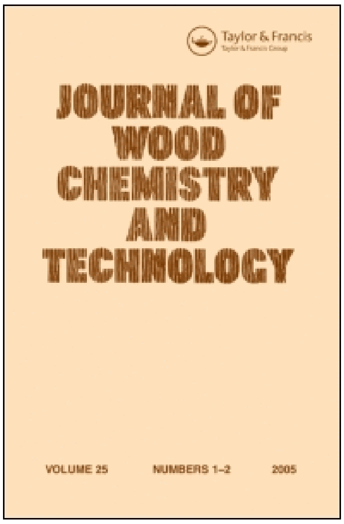

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CHEMICAL MODIFICATION OF CHEMITHERMOMECHANICAL PULPS PART 1: MECHANICAL, OPTICAL, AND AGING PROPERTIES OF PROPIONYLATED SPRUCE CTMP

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ABSTRACT

The effect of propionic anhydride on the optical, mechanical, and aging properties of hydrogen-peroxide-bleached spruce (*Picea abies*) chemithermomechanical pulp (CTMP) has been examined. The aging properties were evaluated using different aging conditions simulating aging behind window-glass, ambient storage (in the dark), and dry heat exposure. The propionylation treatment was carried out on paper sheets.

Chemical modification with propionic anhydride strongly reduced light-induced yellowing: Up to 80% of the discoloration (calculated from the post color number) could be hindered, although 50% of the free phenolic hydroxyl groups were still present in the propionylated sample. The stability against storage in the dark under ambient conditions (23°C, 50% relative humidity) or exposure to dry heat (105°C) was, however, not improved to the same extent. Propionylation did not extensively change the optical or dry strength properties of the treated paper sheets, whereas the wet tensile strength was substantially improved.

INTRODUCTION

Mechanical pulping technology includes many positive features, such as efficient utilization of wood or non-wood materials, significantly lower operating and capital costs compared with chemical pulping technology, and the potential to produce pulp in a zero liquid effluent process.[1] Furthermore, mechanical pulps have a high light scattering ability and opacity, good dimensional stability, high bulk (improves stiffness), the possibility to be bleached to high brightness levels (86-88% ISO), good printing properties and smoothness (due to a high content of fines), i.e., characteristics that are essential for many high-quality paper and board grades. However, the use of mechanical pulps as constituents in some paper products is severely restricted by the well-known tendency of mechanical pulps to undergo color reversion (yellowing) upon exposure to daylight and/or long-term storage at ambient temperatures. The production of mechanical pulps (38 million tons per year 1997[2]) could increase considerably if new cost-efficient technologies could be developed that halt or substantially retard the yellowing process.[3,4]

It is generally accepted that the photoyellowing process is due mainly to photooxidation of lignin.[5-8] Although significant progress has been made over the last decades in understanding and elucidating the mechanism of yellowing,[9,10] the course of the reactions is still not fully understood and requires further studies. Insufficient knowledge of the precise reaction pathways leading to discoloration has made it difficult to develop stabilizing treatments that meet all the needs of the paper industry.

A number of potential treatments have been proposed to photostabilize lignin-containing materials. The use of compounds (alone or in combination), such as ultraviolet absorbers,[8,11-18] sulfur-[8,13,19-25] and phosphorus-containing compounds,[13,26-28] polyethers,[15,20,29-34] ascorbic acid,[13,20,35,36] chelating agents,[20,37] and fluorescent whitening agents[17,38,39] have been examined as photostabilizing additives for mechanical pulps. Although some of these treatments improve the photostability, the stabilizing activity is, in many cases, reduced during long-term storage and/or is based on high charge levels of additive for efficient protection and, therefore, not a realistic alternative. Other approaches have also been tested, including the reduction of α-carbonyl groups,[7,35,40-48] hydrogenation of ring-conjugated ethylenic groups,[42,43,49-51] and acylation or alkylation of hydroxyl groups.[7,40,41,43,47,48,52-55] Although some of these approaches can decrease the overall extent of yellowing, no treatment has yet become technically or economically feasible. This is due to the large amount of chemicals required for successful protection, incompatibility with papermaking practice, and to the deterioration in strength properties often accompanying the treatments.

