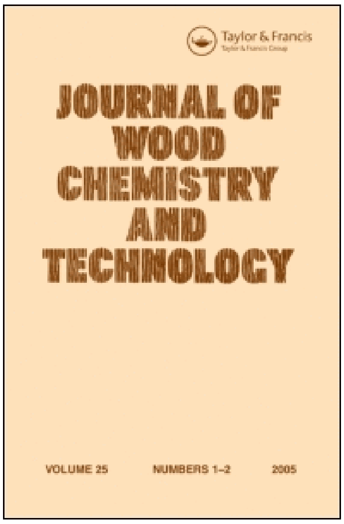

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FLUORESCENT DETECTION OF *o*-QUINONES FORMED IN LIGNIN-CONTAINING PULPS DURING IRRADIATION

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ABSTRACT

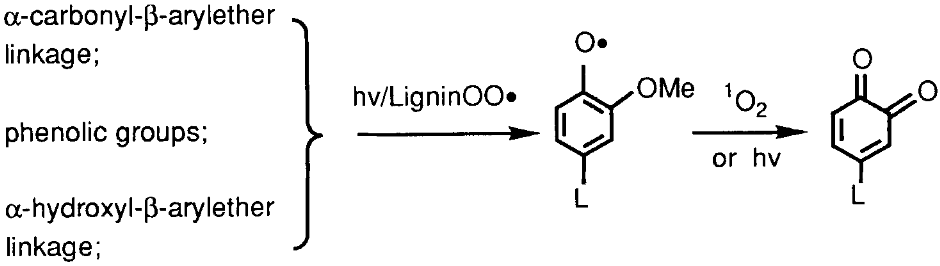
o-Quinones are thought to play a key role in the photoyellowing of mechanical pulps. The facile reaction between *o*-quinones and *o*-phenylenediamine to give fluorescent phenazines is examined as a possible way to detect quinonoid intermediates in pulp sheets. The method was tested on *o*-quinone-rich mechanical pulp sheets prepared by chemical treatment with Fremy's salt (potassium nitrosodisulphonate). The presence of photochemically generated *o*-quinone groups in peroxide-bleached mechanical pulps was inferred from the fluorescence observed from o-phenylenediamine treated sheets. This fluorescence increased with increasing radiation time up to a limiting value. The quinones (but not their phenazine derivatives) are stable upon storage in the dark.

INTRODUCTION

Extended use of high-yield pulps is restricted by their rapid yellowing when exposed to daylight. The overall mechanism is still not completely understood. Many questions remain concerning the nature of the photoreaction products that impart the yellow colour to paper.

Based on studies on pulps[1], extracted lignin[2] and model compounds[3,4,5,6], quinonoid compounds derived from photochemical reactions of lignin are often held responsible for the colour of irradiated pulps. In a general mechanism (scheme 1)[7], quinones are formed from the key reactive intermediates, phenoxy radicals.

However, experimental proof of the presence of photochemically generated *o*-quinones in pulp has been rather elusive. Lebo *et al.*[8] and Argyropoulos *et al.*[9], using ^{13}P NMR, found evidence for the existence of *o*-quinones in irradiated mechanical pulps and in pulps which had undergone oxidation with Fremy's salt or peroxide, or reduction with sodium borohydride. Yet doubt has been cast on the idea of quinone formation by Terasawa and coworkers in a study[10] of light-induced yellowing of spruce and pine mechanical pulps. They observed no bleaching when the irradiated pulps were treated with sodium hydrosulfite, which should readily reduce quinones to uncoloured hydroquinoids. Holmbom *et al.*[11] found no evidence for the presence of quinonoid structures in irradiated stoneground wood and spruce lignin. Their method, involving perethylation and oxidative degradation followed by GC and GC MS analysis of the products was claimed to allow detection of 0.2 such structures per 100 C_9 units. No clear evidence for quinone formation during irradiation was found by FTIR[12], partly because the quinone or quinomethide carbonyl bands near 1640 cm-1 are strongly overlapped by that of water. However, detection of small amounts of reactive intermediates in solid samples is difficult, and if broad-band radiation is used, reaction products resulting from a chromophore absorbing at one wavelength may well undergo further reactions upon absorbing light of another wavelength. In fact, many quinonoids are photoactive and can be converted to other coloured products[13].

