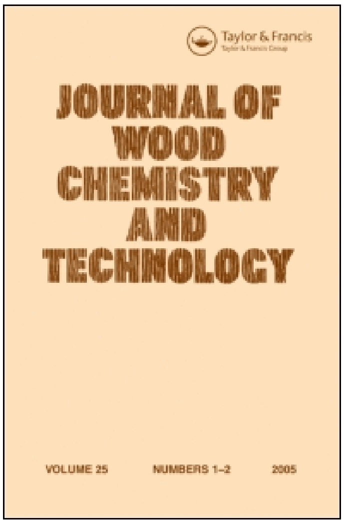

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article van der Zee, Marina E. and Sierra-Alvarez, Reyes(1996) 'Brightness Improvement Of Douglas Fir Thermomechanical Pulp By Edta And Ascorbic Acid Treatments On Chips', Journal of Wood Chemistry and Technology, 16: 2, 155 — 167

To link to this Article: DOI: 10.1080/02773819608545816

URL: http://dx.doi.org/10.1080/02773819608545816

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 16(2), 155-167 (1996)

BRIGHTNESS IMPROVEMENT OF DOUGLAS FIR THERMOMECHANICAL PULP BY EDTA AND ASCORBIC ACID TREATMENTS ON CHIPS

Marina E. van der Zee and Reyes Sierra-Alvarez
Section of Wood Science, Department of Forestry
Wageningen Agricultural University,
P.O. Box 342, 6700 AH Wageningen, The Netherlands.

ABSTRACT

This investigation studies the use of Douglas fir wood as feedstock for thermomechanical pulp (TMP). Douglas fir wood extractives include flavonoids and other polyphenolic compounds, which make the pulp susceptible to discolouration. Pulp darkening is promoted by the formation of metal-chelates and phenolic oxidation products. The effectiveness of various wood pretreatments to prevent the discoloration of polyphenolic extractives in Douglas fir wood was investigated in lab-scale experiments. Iron-mediated brightness losses (up to 5.1% ISO) could be prevented by wood pretreatment with 0.2% EDTA. Treatment of wood meal slurries at temperature levels comparable to those applied in thermo-mechanical pulping caused wood discoloration due to polyphenol oxidation. The brightness losses could be reduced by the addition of 0.5% ascorbic acid. The anti-oxidizing agent was more effective with sapwood compared to heartwood. EDTA pretreatment allowed an increase in the proportion of heartwood from 12% to 39% (w/w) that could be tolerated as feedstock for the production of dithionite bleached TMP with a brightness of 60% ISO. Wood chip impregnation with both EDTA and ascorbic acid only proved advantageous over EDTA alone in Douglas fir samples consisting almost exclusively of sapwood.

INTRODUCTION

The growing demand for pulpwood in recent years has resulted in an increased utilization of wood species with less favourable characteristics as compared to conventional feedstocks. A promising new raw material for mechanical pulping is Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco]. The intrinsic qualities of the fibre for thermomechanical pulp (TMP) are good[1]. The use of Douglas fir in TMP manufacturing is, however, severely limited by the low brightness levels of the pulp.

Douglas fir sapwood does not present brightness problems in TMP. In contrast, the optical properties of mechanical pulps obtained from heartwood are very poor, and the required brightness levels can only be attained with very high bleaching dosages[2,3]. The heartwood extractives contain high levels of flavonoids and other polyphenolic compounds which are the main source of chromophoric compounds. These extractive constituents are largely responsible for the dark colour and poor bleachability of Douglas fir heartwood[4]. Pulp discoloration is intensified by the transformation of polyphenolic extractives into darkly-coloured oxidation products[5] and metal chelates[6-8]. The development of feasible methods for improving the brightness of Douglas fir pulps, would eliminate the main limitation restricting the use of this abundant wood species by mechanical pulp mills. Additional economic and environmental benefits can also be anticipated by the reduction of the chemical charge required for pulp bleaching.

In this study, the effectiveness of various wood pretreatments to prevent the discoloration of polyphenolic extractives in Douglas fir wood was investigated. The pretreatment methods selected were based on the use of sulfur-free additives for minimizing colour-forming reactions occurring during the thermomechanical pulping process.