Since much of the competitiveness of mechanical pulps is based on a low production cost, a photostabilizing treatment must be inexpensive unless other positive features, such as improved mechanical or optical properties, improved runnability or printability of the paper, etc., is a result of such a treatment. Acetylation of both unbleached and bleached high-yield pulps is an efficient way to retard much of the photoinduced discoloration and, simultaneously, increase the strength properties of paper in the wet state provided that the paper product and not the pulp is acetylated.[56] Acetylation can also retard the heat-induced discoloration of different types of lignin-containing pulps.[57] However, the acetylation reaction is not specific to lignin, i.e., polysaccharides also participate in the acylation reaction. Other linear chain dicarboxylic acid anhydrides, such as propionic, butyric, valeric, hexanoic, and heptanoic anhydride have been used mainly for modifying wood to improve its behavior in adverse environments[58,59] but also for chemically modifying chemithermomechanical pulp (CTMP) to generate a less hydrophilic and thermally more stable product.[60] Long chain anhydrides react, however, at a significantly lower rate with lignocellulosic materials than acetic anhydride.[58-63]

In this paper, the propionylation of paper made from spruce CTMP has been examined and evaluated in terms of the derivatization degree of phenolic hydroxyl groups as well as the effect on optical, mechanical, and aging properties of modified paper.

EXPERIMENTAL

Pulps and Paper Samples

Commercially produced hydrogen-peroxide-bleached spruce (*Picea abies*) chemithermomechanical pulp (CTMP) was used as received for the experiments described in this work. The pulp (dried sample) was supplied by Rottneros Bruk AB, Sweden. Handsheets with a grammage of 60 g/m^2 were prepared according to SCAN-M 5:76. The paper sheets were then conditioned at 23°C and 50% relative humidity according to SCAN-P 2:75 before modification with propionic anhydride.

Propionylation Procedure

The CTMP handsheets were propionylated at 100°C using propionic anhydride (97%, Sigma-Aldrich), according to the procedure previously used for acetylation of mechanical pulps.[56] No catalyst or co-solvent was used in order to avoid any contamination that could influence the aging stability.

Analyses

The degree of propionylation was determined by weighing the handsheets prior to and after reaction and is given as a percentage of the dry weight of the paper. The phenolic hydroxyl content (PhOH) was determined according to the procedure previously described by Lai et al.[64] The lignin content was determined as Klason lignin and as acid-soluble lignin measured spectrophotometrically at 205 nm ($\varepsilon = 110$ l/g·cm). The lignin content was found to be 26.8%.

Accelerated Light-Induced Aging

The paper samples were subjected to an accelerated light-induced yellowing in a SUNTEST CPS (Heraeus HANAU, Hanau, Ger.) light-aging tester equipped with a xenon burner and filters (ultraviolet and window-glass), which eliminate radiation of wavelengths below 310 nm. The spectral distribution of the transmitted light was similar to that of average indoor daylight.[cf. 65] The temperature was kept close to room temperature by means of a cooling fan. The irradiance was controlled by an optical sensor that compensates for possible main voltage fluctuations and burner aging. Untreated paper sheets were used in all radiation experiments as controls.

Accelerated Heat-Induced Aging

Accelerated heat-induced aging was performed at 105 ± 2°C according to TAPPI Test Method T 453 pm-85 (effect of dry heat).

Ambient Aging

Ambient aging was done by keeping the paper samples in the dark at 23°C and 50% relative humidity.

Paper Properties

Brightness and color changes according to the CIELAB color scale (L^*-, a^*-, and b^*-values) were measured using an Elrepho 2000 spectrophotometer. The optical properties were averaged from two to six sheets (three measurements on each sheet of paper). The reflectance of a single sheet of paper (60 g/m^2) over a completely black, nonreflecting surface (over a hollow black body, reflectance <0.5%) and the reflectance over a stack of paper (high enough to inhibit any transparence of light) were recorded. The specific light scattering coefficient (s, at 457 nm) and the specific light absorption coefficient (k, at 457 nm) were then calculated using the Kubelka-Munk theory. The post color (PC) number (at 457 nm) was calculated for the propionylation treatment (PC_1) and for the light-induced, heat-induced, and ambient aging (PC_2).[66, cf. 20] The sum of PC_1 and PC_2

represents the total effect of the treatment: PC = PC_1 + PC_2. Tearing resistance and tensile strength were determined according to SCAN-P11:73 R and SCAN-P 38:80, respectively. Wet tensile strength was measured using a wet strength device (Finch device) described in the TAPPI Test Method T 456 om-87. The distance between the upper clamp and the horizontal rod in the Finch device was 50 mm and the immersion time was 30 s. The mechanical properties were averaged from at least six sheets.

