

FINAL BLEACHING OF EUCALYPT KRAFT PULP USING HYDROGEN PEROXIDE

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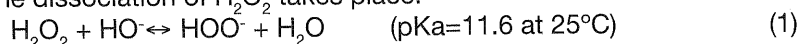
ABSTRACT

The present study was performed to analyze the effect of replacing chlorine dioxide with hydrogen peroxide in a final bleaching stage of a conventional ECF sequence (D_0ED_1P instead of $D_0ED_1ED_2$). D_1 pulps with diverse brightness levels were used. Different operating conditions were applied to them to attain an ISO brightness of 90 ± 0.5 % in the D_0ED_1P pulp. The results were compared with the corresponding $D_0ED_1ED_2$ pulps. The pulp quality was evaluated by measuring brightness, brightness reversion and intrinsic viscosity. Chemicals consumption was also determined. The bleached pulps were submitted to beaten for papermaking potential evaluation. From the factorial experimental design, 2^3 , it was concluded that hydrogen peroxide charge is the variable that mostly affects positively the brightness and negatively the viscosity whereas brightness reversion is negatively affected by temperature and time. The brightness reversion was confirmed to be lower for P pulps. However, the hydrogen peroxide performance has shown dependence on D_1 pulp brightness: it was efficient for pulps with high ISO brightness (~89%), but very high charges were needed to bleach pulps with brightness of ~84%. In spite of having viscosity values 100 to 200 dm^3/kg lower, P pulps showed a higher beatability than D_2 pulps, for the same degree of drainability ($SR=30$), requiring less number of PFI mill revolutions. In addition, the tensile index was higher for the same number of PFI mill revolutions and the opacity and bulk were higher for the same tensile index. The positive effect of hydrogen peroxide on brightness stability without impairing the papermaking properties is, therefore, confirmed, despite the viscosity loss observed.

INTRODUCTION

Recent studies from Brazilian researchers suggest that the substitution of the last chlorine dioxide stage (D_2 stage) in an ECF bleaching sequence by a final peroxide stage (P) has a positive effect on brightness stability while preserving viscosity and pulp strength (Suess, Filho 2004; Süß *et al.* 2000; Henrique *et al.* 2000, Santos *et al.* 2000). This fact has been attributed to the presence of certain type of chromophores (particularly carbonyl structures) in the residual lignin or even produced from the reaction between chlorine dioxide and lignin (Lachenal *et al.* 2005; Mateo *et al.* 2004). These structures are easily cleaved with alkaline peroxide. Therefore, chlorine dioxide has been shown to be the most efficient reagent to remove chromophores originated from precipitated lignin if they are mainly of phenolic type. On the other hand, hydrogen peroxide is the most efficient reagent on the last existing chromophores at the end of an ECF bleaching sequence (mainly of quinone type) (Suess, Filho 2004; Mateo *et al.* 2003; Mateo *et al.* 2001).

To bleach chemical pulps, peroxide stages are used in alkaline environment (pH 10.0 – 11.5) where the dissociation of H_2O_2 takes place:



The perhydroxyl anion, HOO^- , is indeed the active agent responsible for chromophores destruction (Lachenal *et al.* 1995). The amount of this anion is dependent on pH and tempera-

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ture. However, high temperatures and the presence of transition metal ions (such as Mn, Fe and Cu) lead to the formation of radicals (Dence, Reeve 1996). Although they also contribute to the chromophores destruction, these unselective chemical species increase the peroxide consumption, could produce new chromophores, and can degrade polysaccharides lowering pulp intrinsic viscosity (Heikillä, Vuorinen 2000; Dence, Reeve 1996; Devenyns, Plumet 1994; Lachenal *et al.* 1980). To diminish these negative effects metals control is necessary. For that, an acidic or a chelation treatment prior to peroxide stage should be employed or to add stabilizers (such as magnesium sulphate) into the P stage (Lapierre *et al.* 1995). A low metal amount is expected after successive acidic D stages as in a conventional ECF bleaching sequence. However, acid stages remove metals unselectively and a minimum Mg/Mn ratio of 30 is needed to decrease the side reactions leading to the formation of undesirable radicals for a hydrogen peroxide bleaching stage applied to softwood pulps (Throughton *et al.* 1994).

