AGEING OF EUCALYPTUS PULPS: EFFECTS ON BRIGHTNESS AND VISCOSITY

Annbritt Forsström, Pia Hellström Thomas Greschik
Eka Chemicals AB, SE-445 80 Bohus, Sweden
annbritt.forsstrom@eka.com;pia.hellstrom@eka.com; thomas.greschik@eka.com

SUMMARY
The brightness and viscosity loss after dry and moist heat-induced ageing was studied. The evaluation was made using totally chlorine free (TCF) and elemental chlorine free (ECF) laboratory bleached industrial oxygen pre-delignified kraft pulps (*Eucalyptus grandis / Eucalyptus saligna*), prepared to contain varying levels of hexenuronic acid (HexA) and transition metals (iron, copper and manganese). Accelerated heat-induced ageing procedures (70°C; 64 hours) were performed to mimic dry and humid conditions.

A substantial heat-induced brightness reversion was obtained at humid conditions, especially for pulps with a high HexA content. All transition metals added to the pulps increased the brightness reversion significantly; iron and copper more than manganese even at rather low addition levels. The brightness loss was found to correlate with the loss in pulp viscosity during ageing. Increased pH during sheet forming was found to be beneficial for the heat-induced brightness stability and for maintaining pulp viscosity.

INTRODUCTION
Hexenuronic acids are formed during kraft pulp cooking when 4-O-methylglucuronic acid groups in glucuronoxylan are converted to 4-deoxy-4-hexenuronic acid groups (HexA). Since xylan is more abundant in hardwoods than in softwoods, the amount of HexA is higher in hardwood kraft pulps. A number of publications have investigated heat-induced brightness reversion in both dry and humid atmospheres using different wood raw materials and different elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching sequences. It has been shown that hexenuronic acid groups, carbonyl groups and lignin residues may be involved in the brightness reversion reactions [1-9]. Today, there is a renewed interest in heat-induced brightness reversion issues due to the rapid growth of eucalyptus kraft pulp capacity in the world.

Eucalyptus pulps, produced by modern cooking methods, contain high amounts of HexA, 60-70 mmol/kg, and are therefore susceptible to heat-induced ageing [10]. In most cases the HexA groups survive TCF and ECF bleaching and therefore almost all bleached kraft pulps contain measurable amounts of HexA groups. Pulps with high content of HexA are also known to bind metal ions and are consequently sensitive to metal contamination from process equipment and process water. It is also known that metals introduced during pulp production are more detrimental to brightness reversion than metals originally present in the wood [11].

The aim of this study was to evaluate the effects of hexenuronic acid content, moisture and metal content on the dry and moist heat-induced brightness reversion of eucalyptus kraft pulps. The effects of ageing on the pulp viscosity were also studied in some details.

EXPERIMENTAL
Pulp samples
The experiments were carried out on industrial oxygen delignified kraft pulp, (Eucalyptus grandis / Eucalyptus saligna), with a kappa number of 8.8 an ISO brightness of 61%, a viscosity of 942 dm^3/kg and a hexenuronic acid content of 62 mmol/kg. To obtain different levels of HexA prior to bleaching, the pulp was subjected to acid hydrolysis (pH 3) at 90˚C for specified retention times (5-480 minutes). The pulps were then bleached in a TCF sequence, (Q+Mg)P(Q+Mg)P to maintain the HexA content. For comparison, an ECF sequence, D(EPO)DnD, was also used. The ECF sequence was performed according to Eka Chemical's modified procedure with increased temperatures in the D1 and D2 stages to reach a low level of HexA [12]. The bleaching stages were performed in polyethylene bags in water baths and the pressurized stages in autoclaves. All trials were made at a pulp consistency of 10%.

Analyses and methods
Handsheets were prepared according to the ISO standard method 3688. The pH of the pulp suspension was adjusted to 5 using a sodium acetate buffer solution prior to sheet making. ISO brightness was measured according to ISO standard method 2470, whereas kappa number and intrinsic viscosity were determined according to ISO standard methods 302 and 5351, respectively.