RESULTS AND DISCUSSION

Propionylation Reaction

To assess the effect of propionylation on mechanical, optical, and aging properties of high-yield pulps, a series of handsheets made from hydrogen-peroxide-bleached spruce chemithermomechanical pulp (CTMP) were propionylated at 100°C for different periods of time. As can be seen in Table 1, the degree of derivatization was low with a weight gain of only 4.0% after a reaction time as long as 60 minutes. This is about 4 times lower than the corresponding acetylation treatment of H_2O_2-bleached softwood mechanical pulps (cf. the data published in references 56 and 65), a difference that is further increased if the comparison is made on a molar basis. The number of free phenolic hydroxyl groups (PhOH) dropped from about 10.8 (per 100 phenylpropane, C_9, units) to 5.4 after 60 minutes reaction time, i.e., a reduction of 50% (Table 1). A complete propionylation of all hydroxyl groups in softwood lignin corresponds to a weight gain of about 12% calculated on dry wood [calculations are based on an average mass of a C_9 unit of 184 g/mol,[67] lignin content of 26.8%, and a total number of hydroxyl groups of 1.45 per C_9 unit.[68]]. A complete propionylation of all phenolic OH groups corresponds to a weight gain of approximately 1%. This means that other hydroxyl groups are also propionylated, at least at high derivatization degrees. The significantly lower overall reactivity of propionic anhydride (compared with acetic anhydride) is in

TABLE 1
Change in Optical Properties upon Propionylation of Hydrogen-Peroxide-Bleached Spruce CTMP. Propionylation Times (min.) are given Within Parentheses.

Pulp	Weight gain[1] (%)	PhOH/ C_9[2]	Brightness (%)	k_{457} (m^2/kg)	s_{457} (m^2/kg)	Opacity (%)	L*	a*	b*	PC_1 number[3]
Control	---	0.108	78.4	1.46	49.0	83.5	95.0	-1.4	8.5	---
Propionylated (5)	0.6	0.077	77.6	1.56	48.4	83.0	95.3	-1.6	9.5	0.24
(20)	2.2	0.069	77.1	1.63	48.1	83.1	95.3	-1.4	10.0	0.41
(60)	4.0	0.054	76.2	1.77	47.6	83.4	95.3	-1.4	10.5	0.73

[1] On oven-dried paper.
[2] Calculated using a lignin content of 26.8% and a C_9 molecular weight of 184 g/mol.[67]
[3] The post color (PC_1) number at 457 nm (due to propionylation) was calculated according to Giertz.[66]

agreement with previously published data for various types of lignocellulosic materials.[58-63]

Optical Properties

Table 1 shows the change in optical properties during propionylation. As can be seen, the propionylation treatment slightly lowered the light scattering ability (decreased the s-value) and introduced new chromophores that contributed to absorption at 457 nm (increased the k-value). This results in a small decrease in brightness; a reaction time of 5 minutes reduces the brightness by 0.8 brightness units and a reaction time of 60 minutes by 2.2 brightness units (Table 1). The change in optical properties, evaluated according to the CIELAB color system, was manifested as an increase in yellowness (b^*) whereas lightness (L^*) and redness (a^*) were practically unaffected, i.e., the propionylation treatment increased the yellowish cast of the paper. To summarize, the change in optical properties that occurred upon propionylation was small, at least at low derivatization degrees.

Mechanical Properties

As can be seen in Table 2, the tearing resistance was slightly lower and the tensile strength somewhat higher for propionylated CTMP than for the corresponding control. This is in accordance with the results obtained for the acetylation of unbleached and bleached mechanical pulps.[56] Tensile strength and tearing resistance depend on the number of hydrogen-bonding seats at the fiber contact points, the strength of each of the individual hydrogen bonds formed, and on the strength of individual fibers. The moderate change in mechanical properties obtained in this investigation suggests that propionylation of paper neither diminishes the number of hydrogen bonds between fibers nor weakens the fiber structure to any great extent. The equilibrium moisture content decreases with an increase in the degree of propionylation (see Table 2) which can be explained by

TABLE 2
Change in Mechanical Properties upon Propionylation of Hydrogen-Peroxide-Bleached Spruce CTMP. Tensile Index (Nm/g) and Tear Index (Nm^2/kg) are given Within Parentheses.

