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Attempt to photostabilize paper made from high-yield pulp by application of UV screens in conjunction with thiols

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Abstract

The stabilization against photoinduced brightness reversion of peroxide-bleached stoneground wood pulp by two phenolic UV screens (methyl 3-hydroxy-4-benzoylphenoxy acetate (DHBE) and methyl 3-(2″-benzotriazinyl)-4′-hydroxy-5′-terbutylphenyl propanoate (HBTE)) and two polyethyleneoxythiols (2-(2′-methoxyethoxy)ethanethiol (MSH) and 2,2′-oxydiethanethiol (DSH)), individually or in combination (DHBE + MSH and HBTE + DSH), was investigated. A synergistic photostabilization effect was observed between the thiol and the UV absorber, but was not retained during irradiation due to thiol consumption probably by Michael-type addition on the quinones, generated by light. Moreover, during the irradiation, the HBTE derivative was found to be very stable on paper in contrast with the DHBE compound. This effect was related to the presence in HBTE of a bulky substituent (tert-butyl) adjacent to the phenolic group which locks the molecule in a favorable conformation for proton transfer in the ground and excited states.

Keywords: Photostabilization; High-yield pulp; UV screen; Thiols

1. Introduction

Paper made from bleached high-yield pulp (HYP) exhibits intense color reversion when exposed to daylight. Undoubtedly, the main chemical species which causes yellowing is lignin [1]. The origin of the formation of colored species has been the subject of much research [2,3]. The results have provided a theoretical basis on which brightness stabilization can be developed and investigated. Due to the key role played by phenoxy radicals in the yellowing process, approaches which have shown some success, albeit of limited commercial value, have included the incorporation of reducing agents, such as thiols [4,5], sulfoxylates [6] and polyethylene glycol [7], and phenolic UV screens, such as 2,4-dihydroxybenzophenone [4,7,8] and 2-hydroxybenzotriazole [9]. In contrast, non-phenolic alkyl cinnamates, which display very good UV screen properties, are very poor stabilizers of bleached HYP [10]; this finding supports the idea that phenolic UV screens work mainly as antioxidants. Moreover, the protection of phenolic UV absorbers is enhanced by using these derivatives in conjunction with a reducing agent and also by lowering the pH of the paper [11]. Therefore we have examined the stabilizing effect, on bleached lignin-rich paper, of the combination of a thiol and a phenolic UV screen. Two systems were considered: (1) 2-(2′-methoxyethoxy)-ethanethiol (MSH) and methyl 3-hydroxy-4-benzoylphenoxy acetate (DHBE); (2) 2,2′-oxydiethanethiol (DSH) and methyl 3-(2″-benzotriazinyl)-4′-hydroxy-5′-terbutylphenyl propanoate (HBTE) (Fig. 1).

2. Results and discussion

2.1. *Photostabilization of peroxide-bleached stoneground wood pulp using the thiol MSH and the UV screen DHBE*

The phenolic UV absorber DHBE and the thiol MSH, individually and in combination, were applied to an industrial bleached stoneground wood pulp (SGWP) at a concentration level of 2% (DHBE 2%, MSH 2%, DHBE 1% + MSH 1%), followed by exposure to UV light (medium pressure mercury lamp (400 W) filtered by Pyrex glass). The brightness changes were monitored at specific intervals during irradiation by measuring the light reflection at 457 nm (BI) according to standard procedures. The results expressed as the

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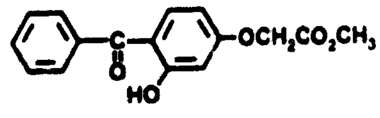
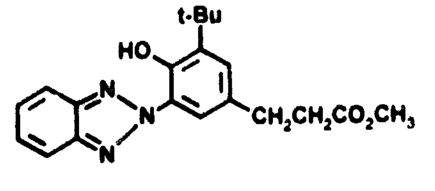
$CH_3OCH_2CH_2OCH_2CH_2SH$ $HSCH_2CH_2OCH_2CH_2SH$

(MSH) (DSH)



(DHBE)



(HBTE)

Fig. 1. Formulae of the compounds studied.

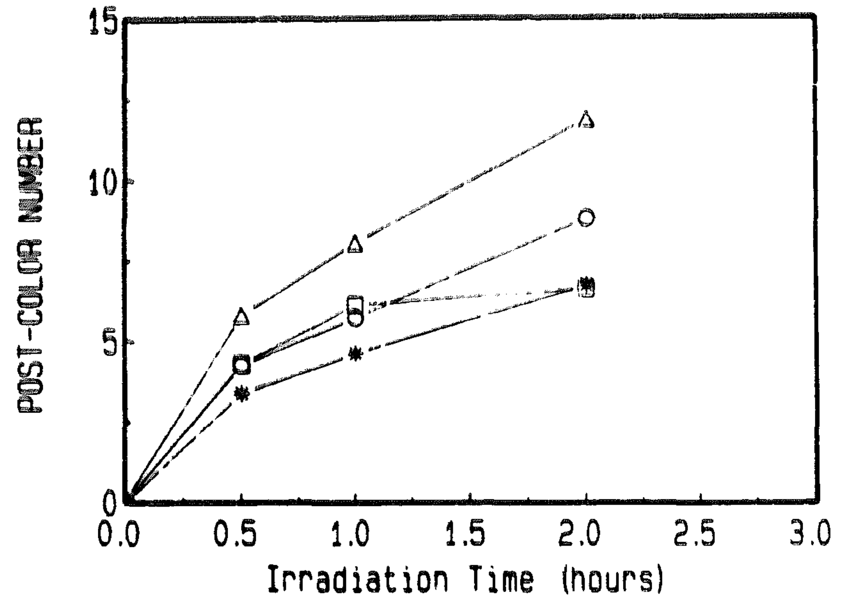


Fig. 2. Photoyellowing, expressed as the post-color number (see Section 2.1), of peroxide-bleached SGWP impregnated with DHBE and MSH and irradiated with UV light (400 W medium pressure mercury lamp filtered by Pyrex glass): △, control; □, DHBE 2% odp; ○, MSH 2% odp; *, DHBE 1% + MSH 1%.