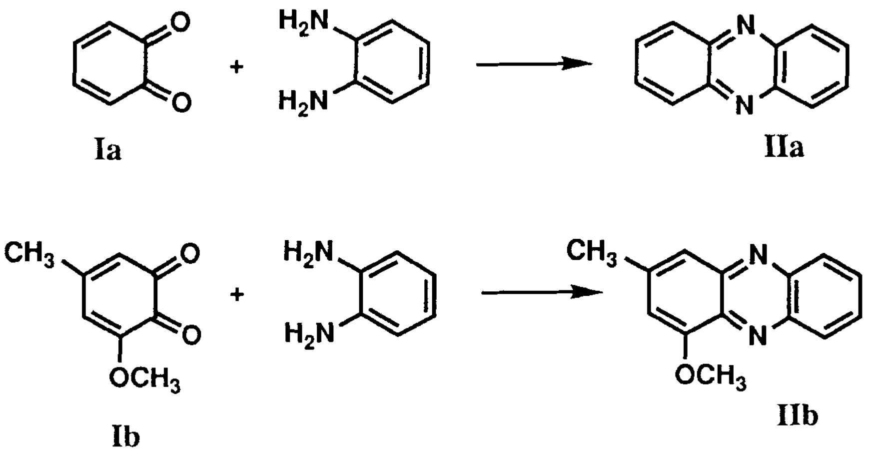


Scheme 1

As a sensitive analytical tool, spectrofluorometry has been applied to the study of paper yellowing[14,15,16,17], although little information about quinones has been obtained, since quinones generally are not fluorescent due to their low-lying n-π* state. A suitable labelling technique is required. The ideal label would be a non-fluorescing reagent that reacts specifically with *o*-quinones to give a fluorescent species with an emission at wavelengths well removed from those for fluorescent chromophores in the pulp. Phenazines, readily formed from the reaction of *o*-quinones with *o*-phenylenediamine (scheme 2), often fluoresce[18]. In this paper we report the use of this reaction to detect the formation of *o*-quinones in irradiated lignin-containing paper by fluorescence spectroscopy.

EXPERIMENTAL

o-Phenylenediamine (Aldrich) was recrystallized twice from cyclohexane. Trichloroacetic acid was distilled before use. Phenazine II_a was obtained, typically, by mixing 108 mg *o*-phenylenediamine and 108 mg *o*-benzoquinone in 20 ml water containing 1 ml of a 5% trichloroacetic acid solution at 70°C for 5 min (yield 74%), a procedure similar to that described by Morrison[19]. After the usual work-up and purification by column chromatography, the product was identified by infrared spectroscopy and thin-



Scheme 2

layer chromatography. A solution of protonated phenazine was prepared[20] by dissolving 20 mg of I in 100 mg ethanol containing 1% trichloroacetic acid; 50 µl of this solution was loaded on a peroxide-bleached thermomechanical pulp (BTMP) sheet with a microsyringe. *o*-Benzoquinone was obtained by periodate oxidation of guaiacol, as described in the literature[21].

3-Methoxy-5-methyl *o*-quinone (Ib) was prepared by oxidation of 2-methoxy-3-methyl phenol with Fremy's salt, following a similar procedure of Teuber and Staiger[22]. Conversion of Ib to phenazine IIb was carried out as follows: solutions of 450 mg of Ib in 10 ml benzene and of 320 mg of *o*-phenylenediamine in 30 ml ethanol were mixed and heated to 60° with stirring for 10 minutes. Extraction with $CHCl_3$ and purification yielded 479 mg IIb as yellow crystals whose melting point (158-160°C), ^1H NMR and i.r. spectra confirmed the identity of the product.

DTPA (diethylenetriamine-pentaacetic acid) treated BTMP was first reduced with sodium borohydride and subsequently treated with a solution of

0.1N HCl in MeOH/dioxane(1:1) to convert α-carbonyl or carbinol groups to >CH(OMe) groups, as α-carbonyl groups deactivate and block the oxidation at the 6-position of the guaiacol structures, thus preventing successful conversion to *o*-quinone with Fremy's salt[23]. After careful washing of the pulps with distilled water, reaction with Fremy's salt was performed under the following conditions: for 5 g (oven dry) of pulp, at a consistency of 20%, 280 mg of Fremy's salt and 75 mL of 5% KH_2PO_4 solution was used. The mixture was stirred and maintained at 60°C for 20 min, washed with distilled water and filtered. The pulp was then mixed with 29 mg phenylenediamine in aqueous solution at pH of 5 and stirred at 60°C for 20 min. After filtering, the pulp was washed twice with a mixture of water and acetone to remove residual diamine before making hand sheets.

Monochromatic light irradiation of handsheets was carried out using the 450 W Xenon lamp and single grating monochromator of a Spex DM-3000 spectrophotometer, with incident light striking normal to the paper surface. A Mineralight® lamp (model 52-G, UVP Inc. San Gabriel, CA.) with a pyrex filter to eliminate light < 300 nm was used for broad band irradiation. Thick sheets (25-30 g/m^2) were used in this study. Irradiation time was 15 minutes unless otherwise stated.

For the *o*-phenylenediamine treatment, samples were suspended in a solution of *o*-phenylenediamine (0.01 M) in ethanol (95%) containing 0.4% chloroacetic acid at 50-55°C for about 2 min. They were then washed with acetone/EtOH 2:1 to eliminate residual diamine, and dried at room temperature in the dark.

Fluorescence spectra were measured with a Spex DM-3000 spectrofluorometer. All spectra are corrected, and are the averaged results of at least 3 sets of experiments.