In this context, the aim of the present study was to evaluate the quality of an *E. globulus* kraft pulp by employing hydrogen peroxide in a final bleaching stage of a conventional sequence instead of chlorine dioxide; that is, to use D_0ED_1P instead of the conventional $D_0ED_1ED_2$, where E means extraction stage in alkaline media. A first goal was to correlate operating variables (namely temperature, time and hydrogen peroxide charge) with the final properties of the pulp by performing experiments based on a statistical plan. The second objective was to evaluate the influence of initial brightness on the performance of the hydrogen peroxide stage by producing, in the lab, D_1 pulps with different ISO brightness levels. In an earlier study employing industrial and laboratorial pulps the results were not conclusive regarding the papermaking potential (Campos *et al.* 2005): a laboratorial P pulp produced from an industrial D_1 pulp with a very high ISO brightness had worse properties in comparison with industrial D_2 pulp; the opposite was observed for P and D_2 pulps produced in the lab utilizing a D_1 pulp with low brightness.

MATERIALS AND METHODS

Industrial *Eucalyptus globulus* kraft pulps were collected before entering the D_1 stage of a conventional ECF bleaching sequence in a Portuguese mill. After being washed with water, these pulps were bleached in the laboratory with several chlorine dioxide charges to produce D_1 pulps with different ISO brightness levels. A D_1 pulp labelled L, having an ISO brightness of 82.9% and a viscosity of 1054 dm³/kg, was bleached with peroxide by applying different operating conditions following a 2³ statistical plan (8 experiments) plus two replications at the center point. The high and the low levels of temperature, time and peroxide charge are presented in Table 1. The results were treated using the software Design-Expert 6.0.11. To complete the study of operating conditions, the effect of magnesium sulphate (0.05–0.2% o.d.p.) or diethylenetriaminepentaacetic acid (DTPA, 0.1% o.d.p) addition to the P stage, in order to preserve viscosity, was also analysed. Three other D_1 pulps, labelled A, B and C with three different brightness levels (84.7, 86.9 and 88.7%), were used to compare the performance of hydrogen peroxide and chlorine dioxide. Therefore, a P stage was applied to these pulps in order to attain an ISO brightness of 90±0.5%; to the same D_1 pulps a final D_2 stage was applied to also attain the same brightness level. All the bleaching experiments were performed in sealed polyethylene bags using 10% consistency with 25 g odp. The operating conditions are shown in Table 1. After bleaching, chemical consumptions were determined and the bleached pulp samples were characterized in terms of intrinsic viscosity, brightness, and brightness reversion. The ageing tests were carried out using the T 260–om procedure (1h, 100°C and 100% relative humidity environment). 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 scattering (s) which in turn is related with the reflectance of an opaque sheet of paper (of infinite thickness), R_∞ , by the Kubelka-Munk equation:

$$PC\ number = 100 \left[(k/s)_{after\ ageing} - (k/s)_{before\ ageing} \right] \quad k/s = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (1)$$

The metal content of some pulps was also measured in order to determine the Mg/Mn ratio. The papermaking potential of fully bleached P and D₂ pulps was evaluated after beating in a laboratory PFI mill at 0, 1000 and 2000 revolutions. Handsheets were prepared for the analysis of physical, optical and structural properties.