post-color number (PCN) vs. irradiation time are shown in Fig. 2.

$$PCN = [(K/S)_t - (K/S)_{t=0}] \text{ and}$$

$$K/S = [(1-R_\infty)^2/(2R_\infty)]$$

As previously observed for other thiols [4–6], a brightening effect was observed for MSH after impregnation (BI = 74.4 before and 75.3 after). This effect is probably caused by Michael addition of the thiol to some of the remaining quinone chromophores. The UV/Vis diffuse reflectance spectra presented as an example in Fig. 3 for DHBE and MSH (before and after 2 h UV irradiation) show clearly the bleaching effect by the thiol MSH, the screening effect between 300 nm and 400 nm by DHBE and the photoprotecting effect on the whole spectrum.

During the first hour of irradiation, the extent of protection provided by the thiol and the UV absorber is the same. A synergistic effect between the thiol and the phenolic UV absorber, when the two are used together, is also observed for the same period of time. After 2 h, a strong decrease in the protecting action of the thiol is observed. It has been shown previously [10] that both phenolic UV absorbers and thiols mainly work as antioxidants. When they are both present in the paper, the thiol may protect the phenolic functionality of the UV absorber, and so increase its effect, the overall action being synergistic.

The above experiments were conducted at high light intensity compared with that encountered during aging. For this reason, similar irradiations were performed at lower intensity with four 18 W fluorescent tubes (two black light and two visible light emitting lamps). With this set-up, 22 h of irradiation corresponds approximately to 1 h with the 400 W mercury lamp. The results of irradiation are presented as a bar chart in Fig. 4. The same trend in the protective action is observed at high and low light intensities. However, the stabilizing effect of MSH is slightly less than that of DHBE; this is probably due to partial thermal breakdown of the thiol by auto-oxidation in air during the 22 h compared with only 1 h for the high intensity experiments.

The DHBE and MSH additives work as antioxidants, i.e. they are capable of reducing phenoxy and peroxy radicals, hydroperoxides, etc. After a certain period of irradiation, their activity decreases markedly. This may be due to decomposition of the antioxidants or grafting onto the pulp. This has been observed previously for certain phenols [12] and thiols [13,14]. To confirm this view, after 2 h of irradiation, the papers were extracted several times with a mixture of methanol and dichloromethane and, after evaporation of the solvent, the amount of DHBE and thiol not consumed during irradiation was estimated by gas chromatography. The results, reported in Fig. 5, indicate a similar consumption of the UV screen when it is applied alone or in combination with the thiol. The consumption of the thiol is more important than that of the UV screen. Also, the consumption of MSH is higher when irradiated alone compared with as a mixture. The UV screen protects the thiol against photodegradation and may also explain the synergistic effect between DHBE and MSH. Both compounds are probably grafted onto the lignocellulose matrix as shown in the next section for the dithiol DSH.

Fluorescence measurements have recently been used to study the light reversion of various lignin-containing pulps and softwood [15]. It was found that bleaching the pulp leads to a substantial increase in the intensity of emission especially in the blue region of the spectrum (approximately 420 nm). In contrast, irradiation of the bleached pulp with UV light lowers the total fluorescence and increases the relative intensity in the longer wavelength region (approximately 520 nm). The fluorescence spectra, before and after UV irradiation with the 400 W mercury lamp, were measured for papers without additives and with DHBE and MSH. The presence of the additive does not strongly perturb the spectra, except for DHBE where the emission is relatively reduced when excited at 365 nm. At this wavelength, the UV screen absorbs the light and acts as an inner filter. Therefore fluorescence is not the most appropriate technique for studying the influence of additives on the photostabilization of the pulp. As an exam-

