

## PERFORMANCE OF A FINAL HYDROGEN PEROXIDE STAGE IN DIFFERENT ECF BLEACHING SEQUENCES

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### SUMMARY

The performance of a final hydrogen peroxide stage (P), applied instead of the conventional chlorine dioxide stage (D) in the ECF bleaching of *E. globulus* kraft pulps, has been studied. Two industrial DED and OQ(PO)D bleached pulps were further bleached in the laboratory either with a D or a P stage until  $90 \pm 0.5\%$  ISO brightness. The papermaking potential of the four fully bleached pulps was assessed with respect to pulp beatability and strength/optical properties of the produced handsheets. The decomposition of peroxide in the final P stage of the DEDP and OQ(PO)DP sequences was estimated. While chlorine dioxide charge was nearly the same for both sequences, a much higher peroxide charge was needed in DEDP. The differences on bleachability with a final P stage were related to bleaching history impact on the nature and content of transition metals, residual chromophores as well as on additives performance. Decomposition reactions contribute significantly to peroxide consumption, especially at higher temperatures. Depending on the bleaching history, autoxidation reactions could contribute to the brightness gain at the final P stage. The papermaking properties revealed the advantages of final peroxide bleaching regarding pulp brightness stability, beatability, tensile strength, air resistance, bulk and opacity.

**Keywords:** chlorine dioxide, decomposition, bleaching history, hydrogen peroxide, pulp properties

### INTRODUCTION

Although the multi-stage process of kraft pulp bleaching has appreciably evolved from the 1950s with the introduction of chlorine dioxide and new equipment (e.g. medium consistency pumps and designed plug-flow towers at target consistency), only in the 1990's environmental issues became the key-drivers in bleaching trends [1]. As a result, extensive research was then devoted to minimize the environmental impact of the bleach plant effluents, largely associated with polychlorinated compounds. The use of chlorine dioxide instead of chlorine, oxygen delignification, hydrogen peroxide and/or ozone bleaching, together with an increased water-closure, were progressively studied and implemented. This "green period" gave rise to the well established elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching sequences as well as the intermediate ECF-light sequences.

Besides this imperative environmental side, the most modern 21<sup>st</sup> century fibrelines of today are focused on optimizing energy efficiency, capital and operating costs and improving product quality[2]. In the bleaching process the focus is put on the production of cost-effective high brightness pulps with a high degree of strength and brightness stability, mostly for the production of high grade bleached pulps such as those for printing and writing (P&W) paper grades. On the other hand, the increased market demand for hardwood bleached pulp, notably eucalypt pulp, has motivated many studies addressing further developments in the cooking and bleaching processes using this raw material.

The current technology of eucalypt pulp bleaching for the production of P&W paper grades is debatable[3]. In spite of advantageous in terms of market requirements, bleaching flexibility is seldom practiced, being chlorine dioxide based ECF sequences (DEDD or DEDED) the prevailing bleaching technology. Before bleaching, the kraft cooking and the pre-delignification stage (oxygen for the most

part) are usually optimized in an integrated way. In the specific case of hardwood pulp bleaching, hexeneuronic acids (HexA) are an extra important variable affecting bleaching efficiency and pulp quality, specifically brightness reversion. As for final bleaching, this area has been more comprehensively studied in recent times given the importance of the last stages to reach target brightness and on the overall bleached pulp quality [4-8]. In fact, it has been a far less understood area mainly because of the difficulties on the assessment of the few remaining chromophores.

The ever-increasing demand for high brightness paper has raised higher consumption of bleaching chemicals and of expensive optical brighteners. Accordingly, final bleaching optimization is of utmost importance. Among bleached pulp properties, brightness reversion is the most important property of high brightness pulps, since this is a property that can markedly change during post-bleaching conditions, thus counteracting the expensive final bleaching costs. Final bleaching has therefore a key-role in dictating the extent of brightness reversion and the process economics as a whole.

