ABSTRACT: The compromise between reaching pulp target brightness and guaranteeing a high-quality bleached pulp is often difficult to manage because of the nature of the last chromophores present. This study reports the performance of either hydrogen peroxide or chlorine dioxide in a final bleaching stage applied to three eucalypt $D_0E_{0P}D_1$ kraft pulps to reach a target ISO brightness of $90\pm0.5\%$. The $D_1$ pulps had ISO brightness values of 84.7\%, 86.9\%, and 88.7\% (pulps A, B, and C, respectively). The experimental results revealed that while chlorine dioxide charge was linearly correlated with $D_1$ brightness, a much higher hydrogen peroxide charge was needed to bleach pulp A compared with pulps B and C. All P pulps had lower brightness reversion and better beatability than $D_1$ pulps. In addition, we observed better physical and optical papermaking properties in P pulps (except for tear index for pulp A), although these pulps exhibited lower intrinsic viscosity. Therefore, the best choice for completing that particular ECF sequence is to push chlorine-dioxide bleaching action in $D_1$ until at least 87% ISO brightness is reached, with the purpose of degrading phenolic units as much as possible, and then to advance with peroxide to boost brightness at the cost of quinone destruction.

Application: Considering the chromophore content at the end of an ECF pulp-bleaching sequence, a final P stage may offer better pulp quality than a final $D_1$ stage. In this context, it is advisable to use $D_1$ pulps with ISO brightness of approximately 87\% or higher.

Elemental-chlorine-free (ECF) and total-chlorine-free (TCF) pulp bleaching sequences have ushered in a new phase of modern multistage bleaching technology focused on the development of efficient environmental protection. The main driving force behind this shift in bleaching concepts was new requirements for reduction of the adsorbable-organic-halogen (AOX) level in effluents from earlier chlorine-based bleaching technologies [1]. This goal of minimizing the environmental impact of pulp mills gave oxygen-based bleaching chemicals such as oxygen, hydrogen peroxide, and ozone a more prominent role.

Hydrogen peroxide is well known for its twofold nature as a pulp delignifying and bleaching agent. Nowadays, as a result of its versatility, it is widely used, not only as a full bleaching stage, but also as a reinforcement agent in alkaline extraction and after oxygen delignification [2]. Not surprisingly, hydrogen peroxide is believed to play a key role in TCF advanced bleaching sequences to achieve high brightness within the so-called minimum-impact mill concept. Nevertheless, ECF is still the preferred bleaching technology in many mills, including the Portuguese pulp and paper industry, a fact that can be attributed mainly to the high production costs of TCF pulps, which offer lesser pulp quality, with emphasis on lower viscosity. On the other hand, there is an ever-increasing demand for high-brightness paper, which has forced higher consumption of bleaching chemicals in market pulp mills and of optical brighteners in integrated pulp mills. A clearer knowledge of final bleaching conditions could definitely improve pulp quality and process economics.

In this context, past research has shown the benefits of replacing the usual final chlorine dioxide stage ($D$) of an ECF kraft pulp sequence (in some cases in conjunction with the preceding extraction stage, $E$) with a final peroxide stage ($P$). A boost in final brightness [3–6], a decrease in brightness reversion [5–8], and chlorine dioxide savings [4,5,7] are examples of such benefits. This remarkable performance of the final $P$ stage is undoubtedly related to the change in the bleaching environment as the pulp moves from an acidic $D$ stage to an alkaline $P$ stage, and to the chemical nature of the last remaining chromophores present in the pulp, which are more prone to react with hydrogen peroxide than with chlorine dioxide.

Despite this evidence, some mill personnel are reluctant to apply a final $D$-stage substitution. This can be explained partly by lack of knowledge about peroxide performance as a final bleaching agent and partly by lack of knowledge of the initial pulp conditions that could ensure best results. The authors found that previous studies of final bleaching optimization with peroxide paid little attention to initial brightness effects on its performance, and moreover the initial brightness values mentioned are too low to achieve conclusive results. Instead of the kappa number dependence [9,10], the values of which are difficult to measure with accuracy at the end of the bleaching sequence, the current approach is to consider chromophore content as a variable affecting final peroxide-
bleaching performance. It has already been reported for a TCF bleaching sequence that total hydrogen-peroxide charge to reach full brightness was highly dependent on the pulp brightness entering the bleach plant [11].

A key motivating factor for this study was also the intriguing results previously obtained concerning the effects of initial brightness on the performance of the last P stage [12]. As a result, the main goal of the present work was to evaluate the effects of initial brightness on the quality of eucalyptus bleached-kraft pulp subjected to a $D_0E_{\text{op}}D_1$ sequence complemented with a final P stage as a replacement for a $D_1$ stage.