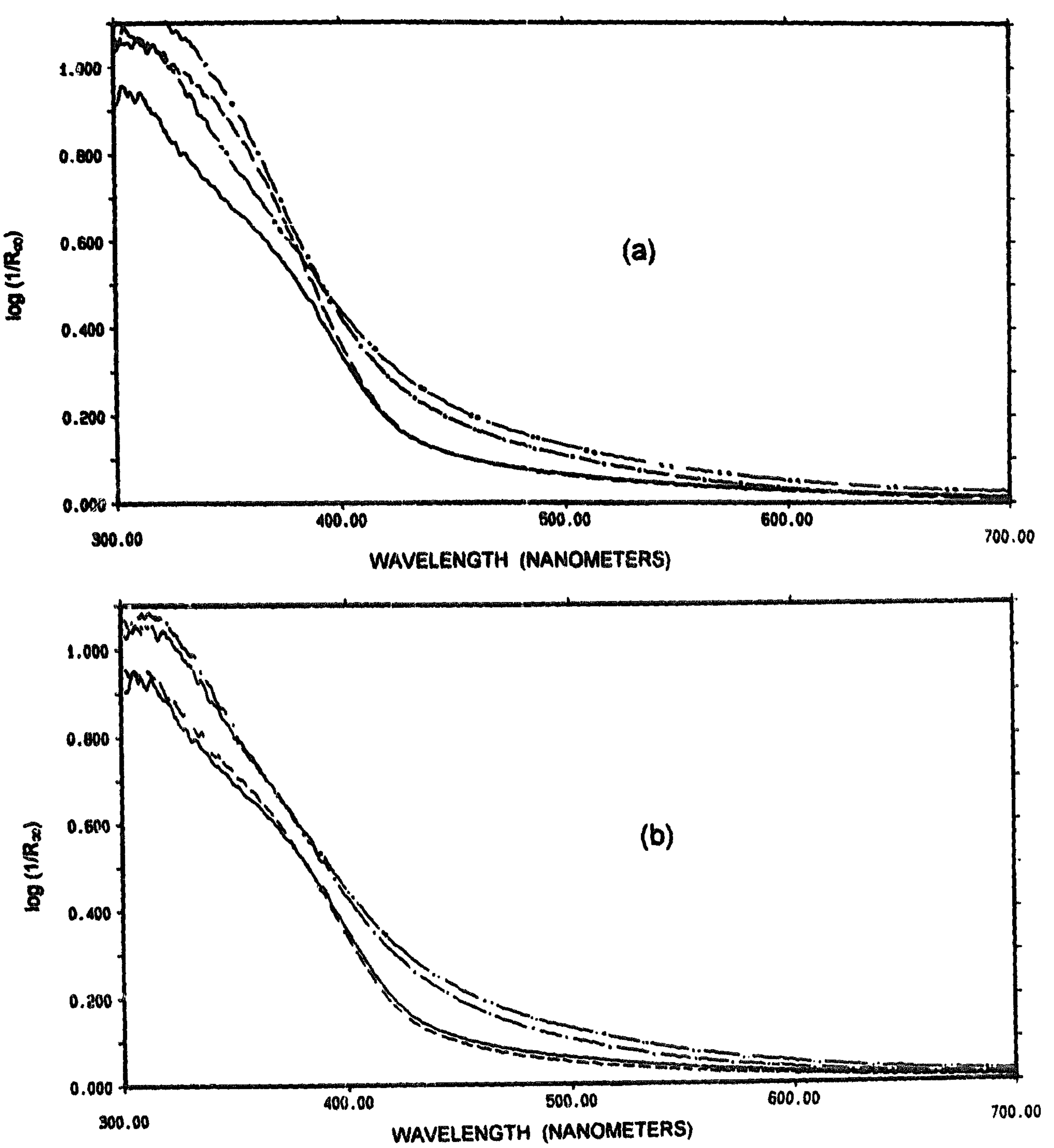


Fig. 3. Diffuse reflectance spectra expressed by log($1/R_\infty$) vs. wavelength. (a) Full line, bleached SGWP before irradiation; – · · –, bleached SGWP after 2 h of irradiation with the 400 W mercury lamp; – – –, bleached SGWP + DHBE 2% odp before irradiation; – · –, bleached SGWP + DHBE 2% after 2 h of irradiation. (b) Full line, bleached SGWP before irradiation; – · · –, bleached SGWP after 2 h of irradiation; – – –, bleached SGWP + MSH 2% odp before irradiation; – · –, bleached SGWP + MSH 2% after 2 h of irradiation.

ple, the spectra recorded for bleached SGWP impregnated with MSH are shown in Fig. 6.

2.2. *Photostabilization of peroxide-bleached pressurized SGWP using the dithiol DSH and the UV screen HBTE*

Of the phenolic UV absorbers, hydroxyphenylbenzotriazole-type molecules (HBT, Tinuvin 1130) were found to prevent the photoyellowing of paper very efficiently [10,11]. Their stabilizing action is related to the excited state intramolecular proton transfer mechanism which takes place via an intramolecular hydrogen bond [16–18] and physical quenching of the excited states [17]. Their photostability, on UV irradiation, appears to be increased by the presence of a bulky substituent near the hydroxyl group of the phenol [18]. This substituent hinders the development of an open form, in both the ground and excited states, which gives photodegraded products [18]. The HBTE derivative should be more stable towards irradiation on the lignin-rich pulp than the DHBE derivative. Moreover, the synergistic action between the UV screen and antioxidant, noted for the pulp [11], has also been observed when an HBT absorber and hindered phenol were applied to wool [19]. For this reason, it was anticipated that the use of a dithiol compound (DSH), incorporating two antioxidant groups, in conjunction with an HBT-type UV screen (HBTE) would yield better stabilization of bleached HYPs than the combination DHBE–MSH.