Table 1 – Properties and experimental bleaching conditions in final chlorine dioxide or hydrogen peroxide stages applied to D₁ pulps (L, A, B and C pulps)

	Pulp L		Pulp A		Pulp B		Pulp C	
ISO Brightness, %	82.9		84.7		86.9		88.7	
Viscosity, dm ³ /kg	1054		950		990		1050	
Final Stage	P (factorial plan)	P with additives	D	P	D	P	D	P
Temperature (°C)	70-90	70	70	70	70	70	70	70
Time (min)	60-120	90	180	60	180	60	180	60
H ₂ O ₂ charge (% o.d.p.)	1-2	2		2.5		1.2		0.65
NaOH charge (%o.d.p.)	~0.9	1.1		0.7		0.6		0.5
MgSO ₄ ·7H ₂ O (%o.d.p.)		0.05-0.2 (0.05+0.1DTPA)		0.05		0.05		0.05
ClO ₂ charge ^A (% o.d.p.)			1.10		0.80		0.35	
ISO Brightness, %	88.3-89.6	89.6-90.0	90.5	90.5	90.2	90.8	89.8	90.3
Viscosity, dm ³ /kg	724-884	904-958	970	690	990	850	1000	910
Brightness reversion, %	3.0-3.9	3.5-3.7	4.3	3.6	4.2	3.4	4.4	3.0
PC number	0.47-0.55	0.01-0.52	0.61	0.48	0.60	0.44	0.66	0.40

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

RESULTS AND DISCUSSION

In the first part of this study, the laboratorial D₁ pulp, labelled L pulp, with an ISO brightness of 82.9%, was bleached with peroxide using a 2³ factorial plan where the operating conditions were varied in the range shown in Table 1. In order to correlate the input variables with the output variables in the chosen operation range, the following general equation was used:

$$Y = \alpha_1 + \alpha_2.A + \alpha_3.B + \alpha_4.C + \alpha_5.AB + \alpha_6.AC + \alpha_7.BC + \alpha_8.ABC \quad (2)$$

where A, B and C represent temperature, time and hydrogen peroxide charge, respectively, and the variable Y represents brightness, viscosity or brightness reversion. As shown by the coefficients values of Table 2, hydrogen peroxide charge is the variable that has affected most significantly pulp ISO brightness and viscosity (with opposite effects) whereas brightness reversion is mostly affected by temperature in a negative way. Two supplementary experiments were carried out to validate the model using the central points of the statistical plan (middle level of variables values). The regression fitted quite well to the test points, being the relative errors of 0.3%, 3.2% and 1.5% for brightness, viscosity and brightness reversion respectively. Therefore, it can be concluded that the model is valid in the range of operating conditions studied.

Table 2 – Coefficients α_i of the predicted output variable equations

Coefficients, α_i	α_1	α_2	α_3	α_4	α_5	α_6	α_7	α_8
Brightness (% ISO)	89.0	-0.057	0.061	0.46	-0.12	$6.0 \cdot 10^{-4}$	-0.094	0.029
Viscosity (dm ³ /kg)	795	-23	-5.4	-48	3.9	6.4	-1.6	-3.9
Brightness reversion (% ISO)	3.5	-0.29	-0.17	0.055	0.055	0.039	0.0025	-0.049

Figure 1 illustrates the results obtained for pulps resulting from the factorial design - pulps 1 to 10. In the same figure, results for pulps produced with the inclusion of additives in the P stage, are also shown (pulps 11-14). The addition of magnesium sulphate has preserved pulp viscos-

ity and had a positive effect on brightness gain. Moreover, an increase in both viscosity loss and peroxide consumption is observed as MgSO_4 charge decreases from 0.2 to 0.05 % odp (pulp 11-13). When DTPA is added simultaneously with MgSO_4 – pulp 14, compared with pulp 13 – a decrease in peroxide consumption can be noticed. This fact is due to the ability of these additives to block non-desirable side reactions of hydrogen peroxide, by decreasing the catalyst capacity of the pulp transition metals, which mainly contribute to the polysaccharides degradation.