The hexenuronic acid content was determined by acid hydrolysis of the pulp in a formiate buffer solution followed by measurements of the UV absorption at 243 nm (ε=8700 $lmol^{-1}cm^{-1}$) of the formed 2-furancarboxylic acid (FA) in the hydrolysate [13]. FA was also analyzed in the filtrates after reslushing of aged handsheets by measurements of the UV absorption as described above. The metal ion content of the pulps (after wet combustion with HNO_3 using a microwave system) and in filtrates was determined with an ICP (inductively coupled plasma) instrument (Iris Thermo Jarrell Ash)

Different amounts of the transition metals in pulps were obtained by treating the bleached pulps with aqueous $CuSO_4$, $FeSO_4$ and $MnSO_4$ solutions at room temperature (22˚C) and at 3% pulp consistency for five minutes. The pulps were then thoroughly washed to secure that the remaining metals were fiber bound.

When evaluating the effect of pH in sheet forming, the pH in the pulp suspension was adjusted with sulfuric acid and sodium hydroxide and kept for about five minutes to ensure stable pH levels.

Accelerated heat-induced ageing

Heat-induced brightness reversion was performed on ISO handsheets after conditioning at 23˚C and 50% relative humidity for two hours. The handsheets were then aged at 70˚C for 64 hours in three different ways:

Method A. Placed in double polyethylene bags in a water bath.

Method B. Placed in sealed polypropylene bottles in a heating cabinet.

Method C. Sheets placed in a heating cabinet (dry conditions).

Since all pulps were bleached to about the same ISO brightness (TCF: 87.7-88.4% ISO; ECF: 88.7% ISO, cf. Table 1) the reversion is reported as a loss in ISO brightness units.

RESULT AND DISCUSSION

Ageing methods

Accelerated heat-induced ageing tests can be performed in dry or humid atmospheres. It is important that the conditions chosen are as close as possible to the conditions of an actual reversion situation to obtain relevant ageing results. It is evident that moist ageing methods should mimic the conditions prevailing during storage and transportation of pulp and paper better than the dry ageing methods. Therefore the accelerated heat-induced ageing methods used in this investigation includes both dry and moist conditions.

Prior to the heat-induced ageing, all handsheets were conditioned at 23˚C and 50% relative humidity for two hours to achieve an initial moisture content of 6%. The moisture content during ageing varied depending on the accelerated ageing method used (Figure 1). When ageing according to method A (double polyethylene bags, water bath), the moisture content in the paper sheets was found to increase; after 64h at 70˚C, the moisture content was 12-13%. In ageing method B (sealed polypropylene bottles, heating cabinet), the moisture content was kept constant at 6%. When ageing at dry conditions, method C, the moisture content decreased from 6% to 0% within 7 minutes and remained at that level for the whole ageing time period. The moisture content versus ageing time for the three employed ageing methods can be found in Figure 1. The final moisture content after 64 hours of ageing for method A (13%), method B (6%) and method C (0%) are hereafter used when reporting the different ageing results.

