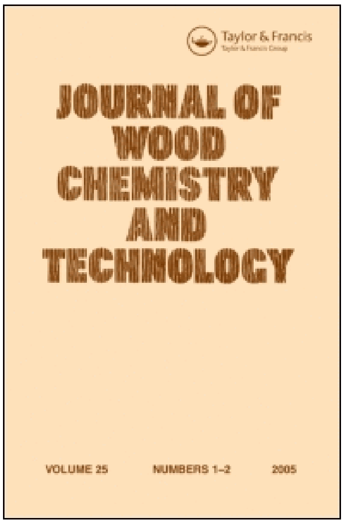

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Light-Induced Yellowing of Mechanical and Ultra-High Yield Pulps. Part 3. Comparison of Softwood TMP, Softwood CTMP and Aspen CTMP

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LIGHT-INDUCED YELLOWING OF MECHANICAL AND ULTRA-HIGH YIELD PULPS. PART 3. COMPARISON OF SOFTWOOD TMP, SOFTWOOD CTMP AND ASPEN CTMP.

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ABSTRACT

We have compared the light-induced yellowing of three peroxide-bleached mechanical pulps: softwood TMP (spruce/balsam fir mixture), softwood CTMP (spruce), and aspen CTMP. We attribute dissimilarities in the absorption difference spectra of softwood TMP and softwood CTMP to photobleaching of residual coniferaldehyde groups present in peroxide-bleached TMP. We also interpret an earlier report of photobleaching by ascorbic acid as coniferaldehyde photobleaching. Coniferaldehyde-free softwood pulps showed a broad absorption maximum at 360 nm and a shoulder at about 416 nm. The 360 nm peak resulted from the coalescence of two absorption peaks with $\lambda_{max} \approx$ 330 nm and 360 nm. Irradiated aspen CTMP had an absorption maximum at 360 nm, but no shoulder at wavelengths above 400 nm. The difference spectra of the irradiated pulps were compared with those for pulps where quinone groups were introduced by oxidation with either Fremy's salt or sodium periodate. These experiments suggested that even if one attributes all the absorption increase above 400 nm to formation of simple o-quinones, these quinones cannot account for the magnitude of the peak at 360 nm. The kinetics for increases in absorption coefficient were fit by a sum of two exponential terms. Within the error of the fitted parameters, all three pulps had identical rate constants.

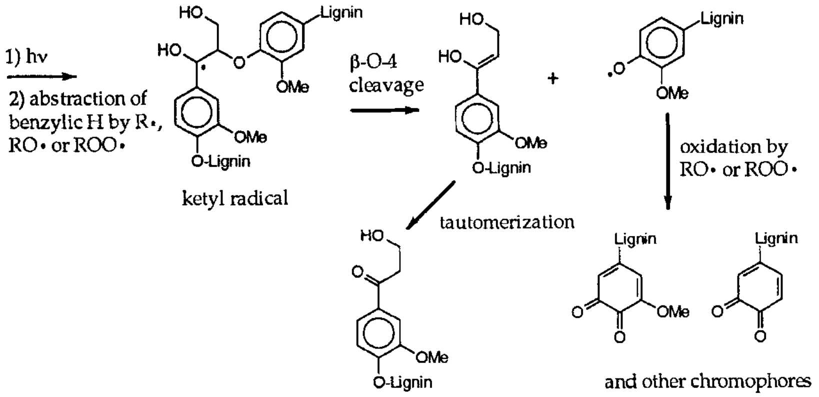
INTRODUCTION

There is continuing interest in expanding the use of bleached mechanical or ultra-high yield pulps beyond their traditional markets of newsprint and short-life advertising papers. These pulps make efficient use of the wood resource, they have attractive bulk, absorbency, optical and printing properties, and new installations have much lower capital costs than kraft mills. Although inferior to chemical pulps in strength, improvements in refining technology have increased their strength sufficiently that mechanical pulps could replace some of the chemical pulp component in higher-value furnishes. However, rapid light-induced discolouration of lignin in mechanical fibre remains as the primary impediment to realization of this potential.

Early work on the mechanism identified phenoxy radicals as key intermediates, and proposed reactions of phenolic groups and of α-carbonyl β-guaiacyl ether structures as likely sources of the radicals[1]. More recently, we[2] showed that, while such reactions undoubtedly occur, they account at most for 30% of the increase in absorption coefficient observed during irradiation of peroxide-bleached softwood thermomechanical pulp (TMP). We proposed that degradation of guaiacylglycerol β-guaiacyl ether structures, via the corresponding ketyl radical (**Scheme 1**), accounts for up to 70% of the phenoxy radicals produced (and 70% of the increase in absorption coefficient) during light-induced yellowing.

This mechanism accommodates several experimental facts which earlier mechanisms did not.

1. Methylation experiments indicate that only about 20% of the increase in absorption coefficient results from transformation of the existing phenolic groups to chromophores. Also, irradiation causes formation of free phenolic groups in pulps where existing phenolic groups have been methylated[2].



SCHEME 1

2. Cleavage of α-carbonyl β-guaiacyl ether structures accounts for only about 7% of the increase in absorption coefficient[2].
3. Irradiation destroys guaiacylglycerol β-guaiacyl structures in softwood TMP[3].
4. Carefully executed UV-visible and FT-IR experiments indicate that aromatic carbonyl groups are formed during irradiation of softwood TMP[4].
5. Laser flash photolysis[5, 6], pulse radiolysis[5], and transient magnetic resonance experiments[7, 8] all indicate that ketyl radicals such as that shown in **Scheme 1** cleave virtually instantaneously to the corresponding phenoxy radical and acetophenone enol.