EXPERIMENTAL

Raw Materials

Douglas fir logs were debarked and sapwood and heartwood were separated and chipped discretely. Chips to be used for pulping experiments were stored in airtight bags at -20°C. A fraction of the chips was dried in a climate room at 25°C under suppressed humidity. The dried chips were milled in a cutting mill, and the fraction between 250 and 425 μm was used for wood meal experiments.

Treatment of Wood Meal Samples

Wood meal samples (3.0 g) were impregnated with 12 mL of a solution containing either L(+)-ascorbic acid (0 to 4% based on o.d. wood weight), $Fe_2(SO_4)_3$ (0 to 100 μg Fe (III)/g o.d. wood (0-

100 ppm), EDTA (0 to 0.4% based on o.d. wood weight) or a combination of these chemicals till complete saturation. The wood slurry was mixed by stirring and then heated in an autoclave at 135°C for 5 min. The treated samples were washed with distilled water and dried in an oven with forced-ventilation at 30°C.

Wood Chip Pretreatment and Refining

Ascorbic acid (0.5% on o.d. wood) and/or EDTA (0.2% on o.d. wood) was added to frozen Douglas fir chips. Demineralized water was added to a consistency of 10 to 15% and mixed thoroughly by stirring. The chip samples were subsequently autoclaved at 135°C for 5 min., and then defibrated and refined under atmospheric pressure on a Sprout-Waldron laboratory refiner to a freeness of around 65°SR. Wood chip mixtures with heartwood to sapwood ratios of 1:0, 1:1, 1:3, and 0:1 (w/w) were tested.

Pulp Bleaching

The pulp was bleached with dithionite under the following conditions: consistency: 5%; bleaching time: 2 hrs; temperature: 60°C; dithionite dosage: 0-1.5% based on o.d. pulp. The bleach liquor was made fresh for each series of experiments in degassed water at 4°C.

Brightness Measurements

The brightness of pulp handsheets was determined by means of an Elrepho brightness measuring device at 457nm assording to TAPPI standard 452. Wood meal samples were placed in a round glass cuvette, designed for brightness measurements of powders, and their brightness determined in a colorimeter (Tricolor LFM3, DRLANGE) using the Z-filter (maximum around 450nm).

RESULTS

Wood Meal Experiments

Fig. 1 shows the brightness change of sapwood meal samples pretreated with ascorbic acid. Wood impregnation with ascorbic acid before heating of the wood meal slurry to 135°C resulted in improved brightness levels. A clear optimum was found at an ascorbic acid dosage of 0.5%, which resulted in an average brightness increase of 4.2% ISO.

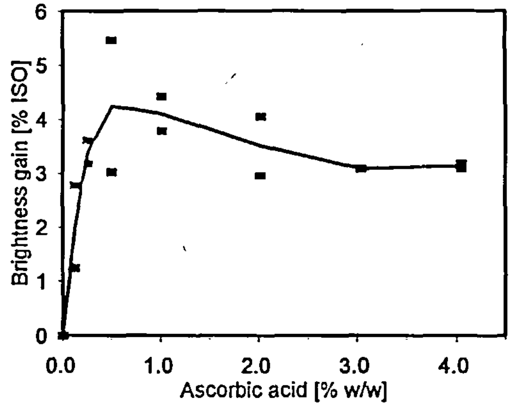


FIGURE 1. Effect of treatment with ascorbic acid (T = 135°C, t = 5 min.) on the brightness of Douglas fir sapwood meal.

The negative impact of iron(III) on the brightness of Douglas fir wood meal is shown in Fig. 2. The addition of 10 ppm Fe(III) to sapwood and heartwood samples was sufficient to cause brightness losses of 1 and 2% ISO, respectively. An increase of the iron dosage to 100 ppm caused a further reduction of the brightness levels by 3.9 and 5.1% ISO, respectively.

Fig. 3 compares the brightness levels of wood meal samples impregnated with Fe(III), with and without the simultaneous addition of EDTA. The chelating agent was found to be highly effective in preventing the iron induced loss in brightness. Dosage of 0.2% EDTA proved sufficient to prevent wood discoloration in the presence of very high iron concentrations (100 ppm). EDTA addition did not generally alter the brightness of iron-deficient wood meal. However, a small improvement in the optical properties of sapwood treated with 0.4% EDTA was observed.