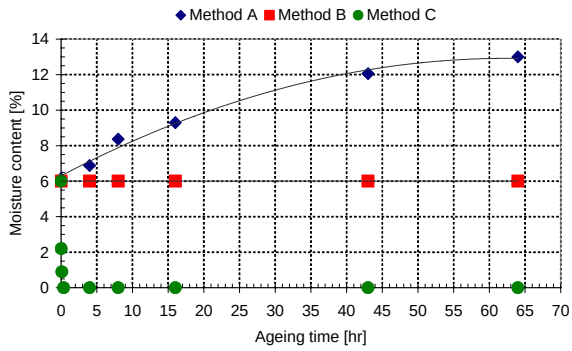

Figure 1. The humidity profile for the different ageing methods used

Preparation of pulps

Hexenuronic acid content

To evaluate the effect of hexenuronic acids on the brightness and viscosity loss during heat-induced ageing of eucalyptus kraft pulps, pulps with different amounts of HexA were prepared. Acid hydrolysis for specified retention times prior to bleaching was used to obtain the different HexA contents (Table 1). The pulps were then bleached in a TCF sequence [(Q+Mg)P(Q+Mg)P] to reach the targeted brightness of 88±0.5% ISO. To obtain a HexA level of 5 mmol/kg, an Eka modified ECF sequence [D (EPO) DnD, with high temperature in D1 and D2] was used.

The four different acid hydrolysis/TCF bleaching sequences covered the HexA range between approximately 5 and 50 mmol/kg. For a TCF bleached pulp, a HexA content of 5 mmol/kg is extremely low and was prepared only for studying the influence of a low level of HexA. For comparison, an ECF bleaching sequence was used to obtain a HexA content of 5mmol/kg. Generally, the HexA content in pulps bleached using TCF sequences are between 20-50 mmol/kg whereas most ECF sequences generates HexA levels between 5-20 mmol/kg.

The HexA levels reached after bleaching were 52, 26, 22 and 5 mmol/kg for the TCF bleached pulps and 5 mmol/kg for the ECF bleached pulp.

A summary of the bleached pulp characteristics is shown in Table 1.

Table 1. The characteristics of the TCF and ECF bleached pulps.

Sequence	HexA content [mmol/kg]	Brightness [%ISO]	Kappa number	Viscosity [dm^3/kg]
A_5QPQP	52	88.4	5.9	786
A_{120}QPQP	26	87.7	3.6	708
A_{240}QPQP	22	87.7	2.3	716
A_{480}QPQP	5	87.7	1.4	697
ECF Eka modified	5	88.7	0.88	831

Metal content

The bleached pulps shown in table 1 were treated with aqueous copper, iron and manganese sulfate solutions with different concentrations to obtain a low (about 10 ppm) and a high (about 50 ppm) level of fiber bound metals. The resulting metal content in so treated pulps can be found in Table 2. The Fe, Mn and Cu content of the untreated pulps were 2.5, <0.1 and 0.3 mg/kg for the TCF bleached pulp and 2.5, 0.6 and 0.9 mg/kg for the ECF bleached pulp.

Table 2. Metal content in the pulps after treatment with $CuSO_4$, $FeSO_4$ and $MnSO_4$.

HeXA [mmol/kg]	Fe [mg/kg pulp]		Mn [mg/kg pulp]		Cu [mg/kg pulp]	
	Low	High	Low	High	Low	High
TCF pulps						
52	5.4	29	8.5	42	9.8	45
26	5.6	36	8.0	43	9.6	53
22	7.4	39	8.0	41	9.3	55
5	10	41			10	46
ECF pulp						
5		49				50

The iron levels examined in this study, i.e., 2.5-49 mg/kg, are relevant for bleached eucalyptus kraft pulps. High levels of manganese and copper could, for some mills, be a reality due to metal contamination from equipments or process waters. There was no decrease in brightness due to the addition of the metal sulfates with one exception; a brightness loss of 2.5% ISO was obtained for the high charge of $FeSO_4$ for both TCF and ECF pulps.

Heat-induced ageing

Effect of moisture and hexeneuronic acids

The moisture content has been found to be of utmost importance for the heat-induced brightness reversion [1,2,3,6]. Figure 2 shows the brightness reversion as a function of moisture content for bleached eucalyptus kraft pulps with various HexA contents (no metals added). It is evident that the moisture content and hexenuronic acid content have a decisive role for the heat-induced discoloration. The TCF bleached pulp with the highest HexA content lost more than 20 brightness units when ageing according to method A (highest moisture content) whereas it only lost about 3 brightness units when aging under dry conditions (method C). The pulps with low HexA contents 5 mmol/kg lost between one and five brightness units depending on the ageing method used.

