

NEW INSIGHTS ON BRIGHTNESS STABILITY OF EUCALYPTUS KRAFT PULP

Eiras, K. M. M.¹, Colodette, J. L.² and Barbosa, L. C. A.²

¹ Ph.D. Researcher
Suzano Papel e Celulose
Mucuri, BA, Brazil. keiras@suzano.com.br

² Ph.D. Full Professors
Federal University of Viçosa
Viçosa, MG, Brazil.

ABSTRACT

Eucalyptus pulps bleached with ECF sequences containing ozone, chlorine dioxide and a final peroxide stage present high brightness stability in relation to pulps bleached with conventional ECF sequences. The reasons why this chemistry is so effective are unknown. This study compares the brightness stability of ECF pulps bleached with the OZ/ED(PO) and OZ/EDP sequences with those of more conventional ECF sequences such as OD_{HT}(PO)DD and OD_{HT}(PO)DP. The brightness stability profiles across the OZ/ED(PO) and OD_{HT}(PO)DD sequences are discussed. In addition, the relative importance of ozone, chlorine dioxide and peroxide doses on dry and wet heat reversion of pulps bleached with the sequence OZ/EDP is discussed. Furthermore, the composition of aromatic compounds present in pulps bleached with the sequences OZ/EDP and OD_{HT}(PO)DD, measured by Py-GC/MS, and their impact on reversion is evaluated. A tentative mechanism for eucalyptus pulp heat reversion is presented. The OZ/ED(PO) bleached pulp showed a PCN (0.06) almost four times lower than that of the OD_{HT}(PO)DP bleached one, a lower kappa and HexA's content and a higher carboxyl and reducing group content. The profile of brightness stability across the OZ/ED(PO) sequence indicated a decreasing trend across the various stages whereas that of the OD_{HT}(PO)DP one showed a decreased trend in the acid stages and an increased trend in the alkaline stages. The distribution of chlorine dioxide and peroxide in the OZ/EDP sequence affected brightness stability with the highest values being achieved when high chlorine dioxide doses are used in the D-stage and low peroxide doses (1-5 kg/odt) are used in the P-stage. The levels of trace aromatic compounds in the bleached pulp do not correlate with brightness stability. The production of high brightness and low brightness stability eucalyptus pulps can be achieved with processes that apply enough charge of electrophilic oxidants to eliminate HexA's, followed by a final nucleophilic oxidation stage with a minimal but well calculated charge of oxidant in order to extract the so-called "unknown reducing substances" and oxidize potential chromophores that are formed

under alkaline conditions. Reversion caused by HexA's is more severe when pulp is dried under acidic conditions. The opposite is observed for reversion caused by the "unknown reducing substances". A final nucleophilic bleaching stage run at slight alkaline conditions is effective to prevent brightness reversion of all eucalyptus pulps.

INTRODUCTION

Our previous studies (EIRAS & COLODETTE, 2005 and EIRAS et al., 2005), indicated that pulps bleached with sequences containing hot acid (A) and/or hot chlorine dioxide (D_{HT}) stages and/or ending with an alkaline peroxide stage show good brightness stability. It was also shown that chlorinated organics present in the pulp may accelerate reversion. In this study an attempt is made to understand these trends on the basis of the pulp fine chemistry. The brightness stability of pulps bleached with the sequences OD_{HT}(PO)DP and OD_{HT}(PO)DD were compared with those of sequences containing ozone such as OZ/ED(PO) and OZ/EDP. Sequences containing ozone stages are interesting to understand the reversion problem since they usually result in low reversion pulps that contain high reducing groups and low HexA's and chlorinated organic contents. WENNERSTRÖM (2005) showed that a peroxide stage after Z/(EO)D treatment increases brightness by 1%ISO and reduces the brightness reversion by 0.5%ISO. The high stability of pulps bleached by ozone has been attributed to effective hexenuronic acid elimination (BUCHERT et al., 1996; RAGNAR and DAHLLÖF, 2002; WENNERSTRÖM, 2005). WENNERSTRÖM (2005) reported that 89-95% of HexA's are eliminated after ozone stage and only 67-73% are removed after a hot chlorine dioxide stage. Even though the ozone stage increases pulp reducing group content (BOKSTRÖM and WENNERSTRÖM, 2001), such groups can be converted or eliminated in a subsequent alkaline peroxide stage. These groups may also be eliminated by an alkaline extraction stage and to a lesser extent by chlorine dioxide. BOKSTRÖM and WENNERSTRÖM (2001) have indicated that pulps bleached with ozone contain less carboxylic acid groups. Pulp bleached by ozone sequences consumes less active chlorine to reach the brightness target, WENNERSTRÖM (2005).