Pulp	Weight gain[1] (%)	Moisture content[2] (%)	Tensile strength (kN/m)	Tearing resistance (mN)	Relative wet tensile strength[3] (%)
Control	---	7.2	2.28 (38.0)	355 (5.90)	0
Propionylated	0.6	6.7	2.48 (41.1)	345 (5.70)	59
	2.2	6.2	2.52 (41.1)	340 (5.55)	87
	4.0	5.2	2.49 (40.0)	340 (5.45)	91

[1] On oven-dried paper.
[2] Equilibrium moisture content of handsheets conditioned at 23°C and 50% relative humidity according to SCAN-P 2:75.
[3] Percentage of the dry tensile strength.

the fact that hydrophilic hydroxyl groups are replaced with more hydrophobic propionyl groups, i.e., the amount of bonded water is reduced. This may contribute to the improvement in tensile strength observed.

The wet tensile strength increased rapidly and was about 60% (of the dry tensile strength) after 5 minutes and more than 90% after 60 minutes reaction time. The lowered equilibrium moisture content and the introduction of hydrophobic groups most likely increased the dimensional stability of the paper which could be one explanation for the obtained wet strength. An improvement in wet strength has previously been reported for acetylated paper made from both chemical[69] and mechanical pulps.[56]

Aging Properties

To establish if propionylation altered the aging response towards light and heat, a series of experiments were performed simulating aging behind window-glass, ambient storage in the dark, and dry heat exposure. The change in optical properties during accelerated light-induced yellowing of untreated and propionylated CTMP is shown in Figure 1 and in Table 3. The propionylation treatment efficiently inhibited light-induced yellowing even after an extensive period of exposure to the UV/VIS radiation from the xenon lamp. Approximately 50% of the yellowing was hindered at the low derivatization degree (5 minutes reaction time, calculated from the PC_2-number) and about 80% at the high degree (60 minutes reaction time). The propionylation treatment gave the same photostability for the rapid initial phase of yellowing as for the slower, less detrimental phase (cf. the PC_2-values after 1 and 24 h, Table 3). Irradiation decreased the L^*-value and increased the b^*-value for both the control and the modified samples, but, the extent of the change was much smaller after propionylation. These findings agree well with results from earlier investigations of acetylated lignocellulosic materials.[39,48]

Table 4 shows the yellowing of untreated and chemically modified CTMP stored in the dark for 260 days under ambient conditions (23 °C and 50% relative humidity). Storage in the dark lowered the brightness for both the control and the modified CTMP samples. The handsheets propionylated for 20 and 60 minutes were somewhat more stable, as indicated by the PC_2-value. The stabilizing effect was, however, small and approaches the error margins of the optical measurements. The color changes that took place during storage were the same as the changes observed during accelerated light exposure, i.e., a decrease in the L^*- and an increase in the b^*-values. The final brightness was in the range 71.4 to 73.1%, about 4-6 brightness units lower than for the corresponding unaged handsheets (cf. Table 4).

Table 5 shows the effect of dry heat (105°C) on the optical properties of untreated and propionylated CTMP. Propionylation improved the stability under dry heat conditions at long term exposure even if the improvement was not as pronounced as that observed in the case of light-induced yellowing (cf. Table 3). About 10-15% of the yellowing was hindered at low derivatization degrees and about 30% at the high degree (calculated from the PC_2-number). The limited

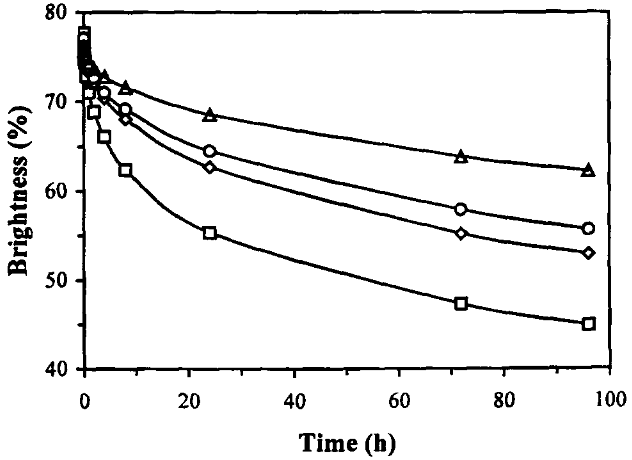

FIGURE 1. The change in brightness after accelerated light-induced yellowing of hydrogen-peroxide-bleached spruce CTMP. Legends: (□), control; (◇), propionylated 5 min.; (o), propionylated 20 min.; (Δ), propionylated 60 min.