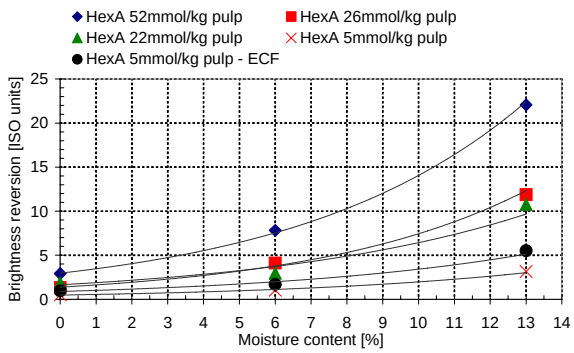

Figure 2. The heat-induced brightness reversion of TCF and ECF eucalyptus kraft pulps with different hexenuronic acid contents as a function of moisture content during ageing. No metals added.

The results show that the pulp with high HexA content is very sensitive to moist heat-induced ageing, but even at dry conditions, there is a significant brightness loss. Furthermore, the brightness reversion for the ECF bleached pulp was similar or slightly higher than the brightness reversion for the TCF bleached pulp at about the same HexA content, 5 mmol/kg. Interestingly, the relationship between the HexA content and the brightness reversion was found to be linear with the slopes of the lines depending on the moisture content during ageing (Figure 3).

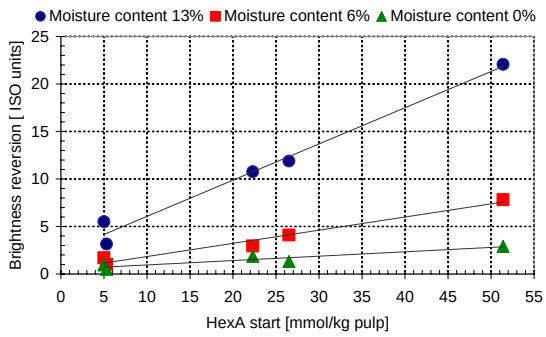

Figure 3. The heat-induced brightness reversion of TCF and ECF eucalyptus kraft pulps as a function of HexA content. The pulps were aged according to ageing methods A-C. No addition of metals.

It has previously been reported that hexenuronic acids are hydrolysed during heat-induced ageing to 2-furancarboxylic acids and 5-formyl-2-furoic acids [7,8]. The decrease of HexA content measured here as the difference between the HexA content in the pulp prior to and after ageing. is in figure 4 referred to as reacted

HexA. As seen in Fig 4 there is a clear correlation between reverted brightness and reacted HexA for all the pulps used in this study i.e. different HexA and metal contents and different ageing methods. This correlation indicates that brightness reversion and HexA degradation are interrelated. i.e. more degradation reactions, more brightness reversion and vice versa.

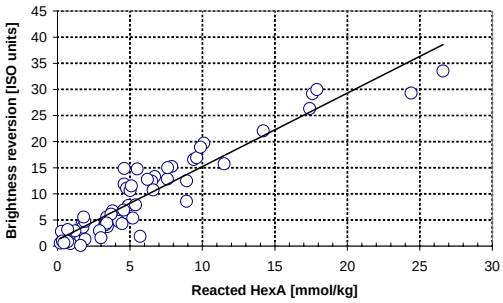

Figure 4. The relationship between reacted HexA and brightness reversion

The decrease in the HexA content has been proposed to be a result of acid hydrolysis and low molecular organic acids are known to be formed during the heat-induced brightness reversion [2,8,14]. Acid hydrolysis of the carbohydrates may also result in a decreased pulp viscosity. The effect of moisture content on the pulp viscosity loss after accelerated heat-induced ageing for 64 hours is shown in Figure 5.