It has been demonstrated that TCF pulps bleached with sequences containing ozone and peroxide are more stable than those bleached with sequences containing peroxide only. Ozone reacts twice faster with alcohols and other cyclical structures than peroxide due to its lower activation energy (8.7 kcal/mol) in relation to peroxide (12 kcal/mol) (DENISOV, 1977).

The objective of this study is to compare the brightness stability of ECF pulps bleached with sequences containing ozone, chlorine dioxide and peroxide stages, OZ/ED(PO) and OZ/EDP, with those of more conventional ECF sequences such as

OD_{HT}(PO)DD and OD_{HT}(PO)DP. In addition, it is investigated the impact of pulp slurry pH and pulp bleaching pH on brightness stability, and a tentative mechanism for eucalyptus pulp heat reversion is presented.

EXPERIMENTAL

Three different industrial *Eucalyptus urograndis* kraft pulps were used throughout this study. The main characteristics of these pulps are described along with the brightness stability data in the tables of results. Pressurized peroxide bleaching (PO) and hot chlorine dioxide (D_{HT}) stages were performed with 280-300 g oven dried pulp samples in a teflon-lined mixer/reactor (Quantum Technologies, model Mark V). The desired charges of chemicals were added to the reactor after the desired pulp temperature was reached and the reaction pressure was adjusted with oxygen when necessary. After the pre-established reaction time elapsed, the reactor pressure was released, the pulp was discharged into a 120 mesh screening box and 300 mL of liquor were squeezed from the pulp for analysis. Sequential chlorine/chlorine dioxide, chlorine dioxide (D), alkali extraction (E) and hydrogen peroxide (P) bleaching stages were performed in polyethylene bags. In all cases, the required amounts of water and reagents were mixed with the pulp at room temperature and the mixtures heated to the desired temperature in a microwave oven. The samples were then placed in a heating bath for the desired reaction time. All bleaching stages were carried out in duplicate under the general bleaching conditions shown in Table 1. Inter-stage washings simulated a vacuum filter operating at a dilution factor of two (inlet and outlet consistencies of 2% and 12.5%, respectively). After bleaching, pulp was diluted to 0.3% consistency, pH was adjusted to 5.0 with SO₂/H₂SO₄ or SO₂/NaOH, and ten hand sheets were formed and dried for 12 hours to 9-10% humidity in an environmentally controlled room (50±2% relative humidity and 23±1 °C). The dry heat reversion tests were performed in conformity with Tappi UM 200 method (4 h, 105±3°C, 0% relative humidity). The wet heat reversion tests were performed according to RAGNAR & DAHLLOF, 2002 (15 h, 90 °C, sheet moisture content of 10%). Reversion results were expressed as post color number (PCN) in conformity with Tappi standard TIS 017-10. Pulp metals contents were measured according to the SCAN-CM 38:96 procedures. Hexenuronic acids and soluble lignin were measured according to TENKANEN, et al., 1999 and GOLDSCHMID, 1971 methods. Pulp kappa number, dichloromethane (DCM) extractives, copper number, carboxyl and xylan contents were determined according to Tappi T236 cm-85, T204 cm-97, T430 om-94, T237 om-93 and T249 cm-85 standard methods, respectively. Pulp samples bleached by D_{HT}EDD, Z/ED and Z/EDP sequences and a purified cotton sample were analyzed by Py-GC-MS in

Shimadzu PQ5050A equipment. The following conditions were applied: silica column DB-WAX (30m X 0.25mm diameter, 0.25 µm wide film) and gas helium flux, pyrolysis at 610 °C, injector at 100 °C, column temperature rate – 40 °C/min to 240 °C for 40 min, detector at 250 °C. The mass ionization detector operated 70eV electron impact and mass array interval 30 and 600Da. Wiley 7 library and RODRIGUES et al. (2001), HERNANDO et al. (2004) and DEL RÍO et al. (2005) were used as reference to identify the compounds.

Table 1. General bleaching conditions

Conditions	D _{HT}	Z/E	(PO)	D ₁	D ₂	P
Consist., %	10	40/10	10	10	10	10
Temp., °C	95	40/60	90	70	70	90
Time, min	120	1/30	60	120	120	120
Pressure, kPa	-	-	300	-	-	-
O ₃ , kg/odt*	-	4-6	-	-	-	-
O ₂ , kg/odt	-	-	6	-	-	-
H ₂ O ₂ , kg/odt	-	-	6-15	-	-	1-15
ClO ₂ , kg/odt	**	-	-	**	**	
MgSO ₄ , kg/odt	-	-	0.15	-	-	-
H ₂ SO ₄ , kg/odt	5	10/0	-	2.5	-	-
NaOH, kg/odt	-	0/7	13	-	2	3-4
Final pH	2.5	2.5/10	11	**	**	**

*oven dried ton

**variable

RESULTS AND DISCUSSION

Brightness reversion can be expressed by variation of b* coordinate, reflectance at 457nm and post color number (PCN) across pulp aging. Natural pulp aging is difficult to mimic in the laboratory and hence it is usually done by some accelerated procedure. In this study wet and dry accelerated aging were used and reversion values were expressed by PCN. Pulp bleached by the Z/ED(PO) sequence (PCN 0.06) was more stable than that bleached by D_{HT}(PO)DP one (Table 2), but in order to reach the 90.5% ISO, this sequence required a unusually high hydrogen peroxide dose in the final (PO) stage (15 kg/odt), which caused a low pulp viscosity. Excess oxidant use in bleaching and low pulp viscosity are considered potential sources of pulp brightness instability; thus, the high stability of Z/ED(PO) pulp is intriguing to say the least.