stabilization effect of propionylation suggests that propionylation only marginally eliminates or retards the reaction pathways leading to colored chromophores during heat-induced aging in a dry atmosphere. Acetylation, on the other hand, reduces both the light-induced and the heat-induced yellowing at rather low derivatization degrees. Although lignin is the most reactive wood component to acetic anhydride,[70] acetylation most likely also derivatizes some of the pulp carbohydrates even at short reaction times. Propionic anhydride is more unreactive; the weight gain obtained after one hour of reaction time (4%) represents the propionylation of only 1/3 of the hydroxyl groups in lignin (see the discussion above). If the reactivity of wood components to propionic anhydride is the same as for acetic anhydride, this means that only a minor part of the pulp carbohydrates have been chemically modified and this could be one explanation for the limited dry-heat stability obtained with propionic anhydride.

Figure 2 shows the relationship between the post color number (after 4 hours of irradiation) and the number of free phenolic hydroxyl groups for untreated and

TABLE 3
Change in Optical Properties during Accelerated Light-Induced Yellowing of Untreated and Propionylated, Hydrogen-Peroxide-Bleached Spruce CTMP.

Pulp	Weight gain[1] (%)	Initial brightness (%)	PC_2 number[2]		PC number[3]		Final brightness[4] (%)	L*	a*	b*
			1 h	24 h	1 h	24 h		24h		
Control	---	78.4	3.0	15.0	3.0	15.0	55.3	89.0	-0.2	18.9
Propionylated	0.6	77.6	1.6	7.9	1.9	8.1	62.7	91.7	-1.1	16.4
	2.2	77.1	1.3	6.5	1.7	6.9	64.3	92.2	-1.1	15.7
	4.0	76.2	0.7	3.5	1.4	4.2	68.5	93.2	-1.2	13.6

[1] On oven-dried paper.
[2] The post color (PC_2) number at 457 nm (due to aging) was calculated according to Giertz.[66]
[3] The post color (PC) number at 457 nm [due to propionylation (PC_1) and aging (PC_2)] was calculated according to Giertz.[66]
[4] Brightness after 24 h irradiation.

TABLE 4

Change in Optical Properties of Untreated and Propionylated Spruce CTMP after Ambient Aging in the Dark (260 Days at 23 °C and 50% Relative Humidity).

Pulp	Weight gain[1] (%)	Initial brightness (%)	Brightness (%)	L*	a*	b*	PC_2 number[2]	PC number[3]
			260 days					
Control	---	78.4	72.8	93.4	-0.8	10.4	2.1	2.1
Propionylated	0.6	77.6	71.4	93.4	-0.6	11.4	2.5	2.7
	2.2	77.1	73.1	94.4	-1.0	11.6	1.5	1.9
	4.0	76.2	72.2	94.1	-1.0	11.9	1.6	2.3

[1] On oven-dried paper.

[2] The post color (PC_2) number at 457 nm (due to aging) was calculated according to Giertz.[66]

[3] The post color (PC) number at 457 nm [due to propionylation (PC_1) and aging (PC_2)] was calculated according to Giertz.[66]

TABLE 5
Change in Optical Properties of Untreated and Propionylated Spruce CTMP after Accelerated Heat-Induced Aging (TAPPI Test Method T 453 pm-85, Effect of Dry Heat, 105°C).

Pulp	Weight gain[1] (%)	Initial brightness (%)	Brightnes (%) 24 h	Brightness (%)	L*	a*	b*	PC_2 number[2]	PC number[3]
				144 h					
Control	---	78.4	66.7	49.7	87.1	3.8	21.2	22.5	22.5
Propionylated	0.6	77.6	65.4	51.3	87.5	4.4	19.9	19.9	20.1
	2.2	77.1	66.0	51.5	87.6	4.3	19.9	19.4	19.8
	4.0	76.2	67.4	54.2	88.8	3.2	19.0	15.6	16.3

[1] On oven-dry paper.
[2] The post color (PC_2) number at 457 nm (due to aging) was calculated according to Giertz.[66]
[3] The post color (PC) number at 457 nm [due to propionylation (PC_1) and aging (PC_2)] was calculated according to Giertz.[66]

