McGarry et al. 2000).

The reactions mainly start at the amorphous part of polymers. Hemicelluloses are thermally deacetylated and hydrolyzed, yielding monomeric compounds. These monomers may react further, e.g., xylose causes the formation of 2-furaldehyde and D-glucose, which gives rise to 5-(hydroxyl-methyl)-2-furfural (HMF). These aldehydes are prone to condensation reactions and must be regarded as likely intermediates in the formation of color. Impregnation of HMF, D-glucuronic acid, and reductic acid on filter paper makes the paper sensitive to aging (Theander and Nelson 1987). Moreover, HMF strengthens both photochemical and thermal yellowing of mechanical and chemical pulps, producing characteristic patterns in the UV-VIS diffuse reflectance spectra that are observed after normal yellowing of the same pulp without addition of HMF (Forsskahl et al. 2000).

Experiments with untreated and acetylated chemi-thermomechanical pulp (CTMP) from aspen when exposed to argon, air, and oxygen atmospheres showed that the degree of photo-yellowing of the untreated CTMP decreased when the air in the surrounding atmosphere was replaced with oxygen-free argon. These results indicated that atmospheric oxygen alone is not responsible for all of the light-induced discoloration or that trace amount of oxygen is however necessary to cause discoloration (Usta and Tutuş 1999; Paulsson et al. 2001). In long-term aging, diethylenetriamine pentaacetic acid (DTPA) spray has been shown to have considerable effect on the stability of brightness, improving the durability of the hornbeam chemi-mechanical pulp (CMP) against optical deterioration in subsequent accelerated irradiation aging (Vaysi et al. 2013). Quinone structures and their precursors, such as hydroquinones and catechols, are important reaction intermediates and products in the photo-yellowing process in ground wood pulps. In fact, the new phenolic and carboxylic groups are formed from quinone radicals during photo-yellowing and long-term accelerated light aging. The α-quinones can be oxidized to muconic acids by peroxide or can be reduced to catechols by dithionite reductive bleaching. These compounds contain new chromophoric groups that in combination with metallic ions may account for the observed unfavorable effects on pulp brightness, including brightness reversion. Peroxide can cleave the aliphatic lignin side chain if the Cα carbon has a carbonyl group (“Dankin reaction”); however, the resulting hydroquinone is also oxidized by secondary radicals arising from peroxide decomposition to a p-quinone (Fig. 1), (Ek et al. 1992).
The mechanism of moist thermal yellowing of fully bleached chemical pulps was studied using dissolving pulp impregnated with various types of degradation products from hexenuronic acid, viz. 2-furancarboxylic acid, 5-formyl-2-furancarboxylic acid, and 2,3-dihydroxy-2-cyclopenten-l-one (reductic acid) either alone or in combination with Fe$^{2+}$ or Fe$^{3+}$ ions. It was found that the two latter acids take part in reactions leading to color formation, whereas 2-furancarboxylic acid does not. It appears that the effect of ions from iron on the color formation depends on their oxidation state. The brightness loss arising from either 5-formyl-2-furancarboxylic acid or reductic acid, present in an amount similar to the content of hexenuronic acid in industrial pulps, was of the same order of magnitude as that observed for industrial pulps aged under the same conditions. The presence of ferrous ions further enhances the discoloration (Sevastyanova 2006).

Recently, the use of high yield mechanical and CMP has been important for the pulp and paper industry. These lignin-rich mechanical pulps are susceptible to photo-oxidative reactions, which cause these pulps to become discolored and to exhibit brightness reversion. Newsprint has shown the largest amount of yellowing when exposed to polychromatic irradiation in the wavelength region of 330 to 385 nm (UV-A region). The color change has been attributed to the formation of new phenolic and carboxylic groups from quinines radicals during photo-yellowing and long-term accelerated light-induced aging (Andrady and Searle 1995).