RESULTS AND DISCUSSION

Paper sheets made from bleached mechanical pulps have their own fluorescence (background fluorescence). Irradiation of these sheets with near-UV light causes a steady decrease in the maximum emission intensity. Despite the substantial increase in absorption in the region of 390 to 450 nm as a result of photoyellowing, the fluorescence intensity from the sheets, when excited at these wavelengths, also declines after irradiation. This is consistent with the formation of nonfluorescent compounds such as quinones.

Fluorescence of Phenazines

If *o*-quinones are formed, treatment of the irradiated sheet with *o*-phenylenediamine should lead to phenazine-type fluorescent chromophores, provided that other lignin structures are not affected by the diamine treatment under the same conditions. For this purpose, we have tested several lignin model compounds: 3,4-dimethoxy-α-(2′-methoxyphenoxy)-acetophenone (an α-carbonyl model), 1-(3,4-dimethoxyphenyl-)2-(2′-methoxyphenoxy)ethanol (an α-hydroxy model), 3,4,3′,4′-tetramethoxystilbene, 3,4,3′-trimethoxy-4′-hydroxystilbene, and coniferaldehyde. HPLC (reversed phase SUPELCO LC-18, MeOH-Water, with cyclohexane as internal reference) monitoring showed no reaction of *o*-phenylenediamine with the model compounds under conditions used to derivatize *o*-quinones and pulp samples. (The method can detect >3% loss of starting model compound.) Thus the diamine reaction seems reasonably specific for *o*-quinones. The emission from phenazines would best serve for identification if it is distinct from or superimposed on the background signal. An example is given for protonated phenazine IIa in EtOH solution containing acetic acid (Figure 1), and loaded on a bleached thermomechanical pulp sheet (Figure 2). The free base form of phenazine is nonfluorescent due to its $^1(n-\pi^*)$ nature which undergoes very efficient intersystem crossing to $^3(\pi-\pi^*)$. However, the protonated form is fluorescent[20]. As shown in Figure 2, a new emission band is superimposed on the background fluorescence of the substrate BTMP. The difference emission spectrum, i.e. $\Delta i_f = i_f(\lambda) - i_{f,o}(\lambda)$, where $i_f(\lambda)$ and $i_{f,o}(\lambda)$ are the fluorescence intensities of the loaded sheet and that of substrate, resembles the emission spectrum of IIa in solution, with maximum at about 512 nm (Figure 1 and 2).

Generation of *o*-Quinones in BTMP and their Detection with Diamine

o-Quinones are produced by the reaction of phenols and condensed phenols with Fremy's salt (potassium nitrosodisulfonate)[24]. Conversion of *o*-substituted phenolic structures in lignin to *o*-quinones by treatment of mechanical pulps with Fremy's salt is also documented[23]. We have measured the fluorescence from a BTMP sheet that was treated successively with Fremy's salt and *o*-phenylenediamine. The spectra are presented in Figure 3. Excitation wavelengths were chosen in the range of 372 to 410 nm because the spectra show most pronounced changes under these conditions. The spectra of untreated BTMP are also included for comparison. Fremy's salt-treated BTMP, with a high concentration of quinones, shows no measurable fluorescence. *o*-Phenylenediamine, adsorbed on solid media where few if any quinones are present such as Whatman filter paper or BTMP, gives fluorescence only when excited by light of $\lambda < 310$ nm, with an emission maximum around 343 nm. Hence, the new band centred around 545 nm is characteristic of fluorescing phenazine-type chromophores formed after consecutive treatment of BTMP with Fremy's salt and *o*-phenylenediamine.

Compared to the model phenazine IIa adsorbed on the same substrate (Figure 2), the new emission band of the treated BTMP sheet shifts to higher wavelengths. Presumably, the methoxyl substituents and the lignin network linked to the phenazine are responsible for the shift. For example, the fluorescence spectra in MeOH solution or on filter paper of phenazine IIb are shown in Figure 4. The structure of the corresponding *o*-quinone (Ib) is a

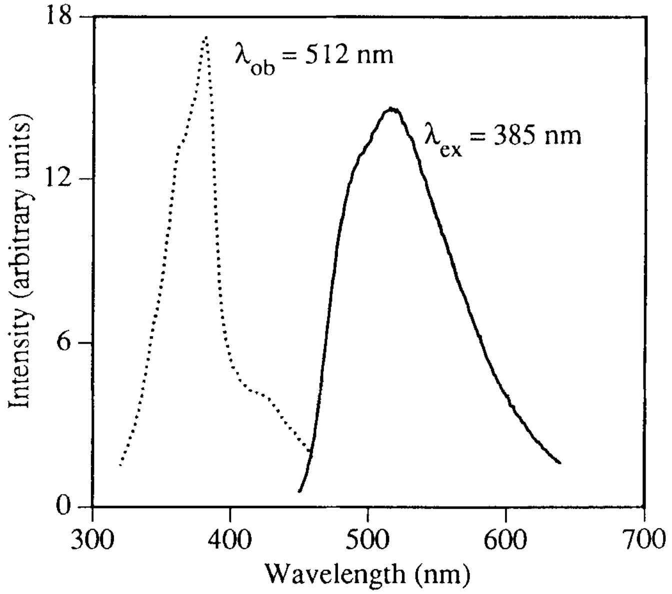


Figure 1. Excitation (dotted curve) and emission spectra of phenazine IIa in ethanol solution containing acetic acid.