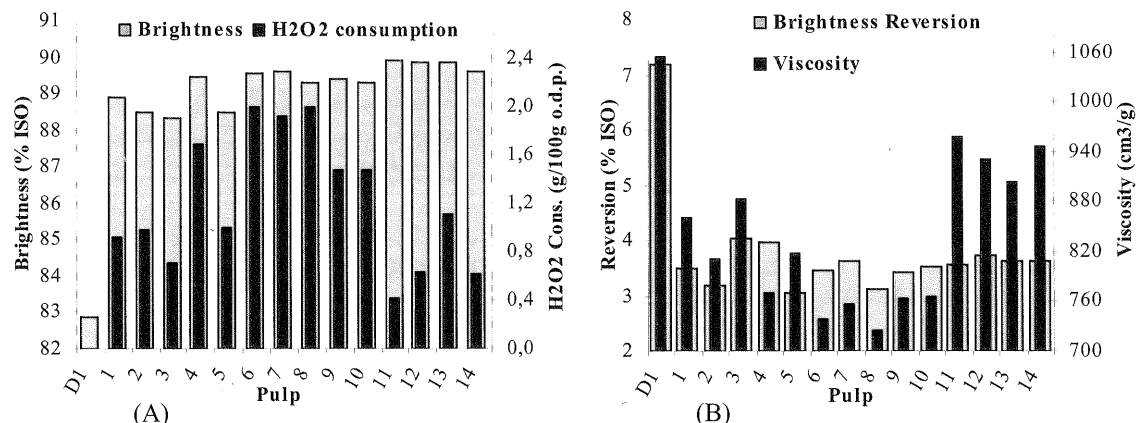


Figure 1 – Comparison between P pulps regarding: (A) brightness and H_2O_2 consumption; (B) brightness reversion and viscosity. D₁ was the starting pulp (pulp L). Pulps 1 to 10 result from the factorial plan applied to pulp L; in pulps 11 to 13, respectively, 0.2, 0.1 and 0.05% of MgSO_4 was added to the P stage; in pulp 14 the mixture 0.05% MgSO_4 + 0.1% DTPA was used instead (see Table 1 for the remaining conditions)

The results of metal analysis carried out on the industrial pulps – D₁(I) and D₂(I) – and on a P pulp produced with the addition of 0.1% $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ are listed on Table 3. The acid D₂ stage reduces unselectively the amount of metals, the transition as well as the alkaline earth ones, being the Mg/Mn ratio close to the critical value of 30. The much higher Mg/Mn ratio in P pulp confirms the efficient addition of magnesium to the P stage to deactivate the remaining transition metals.

Table 3 – Metal content (mg metal / kg o.d.p.) and Magnesium / Manganese ratio of industrial pulps bleached with chlorine dioxide (D_{1,I} and D_{2,I}) and of pulp D_{1,I} further bleached with peroxide (P pulp)

Metal	D _{1,I}	D _{2,I}	P pulp
Magnesium (Mg)	122	98	263
Manganese (Mn)	4.4	3.2	1.6
Mg / Mn	28	31	164

In the second part of this study, a final bleaching stage with peroxide or chlorine dioxide was performed to attain an ISO brightness target of $90 \pm 0.5\%$ using pulps A, B and C with different initial ISO brightness (84.7, 86.9 and 88.7%). Operating conditions and pulp properties (viscosity, brightness and brightness reversion) are presented in Table 1. Regarding the chemical charges, a much higher peroxide charge was needed to bleach pulp A in order to attain the target ISO brightness. Therefore, this pulp has a much lower bleachability towards peroxide than pulps B or C. On the other hand, chlorine dioxide charge correlates in a linear way with the initial brightness as seen on Figure 2. Therefore, pulps A, B and C show similar bleachability towards these reagent. It can be concluded that peroxide brightening must only be used to boost brightness by the last two points. In spite of that, hydrogen peroxide increases brightness stability as shown by the lower reversion in Table 1, regardless of pulp (A, B or C). The latter results are consistent with other works and confirmed at mill tests in Brazil (Henrique *et al.* 2000, Santos *et al.* 2000).