A final bleaching stage is a brightening stage, which aims to attain the last difficult brightness points with the destruction of the remaining chromophores. In this context, the action of peroxide resembles that of the lignin-retaining bleaching stages in mechanical-pulp bleaching. In this sense, final chemical-pulp bleaching with peroxide is carried out under alkaline conditions to ensure the formation of the primary agent responsible for pulp-brightening reactions, the perhydroxyl anion, $\text{HOO}^-$, in accordance with the equilibrium reaction given in Equation [2] ($\text{pK}_a = 11.6$ at 25ºC):

$$H_2O_2 + HO^- \leftrightarrow H\text{OO}^- + H_2O \quad (1)$$

Therefore, alkali pulp brightening with peroxide is a result of the selective reaction of the perhydroxyl anion with certain types of chromophores [13], particularly carbonyl structures (e.g., quinones previously produced in D stages) present in the residual lignin [14,15], whereas unreacted phenols remain intact [16]. The peroxide consumption in the course of a P bleaching stage is, however, not restricted to brightening. Competitive reactions, known to be catalyzed by transition metal ions, also occur in the P stage, producing hydrogen-peroxide decomposition products such as hydroxyl radicals and superoxide anions. Because of the unselектив nature of these species, they can degrade polysaccharides, resulting in a lower pulp intrinsic viscosity. Therefore, maximum peroxide-brightening performance requires a previous metal-management stage using acids or chelants [17] to minimize the peroxide decomposition rate by removing those detrimental transition metals (e.g., Mn, Fe, and Cu).

In the final stage of an ECF bleaching sequence with preceding intensely acidic chlorine dioxide stages, the metal content can be expected to be already low. However, it has been reported that even the lowest achievable level of transition metals is high enough to catalyze peroxide decomposition into free radicals. On the other hand, a certain level of alkaline-earth metals (e.g., Mg and Ca) is required to deactivate the remaining transition metals. This requirement is most significant in the case of acid-treated pulps because unlike chelation, acid stages remove metals unselectively, so the restoration of the appropriate alkaline-earth-metal profile is necessary [18]. Therefore, in the current study, magnesium sulfate was added to the P stage in the case of the most promising bleaching conditions.

### EXPERIMENTAL

*Eucalyptus globulus* pulp was collected before entering the $D_1$ bleaching stage of a Portuguese kraft pulp mill. The $D_0E_{\text{op}}$ pulp (made without oxygen delignification) with an ISO brightness of 78% was bleached in the laboratory at several chlorine dioxide charge levels to obtain three $D_0E_{\text{op}}D_1$ pulps with different ISO brightness levels. These were labeled as pulps A, B, and C and exhibited ISO brightness values of 84.7%, 86.9%, and 88.7%, respectively. These $D_0E_{\text{op}}D_1$ pulps were then bleached with hydrogen peroxide in several trials with various values of retention time, temperature, and sodium hydroxide and peroxide charge to reach 90±0.5% ISO brightness. In the case of the most promising bleaching conditions, 0.05% odp (oven-dry pulp) magnesium sulfate was added to reduce viscosity loss and chemical consumption. With the intent of performing a comparative study, another set of bleaching trials was performed with chloride dioxide using each of the $D_0E_{\text{op}}D_1$ pulps, also with a target of 90±0.5% ISO brightness. Finally, the best $D_0E_{\text{op}}D_0P$ and $D_0E_{\text{op}}D_0P$ pulps (with respect to brightness, intrinsic viscosity, and brightness reversion) were subjected to beating and to the determination of physical, optical, and structural handsheet properties.

<table>
<thead>
<tr>
<th>Bleaching variable</th>
<th>Final D</th>
<th>Final P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>70</td>
<td>70–90</td>
</tr>
<tr>
<td>Time (min)</td>
<td>150–180</td>
<td>60–120</td>
</tr>
<tr>
<td>D* or P charge (% odp)</td>
<td>0.4–1.05</td>
<td>0.7–2.5</td>
</tr>
<tr>
<td>NaOH charge (% odp)</td>
<td>---</td>
<td>0.35–1.0</td>
</tr>
<tr>
<td>MgSO₄·7H₂O (% odp)</td>
<td>---</td>
<td>0.0–0.05</td>
</tr>
</tbody>
</table>

*calculated as active Cl₂; odp – oven-dry pulp.