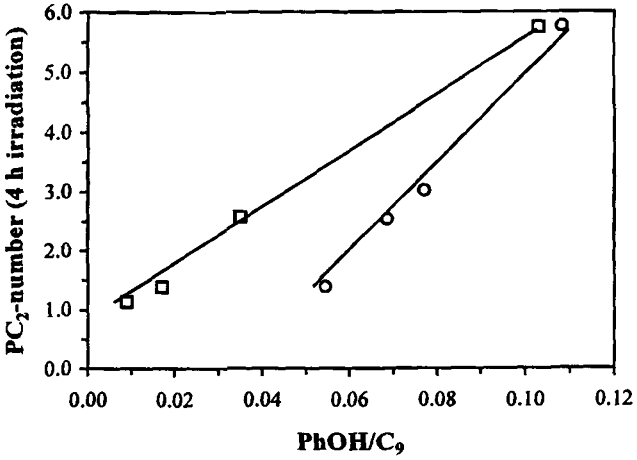

FIGURE 2. Relationship between the post color (PC) number after accelerated light-induced yellowing (4 hours) and the concentration of phenolic hydroxyl groups (PhOH) per phenylpropane (C_9) unit for hydrogen-peroxide-bleached spruce high-yield pulps. Legends: (□), untreated and acetylated TMP (data from reference 48); (o), untreated and propionylated CTMP.

propionylated spruce CTMP. The corresponding values for untreated and acetylated spruce thermomechanical pulp (TMP), aged under the same conditions, are given in the figure for comparison (data from reference 48). It is evident that the free phenolic hydroxyl groups play an important role in the photo-reactions that cause discoloration of hydrogen-peroxide-bleached high-yield pulps. It is also evident that an efficient photostability can be achieved with a somewhat higher amount of phenolic hydroxyl groups still present in the paper sheet when propionic anhydride is used as the modifying chemical (Figure 2). The importance of pulp source (TMP vs. CTMP) or anhydride used for chemical modification (acetic anhydride vs. propionic anhydride) for the obtained results cannot, at this point, be elucidated.

In conclusion, propionylation is as good as acetylation in retarding the photoyellowing characteristics of hydrogen-peroxide-bleached spruce CTMP, and can be done at a substantially lower derivatization degree with a larger number of free phenolic hydroxyl groups still present in the pulp. Furthermore, the optical and mechanical properties of the propionylated handsheets are comparable or better (cf. the wet strength, Table 2) than those obtained for the acetylation treatment. Propionylation was, however, not as efficient in retarding heat-induced (dry heat exposure) discoloration as acetylation. Further studies are underway to address the differences observed between the acetylation and propionylation treatments. The photostabilizing effect of other linear chain dicarboxylic acid anhydrides, such as butyric, valeric, hexanoic, and heptanoic anhydride, will be presented in a forthcoming paper.

CONCLUSIONS

The work presented in this paper demonstrates that the light-induced yellowing of hydrogen-peroxide-bleached spruce CTMP can be strongly retarded by chemical modification with propionic anhydride, even though approximately 50% of the free phenolic hydroxyls are still present. Propionylation, however, did not hinder the discoloration to any great extent when the treated paper sheets were stored under ambient conditions (23°C, 50% relative humidity) in the dark, or exposed to dry heat (105°C).

The propionylation of paper sheets was not detrimental to dry strength properties; a slightly lower tearing resistance and a somewhat higher tensile strength was obtained. The propionylation treatment led, however, to a considerable increase in wet tensile strength even at a low degree of derivatization. The changes in optical properties of the chemically modified paper sheets were minor.

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REFERENCES

1. D.G. Meadows, Tappi J., 79(1), 63 (1996).

2. A.J. Barnet, Pulp Pap. Can., 98(3), 13 (1997).

3. R.A. Cockram, Proc. Int. Mech. Pulp. Conf., June 6-8, Helsinki, Finland, Vol. 1, p. 20 (1989).

4. M.J. Ford and P.M. Sharman, Pulp Pap. Int., 38(10), 29 (1996).

5. L.V. Forman, Pap. Trade J. 111(24), 266 (1940).

6. P. Nolan, J.A. Van den Akker, and W.A. Wink, Pap. Trade J., 121(11), 101 (1945).

7. G.J. Leary, Tappi, 51(6), 257 (1968).

8. K. Kringstad, Tappi, 52(6), 1070 (1969).

9. C. Heitner, In Photochemistry of Lignocellulosic Materials, Chapter 1, p. 2, C. Heitner and J.C. Scaiano (eds.), ACS Symposium Series 531, Washington, DC, USA, 1993.