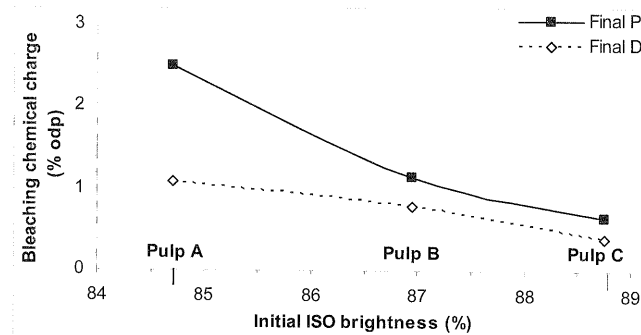


Figure 2 – Influence of initial brightness of D₁ pulp (pulp A= 84.7, pulp B=86.9 and pulp C=88.7) on the chemical charges needed to reach 90±0.5% ISO in the final pulp, using either hydrogen peroxide or chlorine dioxide

Regarding the intrinsic viscosity, peroxide has a negative impact on this property, while chlorine dioxide does not as seen in Table 1. Higher peroxide charges result in higher viscosity loss. However, the introduction of 0.05% odp of MgSO₄·7H₂O in our P stage led to a lower peroxide consumption (for instance, ~12% lower for pulp C), showing the reduction in the catalytic activity of transition metals towards peroxide decomposition.

Pulps A, B and C fully bleached in the final stage with either peroxide or chlorine dioxide were beaten in a PFI mill (0, 1000 and 2000 revolutions) to evaluate optical, physical and mechanical properties of the corresponding handsheets. The results are shown in Figures 3 to 5. As Figure 3A) reveals, all the peroxide pulps show higher beatability, requiring a lower amount of beating energy to achieve the same level of drainability, say 30°SR. In addition, for this level of drainability, fibrillation is more effective because the corresponding handsheets exhibit higher tensile index in comparison with the final D stage (Figure 3B)). Moreover, when the pulps are compared for the same level of tensile index, as in Figures 4 and 5, handsheets obtained from P pulps have a more open structure and higher amounts of air-fiber interfaces as shown by higher values of bulk and opacity. As expected, opacity decreases with the tensile index, just as bulk does, whereas air resistance increases. On the other hand, D pulps show higher tear index in the tensile index range 65-70 N.m/g, but, as peroxide charge decreases (from pulp A to C), the tear index raises and reaches the tear ceiling values observed for D pulps in the tensile index range 80-85 N.m/g. Therefore, pulp C fully bleached with a final P could be beaten to these high values of tensile indexes without a decrease on tear index.

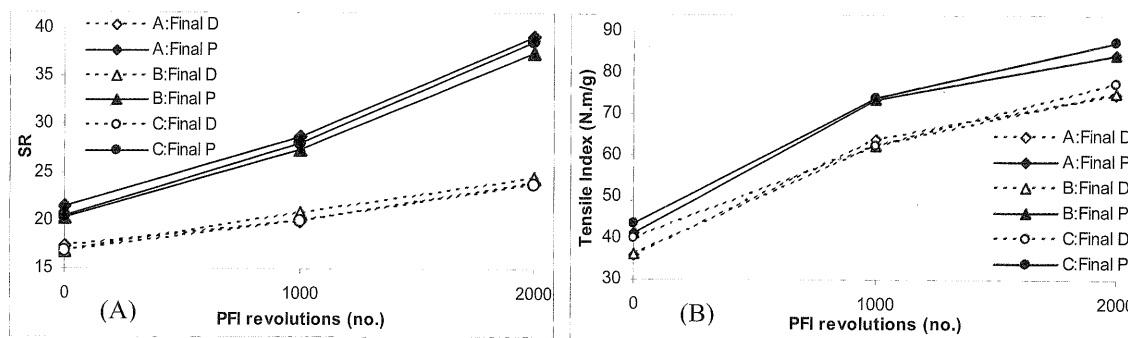


Figure 3 – (A) Pulp drainability (Schopper-Riegler method) and (B) Tensile index versus PFI revolutions for pulps A, B and C further bleached with either chlorine dioxide (D) or hydrogen peroxide (P).