good model for the oxidation product of the phenoxy radical from a α-O-4-2,6-dimethoxy lignin structure, with the methyl group at the place of a linkage to the lignin matrix. The emission maxima are at 562 nm and 546 nm for IIb solution and for filter paper loaded with IIb, respectively. It is thus reasonable that the phenazines detected here and in the following cases derive from methoxy substituted *o*-quinones.

Treatment of Irradiated BTMP with *o*-Phenylenediamine and Fluorescence Detection

a) monochromatic irradiation

When a BTMP sheet is treated with *o*-phenylenediamine after irradiation with monochromatic light of 320 nm for 15 minutes, a green-yellow

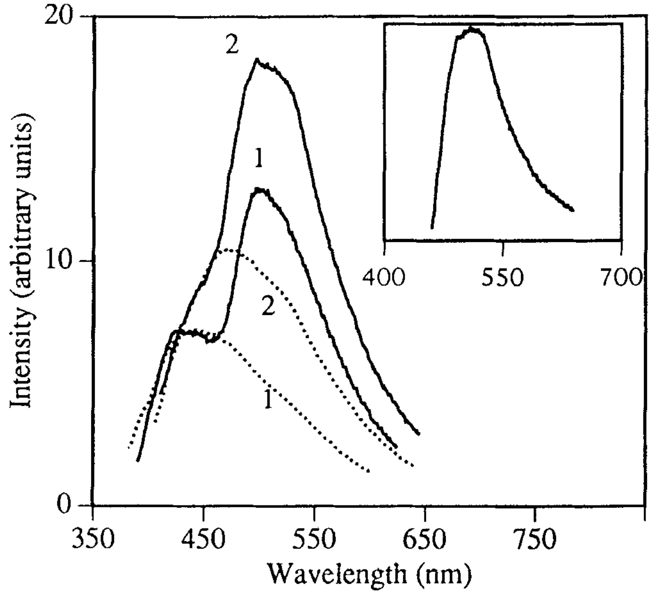


Figure 2. Emission spectra of protonated phenazine IIa loaded on BTMP, with λ_{ex} = 366 nm (spectrum 1) and λ_{ex}=385 nm (spectrum 2). Dotted spectra: blank substrate BTMP. Inset: difference emission spectrum for λ_{ex}=366 nm.

fluorescence from the area exposed to irradiation is visible under a portable TLC UV lamp (365 nm). Figure 5 shows the emission spectra of this fluorescence for excitation at 350 nm and 373 nm along with blank measurements for an irradiated but untreated sample. Although the original maximum intensity of the blank spectrum is comparable to that of treated sheet, a new emission band is superimposed on the blank spectrum. This new band is assigned to some type of phenazine formed as the result of the reaction of the *o*-diamine with photochemically produced *o*-quinones in the sheet.

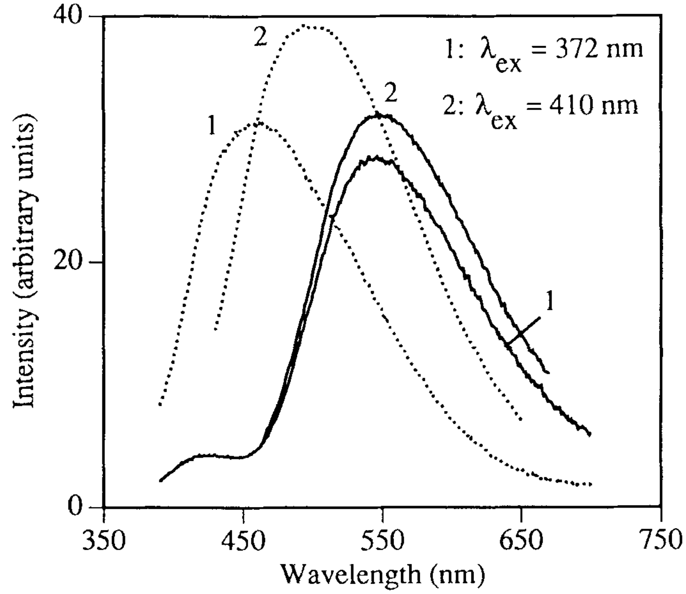


Figure 3. Emission spectra of untreated BTMP (dotted curves) and of BTMP treated with Fremy's salt and *o*-phenylenediamine (solid curves) for excitation at 372 and 410 nm.