A final alkaline hydrogen peroxide stage (P) has been studied for replacing the conventional chlorine dioxide stage (D) or even both the second alkaline extraction and chlorine dioxide stages (ED)[6, 7, 9, 10]. The reported advantages of using a final P stage (DEDP *versus* DEDD) comprise a boost in brightness, a lower brightness reversion of the bleached pulp, chlorine dioxide savings, higher pulp beatability and slightly higher strength properties. In terms of brightness reversion the benefits of a final alkaline hydrogen peroxide stage are related to the impact on xylan structure (removal of chromophores)[8], whereas for pulp beatability and tensile strength the greater fibre swelling governs such improvements [11].

A focal point on hydrogen peroxide bleaching is the control of transition metals-induced decomposition of hydrogen peroxide. Monitoring metals profiles across the bleaching sequence before hydrogen peroxide stages is paramount in order to guarantee optimal results. The use of a prior dedicated acidic washing (A) or chelation stage (Q) is a common practice, as well as the addition of stabilizers (magnesium and/or chelants) into the P stage bleaching liquor. Otherwise, depending on the specific transition metal-catalyst, hydrogen peroxide is readily decomposed into oxygen and water with the possible production of unselective intermediate radical species. Hydrogen peroxide decomposition catalyzed by iron and copper anions involves the generation of radicals. Although manganese produces the fastest decomposition its action is through an ionic mechanism instead [12].

Based on the above considerations, the performance of a final hydrogen peroxide stage in the ECF bleaching of eucalypt kraft pulp strongly depends on the specific pulp bleaching history before entering in the final stage. Besides the important effect of pre-bleaching stages determining the stock composition and the nature of metal ions, the nature of the remaining chromophores should also be considered [13]. Accordingly, this study focuses on a comparison between the performance of a final hydrogen peroxide stage in different ECF bleaching sequences using industrial DED and OQ(PO)D partially bleached pulps. These pulps were further bleached in the laboratory with hydrogen peroxide or chlorine dioxide, the latter used for comparison. The four bleached pulps (DEDD, DEDP, OQ(PO)DD and OQ(PO)DP) were produced in the laboratory under optimized operating conditions in order to attain an ISO brightness target of  $90 \pm 0.5\%$ . Chemicals consumption in each final stage and the papermaking potential (structural, physical and optical properties) of the fully bleached pulps are compared and discussed. Additionally, an attempt was made to estimate the decomposition portion in the total consumption of hydrogen peroxide in both final P stages.

## EXPERIMENTAL

*Eucalyptus globulus* kraft pulps were collected before the final stage of the bleaching plants belonging to different Portuguese pulp mills. These pulps were bleached either by DED (without oxygen pre-delignification) or by OQ(PO)D sequences to ISO brightness of ca. 87.5%. These pulps were washed with distilled water and conditioned in dark at 4 °C. Afterwards, DED and OQ(PO)D pulps were laboratory bleached with a final alkaline hydrogen peroxide stage (P) to study the pulp brightening and degradation kinetics and to assess the extent of hydrogen decomposition. The results on kinetic studies were reported elsewhere [13-14].

All bleaching trials were run at 10% consistency in sealed polyethylene bags immersed in a reciprocal thermostatic water bath. After bleaching, chemicals consumption was determined: hydrogen peroxide and chlorine dioxide residual concentrations in the filtrates were measured by iodometric titration with standardized sodium thiosulphate, whereas sodium hydroxide was titrated, after barium chloride addition and filtration, with standardized hydrochloric acid until pH 8.6. The bleached pulp was then washed with distilled water, manually shredded and conditioned in the dark at 4°C.