Deep investigation on the chemistry of the two pulps (Table 2) showed some interesting facts. Bleached pulp metals content, particularly iron and manganese, could not explain the large brightness reversion difference between the pulps. Hexenuronic acids content, kappa number and soluble lignin correlated with brightness reversion but xylan, carboxyl and especially reducing group content did not correlate with reversion.

Table 2. Brightness reversion and fine chemistry of an oxygen delignified pulp*, bleached with the D_{HT}(PO)DP and Z/ED(PO) sequences

Bleached Pulp Characteristics	D _{HT} (PO)DP	Z/ED(PO)
Final Brightness, % ISO	90.5	90.2
PCN	0.22	0.06
O ₃ , kg/ odt	-	4
ClO ₂ as Cl ₂ , kg/ odt	21.5	6.3
H ₂ O ₂ , kg/ odt	8	15
Total Act. Cl ₂ , kg/ odt	38.2	47.6
Viscosity, dm ³ /kg	799	625
HexA's, mmol/kg	12.2	7.6
Reducing groups, gCu ₂ O/ 100g	0.20	0.46
Carboxyl groups meq/100g	6.1	7.0
Kappa No.	1.4	1.1
Soluble Lignin, %	0.14	0.10
Xylan, %	12.7	13.6
OX, mg/kg	81	22
Metals, mg/kg:		
Fe	11	12
Cu	0.6	0.8
Ca	310	215
Mn	1.4	1

*Original kraft-O₂ Pulp: kappa no. 9.7; viscosity 1046 dm³/kg; HexA's 52.1 mmol/kg; metals contents (mg/kg pulp): Fe 19, Cu 0.6, Ca 1167 and Mn 8.4.

The results shown in Table 2 suggest that reversion is influenced by a combination of various factors which likely operate synergistically. The fact that the OX value for the Z/ED(PO) bleached pulp was four times lower than that of the reference could be a reasonable explanation for its much lower reversion, but this is not an universal trend as shown in our own work (EIRAS et al. 2005). Two questions remains: is the high brightness stability of the Z/ED(PO) pulp derived from the ozone stage, from the chlorine dioxide stage, from the final peroxide stage or from the combination of all? What are the component(s) of the bleached pulp, responsible for brightness reversion, which are actually removed in the ozone stage, in the chlorine dioxide stage, in the final peroxide stage or in all?

Stage-by-Stage Evaluation

Brightness reversion and chemistry of pulps were evaluated after each stage of the Z/ED(PO) and D_{HT}(PO)DP bleaching sequences (results not shown). For the sequence D_{HT}(PO)DP, brightness reversion and pulp reducing groups decreased after alkaline stages (PO or P) and increased after acid stages (D_{HT} and D₁). HexA's and carboxyl groups content decreased all along the sequence. Carboxyl groups derive from HexA's and from lignin structures, with their decrease along the sequence being expected. Thus, the reducing group content is apparently the only parameter that correlates with reversion of the pulp bleached with the D_{HT}(PO)DP sequence. Nevertheless, the OZ/ED(PO) bleached pulp showed a completely different reversion profile across the sequence. Although this pulp had high reducing group content, derived from the ozone stage, the brightness

reversion decreased at this stage, and also decreased at the subsequent chlorine dioxide and hydrogen peroxide stages, resulting in a final pulp of very high brightness stability, in spite of having high reducing group content at the end of bleaching. While reducing group content seems to be a problem for brightness stability of the D_{HT}(PO)DP bleached pulp it is not so for the sequence containing the ozone stage.