The aim of this study was to modify or remove the lignin, extractive substances, metal ions, and coloring agents from pulp in the bleaching process using chemicals (Saint-Cyr et al. 2002; Tutus and Usta 2004; Vaysi and Mirshokraie 2007). Therefore, the objective was to evaluate the effect of thermal yellowing on the brightness reversion of hornbeam CMP bleached with hydrogen peroxide and sodium dithionite.
EXPERIMENTAL

Methods

Pulping

In this study, hornbeam (Carpinus betulus L.) chips were chosen randomly from Mazandaran Wood and Paper Mill (MWPM, Sari, Iran). The moisture of the chips was measured after washing them. Then, the chips were subjected to CMP processing (L/W = 7/1; SO₂: 116 g/L; Na₂O: 106 g/L; and Na₂SO₃: 20% for 60 min at 160 °C). Unbleached pulp yield obtained after the cooking was determined as 85%.

Pulp bleaching

Hydrogen peroxide (H₂O₂) bleaching was applied to the CMP without DTPA (H₂O₂; No DTPA treatment) and with DTPA as chelating agent under the following bleaching conditions: Hydrogen peroxide: 3%; sodium hydroxide to hydrogen peroxide ratio: 0.7%; DTPA charge: 0.3%; Na₂SiO₃: 3%; pulp consistency: 12%; time: 1 h; and temperature: 75 °C. Afterwards, the bleached pulps were beaten to 300 mL freeness (CSF) using a PFI mill (a laboratory refiner according to CPPA-C.7 standard (Bonin et al. 1989). Unbleached CMP was also complementary bleached with sodium dithionite (H₂O₂ + Na₂S₂O₄) under the following conditions: DTPA: 0.3%; pulp consistency: 12%; time: 60 min; and temperature: 65 °C. Then handsheets of basis weight 60 g/m² were produced with bleached and unbleached CMP. Then, 0.5% DTPA solution was sprayed on the handsheets after 5 s, and the optical properties were measured by TAPPI standards (TAPPI 2009). Finally, 60 g/m² hand-sheets were separately made from bleached and unbleached pulps according to TAPPI T205 om-88 (1988).

Table 1. Bleaching Conditions with Hydrogen Peroxide (P) and Sodium Dithionite (Y) in Bleaching Sequences of the Chemical-mechanical Pulp of Hornbeam

<table>
<thead>
<tr>
<th>Row (R.)</th>
<th>Bleaching conditions</th>
<th>Pre-treatment with DTPA</th>
<th>Sodium dithionite (Y)</th>
<th>Hydrogen peroxide (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dryness (%)</td>
<td>4</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>Temperature (°C)</td>
<td>25</td>
<td>65</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>Time (min)</td>
<td>30</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>4</td>
<td>DTPA(%)</td>
<td>0.30</td>
<td>0.25</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>H₂O₂(%)</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>NaOH(%)</td>
<td>-</td>
<td>-</td>
<td>1.50</td>
</tr>
<tr>
<td>7</td>
<td>Na₂S₂O₃(%)</td>
<td>-</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Final pH</td>
<td>5.10</td>
<td>4</td>
<td>9.10</td>
</tr>
<tr>
<td>9</td>
<td>NaOH·H₂O₂ (Weight ratio)</td>
<td>-</td>
<td>-</td>
<td>0.70</td>
</tr>
<tr>
<td>10</td>
<td>Sodium silicate (%)</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
</tbody>
</table>

Thermal properties

Brightness and color changes (i.e., L*, a*, and b* values) were measured on handsheets using a Technibrite Micro TB-1C spectrophotometer (Elrepho Co., Stockholm Sweden) using TAPPI T1215 sp-03 (2007). The handsheets were subjected to thermal aging at 105 °C in the autoclave and time periods 0, 10, 20, 30, and 40 minutes (min) for accelerated thermal aging. The optical properties (brightness, opacity, yellowness, and
greenness) of the handsheets were measured before and after thermal aging according to ASTM and TAPPI standard methods (according to TAPPI T452 om-98 (1996), TAPPI 425 om-96 (1996), ASTM E313 (2015), and TAPPI T527 om-02 (2007), respectively). The specific light scattering (s), light absorption (k) coefficient, k/s ratio, and post color (PC) number were calculated using the Kubelka-Munk theory. The k/s value and PC number were calculated by the following equations (Ek et al. 1991; Mailly et al. 1997; Paulsson et al. 2001),