Based on these results, the conditions employed in further thermomechanical pulping experiments with pretreated wood chips were set at a dosage of 0.5% ascorbic acid and 0.2% EDTA. Note that the brightness levels of pulp handsheets are higher than those of wood meal due to the lower scattering coefficient of the handsheet surface (compare Figs. 2 and 4).

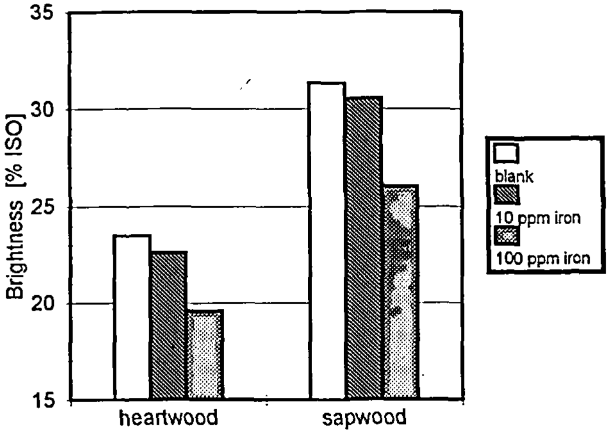
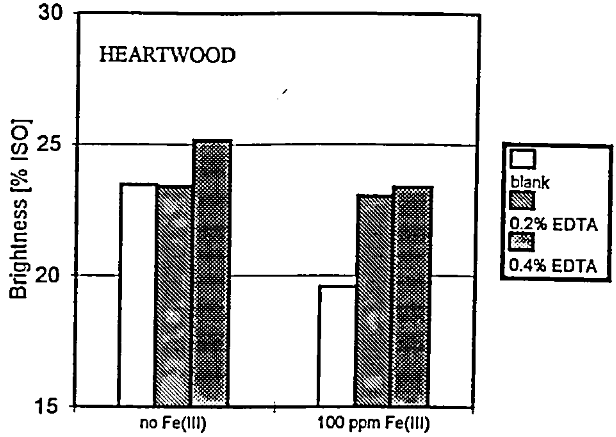


FIGURE 2. Effect of iron (III) (in μg/g wood meal) on the brightness of Douglas fir wood meal. Samples were heated to 135°C for 5 min.

Thermomechanical Pulping Experiments

Fig. 4 compares the brightness levels of unbleached TMP pulp obtained from Douglas fir chip mixtures containing different heartwood ratios, and illustrates the effect of wood pretreatment with ascorbic acid and/or EDTA. A sharp decrease in pulp brightness was found with increasing heartwood contents in the feedstock. The brightness of heartwood pulps was 14% ISO lower compared to sapwood pulp. Wood pretreatment with the additives had distinct effect on the brightness of sapwood and heartwood pulps. Wood impregnation with ascorbic acid provided a minor brightness improvement in heartwood (0.4%), but a brightness gain of 2.7% ISO was attained in sapwood samples. The brightness gain obtained by ascorbic acid increased with increasing sapwood levels in the feedstock. EDTA, on the other hand, improved the brightness of both the sapwood and heartwood pulps by 2.9 to 2.4% ISO, respectively. Sapwood pretreatment with ascorbic acid and EDTA resulted in a cumulative brightness gain exceeding 6% ISO. Hereby, a brightness of 65.5% ISO could be reached which is ample sufficient for newsprint. The brightness gain attained by this combined pretreatment was lower for heartwood samples, amounting to 2.6% ISO.



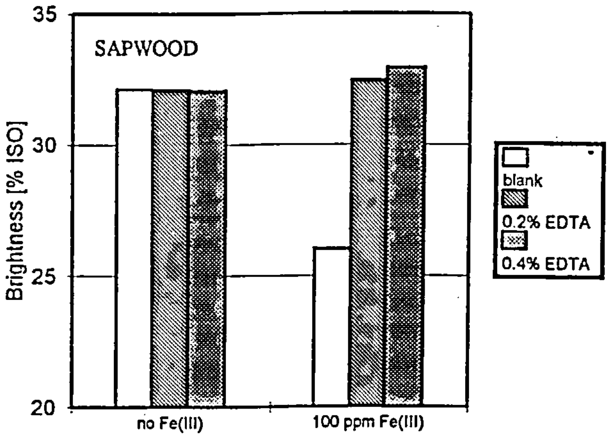


FIGURE 3. Brightness of Douglas fir heartwood and sapwood meal samples impregnated with EDTA and/or Fe(III) (in µg/g wood meal) prior to heating to 135°C for 5 min.