The majority of published work on photochemical discolouration has described the behaviour of softwoods, either stone groundwood (SGW) pulps or TMP. However, the pulps most often suggested as replacements for chemical pulps in higher-value paper grades are bleached chemithermomechanical pulps (CTMP), from both softwoods and hardwoods. In this work we describe light-induced chromophore formation in peroxide-bleached CTMP from both black spruce and aspen, and compare it with the behaviour of peroxide-bleached softwood TMP.

EXPERIMENTAL

Unbleached softwood TMP (a mixture of black spruce and balsam fir), unbleached spruce CTMP and unbleached aspen CTMP were obtained from two eastern Canadian mills. The unbleached pulps were washed at 1% consistency with 0.6% diethylenetriaminepentaacetic acid (DTPA), then bleached at 20% consistency with alkaline hydrogen peroxide for 2 hours at 60 °C. Once-bleached softwood TMP was obtained using 3% peroxide and 1% NaOH on OD pulp; twice-bleached TMP was obtained from two consecutive bleaches using 4% peroxide and 2.5% NaOH. The CTMPs were each bleached with 4% peroxide and 2.5% NaOH. The bleach liquor also contained 3.0% $NaSiO_3$, 0.05% $MgSO_4$, and 0.2% DTPA.

Peroxide-bleached pulps were reduced with sodium borohydride at 1% consistency in a 50/50 volume mixture of water/methanol, at 60 °C for 4 hours. A 50% charge of borohydride (on OD pulp) was added at the start of the reaction, and a second 50% charge was added after 2 hours. In our experience, these conditions give the maximum change in absorption coefficient. The solvent was initially deoxygenated by bubbling with nitrogen, and a slow stream of nitrogen was maintained during the reaction.

Oxidation with Fremy's salt (potassium nitrosodisulphonate, Aldrich) was done by disintegrating 10 g OD of bleached softwood TMP in 600 mL deionized water containing 0.3 g sodium acetate. Crushed ice (500 g) and Fremy's salt (1 g) were added, and the slurry was stirred for 10 h while maintained at ice temperature. An additional 1 g Fremy's salt was added after 2, 4, 6, and 8 hours. The pulp was filtered and washed by dispersing it three times in 1 L of deionized water. After drying, the pulp was extracted with methylene chloride in a Soxhlet extractor.

Oxidation with sodium periodate also used a suspension of 10 g OD pulp in 500 mL deionized water. The suspension was cooled to 0 °C, and an ice-cold solution of 50 g sodium periodate in 400 mL water was added. The slurry was stirred for 6 h. As above, the pulp was washed and extracted with methylene chloride.

L-Ascorbic acid was applied by soaking sheets overnight in a 10% solution of L-ascorbic acid in 20/80 water/methanol. The solvent was deaerated with nitrogen before preparing the solution, and the sheets were kept under nitrogen during soaking and subsequent drying. Loading of ascorbic acid was about 20% by weight.

Low-basis weight sheets (0.010 kg/m^2) were irradiated in a Rayonet RPR-100 photochemical reactor (Southern New England Ultra-Violet) equipped with two blacklight lamps. This reactor normally uses 16 lamps; however we used a smaller number so that overall rates of chromophore formation would be slower, and the rapid initial chromophore formation could be more easily studied. Reflectance spectra were recorded using a Philips PU 8800 uv-visible spectrophotometer equipped with an integrating sphere; absorption coefficents were calculated by measuring the sample reflectance over black and white backings. Complete details of the technique are published elsewhere[9, 10].

Kinetic data were fit using a commercially available program (FitAll, version 5.1, MTR Software, Toronto, Canada) that uses the Marquardt non-linear least-squares algorithm.

RESULTS AND DISCUSSION

Absorption Difference Spectra: Softwood TMP vs Softwood CTMP

Figures 1a and 1b show the uv-visible absorption difference spectra recorded after near-uv irradiation of peroxide-bleached, softwood TMP and CTMP. The apparent absorption maxima were different for each pulp:

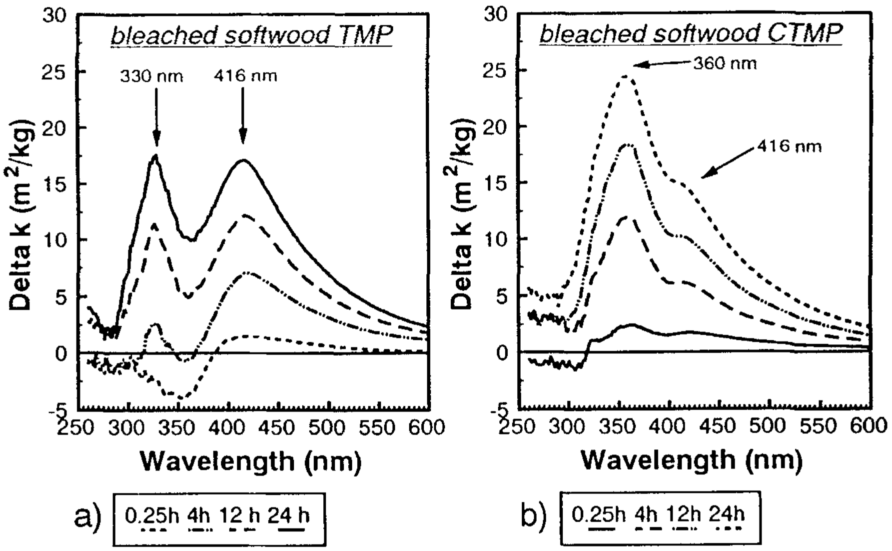


Figure 1: Absorption difference spectra for irradiation of peroxide-bleached mechanical pulps: a) once-bleached softwood TMP, b) once-bleached softwood CTMP.

softwood CTMP had an absorption maximum at 360 nm and a shoulder at 416 nm, while softwood TMP had maxima at 330 nm and 416 nm, and a minimum at 360 nm. These differences suggest that TMP and CTMP undergo different photochemistry; in the following we will show that photooxidation of residual coniferaldehyde in TMP accounts for these spectral differences.