Why High Brightness Stability for Ozone Bleached Pulp

Different charges of ozone (6 kg/odt), chlorine dioxide (5, 15, 25 and 35 kg/odt as Cl₂) and hydrogen peroxide (15, 10, 5, 1 and 0 kg of H₂O₂/odt) were combined in order to bleach an eucalyptus kraft pulp to 90% ISO by the Z/EDP sequence. The factors 2.09 and 2.5 were used to convert peroxide and ozone charges into active chlorine charge. For all cases, the oxidant doses were similar and in the range of 48-51 kg active chlorine /odt of pulp. Heat reversion measured after dry and wet accelerated tests decreased with increasing chlorine dioxide and decreasing peroxide doses up to a certain level. The lowest wet and dry PCN numbers were achieved with chlorine dioxide and hydrogen peroxide doses of 25 and 5 kg/odt pulp, respectively. Decreasing peroxide dose from 5 to 1 kg/odt increased reversion, indicating that a certain amount of peroxide is required to maintain good brightness stability with the Z/EDP sequence. When the hydrogen peroxide stage was suppressed altogether (0 kg/odt), the brightness reversion increased rather sharply. Note that bleached pulp kappa number and HexA's content decreased with increasing chlorine dioxide dose but did not correlate with brightness stability; the lowest kappa number and HexA's content was obtained with the Z/ED₍₃₅₎ strategy, which resulted in the pulp with highest dry and wet PCN values. No correlation was observed between PCN values and pulp organically bound chlorine. The pulps bleached with 5 and 1 kg of peroxide in the last P-stage of the Z/EDP sequence showed the lowest PCN values but not the lowest OX values. The very high reversion values obtained with the Z/ED₍₃₅₎ strategy (Table 3) suggest that electrophilic bleaching with ozone and chlorine dioxide is rather effective to remove pulp readily oxidizable materials (kappa number, HexA's etc.) but incapable of removing certain "unknown materials" that cause brightness reversion. On the other hand, the inefficient removal of readily oxidizable materials during bleaching results in pulps of low brightness stability as well, as seen with the Z/ED_{(5)P}₍₁₅₎ strategy (Table 3).

In summary, good brightness stability is achieved when pulp readily oxidizable materials are removed to a large extent with electrophilic reagents such as ozone and/or chlorine dioxide and the pulp is further treated nucleophilically to remove some "unknown substances" that causes reversion. What are these substances? During the final P-stage treatment (end pH

11.4 – Table 3), are both the HO⁻ and HOO⁻ anions required for the nucleophilic attack of such substances, or HO⁻ alone suffices, or none of these two is required? In order to understand this mechanism, the same experiment described in Table 3 was repeated but now the pH of the final P-stage was adjusted to 4.5 (Table 4). In such pH both the HO⁻ and HOO⁻ anions exists in very low concentrations. The Z/EDP bleached pulps, with the final P-stage run at pH 4.5 showed very poor brightness stability, indicating that the HO⁻ anion is very necessary to remove the so-called “unknown substances” responsible for brightness reversion. Of course, at pH 4.5 there is not much HOO⁻ available either since the hydrogen peroxide pKa is about 10.5 at 90 °C. So, this experiment does not prove whether HO⁻ or HOO⁻ is the specie responsible for minimizing reversion but certainly indicates that the absence of both is very detrimental. The sharp decrease in pulp brightness stability when the final P-stage was carried out at pH 4.5 is explained by severe cellulose degradation caused by the acid peroxide (hydroxyl radicals), which likely generates significant amounts of reducing groups in the pulp. The severe pulp degradation is easily seen by the very low viscosity value (Table 4).

The previous results do not allow for a firm conclusion on the role of alkaline peroxide in the prevention of brightness reversion. A simple alkaline extraction is not recommended as final bleaching stage since it converts colorless traces of lignin phenols into colored quinones. Therefore, hydrogen peroxide needs to be present to oxidize such quinones into colorless muconic acid type structures. The amount of peroxide required is related to the amount of such compounds. Thus, the rule of thumb for production of high brightness stability eucalyptus pulp seems to point towards (1) application of enough electrophilic oxidants (ozone, chlorine dioxide) to decrease pulp readily oxidizable materials (HexA's, lignin etc) content nearly to zero and (2) apply a nucleophilic final stage (alkaline peroxide) with a minimal but well calculated charge of oxidant in order to extract the remaining “unknown substances” and oxidize potential chromophores that may be generated under the alkaline conditions.

Table 3. Brightness stability and chemical characteristics of OZ/EDP bleached pulp using various chemical dosages (P-stage pH = 11.4)

Sequence ¹	Visc dm ³ /kg	Bright-ness, % ISO	HexA mmol/kg	OX ² , mgCl ⁻ /kg	Kappa	Dry ³ PCN	Wet ⁴ PCN
Z/ED ₍₅₎ P ₍₁₅₎	783	91.1	10.1	28	1.0	0.24	3.2
Z/ED ₍₁₅₎ P ₍₁₀₎	805	92.0	4.8	51	0.8	0.16	1.7
Z/ED ₍₂₅₎ P ₍₅₎	854	92.7	2.8	83	0.6	0.14	1.3
Z/ED ₍₃₅₎ P ₍₁₎	856	91.0	1.7	94	0.4	0.16	1.4
Z/ED ₍₃₅₎	981	90.7	1.7	104	0.4	0.46	5.5

*original pulp: kappa no. 10; HexA's 55.3 mmol/kg;

¹subscript numbers refer to ClO₂ (as Cl₂) and H₂O₂ charges (kg/odt);

²Organically bound chlorine;

³Dry reversion: 4 h, 105 °C, 0 % relative humidity;

⁴Wet reversion: 15 h, 90 °C, 10% pulp moisture content.