DEDP and OQ(PO)DP bleached pulps were used to study hydrogen peroxide decomposition at the final stage under laboratory conditions. To estimate hydrogen peroxide decomposition in the final P stage, DED and OQ(PO)D pulps were exhaustively P bleached under harsh conditions (with one or more P stages or cycles) until a brightness ceiling was reached (~93%) as described in a previous study [15]. For the OQ(PO)D pulp, 0.1% (odp) of DTPA and 0.1% (odp) of MgSO<sub>4</sub> were added into the P cycle. The resultant top brightness pulps were labelled DEDP\* and OQ(PO)DP\* and were assumed to be chromophores free. P stages running in the same operating conditions were then applied to these pulps as well as to the starting DED and OQ(PO)D pulps. Therefore, the hydrogen peroxide consumption obtained by using DEDP\* and OQ(PO)DP\* pulps could only be assigned to decomposition reactions whereas for the DED and OQ(PO)D pulps the hydrogen peroxide consumption was a result of both chromophores removal and decomposition reactions [13].

For comparison purposes the conventional industrial DED and OQ(PO)D pulps were laboratory bleached with final P or D stages thus examining the performance of both reagents. The studied ranges of bleaching conditions of the final stages are summarized in Table 1 headed for reaching a final ISO brightness target of  $90 \pm 0.5\%$ . The papermaking potential of the four fully bleached pulps (DEDD, DEDP, OQ(PO)DD and OQ(PO)DP) was assessed with respect to pulp beatability and strength/optical properties of the produced handsheets. Pulp handsheets were prepared according to ISO 3688 for the measurement of ISO brightness following ISO 2470. The artificial reversion tests were run under high temperature and R.H. as detailed in Tappi T 260 standard procedure, and the results were reported as the Post-color number. The handsheets production for physical testing followed ISO 5269/1. Tensile index, tear index, bulk, air resistance (Gurley method) and opacity were measured according to ISO 1924/2, ISO 1974, ISO 534, ISO 5636/5 and ISO 2471, respectively, before and after beating in a PFI mill at 1000 and 2000 revolutions (ISO 5264/2). Pulp intrinsic viscosity was measured as described in ISO 5351.

**Table 1. Ranges of preliminary bleaching conditions used in the final bleaching stages.**

Pulp ID	Final stage	ClO <sub>2</sub> <sup>(a)</sup> (% odp)	H <sub>2</sub> O <sub>2</sub> (% odp)	NaOH (% odp)	T (°C)	time (min)	Obs.
DED	D	0.75 – 0.85	---	---	70	180	Ref. [7]
	P	---	1.20 – 1.50	0.45 – 0.75	60 – 90	60 – 120	
OQ(PO)D	D	0.40 – 0.75	---	---	70	120 – 180	This study
	P	---	0.1 – 0.5	0.7	70	60 – 120	

(a) – as active Cl<sub>2</sub>.

## RESULTS AND DISCUSSION

### *Final bleaching operating conditions*

The DED and OQ(PO)D partially bleached pulps were bleached in the laboratory with a last D or P stage until a target ISO brightness of  $90 \pm 0.5\%$  was reached. The operating conditions are listed in Table 2 together with the data on bleaching chemicals consumption. While the chlorine dioxide charge needed in the final D stage was nearly the same for both pulps (~0.8% odp as active Cl<sub>2</sub>), a remarkable effect of pulp bleaching history is observed on the hydrogen peroxide charge needed in the final P stage (1.2 % odp for DED and 0.1 % odp for OQ(PO)D pulp). In spite of the fact that the use of

stabilizers was not optimized for each pulp, the huge difference can not be merely explained in terms of additives performance. Previous studies have shown that the bleaching sequence has a key role on the nature and content of pulp metals [14]. The use of a chelation stage as in the OQ(PO)D sequence, is advantageous in terms of manganese removal which is acknowledged as the most detrimental transition metal in terms of hydrogen peroxide decomposition [12]. Additionally, it is reasonable to consider that the initial stages can have a contribution on pulp bleachability with hydrogen peroxide at the end of the sequence. Quinone-type chromophores can survive the whole bleaching process [5] and are also co-produced in chlorine dioxide and oxygen bleaching stages[16]. Moreover, chlorine dioxide delignification markedly raises the amount of quinones in pulps [17, 18], as it is the case of the DED sequence, which can thus affect hydrogen peroxide consumption in the course of bleaching. Therefore, both the nature and content of transition metals and quinone-type chromophores are important variables controlling the final bleaching performance of hydrogen peroxide.