To understand the spectra of Figure 1, we must first consider the photochemistry and bleaching chemistry of unbleached softwood TMP. Figure 2a shows the difference spectrum recorded for peroxide bleaching of softwood TMP using industrial conditions (3% peroxide on OD pulp). The strong bleaching with $\lambda_{max} \approx 360$ nm is attributed primarily to oxidation of the coniferaldehyde groups, while bleaching in the visible region ($\lambda > 400$ nm) is attributed to oxidation of quinone structures[11].

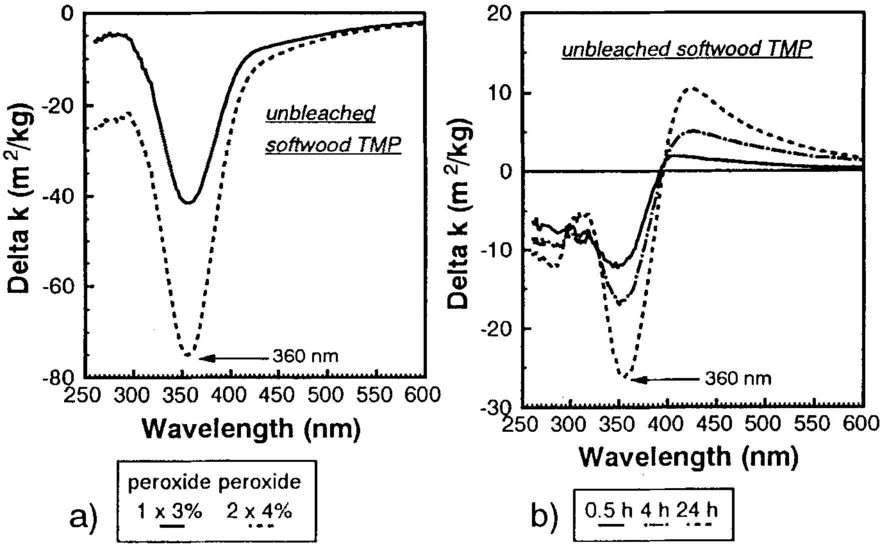


Figure 2: Absorption difference spectra recorded for unbleached softwood TMP: a) effect of bleaching with one or two charges of peroxide, b) effect of near-uv irradiation for 0.5, 4, and 24 h.

In solution, coniferaldehyde model compounds are oxidized rapidly by alkaline hydrogen peroxide[12]. However, two groups have detected residual coniferaldehyde in peroxide-bleached softwood SGW, indicating that peroxide oxidation of coniferaldehyde chromophores in pulp occurs more slowly[13, 14]. Our spectroscopic results suggest that this is also true for bleached softwood TMP. Figure 2a shows that application of a second 4% charge of peroxide caused a further loss of absorption at 360 nm (~ 33 m^2/kg). A third additional charge of peroxide had a minimal effect at this wavelength.

Figure 2b shows the absorption difference spectra obtained during irradiation of unbleached softwood TMP. In accord with earlier reports[15, 16], unbleached TMP discoloured under uv irradiation, as indicated by the absorption increase at wavelengths above 400 nm, but there was also photobleaching at wavelengths below 400 nm, with the bleaching maximum occurring at 360 nm.

The identical position of the peak maxima, and the similarity of the peak shapes in the uv region, suggest that alkaline peroxide and uv irradiation remove a similar chromophore from unbleached TMP. Since it is established that *o*-quinones are formed during irradiation, we attribute the photobleaching that occurs in unbleached TMP to photooxidation of coniferaldehyde. This is consistent with the fact that in unbleached sulphite pulp, where coniferaldehyde has been removed by the sulphite treatment[1], the photobleaching reaction is not observed[15].

These results indicate 1) that residual coniferaldehyde, equivalent to absorption of ~ 33 m^2/kg, exists in softwood TMP bleached using peroxide under commercial conditions[§] and 2) photooxidation of this residual coniferaldehyde will decrease the value of the absorption coefficient at 360 nm.

With the foregoing material as background, we can interpret the difference spectra of peroxide-bleached TMP and CTMP from softwoods. Bleached CTMP contains very little residual coniferaldehyde, a result of the combination of sulphite treatment and peroxide bleaching[17]. Near-uv irradiation causes increases in absorption coefficient due formation of aromatic carbonyl groups, $\lambda_{max} \approx 330$ nm, (Scheme 1), and as yet unidentified chromophores $\lambda_{max} \approx 360$ nm (possibly quinones, see later). These two peaks coalesce into a single broad peak with $\lambda_{max} \approx 360$ nm. The shoulder at 416 nm probably results from the characteristic visible absorption *o*-quinones (see later).

The difference spectra of once-bleached TMP can be interpreted in terms of the same reactions as bleached CTMP, with the addition of the photobleaching of coniferaldehyde. After 0.25 h of irradiation, the photooxidation of coniferaldehyde is manifested as a net bleaching at 360 nm

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[§] The amount of residual coniferaldehyde will vary according to the efficiency of the bleaching sequence.