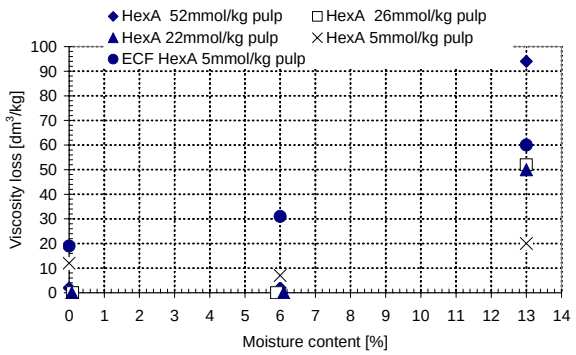

Figure 5. The pulp viscosity loss as a function of moisture content during heat-induced ageing of TCF and ECF eucalyptus kraft pulps with various HexA contents. No addition of metals.

It seems to be a decrease in pulp viscosity for the pulps aged at a high moisture content (13%, method A). The decrease in viscosity is, however, moderate and below 100 dm^3/kg. For the TCF a high HexA content seems to be more detrimental. The ECF bleached pulp seems to be more sensitive compared to the TCF pulp at comparable HexA levels. One explanation could be that the TCF pulps were prepared using an acid hydrolysis stage that decreased the pulp viscosity somewhat (cf. Table 1).

Effects of metal content on brightness reversion

Transition metals such as Fe, Cu and Mn are easily retained in the pulp due to complexation e.g. by HexA groups, which are good chelating agents [15]. Earlier publications have associated brightness loss during ageing with metal content in the pulp [16].

Figures 6 and 7 show the brightness loss after heat-induced ageing as a function of metal ion content for two TCF bleached pulps with a HexA content of 52 and 22 mmol/kg, respectively. The pulps were aged at both dry and moist (6% and 13%) conditions. All metals added to the pulps increased the moist heat-induced brightness reversion especially for the pulp with a high HexA content whereas the dry brightness reversion was largely unaffected. Iron and copper are more detrimental at moist ageing conditions than manganese even at rather low concentrations. These results indicate that pulp metal content, the content of HexA and pulp humidity should be carefully controlled in order to avoid severe brightness reversion.

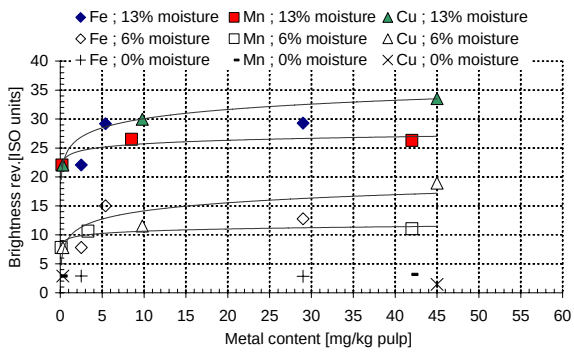

Figure 6. The heat-induced brightness reversion of a TCF eucalyptus kraft pulp (HexA content of 52 mmol/kg) as a function of metal content. The pulp was treated with varying amounts of $FeSO_4$, $MnSO_4$ and $CuSO_4$ and aged using methods A-C).

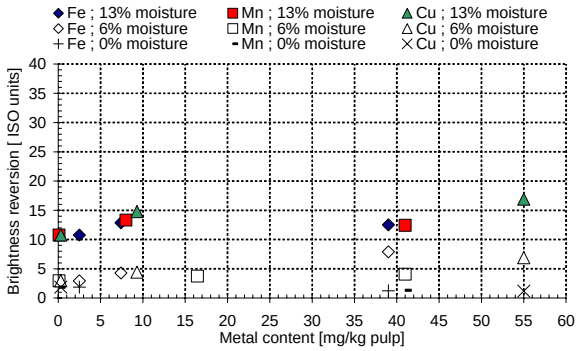

Figure 7. The heat-induced brightness reversion of a TCF eucalyptus kraft pulp (HexA content of 22 mmol/kg) as a function of metal content. The pulp was treated with varying amounts of $FeSO_4$, $MnSO_4$ and $CuSO_4$ and aged using methods A-C).