10. G.J. Leary, J. Pulp Pap. Sci., 20(6), J154 (1994).

11. P.A. Nolan, Pap. Trade J., 121(23), 219 (1945).

12. G. Gellerstedt, I. Pettersson, and S. Sundin, Sven. Papperstidn., 86(15), R157 (1983).

13. P. Fornier de Violet, A. Nourmamode, N. Colombo, J. Zhu, and A. Castellan, Cellul. Chem. Technol., 24(2), 225 (1990).

14. A. Castellan, C. Noutary, and R.S. Davidson, J. Photochem. Photobiol., A: 84(3), 311 (1994).

15. R.S. Davidson, L. Dunn, A. Castellan, and A. Nourmamode, J. Photochem. Photobiol., A: 86(1-3), 275 (1995).

16. X. Pan, L.C. Harvey, and A.J. Ragauskas, J. Pulp Pap. Sci., 22(4), J135 (1996).

17. S. Robert, S. Bourgoing, and E. Leclerc, Proc. 10th Int. Symp. Wood Pulp. Chem., June 7-10, Yohohama, Japan, Vol. 3, p. 218 (1999).

18. G. Cunkle, R. Seltzer, J.-P. Wolf, P. McGarry, Z. Yuan, C. Heitner, and J. Schmidt, Proc. 10th Int. Symp. Wood Pulp. Chem., June 7-10, Yohohama, Japan, Vol. 1, p. 718 (1999).

19. B.J.W. Cole and K.V. Sarkanen, Tappi J., 70(11), 117 (1987).

20. J. Janson and I. Forsskåhl, Nord. Pulp Pap. Res. J., 4(3), 197 (1989).

21. C. Daneault, S. Robert, and M. Lévesque, J. Pulp Pap. Sci., 17(6), J187 (1991).

22. X. Pan and A.J. Ragauskas, J. Wood Chem. Technol., 15(1), 135 (1995).

23. X. Pan and A.J. Ragauskas, J. Pulp. Pap. Sci., 21(1), J25 (1995).

24. C.M. Cook, X. Pan, and A.J. Ragauskas, J. Wood Chem. Technol., 16(3), 327 (1996).

25. A.J. Ragauskas and C.C. Cook, Proc. 9th Int. Symp. Wood Pulp. Chem., June 9-12, Montréal, Canada, p. K6-1 (1997).

26. R.S. Davidson, L.A. Dunn, A. Castellan, N. Colombo, A. Nourmamode, and J.H. Zhu, J. Wood Chem. Technol., 11(4), 419 (1991).

27. J.X. Guo and D.G. Gray, J. Pulp Pap. Sci., 22(2), J64 (1996).

28. J.X. Guo, Y.C. Lin, and D.G. Gray, J. Pulp Pap. Sci., 23(7), J311 (1997).

29. N. Minemura, Mokuzai Gakkaishi, 24(8), 587 (1978).

30. I. Forsskåhl and J. Janson, Pap. Puu, 74(7), 553 (1992).

31. B.J.W. Cool, S.P. Huth, and P.S. Runnels, J. Wood Chem. Technol., 13(1), 59 (1993).

32. R. Maiocchi, L. Villani, and G. Capretti, Proc. 3rd European Workshop on Lignocellulosics and Pulp, August 28-31, Stockholm, Sweden, p. 305 (1994).

33. J. Janson, I. Forsskåhl, and T. Korhonen, Proc. 8th Int. Symp. Wood Pulp. Chem., June 6-9, Helsinki, Finland, Vol. 1, p. 451 (1995).

34. J. Janson and I. Forsskåhl, Nord. Pulp Pap. Res. J., 11(1), 10(1996).

35. J.A. Schmidt and C. Heitner, J. Wood Chem. Technol., 11(4), 397 (1991).

36. A.R. Agnemo, Paper and a Method of Paper Manufacture, International Patent Application, PCT/SE91/00798, Publication Number WO 92/09745, June 11, (1992).