b) broad band irradiation

The same diamine treatment gives slightly different results on BTMP sheets that were irradiated for 48 h with a UV lamp having a wide wavelength distribution. The difference emission spectrum red shifts by 10 to 15 nm with respect to that of the sheet irradiated with monochromatic light (Figure 6). This might be due, in part, to differences in the photochemical reaction of quinones under monochromatic and polychromatic light.

c) samples irradiated for different times

It has been suggested that quinones formed from phenoxy radicals might undergo further photoreactions[13]. To test the effect of different irradiation

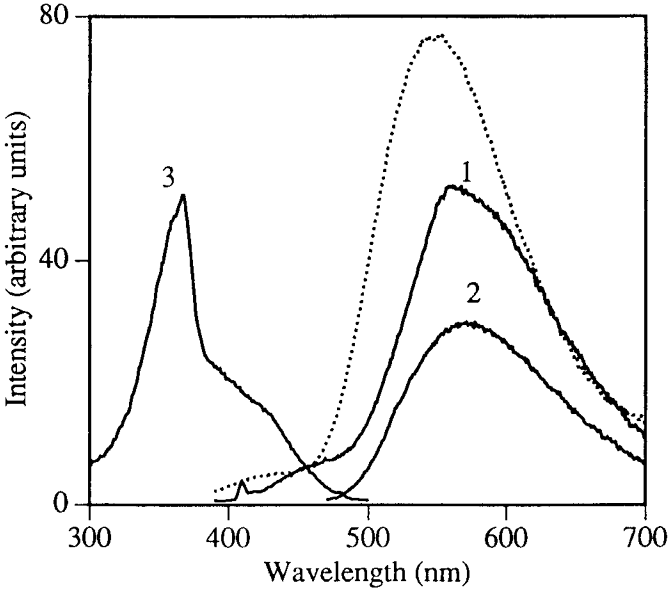


Figure 4. Fluorescence spectra of phenazine IIb solution in MeOH; (1) λ_{ex}=365 nm; (2) λ_{ex}=440 nm; (3) excitation spectrum, λ_{ob}=560 nm. Dotted spectrum: difference spectrum of IIb loaded on filter paper, λ_{ex}=365 nm.

times on quinone detection, BTMP sheets were submitted to 6, 15 and 30 minutes of monochromatic irradiation followed by diamine treatment. The emission spectra of the resulting sheets are presented in Figure 7. It should be remembered that the blank spectra differ from one another for sheets irradiated to different degrees. As can be seen, the ratio of the band attributed to phenazine derivatives to that of the blank increases with irradiation time. Results for irradiation longer than 30 minutes (not shown here) indicate that ratio reaches a platform and remains stable. Extended irradiation also results in a red shift of the phenazine band.

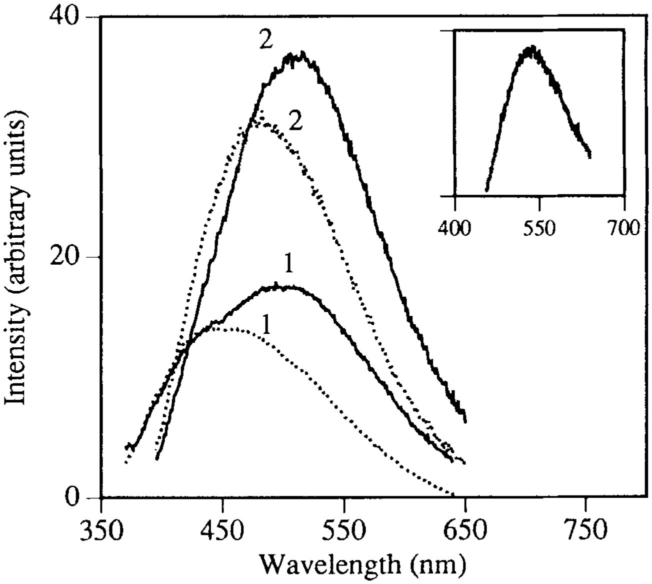


Figure 5. Fluorescence spectra of irradiated BTMP after treatment with *o*-phenylenediamine. Dotted spectra: untreated irradiated BTMP. 1: $\lambda_{ex}=350$ nm; 2: $\lambda_{ex}=375$ nm. Inset: difference emission spectrum for $\lambda_{ex}=350$ nm.

d) stability and detectability of *o*-quinones with storage time

The fluorescence results in Figure 8 show that storage in the dark for up to 30 hrs after irradiation and before diamine treatment has little impact on the detection signal.

e) stability of phenazine fluorescence

The phenazine emission band, on the other hand, show some obvious changes after storage in the dark (Figure 9). A progressive red shift and modification of the spectral shape appear with prolonged storage. Model phenazines are stable in the dark. One possible reason for the instability of the phenazine formed in paper sheets might be reaction of oxygen with residual