The effects of the metal contents on pulps with lower HexA contents (Fig 6) were similar to those seen in Figure 5. The effects were however less pronounced.

Effects of metal content on pulp viscosity

Figures 8 and 9 show the pulp viscosity loss as a function of metal ion content after heat-induced ageing of two TCF bleached pulps with two HexA levels of 52 and 22-26 mmol/kg,. The added transition metals, iron and copper, were found to be detrimental to the pulp viscosity in the moist accelerated ageing procedures employed. Manganese was less detrimental and had only a small negative effect during moist ageing. The viscosity loss was about 300 and 200dm^3/kg for the pulps with hexenuronic acid contents of 52 and 22-26 mmol/kg. The comparison was made at a Fe content of 35 mg/kg employing ageing method A.

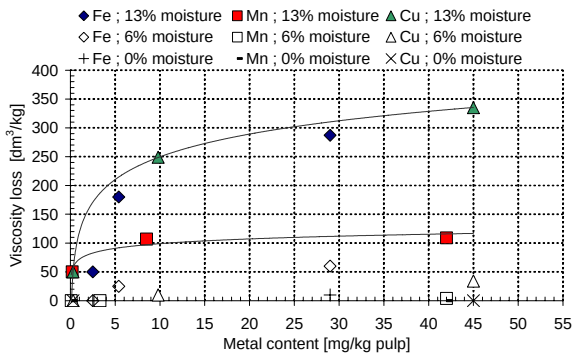

Figure 8. The pulp viscosity loss of a TCF eucalyptus kraft pulp (HexA content of 52 mmol/kg) as a function of metal content during heat-induced ageing. The pulps were treated with varying amounts of Fe, Mn and Cu and aged using methods A-C)

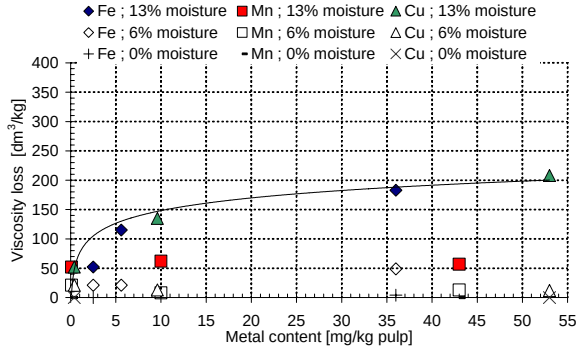

Figure 9. The pulp viscosity loss of a TCF eucalyptus kraft pulp (HexA content of 22-26 mmol/kg) as a function of metal content during heat-induced ageing. The pulps were treated with varying amounts of Fe, Mn and Cu and aged using methods A-C).

Figure 10 shows that there is a linear correlation between brightness reversion and pulp viscosity loss at three different levels; 1) high Fe and Cu content, 2) low Fe and Cu content and 3) high and low Mn content and untreated pulp.

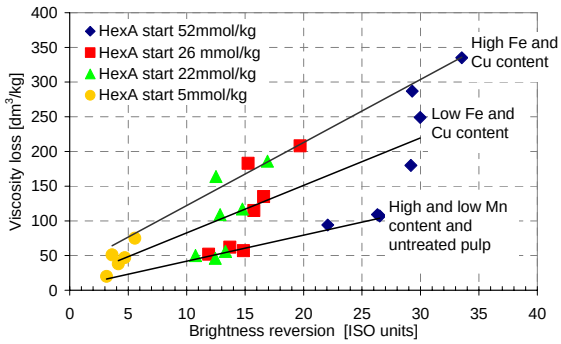

Figure 10. The pulp viscosity loss as a function of brightness loss for TCF eucalyptus kraft pulps with various HexA and metal ion contents. The heat-induced ageing was performed according to method A(13% moisture content).