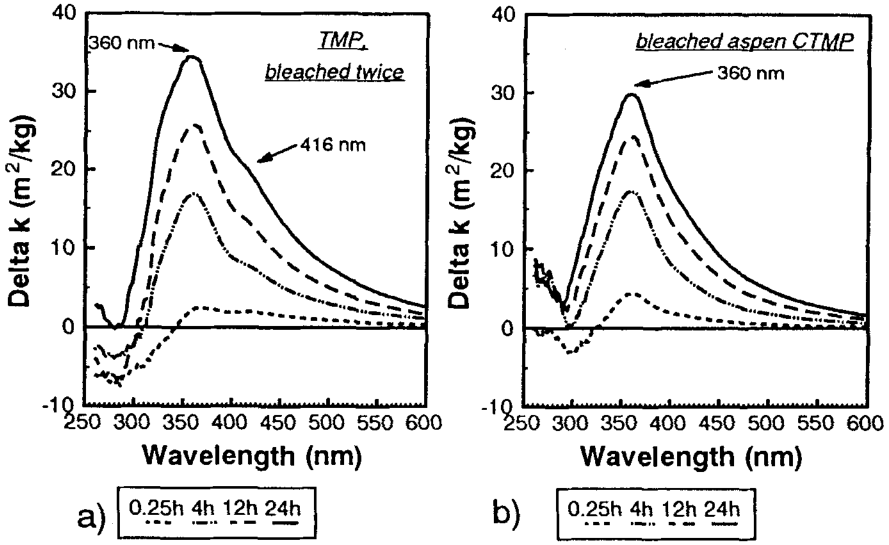


Figure 3: Absorption difference spectra for irradiation of peroxide-bleached mechanical pulps: a) softwood TMP bleached with two 4% charges of peroxide, b) once-bleached aspen CTMP.

(Figure 1a). At longer irradiation times, the decrease in absorption caused by coniferaldehyde photooxidation offsets some of the increase in absorption due to formation of other chromophores. Because the overall absorption increase at 360 nm is suppressed, the 360 nm peak no longer coalesces with aromatic ketone absorption at 330 nm. The absorptions at 330 nm and 416 nm appear as discrete maxima, and a minimum is observed at 360 nm.

Figure 3a shows the absorption difference spectra obtained for irradiation of softwood TMP bleached with two consecutive charges of 4% peroxide. As expected from the argument above, the spectra of this coniferaldehyde-free pulp are identical to those observed for bleached softwood CTMP.

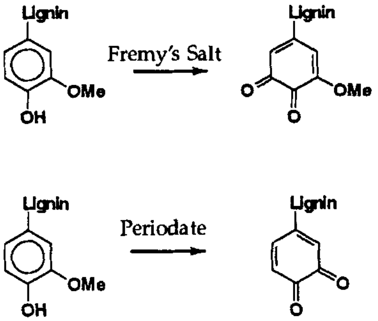
Absorption Difference Spectra: Softwood vs Hardwood

Figure 3b shows the absorption difference spectra obtained for irradiation of peroxide-bleached aspen CTMP. The spectra were characterized by a single maximum at 360 nm. Aspen CTMP does not show the shoulder at 416 nm which was observed for the softwood pulps. Instead, the absorption coefficient fell off smoothly on the long-wavelength side of the absorption maximum, and more gradually than on the short-wavelength side. This indicates that at least one of the chromophores responsible for absorption above 400 nm forms in smaller amounts in aspen CTMP than in softwood TMP and CTMP.

Contribution of o-Quinones to Discolouration

o-Quinones have long been considered as one of the chromophores formed during light-induced yellowing[1]. Evidence in support of this idea includes the loss of methoxyl groups in irradiated groundwood pulp[16, 18, 19], solid-state ^{31}P NMR spectra of trimethylphosphite *o*-quinone adducts[20, 21 139], and fluorescence spectra of *o*-quinone-*o*-phenylenediamine adducts[22]. The exact structure of the *o*-quinones formed remains uncertain. As well, it is not clear whether quinones contribute the the strong absorption increases with $\lambda_{max} \approx 356$ nm that we observed for all these pulps.

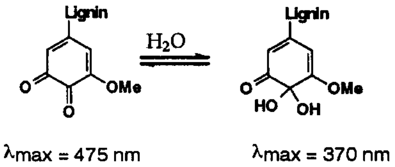
We approached this problem by introducing quinones of known structure into bleached softwood TMP by well-known lignin reactions, and comparing their absorption difference spectra to those of irradiated pulps. The reactions used are shown in Scheme 2. Fremy's salt (potassium nitrosodisulphonate) oxidizes phenolic guaiacyl structures to 3-methoxy-1,2-



SCHEME 2

benzoquinones[23, 24], while sodium periodate will oxidize phenolic guaiacyl groups with demethylation to give simple *o*-quinones[25].

3-Methoxy-1,2-benzoquinones have a unique, two-banded absorption spectrum in aqueous environments, due to an equilibrium between the quinone and a monohydrate adduct[23, 25, 26] (Scheme 3). The quinone chromophore has a broad visible absorption, $\lambda_{max} \approx 470$ nm, while the hydrate has a slightly narrower absorption with $\lambda_{max} \approx 370$ nm[23, 25, 26]. The two-banded difference spectrum obtained after Fremy's salt oxidation of softwood TMP (Figure 4a) is consistent with the formation of this type of quinone. Figure 4a also shows the difference spectrum obtained for periodate oxidation; the single, broad absorption with $\lambda_{max} \approx 420$ nm is consistent with the formation of unmethoxylated *o*-quinones, which do not exhibit the quinone-monohydrate equilibrium[25].