\[ k/s = (1-R_x)^2/2\cdot R_x \]  
\[ \text{PC number} = 100((k/s) - (k/s)_{\infty}) \]  

where s is the light scattering coefficient, k is the light absorption coefficient, t is the irradiation time (min), and R_\infty is the reflectivity of an infinite pile of hand-sheets.

**Statistical Analysis**

Data analysis was performed using SPSS statistical software. To investigate the variables’ interaction, a completely randomized design and one-way variance analysis test, as well as the means grouping by the Duncan method were used.

**RESULTS AND DISCUSSION**

The results of this study showed that with thermal aging (≤ 40 h), the absorption coefficient (k), k/s ratio, opacity, yellowness (b*), greenness (a*), and PC number were increased (almost), whereas the brightness was decreased. The PC number is a scale for paper aging, and has a value of zero at the start of accelerated aging (t = 0 h). In addition, several factors and structural elements have been proposed or considered as initiators or the main cause of the yellowing in high-yield pulp (HYP) and mechanical pulp: Oxygen, α-carbonyl structures, lignin double bond structures, singlet oxygen, various radicals, phenolic groups (catechols), ortho-quinones, para-quinones such as methoxy-p-benzoquinone, lignin β-O-4 structures, hydroquinones, and stilbenes formed from the phenylcoumaran type entities. The yellowing phenomenon has been attributed to a light-induced oxidation (related to thermal aging) of the lignin present in the pulp (Forsskahl et al. 2000; Tran 2003).

Handsheets bleached with H_2O_2 revealed the highest PC number and the least brightness stability. In the H_2O_2 bleaching, absorption coefficient, k/s ratio, greenness, and PC number were decreased, and brightness was increased. Following aging up to 40 h, all optical properties, except for brightness, increased. These changes were most noticeable up to 20 h of thermal aging. Based on these findings, the overall mechanism of thermal yellowing is suggested to involve several stages, including the degradation of hexenuronic acid and the formation of reactive precursors, such as 5-formyl-2-furancarboxylic acid or reductic acid, which subsequently take part in the yellowing reactions. The presence of ferrous ions further enhances the discoloration (Sevastyanova 2006). Supplementary bleaching with sodium dithionite improved the optical properties of the handsheets as well. Light-induced yellowing is principally associated with lignin-rich pulps (i.e., HYP). The HYP discoloration is dominated by lignin-based reactions including the ketyl, phenoxy, and phenacetyl pathways, phenoxyquinone redox cycle, and stilbene photo degradation.
Quinones and other chromogenic substances are produced through these pathways (Kojima et al. 2014).

Through spraying DTPA solution on the surface of hand sheets, brightness, opacity, and yellowness were improved, whereas the k/s ratio and PC number were decreased. Among various samples examined after thermal aging, it was found that in long-term aging, DTPA spray had a considerable effect on brightness stability and thermal aging. Some metal ions present in water used for papermaking could affect the optical quality of paper and cause a remarkable decrease in brightness and brightness stability. The results showed that brightness loss due to metal ions was as high as 4 to 5 points. Further, it indicated that using DTPA in a small amount could recover the brightness loss in the presence of transition metal ions. Moreover, the results showed that transition metal ions in complexation with lignin-like structures prompted increase in the light absorbency in visible region considerably (Abdulkhani and Mirshokraie 2006).