The performance of the HBTE–DSH additives, evaluated on a slightly different pulp (peroxide-bleached pressurized stoneground wood pulp (PSGWP) instead of peroxide-bleached SGWP) will not drastically change the conclusions. The results are reported in Fig. 7. These experiments show that, for optimum stabilization, a mixture of HBTE and DSH must be applied at a level of 2% of each component. HBTE and DSH were applied to papers made from bleached PSGWP. These papers were exposed for 1 h to UV light (400

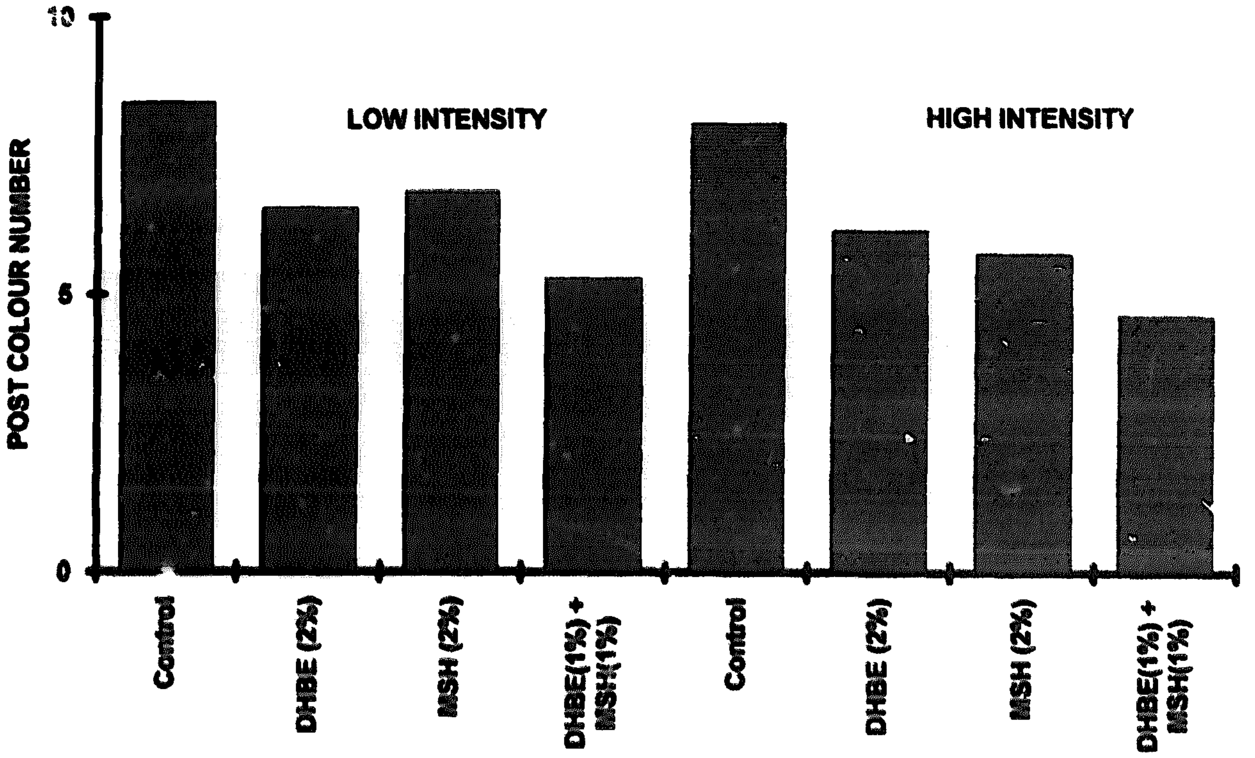


Fig. 4. Photoyellowing of peroxide-bleached SGWP impregnated with the additives and irradiated with high intensity (400 W mercury lamp for 1 h) and low intensity (four 18 W fluorescent tubes (two black light lamps and two visible light lamps) for 22 h) light.

W) and the diffuse reflectance spectra were recorded before and after irradiation (Figs. 8(a)–8(c)). As observed for MSH, the addition of DSH increases the brightness index of the paper (1 point). This can be seen in the visible region of the reflectance spectra (Figs. 8(b) and 8(c)). The combined action of the thiol and the UV screen gives very good photostabilization of the paper between 30 min and 1 h irradiation time; however, the beneficial action of the thiol is almost lost after 3 h.

The consumption, on UV irradiation, of HBTE and MSH incorporated in the paper was evaluated by gas chromatography as for the study on DHBE and MSH. The amount of extractable thiol and UV absorber present after 15 and 30 min and 1, 2 and 3 h of irradiation was obtained by gas chromatography and the results are presented in Fig. 9. In contrast with DHBE, the hydroxybenzotriazole UV screen is stable under the experimental conditions used. This is in accordance with the conclusions drawn by Catalan and Del Valle [18]. The presence of two thiol groups in DSH decreases the amount of thiol extracted after irradiation compared with MSH. As previously observed, the presence of the UV screen gives some protection to the thiol. We may also propose that, in the presence of the UV absorber, the formation of quinone-type structures occurs to a lesser extent and, consequently, there is a lower consumption of the thiol by Michael addition. To confirm the photochemical grafting of the thiol, the papers were overloaded with DSH (10%) and irradiated with the low intensity lamp set-up for 48 h. After extraction using the procedure described above, the sulfur content of the papers was measured to be 0.3%. This should be compared with the non-irradiated paper (0.1%). This result also supports the speculation that the stabilization of HYP by thiols is partially due to the Michael addition mechanism.