1. Ranges of experimental bleaching conditions with chloride dioxide and hydrogen peroxide.

All bleaching trials were run in sealed polyethylene bags immersed in water baths at 10% consistency with 25 g odp. Table 1 summarizes the ranges of bleaching conditions. After bleaching, chemical consumptions were determined, and the bleached pulp samples were washed with three liters of distilled water (~35°C) divided into three equal portions. Intrinsic viscosity was determined according to ISO 5351.

Handsheets for determination of optical properties were prepared using the standard procedure described in ISO 3688. Brightness, brightness reversion, and opacity were measured according to ISO 2470, T 260, and ISO 2471, respectively. Brightness reversion was expressed in terms of % ISO (brightness difference between initial and post-aging values) and of post-color (PC) number. The latter quantity uses the ratio of the specific absorption (k) to the specific light scattering (s), which in turn is related to the reflectance of an opaque sheet of paper of infinite thickness, $R_{\infty}$, by the Kubelka-Munk equation:

$$R_{\infty} = \frac{(1-R_0)^2}{2SR_b}$$
The change in k/s is directly proportional to the amount of chromophores formed during the aging test. Handsheets for determination of physical properties were prepared using the standard procedure described in ISO 5269/1. These properties were evaluated before and after beating in a laboratory PFI mill at 1000 and 2000 revolutions (ISO 5264/2). Tensile index, tear index, bulk, and air resistance (Gurley method) were measured according to ISO 1924/2, ISO 1974, ISO 534, and ISO 5636/5, respectively.

### RESULTS AND DISCUSSION

To accomplish the goals of this research, a final bleaching stage with peroxide or chlorine dioxide was performed to attain an ISO brightness target of 90±0.5% using pulps A, B, and C with different initial ISO brightness values (84.7%, 86.9%, and 88.7%). Optimal bleaching conditions with respect to chemical consumptions and pulp properties (viscosity, brightness, and brightness reversion) are listed in Table II.

In terms of chemical charges needed to reach 90±0.5% ISO brightness, as shown in Fig. 1, an almost linear relation is observed between the chlorine dioxide charge in the D₂ stage and the brightness of the D₁ pulps, while the proportioned peroxide charge needed to bleach pulp A is much higher compared with that required for pulps B and C. Accordingly, it seems preferable to extend chlorine dioxide bleaching in the D₁ stage up to an ISO brightness of approximately 87% or higher before final peroxide bleaching.

In this sense, it is essential to bear in mind the important role attributed to quinone structures in final pulp bleaching. These structures are part of the major colored systems present in lignin and are also side-reaction products of chlorine dioxide and oxygen bleaching stages. On this point, Zawadzki et al. [19] confirmed the importance of the effect of these structures on the final brightness values of DEDED pulps with the finding of a correlation between E₁ and D₂ lignin-quinone contents and D₁ and D₂ brightness values. Further work by Mateo et al. [20] showed that the remaining chromophores of an ECF (D₀E₁D₂₁) pine kraft pulp bleached to 84% ISO brightness were mainly of the quinone type. For a DEDED pulp with 88.1% ISO brightness, it was suggested that the last chromophores were more likely to be of the quinone-phenol type [21]. Theoretically, in both cases, the best ECF bleaching option would be a final P stage complementing the previous D stages.

In spite of the great reduction of hydrogen peroxide charge from pulp A to pulp C, the charges used in this work are still relatively far from those reported by Süss et al. [5], who reported that 0.25% H₂O₂ (at 80ºC for 3h) was needed to bleach a pulp from 87.7% to 90+% ISO brightness. This difference can be partly attributed to the sequence type (OD₁E₁D₂₁), which certainly has an impact on the amount and type of chromophores present in the pulp. Considering that ECF bleaching without oxygen delignification demands more intense chlorine dioxide stages and that there is a dramatic increase in the quinone content in the D₀ stage relative to the brownstock residual lignin value [22], more peroxide charge will be required to achieve quinone destruction. Quinones can be also produced during oxygen delignification, although to a lesser extent than with chlorine dioxide [22]. Using more accurate in-situ methods, Brogdon et al. [23] have confirmed that quinone structures are important in the final bleaching of ECF pulps.