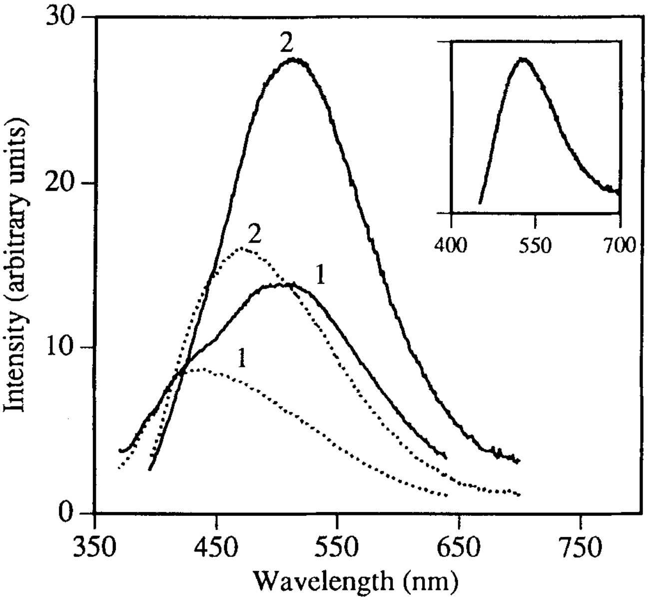


Figure 6. Fluorescence emission spectra of BTMP irradiated with a broad band UV lamp, then treated with *o*-phenylenediamine. Dotted spectra: untreated irradiated BTMP. 1: λ_{ex}=350 nm; 2: λ_{ex}=375 nm. Inset: difference emission spectrum for λ_{ex}=375 nm.

diamine in the paper, to give products that modify or suppress the emission. Obviously, if storage of the sheets is unavoidable prior to emission measurements, they should be treated with diamine solution just before introduction in the spectrofluorometer.

Specificity

The method of quinone conversion used here should be selective towards *o*-quinones to some extent, as a model *p*-benzoquinone gave no fluorescence when treated with phenylenediamine. Although we can not exclude the possibility that emission of our treated samples may be due in part

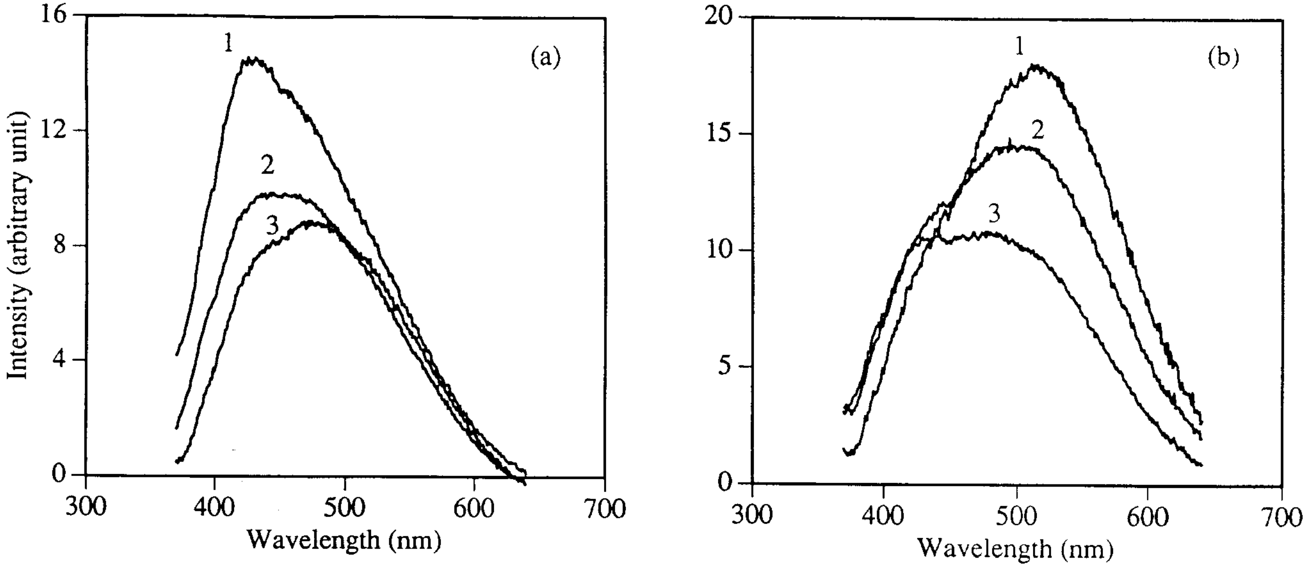


Figure 7. Fluorescence spectra (λ_{ex}=350 nm) of irradiated BTMP (a) and of irradiated and *o*-phenylenediamine-treated BTMP (b). Irradiation time (minutes): (1) 6; (2) 15; (3) 30.