Fig. 5 shows the effect of dithionite dosage in the brightness of pulps obtained from pretreated heartwood and sapwood chips. The brightness gain attained by the addition of EDTA and ascorbic acid is still evident after pulp bleaching. Bleaching of pretreated sapwood pulp with 1% dithionite provided excellent brightness levels of 68% ISO. In contrast, only a maximum of 53%

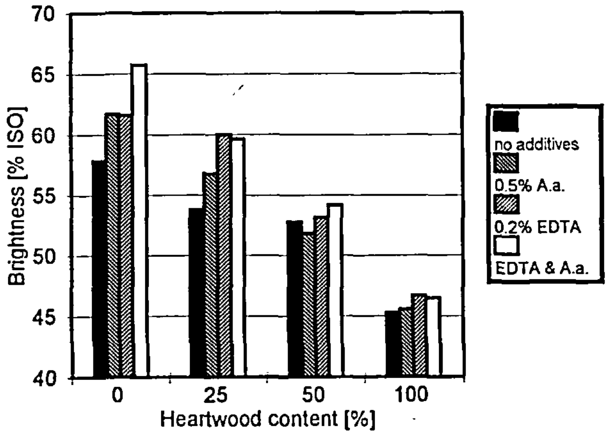


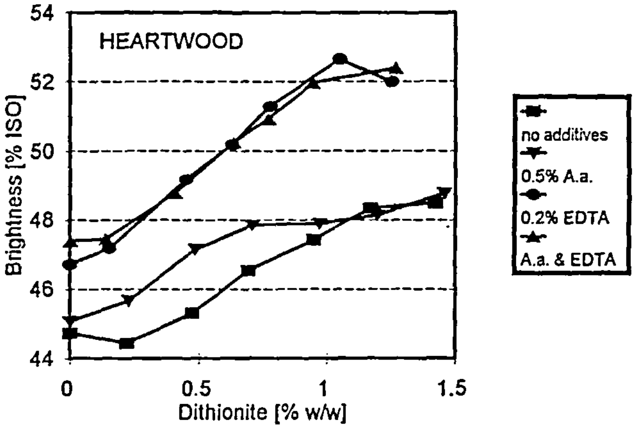
FIGURE 4. The role of sapwood to heartwood ratios on the brightness of Douglas fir thermomechanical pulp handsheets and the effect of EDTA (0.2% on o.d. wood) and/or ascorbic acid (0.5% on o.d. wood) pretreatments on unbleached pulp brightness.

ISO brightness was obtained after bleaching the pretreated heartwood pulp with up to 1.5% dithionite. This brightness level is significantly lower than that required for commercial newsprint.

Fig. 6 illustrates the effect of wood chip pretreatment on the brightness of Douglas fir pulps bleached with 1% dithionite. These results show that when pretreatment is not applied, bleached pulps with a brightness of 60% ISO can only be obtained if the heartwood fraction in the feedstock is lower than 11.6%. The heartwood input that can be tolerated is increased to 39.2% by wood chip impregnation with EDTA. Wood chip pretreatment with both EDTA and ascorbic acid only proved advantageous over EDTA alone in Douglas fir samples consisting almost exclusively of sapwood.

DISCUSSION

Douglas fir TMP produced from heartwood rich feedstocks does not meet the brightness levels required for commercial newsprint production. In this study, the brightness of heartwood pulps was found to be 14% ISO lower as compared to sapwood pulps. The brightness and bleachability of Douglas fir TMP decreases with



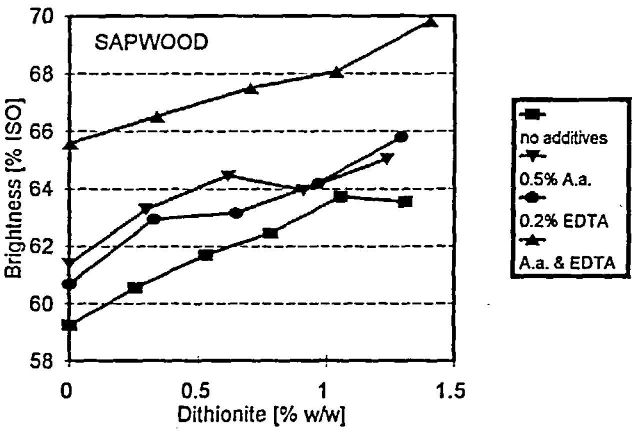


FIGURE 5. Brightness of bleached thermomechanical pulp produced from Douglas fir heartwood and sapwood as a function of the dithionite dosage. Wood chips were impregnated with 0.2% EDTA and/or 0.5% ascorbic acid prior to refining.