**Table 2. Selected final bleaching conditions for reaching 90±0.5% ISO brightness (T = 70°C).**

Pulp ID	Final stage	ClO <sub>2</sub> <sup>(a)</sup> (%odp)	H <sub>2</sub> O <sub>2</sub> (%odp)	NaOH (%odp)	time (min)	Final pH	Relative consumptions (%)			Obs
							ClO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	NaOH	
DED	D	0.80	---	---	180	3.5	96	---	---	Ref. [7]
	P <sup>(b)</sup>	---	1.20	0.60	60	11.2	---	94	46	
OQ(PO)D	D	0.75	---	---	120	3.4	98	---	---	This study
	P <sup>(c)</sup>	---	0.10	0.70	120	11.5	---	69	57	

(a) – as active Cl<sub>2</sub>; (b) – with the addition of 0.05% odp MgSO<sub>4</sub>·7H<sub>2</sub>O; (c) – with the addition of 0.05% odp DTPA

### **Hydrogen peroxide decomposition**

As it is known, hydrogen peroxide performance during bleaching is dependent on its decomposition which is catalyzed by the presence of transition metals. In Table 3 the total consumption of hydrogen peroxide (due to both chromophores removal and decomposition reactions) in the final P stage of the DED and OQ(PO)D starting pulps are presented. Additionally, the hydrogen peroxide consumption assigned only to decomposition reactions was estimated by using the top brightness pulps (DEDP\* and OQ(PO)DP\*, assumed chromophores free).

**Table 3. Consumption of hydrogen peroxide after 60 min in the final P stage of the DEDP and OQ(PO)DP bleaching sequences.**

P stage conditions <sup>(a)</sup>	Total consumption (%odp)		Consumption due to decomposition (%odp) <sup>(b)</sup>		Decomposition/Total (%)	
	DEDP	OQ(PO)DP	DEDP*	OQ(PO)DP*	DEDP	OQ(PO)DP
0.5% odp H <sub>2</sub> O <sub>2</sub> ; 70°C	0.23	0.15	0.05	0.09	22	60
2.0% odp H <sub>2</sub> O <sub>2</sub> ; 70°C	0.61	0.97	0.07	0.09	12	9
0.5% odp H <sub>2</sub> O <sub>2</sub> ; 90°C	0.36	0.21	0.16	0.19	44	90
2.0% odp H <sub>2</sub> O <sub>2</sub> ; 90°C	1.45	1.06	0.82	0.52	57	49

(a) the same as those used in the study of brightening kinetics previously reported (with 0.05 % odp DTPA)[13].

(b) very high brightness pulps: DEDP\* and OQ(PO)DP\* pulps possessing 93.4 and 92.5% ISO brightness, respectively.

As can be inferred from the results, the contribution of hydrogen peroxide decomposition to total consumption is enhanced at 90°C for both pulps. After 60 min, hydrogen peroxide consumption due to

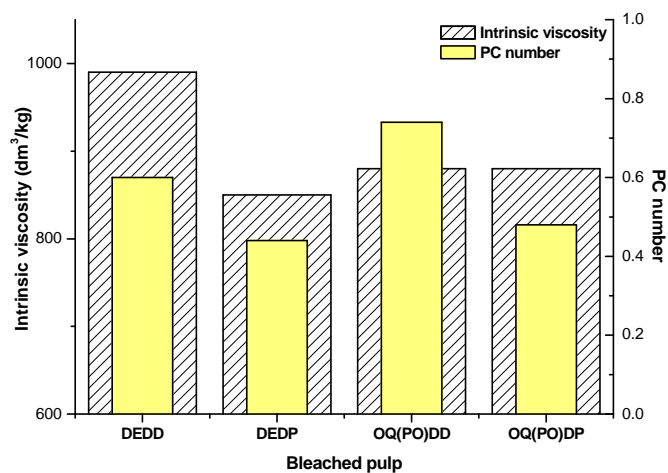
decomposition reactions exceeds 50% under certain bleaching conditions.