To summarize, a high HexA content and a high Cu and/or Fe content of the pulp have a substantial negative effect on the brightness and pulp viscosity during heat-induced ageing, especially at the highest moisture content (13%) used in this investigation whereas manganese is less detrimental. A moisture level of 13% corresponds well to real conditions since the dry solid content of market pulps is about 88-90% [5].

Effect of sheet forming pH

In this part of the study, handsheets were prepared at various sheet forming pH levels from 5-11 by adding sulfuric acid or sodium hydroxide to the pulp suspension. This was done to evaluate the changes in brightness and pulp viscosity after humid accelerated heat-induced ageing. The humid brightness reversion was then performed according to methods A and B as previously described. The eucalyptus pulps used had a HexA content of 52 mmol/kg and a Cu content of 0.4 or 70 mg/kg. Copper was chosen due to its detrimental effect on brightness and pulp viscosity during ageing (cf. Figures 6-10).

An increased pH of the pulp suspension during sheet forming decreased the humid heat-induced brightness reversion substantially (Figure 11). At pH 5, the brightness reversion was about 30 ISO brightness units and at pH 8.5 and higher below 5 ISO brightness units, i.e., a reduction with more than 80%.

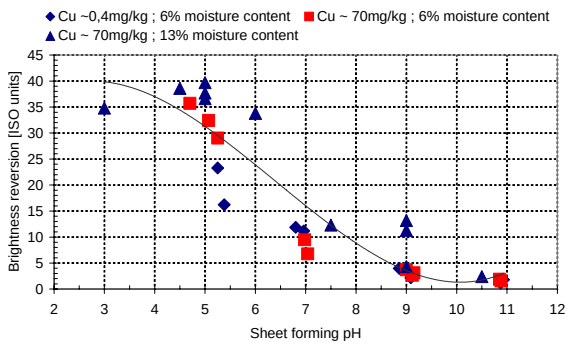

Figure 11. Heat-induced brightness reversion as a function of pH during sheet forming. The TCF pulp with a HexA content of 52 mmol/kg and moist ageing methods A and B were used.

An increased pH of the pulp suspension during sheet forming also gives a positive effect on pulp viscosity after ageing, see Figure 12. If the pH is increased from 5 to 9, the viscosity loss is reduced with about 300 dm^3/kg for the pulp aged according to method A (13% moisture content). At lower moisture contents (6%) and pH above 7, the viscosity loss is very low irrespective of the Cu content.

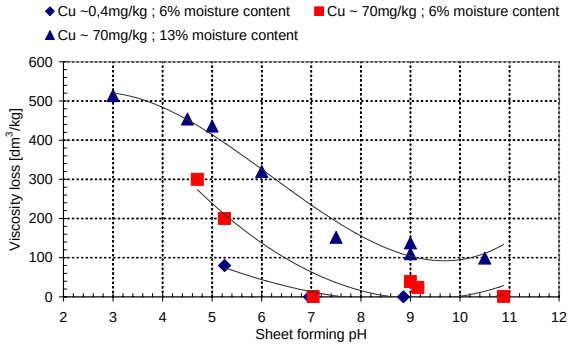

Figure 12. The decrease in pulp viscosity after heat-induced ageing as a function of pH during sheet forming. The eucalyptus kraft pulp used had a HexA content of 52 mmol/kg and moist ageing methods A and B were used.