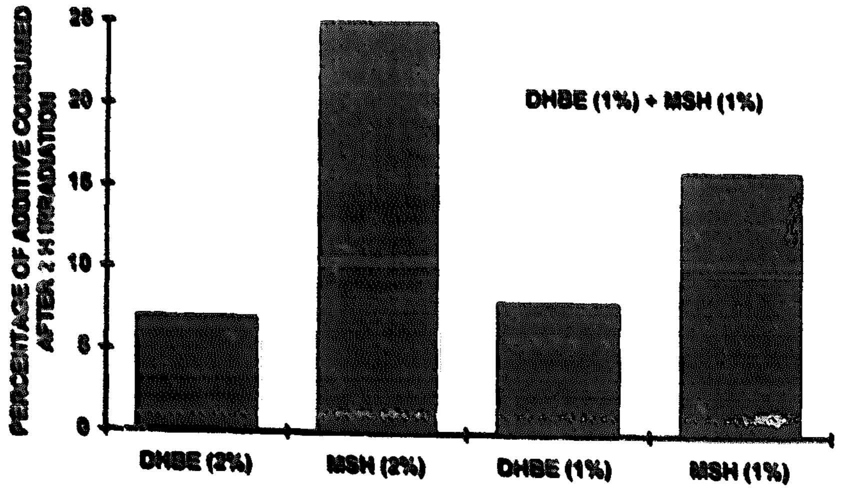


Fig. 5. Percentage of additive consumed after 2 h of irradiation of impregnated bleached SGWP with the 400 W mercury lamp.

3. Conclusions

The results of this study have shown that phenolic UV screens based on hydroxybenzophenone-type (DHB) and hydroxyphenylbenzotriazole-type (HBT) structures, applied in conjunction with diethyleneoxythiols, are particularly effective in the photostabilization of peroxide-bleached stoneground wood pulps. The action of the thiols decreases strongly as irradiation with UV light proceeds due to consumption of the material probably by Michael addition of the thiol to quinones. In contrast with DHB-type UV screens, the HBT structures were found to be stable on paper and appear to be very appropriate for photostabilizing these materials. The development of new reducing species, which are relatively stable to UV irradiation and capable of destroying peroxides when they are used in conjunction with HBT-type UV absorbers, may yield sufficient photostability for the development of the use of bleached high-yield pulps in higher paper grade quality.

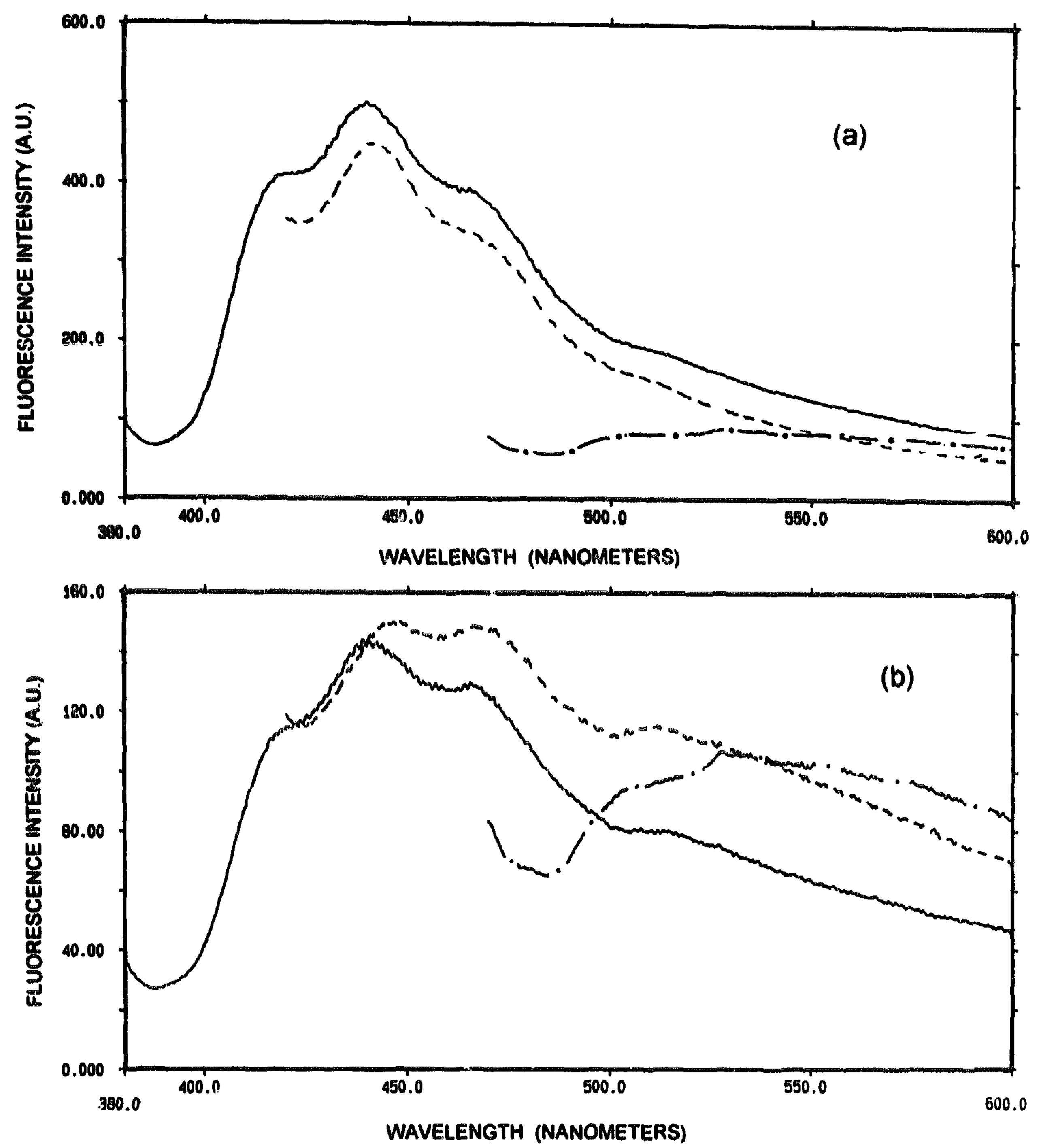


Fig. 6. Corrected fluorescence spectra of peroxide-bleached SGWP impregnated with MSH 2% odp: (a) before irradiation; (b) after 2 h of irradiation with the 400 W mercury lamp. Full line, $\lambda_{exc} = 365$ nm; – – –, $\lambda_{exc} = 400$ nm; – · –, $\lambda_{exc} = 450$ nm.