Changes in PC number were more noticeable for the first 20 h of thermal aging (Table 1, Figs. 2 through 7). The DTPA treatment in long-term thermal aging and the use of sodium dithionite and hydrogen peroxide in short to long aging provided better brightness stability, and paper durability in thermal aging. In fact, new phenolic and carboxylic groups are formed from quinone radicals during photo-yellowing and long-term accelerated light aging. These o-quinones can be oxidized to muconic acids by peroxide or they can be reduced to catechols by dithionite reductive bleaching (Fig. 1). These new groups could form chromophoric groups in combination with metallic ions. Such factors may account for the observed unfavorable effects on pulp brightness, including brightness reversion (Ek et al. 1992; Qiu et al. 2003). The yellowing of cellulosic is thought to be caused by three stress factors: chemical (oxidative and/or hydrolytic) stress, photo stress (light and irradiation), and thermal stress (high temperatures). These factors individually cause the yellowing or in combination. As a consequence of these physico-chemical influences, molecular changes arise in the cellulose material, which are reflected by losses in molecular weight (and often crystallinity) (Area and Cheradame 2011; Ahn et al. 2019). The residues from bleaching chemicals (Eiras et al. 2005), hexeneuronic acid (HexA) and similar compounds (Sevastyanova et al. 2006), lignin residues (Jääskeläinen et al. 2009), or the hemicellulose content could act as the important chemical constituents that cause major color generation in pulp used for real-world applications.

**Table 2. Average of Optical Properties of Bleached Horn Beam CMP Pulp Following Thermal Aging**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Brightness (%)</th>
<th>Opacity (%)</th>
<th>Yellowness (%)</th>
<th>k/s *1000</th>
<th>PC *100</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached*</td>
<td>38.73</td>
<td>94.24</td>
<td>25.42</td>
<td>232.11</td>
<td>2.43</td>
<td>71.59</td>
<td>0.99</td>
<td>12.73</td>
</tr>
<tr>
<td>H₂O₂ Bleached*</td>
<td>53.84</td>
<td>82.28</td>
<td>24.01</td>
<td>69.29</td>
<td>2.23</td>
<td>82.97</td>
<td>-0.5</td>
<td>13.96</td>
</tr>
<tr>
<td>Thermal Aging</td>
<td>51.58</td>
<td>82.41</td>
<td>21.96</td>
<td>51.84</td>
<td>0.64</td>
<td>86.69</td>
<td>-0.65</td>
<td>17.15</td>
</tr>
</tbody>
</table>

** Vaysi and Kord 2013

Mean optical properties and paper aging time between different treatments and aging times based on the Duncan test were also studied. According to the results of Duncan tables, there was a significant difference between the mean optical properties in the
treatments at the 99% confidence level (for yellowness at the 95% confidence level). In addition, there was a significant difference between the mean of the properties of brightness, opacity, PC number, and the aging time at the 99% confidence level as well as for the yellowness at the 95% confidence level, but there was no significant difference in other optical properties (Table 3).

**Fig. 2.** Changes of brightness in hand-sheets of hornbeam CMP pulp after thermal aging

**Fig. 3.** The changes of yellowness in hand-sheets of hornbeam CMP pulp after thermal aging
Table 3. One-way Analysis of Variance and Duncan Test between Mean of Treatments and Aging Time

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Brightness</th>
<th>K/S</th>
<th>Opacity</th>
<th>Yellowness</th>
<th>PC</th>
<th>Factor a*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>S.L</td>
<td>F</td>
<td>S.L</td>
<td>F</td>
<td>S.L</td>
</tr>
<tr>
<td>Treatment</td>
<td>25.112</td>
<td>0.0001**</td>
<td>130.68</td>
<td>0.0001**</td>
<td>57.82</td>
<td>0.0001**</td>
</tr>
<tr>
<td>Aging time (h)</td>
<td>5.912</td>
<td>0.0001**</td>
<td>0.469</td>
<td>0.469</td>
<td>3.401</td>
<td>0.01**</td>
</tr>
</tbody>
</table>

1Significant level: S.L, *It is significant at 95% confidence level,, ** It is very significant at 99% confidence level.