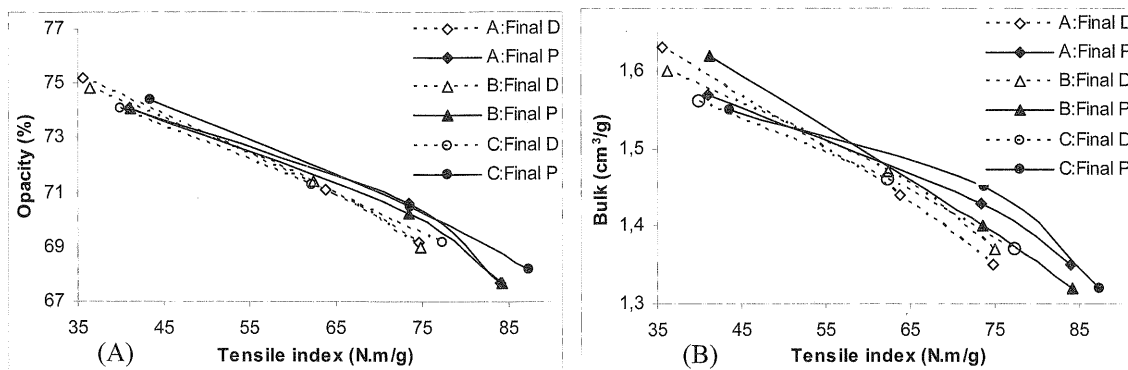


Figure 4 – (A) Opacity and (B) bulk *versus* tensile index for pulps A, B and C further bleached with either chlorine dioxide (D) or hydrogen peroxide (P).

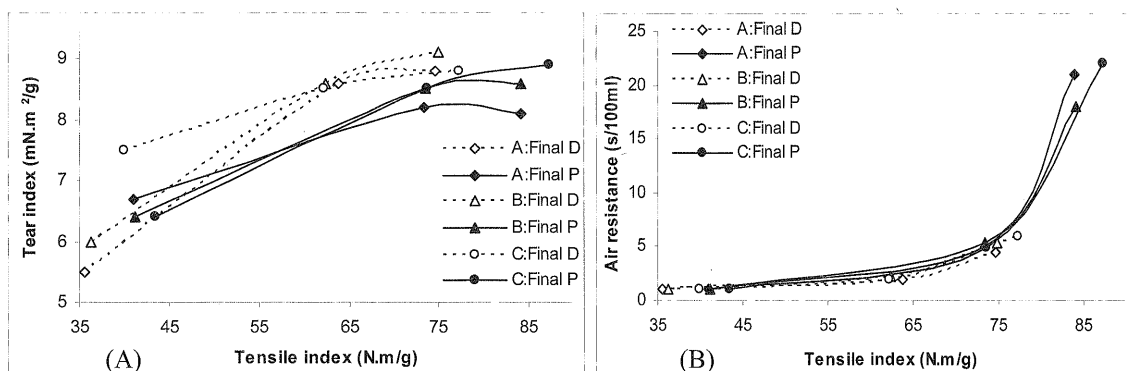


Figure 5 – (A) Tear index and (B) Air resistance (Gurley method) *versus* tensile index for pulps A, B and C further bleached with either chlorine dioxide (D) or hydrogen peroxide (P).

CONCLUSIONS

On the first part of this work, a laboratory pulp with an ISO brightness of 82.9 % was used as raw material for the P bleaching experiments, following a 2^3 factorial plan. From the results of the statistical plan, it can be concluded that peroxide charge is the variable that most positively influences brightness and negatively affects viscosity. Temperature and time also negatively affects brightness reversion. A relationship between the output and input variables were established, being validated with two additional experiments at the centre point of the statistical plan.

In comparison with D_2 pulps, lower brightness reversion values were noticed for P pulps. However, this reagent led to a severe cellulose degradation that caused significant viscosity losses. When small amounts of magnesium sulphate (0.05 to 2.0 kg $MgSO_4 \cdot 7H_2O$ / 100kg pulp), alone or mixed with 0.1% DTPA, were introduced into the peroxide stage lower viscosity loss as well as lower hydrogen peroxide consumption were observed. Additionally, a slight rise on brightness has also been observed.