4. Experimental details

4.1. Materials

The pulp used for preparing the paper handsheets for the study on the couple DHBE–MSH was kindly provided by the Centre Technique du Papier (Grenoble, France) and the paper handsheets used for the study of the HBTE–DSH system were kindly supplied by KCL (Espoo, Finland).

The first pulp, used as a model for bleached HYP, was a peroxide-bleached SGWP, and has been used previously [15c]. The second pulp used in this study was a peroxide-bleached pressurized SGWP and was chosen as common pulp by partners in "The Forest Program MA 2B 0018". The pulp was made of 85% bleached PGW and 15% bleached Kraft; it also contained 4% kaolin.

Reagents were supplied by Aldrich Chemical Company and were used without further purification. The synthesis of DHBE has been described elsewhere [11b]. The HBTE com-

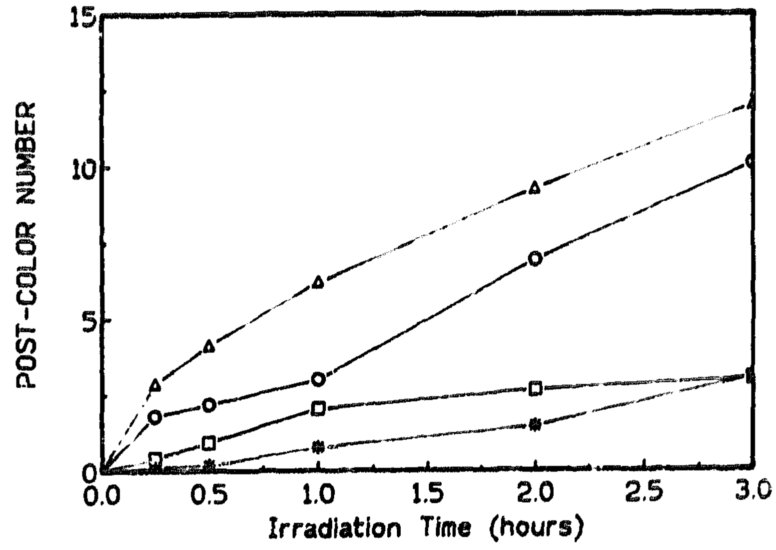


Fig. 7. Photoyellowing, expressed as the post-color number (see Section 2.1), of peroxide-bleached pressurized SGWP impregnated with HBTE and DSH and irradiated with UV light (400 W medium pressure mercury lamp filtered by Pyrex glass): Δ, control; □, HBTE 2% odp; O, DSH 2% odp; *, HBTE 2% + DSH 2%.