Table 4. Brightness stability and chemical characteristics of OZ/EDP bleached pulp using various chemical dosages (P-stage pH = 4.5)

Sequence ¹	Visc dm ³ /kg	Bright-ness, % ISO	HexA mmol/kg	OX ² , mgCl ⁻ /kg	Kappa	Dry ³ PCN	Wet ⁴ PCN
Z/ED ₍₅₎ P ₍₁₅₎	316	87.1	9.6	32	1.2	1.545	14.6
Z/ED ₍₁₅₎ P ₍₁₀₎	350	88.0	4.2	58	0.9	1.231	11.9
Z/ED ₍₂₅₎ P ₍₅₎	499	88.7	2.3	89	0.7	0.999	8.77
Z/ED ₍₃₅₎ P ₍₁₎	771	89.6	1.6	105	0.5	0.644	6.41
Z/ED ₍₃₅₎	981	90.7	1.5	111	0.5	0.463	5.54

*original pulp: kappa no. 10; HexA's 55.3 mmol/kg;

¹subscript numbers refer to ClO₂ (as Cl₂) and H₂O₂ charges (kg/odt);

²Organically bound chlorine;

³Dry reversion: 4 h, 105 °C, 0 % relative humidity;

⁴Wet reversion: 15 h, 90 °C, 10% pulp moisture content.

Brightness Reversion Mechanism

The so-called “unknown substances” referred to in the previous session that cause pulp brightness reversion may have different origins. No matter how low the kappa number is (≤ 1 in all cases, Table 3) there is always some trace aromatics left in the bleached pulp. In addition, reducing groups can be generated during electrophilic bleaching stages (ozone, chlorine, chlorine dioxide etc.). Furthermore, trace amounts of hexenuronic acids will always be present in bleached pulps since their reaction rate with electrophilic oxidants is low. It seems that a mechanism involving reducing groups, hexenuronic acids and trace amounts of aromatics remaining in the pulp is responsible for eucalyptus kraft pulp brightness reversion. Reagents that are able to create reducing groups (ozone and chlorine dioxide) should be avoided as last stage of a bleaching sequence. Hexenuronic acids and trace aromatics derived from lignin and/or extractives must be removed to the maximum extent with ozone and/or chlorine dioxide. These trace aromatics may be linked to hemicelluloses and cellulose through the so-called lignin-carbohydrate complexes (AXELSSON, 2005). The majority of trace phenolic compounds can be eliminated by applying high charges of chlorine dioxide intercalated with alkaline extractions and efficient washing.

Trace aromatic compounds

The compositions of trace aromatics present in certain fully bleached pulps were determined by the Py-GC/MS technique. Some significant compounds found in such pulps are shown in Figure 1 and Table 5. It is worth noting that despite having 91% ISO brightness, these pulps contained a large number of different aromatic compounds, likely derived from pulp traces of lignin and phenolic extractives. The same types of aromatic compounds were found in the OZ/EDP and D_{HT}EDD bleached pulps, although they occurred in different proportions. These results are in principle unexpected since ozone and chlorine dioxide act by different mechanisms. Cotton fibers were used as reference to determine the accuracy of the analytical technique (Py-MS/CG). In this reference material only

one aromatic compound was identified in the cotton (pirocatechol) but in very low concentration (1.34% area). The bleached pulps (kappa number <0.5) showed much larger amount of this compound and many other types of compounds. Most of the aromatic compounds identified are likely derived from lignin residues or lignin-carbohydrate complexes. The presence of a final hydrogen peroxide stage in the sequence did not influence the aromatic compounds content. Even when peroxide charges reached 10 or 15 kg/odt, the relative percentage of aromatic compounds were still high as can be seen for the Z/ED₁₅P₁₀ (8.18 %) and Z/ED₅P₁₅ (9.24 %) bleached pulps. The pulp bleached by the Z/ED₁₅P₁₀ sequence had one of the highest relative aromatic compound areas (8.18%) and yet the lowest brightness reversion (PCN 0.16) whereas the Z/ED₃₅ bleached pulp had the lowest relative aromatic compound area (3.3%) and the highest brightness reversion (PCN 0.46).