37. Y. Ni, A. Ghosh, Z. Li, C. Heitner, and P. McGarry, J. Pulp Pap Sci., 24(8), 259 (1998).

38. S. Bourgoing and S. Robert, Proc. 9th Int. Symp. Wood Pulp. Chem., June 9-12, Montréal, Canada, p. 10-1 (1997).

39. M. Paulsson and A.J. Ragauskas, Nord. Pulp Pap. Res. J., 13(2), 124 (1998).

40. D.F. Manchester, J.W. McKinney, and A.A. Pataky, Sven. Papperstidn., 63(20), 699 (1960).

41. D.H. Andrews and P. DesRosiers, Pulp Pap. Mag. Can., 67(C), T119 (1966).

42. S.Y. Lin and K. Kringstad, Tappi, 53(9), 1675 (1970).

43. U. Tschirner and C.W. Dence, Pap. Puu, 70(4), 338 (1988).

44. P. Fornier de Violet, A. Nourmamode, N. Colombo, and A. Castellan, Cellul. Chem. Technol., 23(5), 535 (1989).

45. M. Ek, H. Lennholm, and T. Iversen, Nord. Pulp Pap. Res. J., 5(4), 159 (1990).

46. R.C. Francis, C.W. Dence, T.C. Alexander, R. Agnemo, and S. Omori, Tappi J., 74(12), 127 (1991).

47. A. Castellan, A. Nourmamode, C. Noutary, and D. Lachenal, Cellul. Chem. Technol., 26(4), 451 (1992).

48. M. Paulsson, R. Simonson, and U. Westermark, Nord. Pulp Pap. Res. J., 10(1), 62 (1995).

49. A. Castellan, A. Nourmamode, P. Fornier de Violet, N. Colombo, and C. Jaeger, J. Wood Chem. Technol., 12(1), 1 (1992).

50. T.Q. Hu, B.R. James, and C.-L. Lee, J. Pulp Pap. Sci., 23(4), J153 (1997).

51. T.Q. Hu, B.R. James, and C.-L. Lee, J. Pulp Pap. Sci., 23(5), J200 (1997).

52. R.P. Singh, Tappi, 49(7), 281 (1966).

53. A.F.A. Wallis and R.H. Wearne, Appita, 36(3), 192 (1982).

54. M. Ek, H. Lennholm, G. Lindblad, and T. Iversen, Nord. Pulp Pap. Res. J., 7(3), 108 (1992).

55. M. Paulsson, R. Simonson, and U. Westermark, Nord. Pulp Pap. Res. J., 11(4), 227 (1996).

56. M. Paulsson, R. Simonson, and U. Westermark, Nord. Pulp Pap. Res. J., 9(4), 232 (1994).

57. M. Paulsson and A.J. Ragauskas, Nord. Pulp Pap. Res. J., 13(3), 191 (1998).

58. R.M. Rowell, In The Chemistry of Solid Wood, Chapter 4, p. 175, R.M. Rowell, (ed.), ACS Symposium Series 207, Washington, DC, USA, 1984, and references cited therein.

59. C.A.S. Hill and D. Jones, Holzforschung, 50(5), 457 (1996).

60. H.-P. Rensch and B. Riedl, Thermochim. Acta, 205, 39 (1992).

61. I.S. Goldstein, E.B. Jeroski, A.E. Lund, J.F. Nielson, and J.W. Weaver, For. Prod. J., 11(8), 363 (1961).

62. H.-P. Rensch and B. *Riedl, J. Wood Chem. Technol., 13(2), 167 (1993).*

63. B.S.W. Dawson, R.A. Franich, H.W. Kroese, and D. Steward, Holzforschung, 53(2), 195 (1999).

64. Y.-Z. Lai, X.-P. Gou, and W. Situ, J. Wood Chem. Technol., 10(3), 365 (1990).

65. M. Paulsson and A.J. Ragauskas, Nord. Pulp Pap. Res. J., 13(2), 132 (1998).

66. H.W. Giertz, Sven. Papperstidn., 48(13), 317 (1945).

67. S.A. Rydholm, Pulping Processes, Chapter 4, p. 186, Interscience Publishers (John Wiley & Sons, Inc.), New York, NY, USA, 1965.

68. K. Lundquist, Acta Chem. Scand., B34(1), 21 (1980).

69. L.O. Klinga and E.L. Back, Sven. Papperstidn., 69(3), 64 (1966).

70. R.M. Rowell, R. Simonson, S. Hess, D.V. Plackett, D. Cronshaw, and E. Dunningham, Wood Fiber Sci., 26(1), 11 (1994).