In a complementary study[13], the OQ(PO)DP pulp has shown a much higher bleachability (brightness gain/peroxide consumption) in the final P stage compared to the DEDP pulp. As in Table 3 the decomposition reactions are a significant part of total peroxide consumption in the bleaching of the OQ(PO)D pulp, particularly at a lower peroxide charge of 0.5% odp, decomposition products, i.e. radicals, have contributed to the brightness gain. In fact, this is consistent with previous results on pulp degradation kinetics in the final P stage of both sequences and on the metals profiles across the sequences as well [14]. In that study [14], it was evidenced that hydrogen peroxide decomposition was for the most part due to manganese(III) bound to the DED pulp, whereas for the more degraded OQ(PO)D pulp, the higher content of copper and iron, together with a lower magnesium content (lower Mg/(Fe+Cu) ratio), was the main factor determining peroxide decomposition. The twofold role of radicals as pulp brightening and degradation agents is thus highlighted in the final stage of the OQ(PO)DP sequence due to Fe- and Cu-induced decomposition of hydrogen peroxide. In contrast, in the final stage of the DEDP sequence, since Mn-induced decomposition does not generate radicals, such decomposition do not equally contribute to the brightness gain.

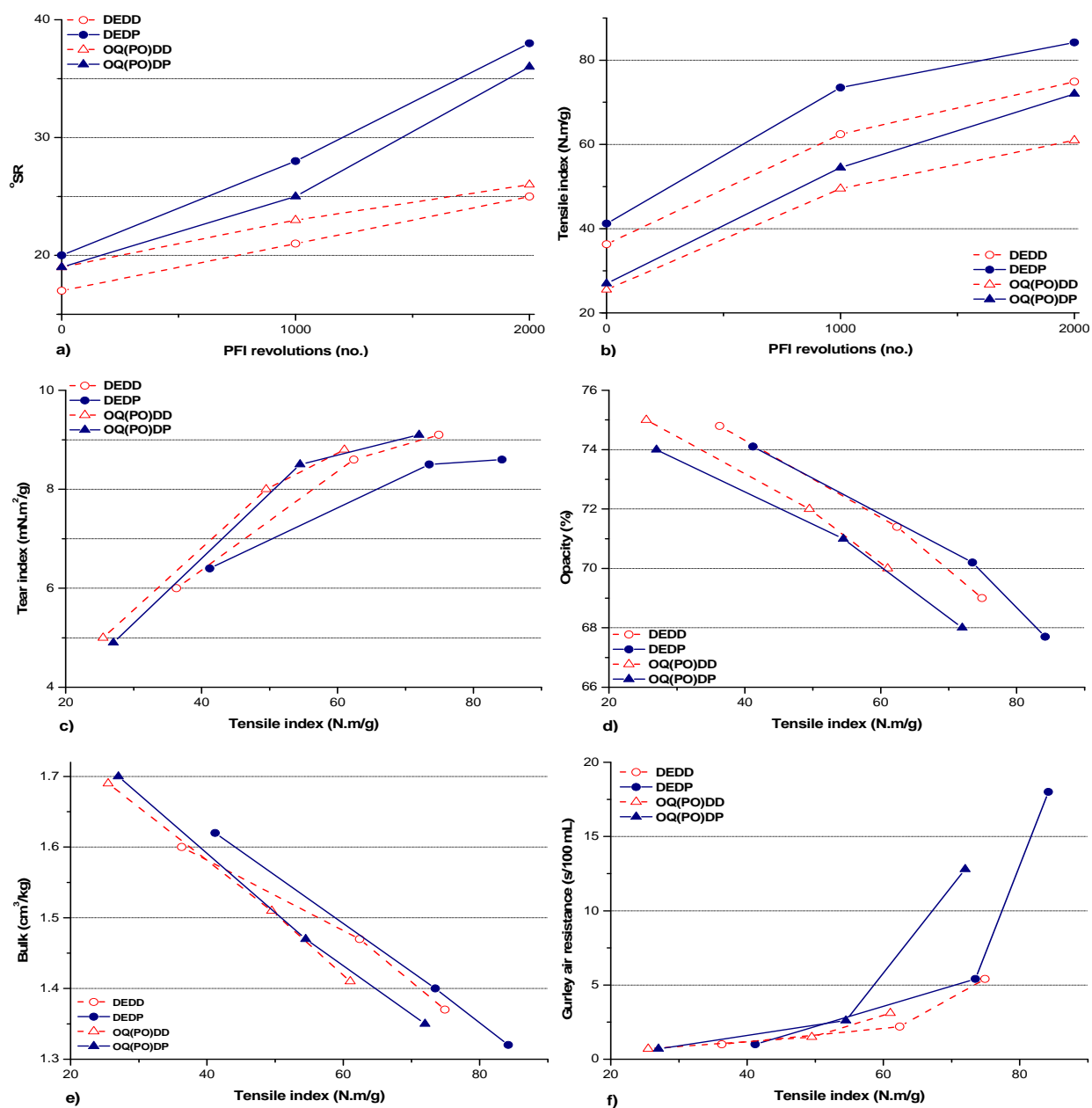
The above results stress the significant impact that pulp bleaching history has on pulp brightening and degradation kinetics in the final P stage. In other words, the bleaching history establishes not only the extent but also the nature of peroxide decomposition. Consequently, the different decomposition pathways and determining steps renders dissimilar decomposition kinetic laws affecting the overall pulp brightening and degradation reactions in the final P stages, which will be clarified by modelling the kinetics in an upcoming study.