**Table II. Optimal conditions for final D and P bleaching of pulps A, B, and C (P stage: T=70ºC, t=60 min, [MgSO₄] = 0.05% odp; D stage: T=70ºC, t=180 min) and pulp properties.**

<table>
<thead>
<tr>
<th>D₀E₁D₂₁ pulp</th>
<th>Final stage</th>
<th>[ClO₂]* (% odp)</th>
<th>[H₂O₂] (% odp)</th>
<th>[NaOH] (% odp)</th>
<th>Intrinsic viscosity (dm³/kg)</th>
<th>ISO brightness (%)</th>
<th>Brightness reversion %</th>
<th>PC number</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>D₂</td>
<td>1.10</td>
<td>---</td>
<td>---</td>
<td>970</td>
<td>90.5</td>
<td>4.3</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>---</td>
<td>2.50</td>
<td>0.7</td>
<td>690</td>
<td>90.5</td>
<td>3.6</td>
<td>0.48</td>
</tr>
<tr>
<td>B</td>
<td>D₂</td>
<td>0.80</td>
<td>---</td>
<td>---</td>
<td>990</td>
<td>90.2</td>
<td>4.2</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>---</td>
<td>1.20</td>
<td>0.6</td>
<td>850</td>
<td>90.8</td>
<td>3.4</td>
<td>0.44</td>
</tr>
<tr>
<td>C</td>
<td>D₂</td>
<td>0.35</td>
<td>---</td>
<td>---</td>
<td>1000</td>
<td>89.8</td>
<td>4.4</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>---</td>
<td>0.65</td>
<td>0.5</td>
<td>910</td>
<td>90.3</td>
<td>3.0</td>
<td>0.40</td>
</tr>
</tbody>
</table>

* as active Cl₂.
nones are a significant product formed during the $D_0$ stage. As a matter of fact, $D_0$ stages definitely comprise both delignification and darkening reactions, which have been suggested to have a detrimental impact on final brightening efficiency. This important impact on pulp bleachability attributed to quinones is corroborated by Lachenal et al. [24], who found that pulps richer in quinone groups are more difficult to bleach by ClO$_2$-based ECF sequences.

The differences between hydrogen peroxide and chlorine dioxide reactions with pulp chemical structures are proposed here to explain the results presented in Fig. 2 concerning brightness reversion. Brightness reversion has been attributed to several compounds and bleaching conditions. Among these, oxidized structures like carbonyl groups are important contributors, as described by Adorjan et al. [25], who found a linear correlation between carbonyl content and PC number. Moreover, final bleaching in $D$ stages (where the amount of residual lignin is very low) shows a greater potential to form carbonyl groups in the cellulose and remaining hemicellulose moieties, resulting in greater brightness reversion. Therefore, as perhydroxyl anion reacts preferentially with carbonyl structures such as quinones, a brightness gain can be obtained with a concomitant low reversion (higher brightness stability), as shown in Fig. 2. These lower brightness-reversion values for pulps bleached with a final peroxide stage are consistent with the other work already mentioned and have also been confirmed in mill tests in Brazil [26,27].

As for intrinsic viscosity, it can be seen in Fig. 2 that peroxide has a negative impact on viscosity, while chlorine dioxide does not. Higher peroxide charges result in higher viscosity loss. In the present work, the charges of the stabilizer (MgSO$_4$.7H$_2$O) were not fully optimized and were insufficient from the viscosity point of view. Other authors have shown the positive effect of magnesium ions on peroxide bleaching using higher charges [4,7,12]. However, the introduction of 0.05% odp of MgSO$_4$.7H$_2$O in the $P$ stage led to a lower peroxide consumption (for instance, ~12% lower for pulp C), showing a reduction in the catalytic activity of transition metals toward peroxide decomposition.

As mentioned before, pulps A, B, and C fully bleached with either peroxide or chlorine dioxide were subjected to an evaluation of their papermaking potential. As can be seen in Fig. 3, the current results concerning pulp beatability, based on pulp drainability according to the Schopper-Riegler (SR) scale, reveal that peroxide pulps need fewer PFI revolutions to achieve the same beating degree, thus enabling important energy savings in paper mills.

Tensile-index results displayed in Fig. 4 show that final bleaching with peroxide enables a higher development of this index with beating and provides handsheets with better tensile strength in comparison with the final $D$ stage. Regarding tear-index results, presented in Fig. 5, it is difficult to establish a general trend common to all pulps. However, as peroxide charge decreases (equivalent to an increase in chlorine dioxide charge in $D_1$) from pulp A to pulp C, the tear index improves, reaching the highest values observed for $D$ pulps except for pulp A. Handsheet physical resistance results from fiber intrinsic resistance and the degree of bonding between fibers. In the case of a hardwood pulp, bonding is of utmost importance because of the short fiber length of hardwoods. Mainly because of fibrillation, it can be seen in Figs. 4 and 5 that beating provides an improvement in handsheet physical resistance, but at the cost of intrinsic fiber resistance. Figure 5 shows that P pulps attain the tear ceiling values at higher tensile indices. Pulp C bleached with a final $P$ stage could be beaten to tensile indices of 80–85 N.m/g without a decrease in tear index.