Table 5. Aromatics compounds detected by Py-GC/MS technique in various bleached eucalyptus kraft pulps

Aromatic Compounds	%Area			
	Z/ED ₅ P ₁₅	Z/ED ₁₅ P ₁₀	Z/ED ₃₅	D _{HT} EDD
5-Methylbenzene-1,3-diol	0.3	0.76	-	-
Phenol	0.93	0.66	-	0,67
Unknown	0.51	0.53	-	0,43
3,4-dihydroxybenzaldehyde	0.38	0.25	0.31	0,18
2-acetylhydroquinone	-	-	0.12	-
Benzene-1,2-diol (catechol)	3.75	3.49	2.46	2,17
4-Methylcatechol	1.55	0.57	-	-
4-Hydroxybenzaldehyde	0.45	0.48	-	-
4-hydroxy-2-ethylbenzaldehyde	0.26	0.21	-	-
2-methylbenzene-1,4-diol	0.46	0.57	0.13	0,22
Hydroquinone	0.65	0.66	0.28	0,36
Total	9.24	8.18	3.3	4.03
PCN (dry test)	0.25	0.16	0.46	0.30
PCN (wet test)	3.21	1.70	5.54	3.7

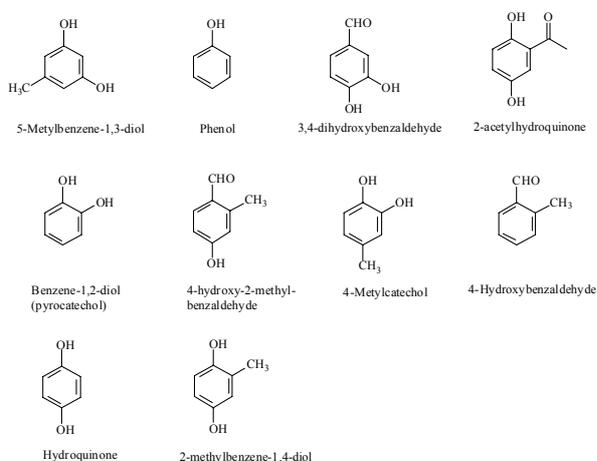


Figure 1. Aromatic compounds identified by Py-GC/MS in OZ/EDP and D_{HT}EDD bleached pulps.

Reducing groups and hexenuronic acids

Modern bleach sequences have been designed to produce pulps with minimum amounts of HexA's and reducing groups. Sequences containing hot acid (A) or hot chlorine dioxide (D_{HT}) as first stage and a hydrogen peroxide as final stage are usually quite effective in minimizing HexA's and reducing groups. Examples of such sequences are the A/D(PO)DP and D_{HT}(PO)DP, which have gained a lot of acceptance in recent years for eucalyptus kraft pulp bleaching. They allow for producing pulps of high brightness and high brightness stability. However, even pulps bleached in these sequences still present some brightness reversion (1.5-2% ISO brightness loss), which has not yet been accounted for. In the previous session it was not possible to correlate brightness reversion with trace aromatics present in the pulp. Thus, reducing groups and trace hexenuronic acids come back to the picture, in an attempt to explain reversion of pulps bleached with highly sophisticated bleaching sequences as the ones cited above.

Table 6 show the effect of pH on heat reversion (dry and wet) of two eucalyptus pulps bleached by the (DC)(PO)DD and D_{HT}(PO)DP sequences. In the first case scenario, the bleached pulp contained virtually no hexenuronic acids (0.2 mmol/kg) and a significant amount of reducing groups (copper no. 0.32 g Cu₂O/100g) and in the other case scenario the pulp contained significant amount of HexA's (11.2 mmol/kg) and low amount of reducing groups (copper no. 0.06 g Cu₂O/100g). The pH of these pulps was adjusted in the range of 3 to 9 and they were tested for wet and dry reversion (Figs. 2 and 3). It is observed that the pulp with high HexA's content is quite stable in the high pH range whereas the pulp containing high content of reducing groups is more stable in the lower pH range. Hence it is concluded that HexA's suffers acid hydrolysis and generate colored substances under heat and moisture. In fact, SEVASTYANOVA, 2005, unequivocally proved that hexenuronic gives rise to compounds such as reductic and 5-formyl-2 furancarboxylic acids under wet reversion conditions and claimed that these compounds are likely the cause of reversion derived from HexA's. On the other hand, the reversion caused by reducing groups is more severe under alkaline conditions (Fig. 5). On the other hand, reducing groups of the carbonyl type and/or trace amounts of aromatics are more susceptible to oxidation under alkaline conditions giving rise to colored substances. What substances are these is still a matter of question.

Table 6. Brightness stability and chemical characteristics of (DC)(EPO)DD and D_{HT}(EPO)DP bleached pulps. Pulp slurry pH adjusted to 5.0 for reversion test (ISO Standard 3688)

Sequence ¹	Brightness, % ISO	Cu # g Cu ₂ O /100 g	Hex m mol / kg	OX ² , mg Cl- / kg	Kappa	Dry ³ PCN	Wet ⁴ PCN
(DC)(EPO)DD	92.1	0.32	0.2	367	0.15	0.38	4.7
D _{HT} (EPO)DP	92.0	0.06	11.2	78	1.40	0.23	3.0

¹original pulp: kappa no. 11.5; HexA's 66.3 mmol/kg;

²Organically bound chlorine;

³Dry reversion: 4 h, 105 °C, 0 % relative humidity;

⁴Wet reversion: 15 h, 90 °C, 10% pulp moisture content.