SCHEME 3

The spectrum obtained for Fremy's salt oxidation (Figure 4a) suggests that the strong absorption peak observed at 356 nm in irradiated mechanical pulps might be attributed to the quinone-hydrate form of 3-methoxy-1,2-benzoquinone chromophores. However, two lines of reasoning argue against this.

Figure 4b shows the difference spectra of bleached aspen CTMP, bleached spruce CTMP and twice-bleached softwood TMP after 24 hours irradiation, and softwood TMP treated with Fremy's salt. The spectra were normalized to the absorption at 356 nm. It is apparent from these normalized spectra that if we assigned the absorption peak at 356 nm in irradiated pulps to a quinone-hydrate structure such as that in Scheme 3 we would expect a much stronger absorption due to the corresponding methoxy-*o*-quinone in the $\lambda > 400$ nm region.

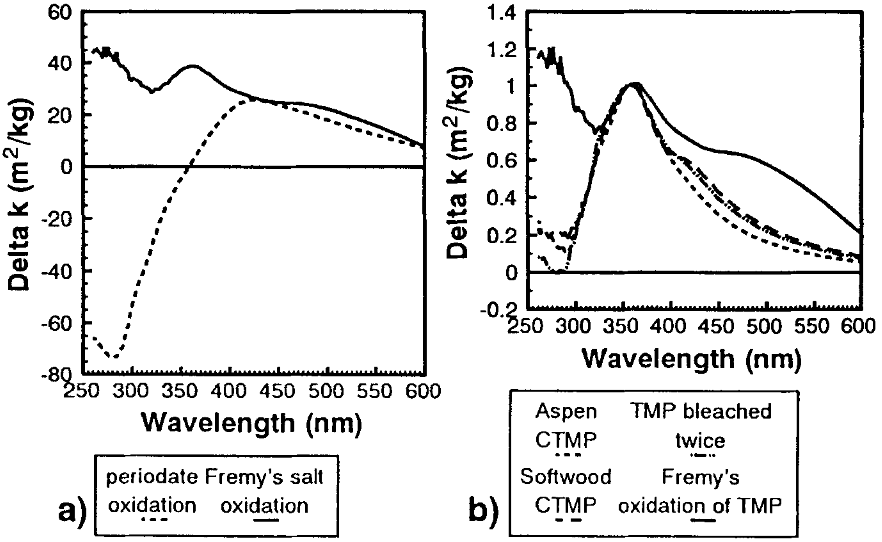


Figure 4: Absorption difference spectra: a) bleached softwood TMP treated with Fremy's salt or sodium periodate, b) spectra normalized at 360 nm: bleached pulps irradiated 24 h and Fremy's oxidized pulp.

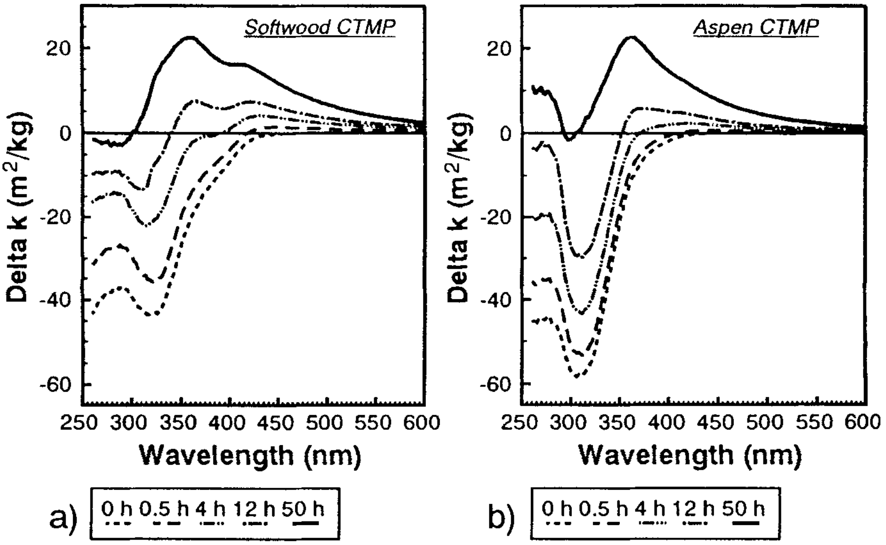


Figure 5: Absorption difference spectra for irradiation of borohydride reduced and peroxide bleached pulps: a) softwood CTMP, b) aspen CTMP.

Since light-induced chromophore formation occurs at least partly with demethylation, one would expect aspen CTMP, by virtue of its syringyl groups, to have larger amounts of methoxy-*o*-quinone chromophores. In fact, the opposite occured. The relative absorption increase $\Delta k(356)/\Delta k(\lambda > 400)$ is smaller for aspen than for the softwood pulps.

This analysis argues against methoxy-*o*-quinones as a major contributor to the absorption band at 356 nm. However, simple diagnostic chemistry suggests that this chromophore is nonetheless some kind of quinone. Sodium dithionite, a mild reducing agent, removes only a small portion of the light-induced absorption increase at 356 nm, while sodium borohydride removes all of it[21 139]. This indicates that the chromophore with $\lambda_{max} \sim 356$ nm does contain conjugated carbonyl groups, unreactive to sodium dithionite.