Opacity is a measure of the ability to obstruct the passage of light [28]. For this reason, opacity increases with the number of air interfaces in the fiber web, which are responsible for higher light scattering. Although a more porous and bulk-
ier handsheet has greater opacity, its physical properties are compromised because of voids in the fiber matrix that hinder fiber bonding. Compromise is always needed between these important papermaking properties, and again final bleaching with peroxide seems to be a good option to fulfill papermaking demands for high-quality paper (Figs. 6–8), because it provides bulkier handsheets with higher opacity. As expected, opacity decreases with tensile index (Fig. 6), just as bulk does (Fig. 7), whereas air resistance increases.

By holding one variable constant, for instance tensile index at 70 N.m/g, it is possible to make a clearer comparison of some of the results discussed above (Figs. 5–8). It is clear that a higher tear index can be obtained for D pulps, but that P pulps have higher opacity and bulk. Nevertheless, it should be stressed that the P pulps show greater papermaking potential because of their better beatability, which enables papermakers to develop greater paper resistance while at the same time adjusting other interdependent paper properties.

**CONCLUSIONS**

A successful multistage ECF bleaching sequence owes a certain amount of its cost-effectiveness, pulp quality, product differentiation, and environmental performance to the final brightening stages, yet the bleaching sequence should be perceived as a whole. This work has thoroughly analyzed the frontier between the D₁ and the final P stage in terms of the effect of chromophore content on final peroxide bleaching performance (to attain an ISO brightness of 90±0.5%) compared with chlorine dioxide bleaching. It follows from the results that pulps bleached with a final peroxide stage have lower brightness reversion and, in general, better papermaking potential (physical and optical properties) than D₂ pulps, even though they exhibit a lower intrinsic viscosity. Further work on optimizing the magnesium sulfate charge is essential to prevent unwanted viscosity loss. An exception was observed for the P pulp with the lowest initial brightness (84.7%), which attained a lower tear index than the corresponding D₂ pulp.

The performance of peroxide as a final brightening agent depends on the initial pulp brightness entering the final stage. Although the chlorine dioxide charge to be used is linearly dependent on D₂ pulp brightness, the hydrogen peroxide charge has a more pronounced dependence, being much higher for pulp with an initial brightness lower than 87%. Therefore, the best synergistic choice for the last part of an ECF sequence is to push the chlorine dioxide bleaching action in D₁ a little further to attain at least 87% ISO brightness and then advance with peroxide as a final stage to boost brightness.

From a literature review of the conditions used in final peroxide bleaching stages, it was perceived that the presence of a D₀ stage instead of an oxygen delignification stage could be a factor determining downstream bleachability in terms of the total peroxide charge to be used in the sequence [5]. This can be explained by the quinone content, which has elsewhere been reported to increase considerably in the D₀ stage [22,23] and therefore requires a greater peroxide charge to react. TJ
AKNOWLEDGEMENTS

The authors are grateful to Grupo Portucel Soporcel for making the D_EOP pulp available, RAIZ (Instituto de Investigação da Floresta e do Papel) for technical assistance with the papermaking properties evaluation portion of the trials, and Fundação para a Ciência e Tecnologia for the PhD scholarship granted to Pedro Loureiro.

Received: March 27, 2007
Accepted: January 14, 2008

LITERATURE CITED


INSIGHTS FROM THE AUTHORS

We chose this topic because it is one of the key subjects within the novel bleaching process, brightness stability being the main driving force.

One difficult aspect of this research was the control of the hydrogen peroxide decomposition. This can be minimized by using additives such as magnesium sulfate or chelants as well. We think the most important findings were the higher beatability exhibited by pulps bleached with a final P stage compared to pulps bleached with a final D stage and the dependence of the P stage performance on the initial pulp brightness.

This work can help mills achieve higher profit from the optimal use of the final P stage for those who already use this final stage. For others, this study shows the advantage of using peroxide at the final ECF stage.

Maria da Graça Videira Sousa Carvalho is an Auxiliary Professor of Chemical Engineering in the Centro de Investigação em Engenharia dos Processos Químicos e dos Produtos da Floresta (CIEPOPF), Department of Chemical Engineering, University of Coimbra, Portugal. Author contact: mgc@eq.uc.pt. Nuno Miguel Vasconcelos Carvalho is a research and development engineer with Portucel Cacia in Portugal. Pedro Emanuel Garcia Loureiro is a PhD student at CIEPOPF.