increasing heartwood contents in the raw material. Douglas fir is characterized by an early development of heartwood (after 6-10 years), and narrow sapwood (4-22 annual rings at breast height)[9]. As a consequence, the heartwood content in industrial Douglas fir wood chip piles is high, generally ranging from 35 to 40%.

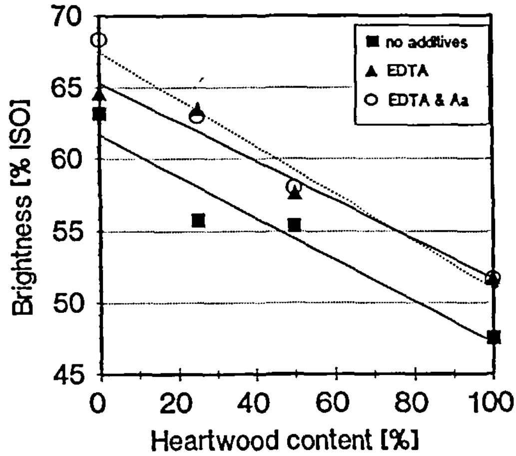


FIGURE 6. Effect of heartwood content on the brightness of Douglas fir thermomechanical pulp bleached with 1% dithionite. Bleached pulps obtained from wood chips impregnated with EDTA (0.2% on o.d. wood) or EDTA (0.2% on o.d. wood) and Ascorbic acid (0.5% on o.d. wood) are compared with pulps from chips devoid of any added chemicals.

The extractive content in Douglas fir heartwood is high, ranging from 2.4 to 8.8% depending on the wood source and the extraction procedure applied[10,11]. Flavonoids, of which taxifolin and quercetin are most abundantly present, represent 80 to 90% of the total phenols extracted. Kelsey and Harmon[12] reported taxifolin contents of 17.3 mg/g and 1.9 mg/g for Douglas fir heartwood and sapwood, respectively. Flavonoids and other polyphenolic extractives are mainly responsible for the poor brightness and bleachability of Douglas fir TMP[2,4,13,14]. The presence of these extractives has also been associated with the poor brightness of mechanical and chemical pulps from other wood species[15]. Furthermore, polyphenol discoloration also causes colour changes during storage of Douglas fir and other wood species[15].

Polyphenolic extractives with ortho-dihydroxygroups, such as quercetin and taxifolin (Fig. 7), are particularly important in relation to colour development. Oxidation of vicinal phenolic hydroxyl groups occurs easily, and results in the formation of the unstable benzoquinones. Subsequent auto-oxidation reactions cause the formation of darkly coloured high-molecular weight polymers,

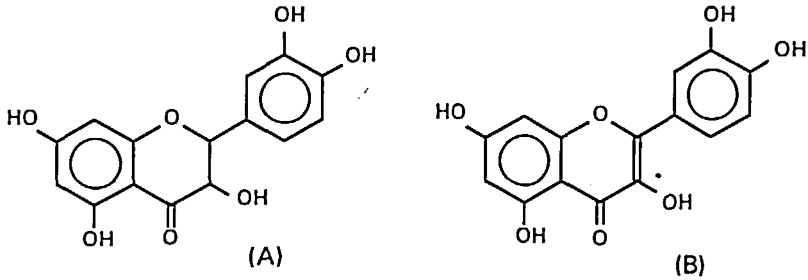


FIGURE 7. Chemical structure of taxifolin (A) and quercetin (B).

leading to the development or intensification of pulp colour[5,15]. Oxidative condensation of polyphenols is promoted at the high temperatures applied in thermomechanical pulping[16-18]. Addition of reducing agents might therefore contribute to reduce the brightness losses caused by the oxidation of polyphenolic extractives. Reducing agents, including ascorbic acid, are known to suppress polyphenol oxidation by rapidly reducing any quinones formed[19].