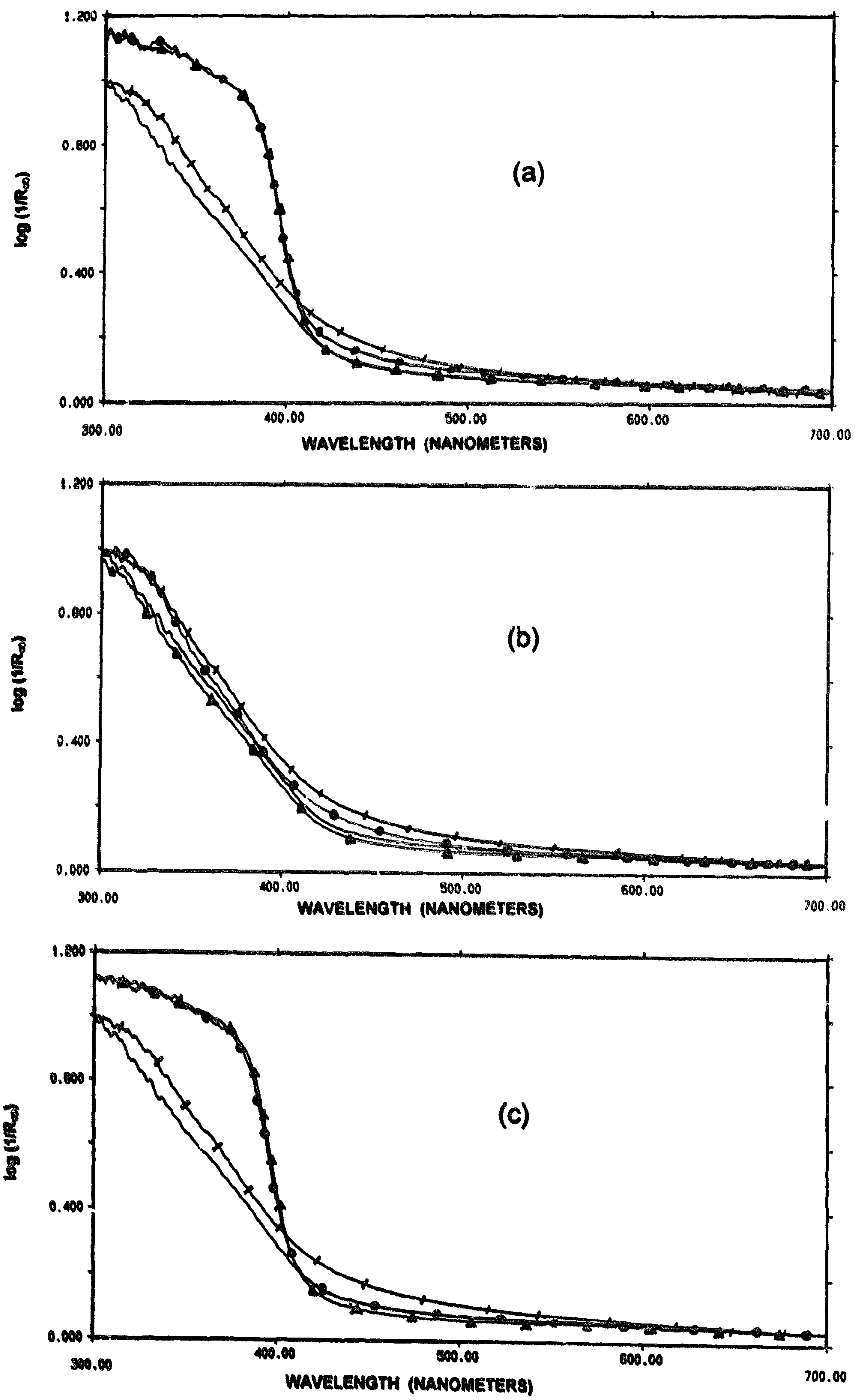


Fig. 8. Diffuse reflectance spectra expressed by $\log(1/R_\infty)$ vs. wavelength. (a) Full line, bleached PSGWP before irradiation; –/–, bleached PSGWP after 1 h of irradiation with the 400 W mercury lamp; ▲, bleached PSGWP + HBTE 2% odp before irradiation; ●, bleached PSGWP + HBTE 2% after 1 h of irradiation. (b) Full line, bleached PSGWP before irradiation; –/–, bleached PSGWP after 1 h of irradiation with the 400 W mercury lamp; ▲, bleached PSGWP + DSH 2% odp before irradiation; ●, bleached PSGWP + DSH 2% after 1 h of irradiation. (c) Full line, bleached PSGWP before irradiation; –/–, bleached PSGWP after 1 h of irradiation with the 400 W mercury lamp; ▲, bleached PSGWP + HBTE 2% + DSH 2% odp before irradiation; ●, bleached PSGWP + HBTE 2% + DSH 2% after 1 h of irradiation.

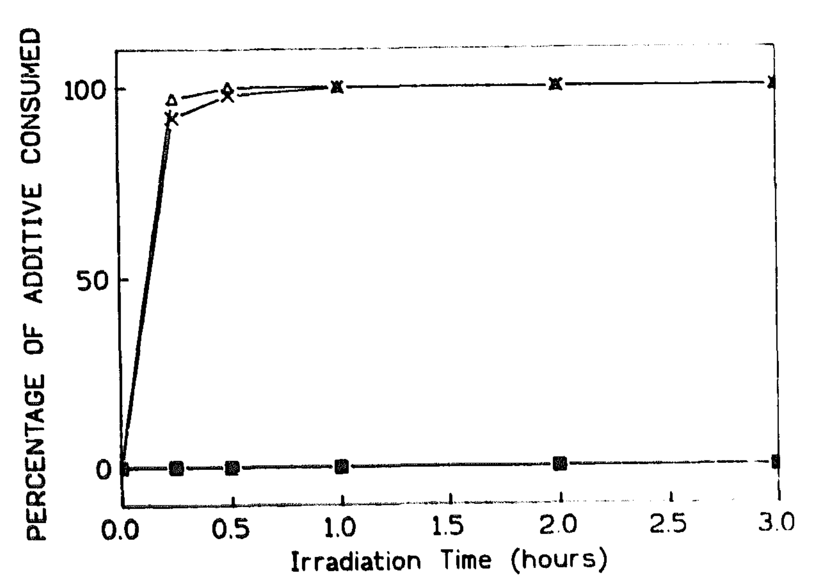


Fig. 9. Percentage of additive consumed during irradiation of the impregnated bleached PSGWP with the 400 W mercury lamp: □, HBTE 2% odp; △, DSH 2% odp; HBTE 2% + DSH 2% (*, HBTE; ×, DSH).

pound was kindly supplied by Ciba Geigy Ltd. (Macclesfield, UK). DSH was an Aldrich chemical. MSH was synthesized from 2-(2′-methoxy)ethoxy-1-iodoethane (4.3×10^{-2} mol) and thiourea (4.6×10^{-2} mol). The mixture of the two compounds was refluxed in ethanol (50 ml) for 4 h. The solvent was then evaporated and, to the viscous liquid obtained, sodium hydroxide (6.9×10^{-2} mol) in water (30 ml) was added. The mixture was stirred at 80 °C overnight. After neutralization with dilute hydrochloric acid and extraction with dichloromethane, the organic layer was evaporated under vacuum (water aspirator). The odorous liquid was chromatographed on silica gel (eluent, dichloromethane–ethyl ether, 1:1 v/v) and the purity was checked by gas chromatography. Yield: 90%. ^{1}H NMR (60 MHz) δ ppm (CCl_4): 1.4 (t, 1H, SH), 2.6 (m, 2H, CH_2S), 3.5 (m, 9H, OCH_2+OCH_3). IR (film) ν cm^{-1}: 2900 (C–H), 2540 (S–H), 1100 (C–O).