Effect of Borohydride Reduction on Bleached CTMP

In earlier work, we presented uv-visible evidence that benzyl alcohol groups in bleached softwood TMP are photooxidized to aromatic ketone groups[2, 10]. Sjöholm *et al.*[27] recently reported ^{13}C NMR results consistent with this reaction.

The difference spectra shown in Figure 5 confirm that oxidation of benzyl alcohol groups to aromatic ketones also occurs in bleached CTMP from both softwood and aspen. Treatment with sodium borohydride causes a bleaching with $\lambda_{max} = 316$ nm and 306 nm for softwood CTMP and aspen CTMP, respectively, which we attribute to reduction of aromatic ketones. These absorption maxima are at somewhat lower wavelengths than observed for borohydride reduction of softwood TMP, where $\lambda_{max} = 320\text{-}330$ nm[2, 10]. In the case of aspen, this difference may be due to the presence of syringyl groups. The differences between softwood CTMP and TMP may be due to the residual coniferaldehyde in TMP. Coniferaldehyde end groups are reduced by borohydride to the corresponding coniferyl alcohol, with a bleaching maximum at 356 nm. Although the reduction of aromatic carbonyl groups is the dominant

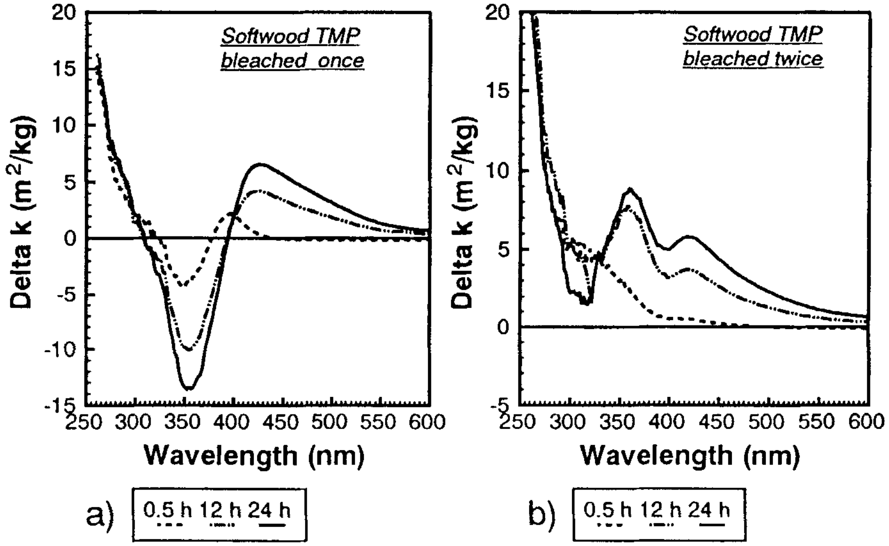


Figure 6: Absorption difference spectra for irradiation of bleached, ascorbic acid treated pulps: a) once-bleached softwood TMP, b) twice-bleached softwood TMP.

feature in the difference spectrum, the reduction of residual amounts of coniferaldehyde may shift the observed maximum somewhat to longer wavelengths.

When the reduced pulps were irradiated, the aromatic ketone absorption recovered. As in the case of softwood TMP (Scheme 1), we attribute this to light-induced cleavage of guaiacylglycerol β-guaiacyl ether linkages, via the corresponding ketyl radical. The enol which results from homolytic cleavage of the C_β-O bond tautomerizes to give the corresponding ketone, and the phenoxy radical is oxidized to coloured chromophores.

Photobleaching by Ascorbic Acid

Figure 6a shows the absorption difference spectra obtained for once-bleached softwood TMP treated with ascorbic acid after 0.5, 12 and 24 hours

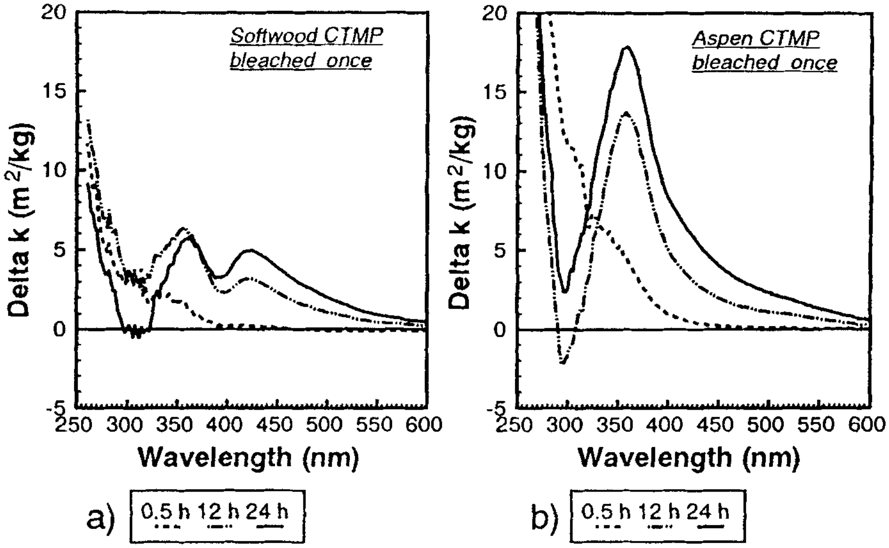


Figure 7: Absorption difference spectra for irradiation of bleached, ascorbic acid treated pulps: a) softwood CTMP, b) aspen CTMP.

irradiation. Photobleaching with $\lambda_{max} \approx 350$ nm was evident, as reported earlier[10]. Comparison with Figure 1a indicates that the increase in absorption coefficient for $\lambda > 400$ nm was about 30% of that observed for untreated pulp, *i.e.*, ascorbic acid inhibited formation of visible-light absorbing chromophores.