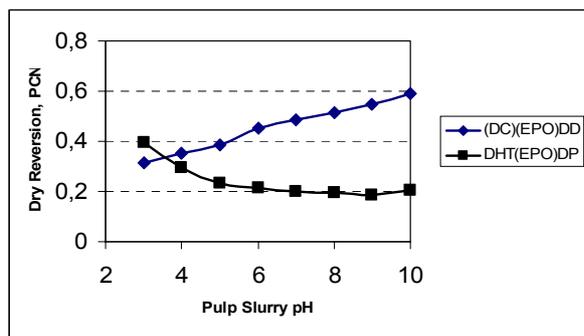


Figure 2. Effect of slurry pH on dry brightness reversion of pulps bleached with the (DC)(EPO)DD and D_{HT}(EPO)DP sequences.

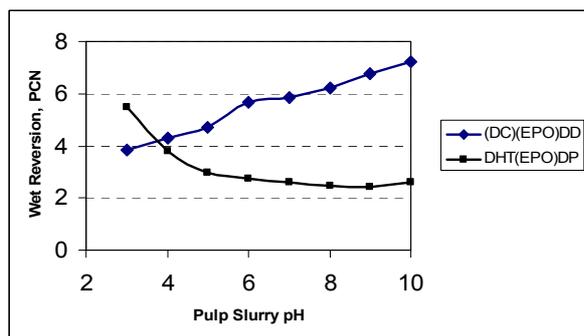


Figure 3. Effect of slurry pH on wet brightness reversion of pulps bleached with the (DC)(EPO)DD and D_{HT}(EPO)DP sequences.

Improving Brightness Stability at Mill Scale

Although brightness stability can be improved by proper adjustment of pulp slurry pH before the drying machine (Figs. 2 and 3), such practice is hindered by the fact that pulp mills prefer to dry their pulp at a slurry pH of 4.7-5.5 to warrant good drainability and improved machine performance. So, as of a rule the pulp slurry will be adjusted to this pH range at the mill. One possible way to gain some brightness stability is by adjusting the pH of the last bleaching stage. Figures 4 and 5 show dry and wet reversion data, respectively, for pulps bleached at variable pH at the last stage (D and P). A D_{HT}(EOP)D bleached pulp was treated with chlorine dioxide or hydrogen peroxide at various pH values. The resulting pulps were tested for dry (slurry pH 5, 100°C, 4 h, 0% humidity) and wet conditions (slurry pH 5, 90 °C, 15

h, 10% humidity). The results shown in Figures 4 and 5 indicate that better brightness stability is achieved when bleaching is carried out at higher pH values. This reflects the fact that the bleached pulps (Table 7) contained significant amount of HexA's (2.8 and 7.6 mmol/kg for final D and P, respectively) and very low amounts of reducing groups (0.11 and 0.07 mmol Cu₂O/100g for final D and P, respectively). It is worth noting that the pH of the pulps bleached at the various pH values was adjusted to 5.0 prior to making the hand sheets that were tested for reversion. Hence, by the use of this practice, i.e., running the last bleaching stage at higher pH values, it is possible to minimize reversion without penalizing the performance or the drying machine. Of course, this practice is valid for bleached pulps rich in hexenuronic acid, which present better brightness stability when containing an alkaline character.

Table 7. Brightness stability and chemical characteristics of D_{HT}(EPO)DD and D_{HT}(EPO)DP bleached pulps. Pulp slurry pH adjusted to 5.0 for reversion test (ISO Standard 3688)

Sequence ¹	Brightness, % ISO	Cu # g Cu ₂ O /100 g	Hex m mol / kg	OX ² , mg Cl- / kg	Kappa	Dry ³ PCN	Wet ⁴ PCN
D _{HT} (EPO)DD ⁵	90.7	0.11	2.8	112	0.45	0.27	1.71
D _{HT} (EPO)DP ⁶	90.7	0.07	7.6	89	1.05	0.15	1.31

¹original D_{HT}(EOP)D bleached pulp: kappa no. 1.2; HexA's 8.7 mmol/kg;

²Organically bound chlorine;

³Dry reversion: 4 h, 105 °C, 0 % relative humidity;

⁴Wet reversion: 15 h, 90 °C, 10% pulp moisture content;

⁵D-stage run at end pH 5.3;

⁶P-stage run at end pH 9.3.