CONCLUSIONS

The heat-induced brightness reversion of totally chlorine free and elemental chlorine free kraft pulps (Eucalyptus grandis / Eucalyptus saligna) was found to be strongly correlated with the hexenuronic acid and moisture contents of the pulps. The transition metals, iron and copper, were strongly detrimental even at low levels, whereas manganese was less harmful. Furthermore, the brightness loss was found to correlate with a loss in pulp viscosity during heat-induced ageing. An increased pH of the pulp suspension prior to sheet making was found to be beneficial for the heat-induced brightness stability and for maintaining pulp viscosity

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REFERENCES

1. Granström, A.; Eriksson, T.; Gellersted,t G.; Röost, C.; Larsson, P. (2001): Variables affecting the thermal yellowing of TCF-bleached birch kraft pulps. Nord. Pulp Pap. Res. J. 16(1), 18-23.
2. Granström, A.; Gellerstedt, G.; Eriksson, T. (2002): On the chemical processes occurring during thermal yellowing of a TCF-bleached birch kraft pulp. Nord. Pulp Pap. Res. J., 17(4), 427-433
3. Granström, A. (2001): On the thermal yellowing of TCF-bleached birch kraft pulp. TRITA-PMT Report 2001:11, Stockholm, Sweden: Royal Institute of Technology, 77pp.
4. Rapson, W.H.; Spinner, J.H. (1979): Brightness reversion in bleached pulp. In Sing, R.P. (ed.) The Bleaching of Pulp. TAPPI Press, ort, land, 357-390.
5. Colodette, J.L.; Eiras, K.M.M.; Oliveira, R.; Ventorim, G. (2004): Influence of eucalypt wood supply on pulp brightness stability. Appita 57(6), 481-487.
6. Sevastyanova, O.; Li, J. Gellerstedt, G. (2004): Influence of different oxidizable structures on the brightness stability of chemical pulps. Eighth European Workshop on Lignocellulosics and Pulp. Riga, Latvia, 22-25 August, 353-356.
7. Sevastyanova, O.; Li, J.; Gellerstedt, G. (2006): On the reaction mechanism of the thermal yellowing of bleached chemical pulps. Nord. Pulp Pap. Res. J. 21(2), 188-192.
8. Chirat, C.; de la Chapelle, V. (1999): Heat- and light-induced brightness reversion of bleached chemical pulps. J. Pulp Pap. Sci. 25(6), 201-205
9. Kawae, A.; Uchida, Y. (2005): Heat and moisture-induced yellowing of ECF-light bleached hardwood kraft pulp. Appita 58(5), 378-381.
10. Colodette, J.L.; Gomide,J.L.; Junior, D.L.; Gomes, C.M.(2006): Improving the Economics of Eucalyptus Kraft Pulp ECF Bleaching, ISETPP, Guangzhou, China, 8-10 November, 330-335
11. Eiras, K.M.M.; Colodette, J.L. (2005): Investigation of eucalyptus kraft pulp brightness stability. J. Pulp Pap. Sci. 31(1), 13-18.
12. Greschik, T.; Björklund, M.; Basta, J.; Blom, C. (2006): Improved brightness stability by optimizing the standard ECF bleaching sequence. ABTCP, Sao Paulo, Brazil, 16-19 October
13. Vuorinen, T.; Fagerström, P.; Buchert, J.; Tenkanen, M.; Teleman, A. (1999): Selective Hydrolysis of Hexenuronic Acid Groups and its Application in ECF and TCF Bleaching of Kraft Pulps. J. Pulp Pap. Sci. 25(5), 155-162.
14. Tenkanen, M.; Forsskåhl, I.; Tamminen, T.; Ranua, M.; Vuorenvirta, K.; Poppius-Levlin, K. (2002): Heat-induced brightness reversion of ECF-light bleached pine kraft pulp. Seventh European workshop on lignocellulosics and pulp. Turku, Finland, 26-29 August, 107-110.
15. Sevastyanova, O. (2005): On the importance of oxidizable structures in bleached kraft pulps. Ph.D. Thesis, Royal Institute of Technology, Stockholm, Sweden
16. Czepiel, T.P. (1960): The influence of selected metal traces on the color and color stability of purified cotton linters. Tappi J. 43(4), 289-