Figures 6b, 7a and 7b show the absorption difference spectra for, respectively, twice-bleached softwood TMP, bleached softwood CTMP, and bleached aspen CTMP, all treated with ascorbic acid. Formation of chromophores absorbing at both visible and near ultra-violet wavelengths was inhibited (compare Figures 1b, 3a and 3b), but there was no photobleaching at 350 nm.

In an earlier paper[10], we speculated that the photobleaching observed for ascorbic acid treated, once-bleached TMP was a consequence of light-driven removal of stilbene by ascorbic acid. The spectra above suggest a simpler

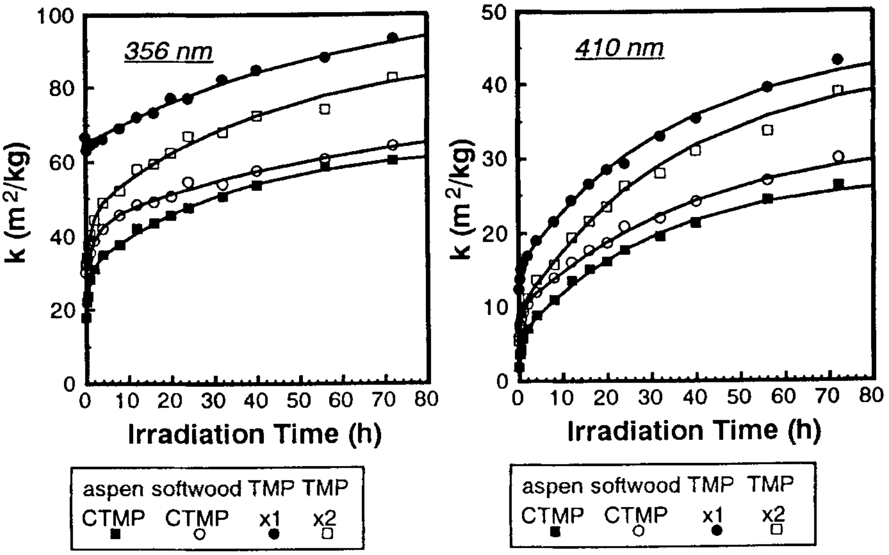


Figure 8: Kinetics of chromophore formation for irradiation of once- (x1) and twice-bleached (x2) softwood TMP, bleached softwood CTMP, and bleached aspen CTMP at 356 nm and 410 nm.

explanation. Ascorbic acid inhibits the light-induced formation of chromophores with $\lambda_{max} \approx 350$ nm, which results in a slower increase in absorption coefficient. In once-bleached TMP this suppression of chromophore formation allows the photobleaching of coniferaldehyde to be observed more readily.

Kinetics

Two wavelengths were chosen for kinetic analysis: 356 nm, because this is where the largest increases in absorption coefficient occur, and 410 nm, because this wavelength corresponds both to yellowing and to the shoulder observed in the difference spectra of the softwood pulps. The kinetics of the increase in absorption coefficient for the four bleached pulps are shown in Figure 8. The curves were adequately fit by a sum of two exponential terms

TABLE 1: Rate Constants for Increases in Absorption Coefficient (brackets denote standard deviation)

Pulp	λ = 356 nm		λ = 410 nm	
	r_1 (h^{-1})	r_2(h^{-1})	r_1(h^{-1})	r_2(h^{-1})
Softwood TMP Bleached Once	-	0.016 (0.01)	2.1 (1.3)	0.028 (0.009)
Softwood TMP Bleached Twice	0.73 (0.30)	0.025 (0.01)	2.1 (0.46)	0.028 (0.006)
Spruce CTMP Bleached Once	0.45 (0.24)	0.016 (0.017)	1.5 (0.75)	0.025 (0.009)
Aspen CTMP Bleached Once	1.1 (0.54)	0.029 (0.015)	1.6 (0.51)	0.033 (0.01)

(equation 1), with the exception of once-bleached softwood TMP at 356 nm, which was adequately described by a single exponential term (equation 2). k^{∞} is the maximum value of the absorption coefficient, r_1 and r_2 are first-order rate

$$k(t) = k^{\infty} - A_1\exp(-r_1t) - A_2\exp(-r_2t) \qquad (1)$$

$$k(t) = k^{\infty} - A_2\exp(-r_2t) \qquad (2)$$

constants with units hour^{-1}, and A_1 and A_2 are the amplitudes associated with each of the rate constants. The values of the parameters obtained for the fitted curves are tabulated in Tables 1 and 2.

The kinetic data indicate that for all pulps chromophore formation can be separated into rapid and slow phases. The rate constant for the rapid phase was 30-100 times larger than that for the slow phase. Each phase undoubtedly comprises several chemical changes that occur with similar rates, but the best

TABLE 2: Pre-exponential Factors for Increases in Absorption Coefficient. (brackets denote standard deviation)

Pulp	λ = 356 nm			λ = 410 nm		
	Δk^∞ (m^2/kg)	A_1 (m^2/kg)	A_2 (m^2/kg)	Δk^∞ (m^2/kg)	A_1 (m^2/kg)	A_2 (m^2/kg)
Softwood TMP Bleached Once	40.3 (23)	40.3 (23)	-	33.3 (5.1)	3.0 (0.5)	30.3 (5.1)
Softwood TMP Bleached Twice	56.9 (6.9)	13.3 (2.9)	43.6 (6.3)	37.2 (3.7)	4.2 (0.5)	33.1 (3.7)
Spruce CTMP Bleached Once	43.2 (18)	12.2 (3.5)	31.1 (18)	26.6 (4.2)	3.7 (0.9)	23.2 (4.1)
Aspen CTMP Bleached Once	46.2 (7.5)	13.1 (3.4)	33.1 (6.7)	25.7 (2.9)	3.9 (0.8)	21.7 (2.8)

that fitting routines can do is provide an average rate constant for the group. As well, the fitting data alone will not distinguish whether the rapid and slow reactions occur consecutively or simultaneously.