### ***Bleached pulp properties***

The intrinsic viscosity and brightness reversion (evaluated by the PC number) of the four fully bleached pulps, all possessing an ISO brightness of  $90 \pm 0.5\%$ , are presented in Fig. 1. As expected, a final P stage reduces the brightness reversion attained with a conventional final D stage, being the difference greater for the case of the OQ(PO)D based pulp. On the other hand, the yellowing tendency of both OQ(PO)DD and OQ(PO)DP bleached pulps is superior compared to the equivalent DED based pulps. The effect of pulp bleaching history on the brightness stability of ECF bleached pulps, by using a final P stage, has been addressed in a previous study[14]. The role of polysaccharide degradation and the nature and content of the remaining metals explained the reported differences on reversion. The more degraded ECF-light pulp once again exhibits a larger tendency for reversion, particularly comparing DEDD and OQ(PO)DD bleached pulps. In fact, contrary to DEDP, the final P stage of the OQ(PO)DP sequence does not impair viscosity compared to the corresponding final D stage. The positive effect of additives in addition to the moderate temperature of 70 °C is an effective way to prevent pulp degradation [13, 14]. In the case of DEDP bleaching (with Mg addition), the use of hydrogen peroxide stabilizers (chelants and/or magnesium) was not fully optimized. As for OQ(PO)DP, the addition of 0.05% odp DTPA was enough to equalize the selectivity attained with the final D stage.