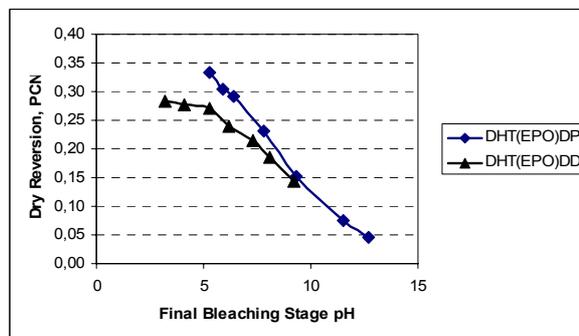


Figure 4. Effect of last-stage reaction pH on dry brightness reversion for pulps bleached with the D_{HT}(EPO)DD and D_{HT}(EPO)DP sequences.

CONCLUSION

The production of high brightness stability eucalyptus pulps can be achieved with processes that apply enough charge of electrophilic oxidants (ozone, chlorine, chlorine dioxide etc.) to reduce pulp HexA's to nearly zero followed by a final nucleophilic oxidation stage with a minimal but well calculated charge of oxidant in order extract the remaining

“unknown reducing substances” and oxidize potential chromophores created under alkaline conditions. Reversion caused by HexA’s is more severe when pulp is dried under acidic conditions. The opposite is observed for reversion caused by the “unknown reducing substances”. A final nucleophilic bleaching stage run at slight alkaline conditions is effective to prevent brightness reversion of eucalyptus pulps.

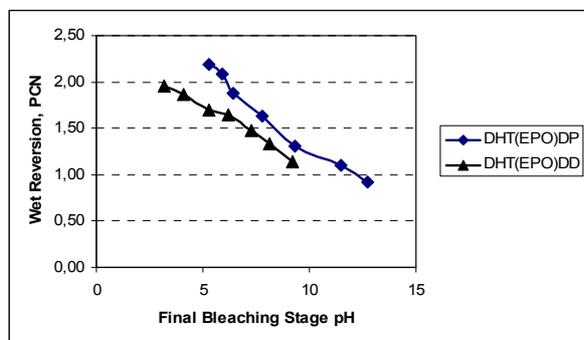


Figure 5. Effect of last-stage reaction pH on wet brightness reversion for pulps bleached with the D_{HT}(EPO)DD and D_{HT}(EPO)DP sequences.

REFERENCES

- AXELSSON, P.; BERGGREN, R.; BERTHOLD, LINDSTRÖM. *Journal of Pulp and Paper Science*, Montreal, CA, v. 31, n. 1, 2005.
- BOKSTRÖM, M.; WENNERSTRÖM, M. ISWPC, Nice, France, *Proceedings...*, 2001.
- BUCHERT, J.; BERGNOR, E.; LINDBLAD, G.; VILKARI, L.; EK, M. *Tappi Journal*, Atlanta, EUA, v. 80, n. 6, p. 165-171, 1996.
- CANADIAN PULP AND PAPER ASSOCIATION. Technical Section. *Standard test methods*. Montreal, 1986.
- DEL RÍO, J. C.; GUTIÉRREZ, A.; HERNANDO, M.; LANDÍN, P.; ROMERO, J.; MARTÍNEZ, A. *J. Anal. Appl. Pyrolysis*, 2005.
- EIRAS, K. M. M.; COLODETTE, J. L. *Journal of Pulp and Paper Science*, v. 31, n. 1, p. 1, 2005.
- EIRAS, K. M. M.; FRANCIS, R.C.; COLODETTE, J. L.; LASSELL, S. IPBC, Stockholm, Sweden, *Proceedings...*, 2005.
- GOLDSCHMID, O. New York, USA: Wiley-Interscience, 1971, p. 241-266.
- HERNANDO, M.; LANDÍN, P.; TROVAL, G.; ROMERO, J. CIADICYP PyGCMS y FT-NIR, 2004.
- PTS METHOD PTS-RH 012/90. *Papiertechnische Stiftung*, HeBstrabe, Munchen, 1990.
- RAGNAR, M.; DAHLLOF, H. *Nordic Pulp and Paper Research Journal*, [S.l.], v. 17, n. 3, p. 228-233, 2002.
- RODRIGUES, J.; GRAÇA, J.; PEREIRA, H. *Journal of Analytical and Applied Pyrolysis*, v. 58-59, p. 481-489, 2001.
- SCAN - SCANDINAVIAN PULP, PAPER AND BOARD. *Testing committee*. Estocolmo: SCAN cm38:96: 1989.

SEVASTYANOVA, O. Doctoral Thesis. KTH Stockholm, Sweden, 2005.

TENKANEN, G. et al. *Journal of Pulp and Paper Science*, Montreal, CA, v. 25, n. 9, p. 306, 1999.

TAPPI - TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY. *Tappi Standard Methods*, Atlanta: TAPPI, 1993, 1996 e 2000.

WENNERSTRÖM, M. *Pulp & Paper Canada*, n. 106, v. 1, p. T9, 2005.