In the second part of this study, D_1 pulps with three different brightness levels (~85, ~87 and ~89 % ISO, named pulps A, B and C, respectively) were produced to evaluate the influence of the initial brightness on the hydrogen peroxide performance. All pulps were fully bleached either with hydrogen peroxide or chlorine dioxide to reach 90 ± 0.5 %ISO and submitted to potential papermaking evaluation. The pulp bleachability towards hydrogen peroxide was proven to depend on D_1 pulp brightness (much lower for A pulp) whereas the different pulps have shown similar bleachability when chlorine dioxide was used (linear dependence on initial pulp brightness). Therefore, a final P stage should be applied to a D_1 pulp with an ISO brightness higher than 87% if the target is 90%.

The viscosity of P pulps was 100 (pulp C) to 200 (pulp A) dm³/kg lower than the values observed in the D₂ pulps. In spite of that, P pulps have shown higher beatability, needing less PFI revolutions to attain 30°SR than D₂ pulps do. Moreover, P pulps exhibited higher tensile index for equal drainability level and the correspondent handsheets were bulkier with higher opacity for the same tensile index. In opposition, D₂ pulps showed better tear index.

REFERENCES

- Campos, M.A.R., Amaral, J.L., Ferreira, L.M.G.A., Carvalho G.V.S. (2005). 9th Chempor Conf., Coimbra: 64-65, CD-Rom.
- Dence, C.W., Reeve, D.W. (1996) «Pulp Bleaching - Principles and Practice». Tappi Press, Atlanta.
- Devenyns, J. and Plumet, L. (1994). 3rd EWLP, Stockholm:139-144.
- Heikkilä, M., Vuorinen, T. (2000). Int.Pulp Bleaching Conf., Halifax: 155-160.
- Henrique, P. M., Costa, M. M., Correia, F. M., Fonseca, M. J. O., Santos, J. R. C., Landim, A. B., Filho, C. L. (2000). 33^o Int. Cong.of Cellulose and Paper, ABTCP, São Paulo Brasil (CD-Rom).
- Lachenal, D., Choudens, C., Monzie, P. (1980). *Tappi J.* **63**(4): 119-122.
- Lachenal, D., Fernandes, J. C., Froment, P. (1995). *J. Pulp Pap. Sci.* **21**(5): J173-J177
- Lachenal, D., Chirat, C., Benattar, N., Hamzeh, Y., Marlin, N., Mateo, C., Brochier, B. (2005) Int. Pulp Bleaching Conf. Proc., Stockholm: 181-187
- Lapierre, L., Bouchard, J., Berry, R.M., Van Lierop, B. (1995). *J. Pulp Paper Sci.* **21**(8): J268-J273.
- Mateo, C., Chirat, C., Ait-Ouaret, R., Lachenal, D., Jeunet, A. (2001). *Nord. Pulp Pap. Res. J.* **16**(4): 385-388
- Mateo, C., Rousseau, C., Chirat, C., Lachenal, D. (2003). 28th Eucepa Conference, Lisbon: 41-45.
- Mateo, C., Chirat, C., Lachenal D. (2004). *J. Wood Chem. Technol.* **24**(3): 279-288
- Santos, L. N. D., Gala, P. A. M., Robles, Y. A. M., de Almeida, J. M., (2000). 33^o Int. Cong.of Cellulose and Paper, ABTCP, São Paulo Brasil (CD-Rom).
- Suess, H. U., Filho, C. L. (2004). 37th Annual conference of ABTCP, São Paulo, Brasil (CD Rom)
- Süß, H. U., Schmidt K., del Grosso, Mahagaonkar, M. M. (2000). *Appita J.* 53(2):116-121.
- Throughton, N.A., Desprez, F., Devenyns, J. (1994). TAPPI Proceedings, TAPPI PRESS, Atlanta: 807-820.