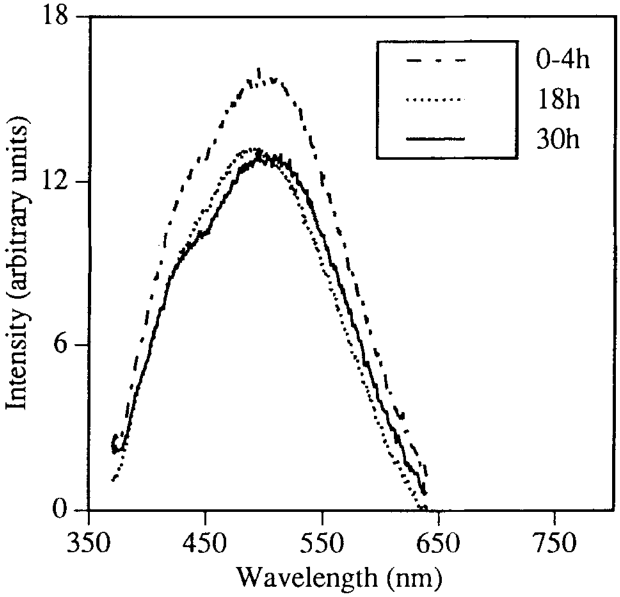


Figure 8. Emission spectra (λ_{ex}=350 nm) of BTMP treated with *o*-phenylenediamine after storage for the indicated times after irradiation.

to products from *p*-quinone structures, as Sawick and Elbert[25] have shown that reaction of *o*-phenylenediamine with 2-hydroxy-1,4-naphthoquinone resulted in fluorescent 4-hydroxy-1,2-naphthylquinoxaline (rose-red emission, but no emission band wavelength given)[25] (scheme 3), we believe there are three reasons to doubt the involvement of *p*-quinones in our results. First, in the above cited study, only 2-hydroxy substituted *p*-quinones gave fluorescent quinoxalines, whereas other *p*-quinones gave negative results. It is obvious, given the role of phenolic hydroxy groups in quinone formation, that no 2-hydroxy-*p*-quinones structures would form in lignin as result of photoyellowing. Secondly, an extented ring conjugation is needed for emission

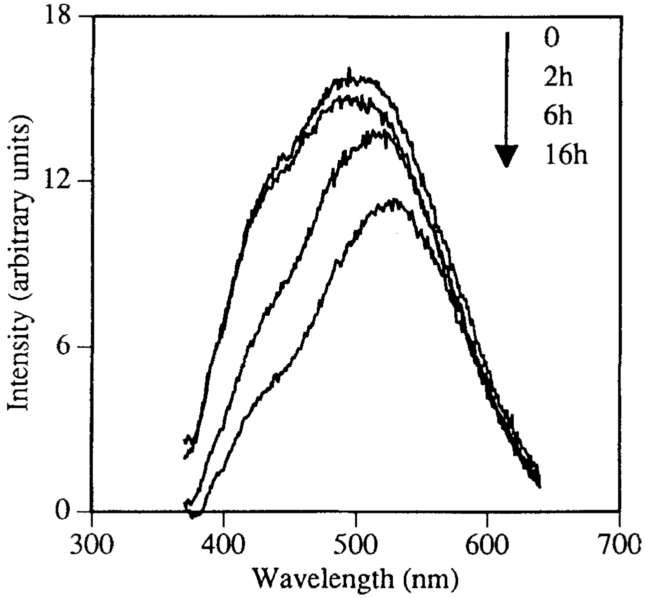
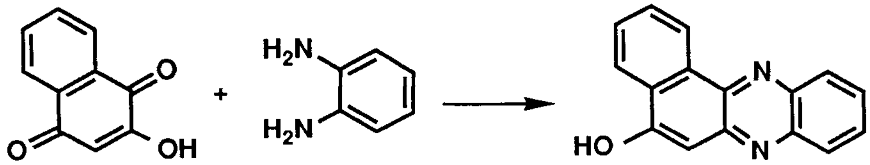


Figure 9. Emission spectra (λ_{ex}=350 nm) for BTMP stored for the indicated times following irradiation and treatment with *o*-phenylenediamine.



Scheme 3

at the green-yellow region ($>$500nm), and since *p*-quinones reacting with *o*-phenylenediamine would not lead to such ring structures, only phenazine derivatives from *o*-quinones are likely to be responsible for the new fluorescence. Finally, if we assume that the Fremy's salt treatment of pulp produces only *o*-quinones as has been suggested[23,26], the resemblance of the emission spectra of pulps treated with Fremy's salt and diamine to the difference emission spectra from irradiated and diamine-treated pulps should be considered as support of specificity towards *o*-quinones.

Interestingly, when a large number of irradiated and diamine-treated sheets were washed with anhydrous acetone, the combined liquid phase, after removal of unreacted diamine and loading on filter paper, gave a weak fluorescence in the same wavelength region as the model phenazine IIa. Note that acetone washing did not modify the fluorescence pattern or intensity of the BTMP sheets by any significant degree. Because the extractable substances represented only a very tiny part of the pulps involved, and because they seem to be of oligomeric nature, no attempt was made to identify all the components and examinate their fluorescence in detail on a solid substrate. It is still possible that some of the photochemically generated quinones were extractable, and that the phenazine derivatives formed from reaction with the diamine might be the origin of this fluorescence emission.