At a given wavelength, the rate constants for the rapid phase were identical for all the pulps, as were those for the slow phase, within the standard deviation of the fitted parameters.

We obtained further information on the chromophore forming reactions by analyzing the pre-exponential factors A_1 and A_2, shown in Table 2. The sum $A_1 + A_2$ gives the maximum *change* in absorption coefficient (k^∞ - k(t=0)) , denoted in Table 2 as Δk^{∞}. Each amplitude has units of absorption coefficient, and is proportional to the concentration of chromophores, or equivalently, the concentration of chromophore precursors.

For CTMP from both aspen and from spruce, Δk^{∞} was about 20-30% smaller than for softwood TMP. Since the pre-exponential factor corresponding to the rapid phase of chromophore formation, A_1, was essentially the same for all the pulps at each analysis wavelength, we attribute the smaller values of Δk^{∞} for the CTMPs to smaller values of A_2, the slow-phase pre-exponential factor. This suggests that sulphonation destroys some of the precursors to slow-phase chromophore formation.

At longer irradiation times the slow phase was dominant. Chromophore formation will be slower in the CTMPs than in TMP, as a consequence of the lower concentration of chromophore precursors. However, the initial rates of chromophore formation will be almost identical for all the pulps. Although the rapid phase contributes only about 4 m^2/kg of the total increase in absorption coefficient at 410 nm, this is sufficient to cause visible discolouration. For practical purposes, there was little difference in the rates of absorption coefficient increases for these three pulps.

Once-Bleached Softwood TMP at 356 nm

The absorption coefficient increase for once-bleached softwood TMP at 356 nm required only a single exponential term to describe its kinetics. As with the *difference* spectra, this anomalous behaviour is readily explained by the photobleaching of residual coniferaldehyde.

Figure 2a shows that the second peroxide bleach of softwood TMP caused a 33 m^2/kg decrease in the absorption decrease at 356 nm, which we attribute to oxidation of residual coniferaldehyde in once-bleached TMP. For twice-bleached softwood TMP, the rapid phase of chromophore formation contributes 13 m^2/kg (Table 2) of the total absorption coefficient increase at

356 nm. The 13 m^2/kg increase in absorption coefficient which occurs at 356 nm due to the rapid phase of photochemical chromophore formation in once-bleached TMP is balanced by the simultaneous 33 m^2/kg decrease in absorption due to photobleaching of coniferaldehyde. Thus, only a single exponential term is required to model the kinetics of chromophore formation at 356 nm in once-bleached TMP, to describe the slow-phase chromophore formation. As further confirmation of this, the rate constant obtained for once-bleached TMP at 356 nm was identical to the slow-phase rate constants obtained at 356 nm for the other three bleached pulps (Table 1), and the amplitude for this single term was essentially the same as the slow phase amplitude for twice-bleached TMP.

CONCLUDING REMARKS

Although there are spectral differences between the pulps studied here, in the main our results imply that the time required to go from initial whiteness to perceptible discolouration will not differ significantly between softwood TMP and CTMP, or between CTMP from aspen or spruce.

As a final point, we would like to comment on the implications of two important features of the mechanism of light-induced yellowing. First, as long accepted, phenoxy radicals are the initially formed intermediates[1,28], and they are subsequently oxidized to chromophores. Second, although diatomic oxygen is probably the stoichiometric oxidant, direct attack of oxygen at phenoxy radicals is very slow[29-31]. Phenoxy radicals react much more readily with oxygen-centered radicals such as alkoxy or perhydroxyl, giving coloured, non-radical products[30].

These two features, formation of phenoxy radicals, and their reaction with perhydroxyl radicals, are characteristic of the radical chain-breaking action of phenolic antioxidants[32]. Autoxidation reactions are propagated by perhydroxyl radicals (ROO•):

$$R\bullet + O_2 \rightarrow ROO\bullet$$

$$RH + ROO\bullet \rightarrow R\bullet + ROOH$$

One phenolic antioxidant can intercept two perhydroxyl radicals, terminating two radical chains:

$$ROO\bullet + PhOH \rightarrow PhO\bullet + ROOH$$

$$ROO\bullet + PhO\bullet \rightarrow \text{non-radical products}$$

The "non-radical products" referred to in the literature on phenolic antioxidants are generally quinones and stilbene quinones[33, 34], the same coloured species which are formed during discolouration of lignin-containing pulps.

It is clear how lignin phenolic groups exhibit this antioxidant behaviour. What Scheme 1 makes clear is that benzylic hydrogens of guaiacylglycerol β-aryl ethers behave analogously: abstraction of the benzylic hydrogen by ROO• gives a phenoxy radical, which reacts with a second perhydroxyl radical.

Thus the photochemical discolouration of lignin-containing pulps is perhaps best viewed as the normal response to ultra-violet light of a material containing 20-25% by weight of a phenolic antioxidant. The challenge to wood chemists is to redirect this chemistry along reaction pathways that give colourless products.

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