Our results show that wood impregnation with the reducing agent ascorbic acid prior to chip refining prevented the oxidative discoloration of Douglas fir sapwood (Fig. 4). This pretreatment however was not effective when applied to heartwood samples, suggesting that irreversible oxidation of heartwood extractives had occurred before wood pulping. In a related study, Barton[20] reported that dosage of ascorbic acid during Western Hemlock pulp handsheet formation only provided minor improvements in brightness. The poor performance of the antioxidant was attributed to the formation of chromophores in earlier processing steps by oxidation of polyphenol extractives analogous to those present in Douglas fir wood. These results suggest that ascorbic acid pretreatment can be beneficial in Douglas fir feedstocks containing high sapwood fractions, and provided that it is dosed prior to refining.

Additional pulp brightness losses can occur during wood pulping by reaction of metallic ions with ortho-hydroxy phenolic extractives, and the subsequent formation of darkly coloured metal-complexes[8,17]. In particular, process waters often contain ferric ions which are released by wear of pulping equipment or may be present in the input water. Complexing agents like EDTA can form colourless chelates with various metal ions. Therefore, EDTA might be effective in preventing the formation of coloured metal complexes with phenolic extractives during pulping of Douglas fir. Indeed, this study demonstrated that wood chip pretreatment with EDTA caused a significant improvement in the brightness of Douglas fir thermomechanical pulp. In contrast to ascorbic acid, EDTA provided similar brightness gains with sapwood and heartwood samples (Fig. 4).

Wood chip pretreatment with EDTA, ascorbic acid or a combination of these chemicals also proved effective in increasing pulp bleachability (Fig. 5). In agreement with Lorås[3] and Betz and Styan[14] the brightness of the dithionite bleached pulps was greatly affected by the initial brightness of the unbleached pulp. Bleaching with 1% dithionite provided an average brightness gain of 3.5% ISO, irrespectively of the heartwood fraction in the feedstock or the pretreatment method applied. Given the low brightness of heartwood rich pulps, this implies that high dithionite charges will be required in order to attain adequate brightness levels. An attractive alternative is the pretreatment of wood chips with EDTA. Fig. 6 shows that this method permits a considerable increase in the heartwood fraction that can be tolerated in the manufacture of bleached Douglas fir TMP. In the production of 1% dithionite bleached pulp with a brightness of 60% ISO, the acceptable heartwood proportion can be increased from 11.6 to 39.2% by EDTA pretreatment. This heartwood fraction is similar to that found in industrial Douglas fir wood chip piles (35-40%). Wood impregnation with ascorbic acid alone or in combination with EDTA only proved advantageous over EDTA pretreatment in Douglas fir samples consisting almost exclusively of sapwood (Fig. 6). These results indicate that wood chip pretreatment with chelators is a promising approach to improve the optical properties of Douglas fir mechanical pulps.

Full-scale trials performed by the paper mill Parenco Newsprint BV (Renkum, The Netherlands) with mixed softwood furnishes (ie. mixtures of Douglas fir, pine (*Pinus sylvestris*) and spruce (*Picea abies*) wood) showed that increasing levels of Douglas fir wood in the furnish resulted in decreasing pulp bleachability (Parenco, personal communication). The negative effect of Douglas fir heartwood extractives in pulp brightness was still evident when the furnish contained only a minor fraction of Douglas fir wood (7%). Mill trials were conducted in order to assess the effectiveness of impregnating wood chips (7% Douglas fir, 30-40% spruce, and 50-60% pine) in the screw-feeder with the chelating agent DPTA. A low dosage of DPTA (approx. 0.4%), provided a brightness improvement of 1.5 to 2% ISO.

CONCLUSIONS

Impregnation of Douglas fir chips with 0.2% EDTA prior to lab-scale thermomechanical pulping proved to be an effective measure to minimize the formation of dark metallic-polyphenol complexes. After pretreatment, dithionite bleached pulps with brightness levels adequate for commercial newsprint could be produced from feedstocks containing heartwood fractions similar to those in industrial Douglas fir wood chip piles.

ACKNOWLEDGEMENTS

We wish to thank R.P. van der Zwan for initializing the project, and A.Th.F. Helmink and J.J. Velthuizen for their assistance. Financial contributions by Parenco Newsprint B.V. and the Commission of the European Community to support the project are gratefully acknowledged.

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