While unequivocal proof of the formation of phenazines in the pulp is difficult to produce, the ease of reaction of *o*-phenylenediamine with *o*-quinones under mild conditions[18], the negative response with other lignin model compounds, and the results with sheets treated with Fremy's salt all indicate that the reaction is reasonably specific.

Application to Other Pulps

Irradiated sheets made from other bleached pulps gave similar positive results. A bleached and irradiated chemithermomechanical pulp (BCTMP), and

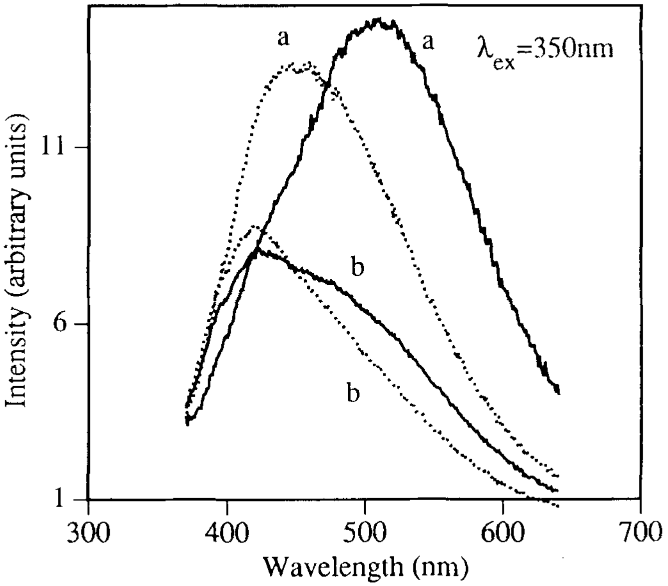


Figure 10. Emission spectra of irradiated BCTMP (a) and $NaBH_4$-reduced BCTMP (b) after *o*-phenylenediamine treatment. Dotted spectra: corresponding irradiated samples.

a BTMP pulp, treated thoroughly with sodium borohydride to remove carbonyl compounds prior to irradiation both showed marked fluorescence in the region attributable to phenazines derived from *o*-quinones (Figure 10). In the latter case, the result indicates that quinones had been regenerated photochemically. The results for an *unbleached* thermomechanical pulp (UBTMP) were less clear. The *o*-phenylenediamine treatment resulted in a lower fluorescent intensity than the original sheet, with a much less pronounced red shift (Figure 11). Thus, there is no clear evidence for the presence of a phenazine derivative. The diamine treatment of unbleached pulps always leads to strong darkening. At present, there is not enough evidence to decide whether this indicates a lower *o*-quinone content for unbleached pulps, or whether reactions

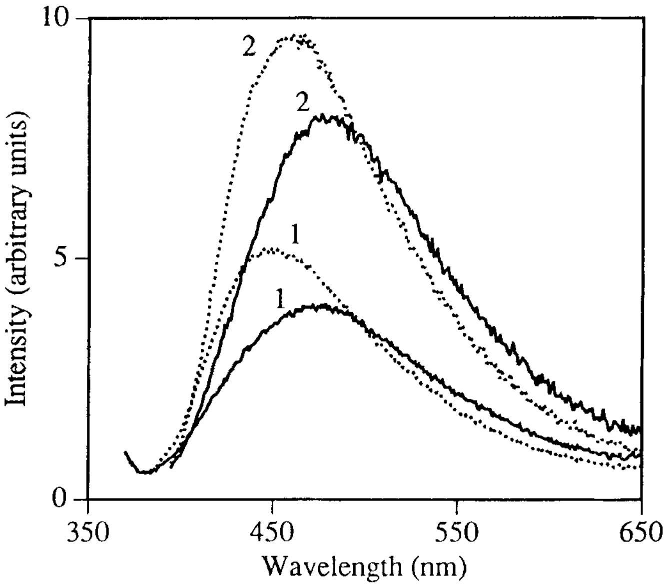


Figure 11. Fluorescence emission spectra of UBTMP treated with *o*-phenylenediamine. Dotted spectra: untreated UBTMP. 1: λ_{ex}=350 nm; 2: λ_{ex}=375 nm.

of the diamine with some structures in unbleached pulps, removed in the bleaching process, give strongly absorbing groups that blur the observed emission.

CONCLUSION

The formation of *o*-quinone structures has been detected by combining a diamine treatment and fluorescence spectroscopy on sheets made from peroxide-bleached thermomechanical and chemimechanical pulps, irradiated with broad band light and with monochromatic light of 320 nm. The emission band of the phenazines is easily distinguished from the background signal. Although the method leads to uncertain results for unbleached pulps, and does not provide accurate identification or quantification of quinone structures, it appears to be a simple way to detect *o*-quinone formation in bleached paper. Scaiano *et al.* have also inferred the formation of *o*-quinones in pulps during irradiation by means of a fluorescent probe based on an entirely different chemistry[27].

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