**Figure 1. Intrinsic viscosity and PC number of the fully bleached pulps.**



**Figure 2. Pulp properties of the DEDD, DEDP, OQ(PO)DD and OQ(PO)DP bleached pulps with  $90 \pm 0.5\%$  ISO brightness.**

The results on the papermaking potential of the produced bleached pulps are presented in Fig. 2, with regard to pulp beating performance and mechanical, structural and optical properties. It is evidenced that less beating is needed for the peroxide bleached pulps towards the same drainability (°SR) compared to chlorine dioxide bleached pulps, as depicted in Fig. 2a. A lower drainability (higher °SR) is attained with DEDP bleaching being the difference between both final stages more significant between DEDD and DEDP. This can be related to the less pulp degradation observed with the previous DED stages compared to OQ(PO)D stages, more precisely considering xylan yield during bleaching. In fact, the DED based pulps exhibited higher xylan relative content (results not shown). Since xylan is the most important source of carboxyl groups in *E. globulus* pulps, it will diminish the

extent of fibre swelling if depleted and therefore negatively contributing to pulp beatability and similarly for strength properties such as tensile strength.

The alkaline P stage causes an electrolytic fibre swelling [11] that reduces the required mechanical energy in the beating process [19]. The effect of fibre charge on promoting swelling and their relationship to paper properties has been stressed for the case of bleached hardwood pulp[20]. It is confirmed that the more swollen peroxide bleached pulps (higher water retention values – not shown) have higher beatability and tensile strength (Fig. 2b) than the corresponding chlorine dioxide bleached pulps in the final stage. After 2000 revolutions, the OQ(PO)DD pulp does not achieve a tensile index of 70 N.m/g, which can be attributed to the observed higher pulp degradation upon bleaching with the ensuing reduction in xylan yield, which is detrimental for the bonding potential of the bleached fibres.

As for tear resistance, the development of this index is different among the bleached pulps. The negative impact of peroxide bleaching in the tear index is only observed for the DEDP bleached pulp and after beating. For the OQ(PO)D based pulps, the development of tear index with beating is parallel until 1000 revolutions with either of the final stages, however peroxide allows reaching a higher tear index after beating to a higher tensile index.

DED based pulps have higher opacity (Fig. 2d) and are bulkier (Fig. 2e). The impact of the final P stage in both sequences slightly increases these properties with beating except for the less obvious differences in opacity attained with the OQ(PO)D based pulps. The peroxide bleached pulps have a greater air resistance (Fig. 2g). Table 4 summarizes the pictorial comparison among the properties of the pulps considering the more conventional final D stage as the reference for both sequences.

**Table 4. Effect of a final P stage on the properties of the two fully bleached pulps having a different bleaching history, beaten to the same tensile index of 60 N.m/g (for both sequences the pulp that had a final D stage is used for comparison).**

Pulp properties	DEDP (in comparison with DEDD)	OQ(PO)DP (in comparison with OQ(PO)DD)
brightness reversion	↓↓	↓
intrinsic viscosity	↓↓	≈
PFI revolutions	↓	↓
tear index	↓	≈
opacity	≈	≈
bulk	↑	↑
Gurley air resistance	↑	↑

Comparing all properties to the same tensile index of 60 N.m/g, DED based pulps have higher opacity and bulk but lower tear index compared to OQ(PO)D based pulps. In terms of papermaking properties, the final P stage was only disadvantageous compared to the corresponding final D stage in the tear index of the DEDP bleached pulp.

## CONCLUSIONS

The pulp bleaching history has a great influence on the performance of a final hydrogen peroxide bleaching stage as concerns bleachability and selectivity parameters and bleached pulp properties. This is also valid for the brightening chemistry while residual transition metals (e.g., Fe and Cu) contribute to autoxidation brightening reactions as a result of hydrogen peroxide decomposition. A lower brightness reversion and higher pulp beatability are beneficial features from the use of a final P stage instead of a final D stage.

**Acknowledgements** The authors gratefully acknowledge Portucel Soporcel Group and Celbi pulp mill for supplying pulp samples, and RAIZ for the technical facilities. FCT is acknowledged for the Ph.D. scholarship granted to Pedro E. G. Loureiro (SFRH/BD/29690/2006).

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