Fig. 4. The changes of opacity number in hand-sheets of hornbeam CMP pulp after thermal aging

Fig. 5. The changes of a* factor in hand-sheets of hornbeam CMP pulp after thermal aging
Fig. 6. The changes of k/s ratio in hand-sheets of hornbeam CMP pulp after thermal aging

Fig. 7. The changes of post color number in hand-sheets of hornbeam CMP pulp after thermal aging

Complementary bleaching with sodium dithionite, after peroxide bleaching, improved the optical behavior of the handsheets in short-term aging, but in longer aging, the least brightness stability and the greatest optical deterioration were observed in unbleached paper and H₂O₂ bleaching and supplementary bleaching with sodium dithionite.

Reportedly, hypochlorite and ozone oxidations introduce all three chemical moieties (carboxyl, aldehyde, and ketone groups), their relative content depending on the
reaction conditions, while hydrogen peroxide oxidation results mostly in ketonic groups being introduced. Some studies (Lewin and Epstein 1962; Mosca et al. 2012) investigated the aging processes in paper and determined that carbonyl groups in the form of aldehyde moieties and conjugated diketones are key chromophores derived from polysaccharides that lowered optical quality in pulps and paper (Rosenau et al. 2005).

Among various samples examined for thermal aging, it was found that DTPA spray considerably increased the brightness stability in long-term aging. The DTPA spray improved brightness stability and it decreased brightness reversion, thus provided better resistance towards optical deterioration. The components of false lignin are likely to be involved in the thermal yellowing of a bleached pulp. The lignin content in a fully bleached chemical pulp is usually low, but traditionally lignin is suspected as a precursor in the formation of chromophores. It may also form complexes with metal ions and thus give rise to a more intense color. The hexenuronic acid groups present in pulp xylan apparently play a dominant role in the brightness reversion of bleached kraft pulp on exposure to heat (Granström et al. 2002; Borrega et al. 2013). Considering the role of the pulp and paper industries as a mainstay in many economies worldwide, the importance of bleaching processes in the pulp and paper industries, and the customer’s notion that bright white materials are of high quality and purity, it is evident that yellowing and brightness reversion of celluloses have been a topic of great interest (Yuan and McGarry 2002; Suess 2010).

**CONCLUSIONS**

This study evaluated the effect of thermal yellowing on the brightness reversion of hornbeam chemi-mechanical pulp (CMP) bleached with hydrogen peroxide and sodium dithionite. The most important results obtained from this investigation can be summarized as follows:

1. With accelerated thermal aging up to 40 h, all optical properties (except for brightness) increased relative to untreated specimens.
2. The post color (PC) number is a scale for paper aging, and zero represents without accelerated paper aging. These changes were more noticeable in the first 20 h of thermal aging.
3. After long-term aging, the least brightness stability and the greatest optical deterioration were observed from the unbleached and peroxide-bleached pulp. This is because the oxidizing agent \( \text{H}_2\text{O}_2 \) converted some of the chromophoric groups (quinones) to acid functional groups during the course of bleaching.
4. Additional bleaching with sodium dithionite improved the optical behavior of the hand-sheets exposed to short-term thermal aging; however, in long-term aging, the lowest brightness stability and the greatest optical deterioration were observed in unbleached paper and a combination of \( \text{H}_2\text{O}_2 \) bleaching with supplementary sodium dithionite bleaching.
5. The DTPA treatment for long-term aging and the use of sodium dithionite and hydrogen peroxide for short-long aging imparted better brightness stability.
6. The results of this study showed that from 0 to 40 h of thermal aging, the optical properties of paper except for brightness and greenness parameters were increased.
This increase was more remarkable up to 15 h of thermal aging. In addition, among different treatments, the DTPA treatment in long-term thermal aging and the use of sodium dithionite and hydrogen peroxide in the short-term aging, have important influences on brightness durability and decrease in color reversion. As a result, there is an increase in paper durability against thermal deterioration.

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