The action of the additives on the pulps was assessed by applying to the paper a solution (tetrahydrofuran (THF) or dichloromethane) of the compound with a syringe. After irradiation, the papers were extracted several times with a mixture of dichloromethane and methanol or THF and methanol and the solvent was evaporated to dryness. For gas chromatography analyses, before evaporation of the extraction mixture, a known quantity of docosane was added. Before injection, the residue was silylated at room temperature with a mixture of bis(trimethylsilyl)trifluoroacetamide, THF and pyridine (5:5:1, v/v/v). Both UV absorbers and thiols were titrated by gas chromatography. The non-consumption of HBTE during irradiation was confirmed by UV absorption spectroscopy on the extracted solution.

Sulfur elemental analyses on the bleached PSGWP papers after photografting of the DSH compound were performed at the Institut du Pin, Université Bordeaux 1 according to usual procedures.

4.2. Spectroscopic measurements

Solution UV absorption spectra were obtained on a Hitachi U3300 spectrometer. For the UV–visible diffuse reflectance spectra, the spectrometer was equipped with an integrating sphere (150 mm diameter).

The brightness index at 457 nm was determined on a Elrepho-Datacolor 2000 reflectometer according to ISO 2470 standard.

Fluorescence spectra were recorded on a Hitachi F4500 fluorometer with the sheet placed at 45° to the light source. Fluorescence emission was observed at 90° to the exciting light (λ_{exc} = 365, 400 and 450 nm).

4.3. Irradiation conditions

For the first study with DHBE and MSH, paper handsheets were irradiated both at low intensity with four 18 W fluorescent tubes (two black light lamps and two visible light lamps) housed in a box and at high intensity with a (Mazda 400 W) medium pressure mercury lamp surrounded by a Pyrex filter, on a merry-go-round in order to ensure uniform irradiation. In both cases, the temperature of the set-up was maintained near 30 °C by fans.

4.4. Gas chromatography analysis

Gas chromatography analysis was performed with a Shimadzu 14A instrument equipped with a Shimadzu CR4A integrator. Gas chromatography used the split mode for injection, a flame ionization detector and a capillary column (DB1, 40 m × 0.32 mm, 1 μm film thickness) with helium flow. The oven was programmed from 180 °C (1 min) to 300 °C at 5 °C min^{-1} and then was held at 300 °C for 35 min. The injector and detector were set at 280 and 300 °C respectively.

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References

[1] P. Nolan, J.A. Van den Akker and A. Wink, *Paper Trade J., 121* (1945) 101.
[2] (a) R.S. Davidson and A. Castellan, *Paper, 10* (1991) 24. (b) A. Castellan, *L'Actualité Chimique, 7* (Suppl.) (1994) 148.
[3] C. Heitner, *ACS Symp. Ser., 531* (1993) 60.
[4] P. Fornier de Violet, A. Nourmamode, N. Colombo and A. Castellan, *Cell. Chem. Technol., 23* (1989) 535.
[5] B.J. Cole and K.V. Sarkanen, *Tappi, 72* (1987) 117.
[6] R.S. Davidson, L.A. Dunn, A. Castellan, N. Colombo, A. Nourmamode and J.H. Zhu, *J. Wood Chem. Technol., 11* (1991) 419.
[7] J. Janson and I. Forsskåhl, *Nordic Pulp Pap. Res. J., 4* (1989) 197.
[8] R.S. Davidson, L.A. Dunn, A. Castellan, N. Colombo, A. Nourmamode and J.H. Zhu, *J. Wood Chem. Technol., 11* (1991) 419.
[9] A. Castellan and R.S. Davidson, *European Community Rep., EUR 14011*, EEC, 1992, p. 121.

[10] C. Noutary, A. Castellan and R.S. Davidson, *J. Photochem. Photobiol. A: Chem.*, *84* (1994) 317.

[11] (a) R.S. Davidson, L. Dunn, A. Castellan and A. Nourmamode, *J. Photochem. Photobiol. A: Chem.*, *86* (1995) 275. (b) A. Castellan, C. Noutary and R.S. Davidson, *J. Photochem. Photobiol. A: Chem.*, *84* (1994) 311.

[12] C. Jaeger, A. Nourmamode and A. Castellan, *Holzforschung*, *47* (1993) 375.

[13] D.Y. Lee and M. Sumimoto, *Holzforschung*, *45* (Suppl.) (1991) 15.

[14] X. Pan and A.J. Ragauskas, *J. Wood Chem. Technol.*, *15* (1995) 135; *J. Pulp Paper Sci.*, *21* (1995) J25.

[15] (a) A. Castellan and R.S. Davidson, *J. Photochem. Photobiol. A: Chem.*, *78* (1994) 275. (b) A. Castellan, H. Choudhury, R.S. Davidson and S. Grelier, *J. Photochem. Photobiol. A: Chem.*, *81* (1994) 117; *81* (1994) 123. (c) R.S. Davidson, L. Dunn, A. Castellan and A. Nourmamode, *J. Photochem. Photobiol. A: Chem.*, *58* (1991) 349.

[16] J. Catalan, P. Perez, F. Fabero, J.F.K. Wilshire, R.M. Claramunt and J. Elguero, *J. Am. Chem. Soc.*, *114* (1992) 964.

[17] J. Catalan, F. Fabero, M.S. Guijarro, R.M. Claramunt, M.D. Santa Maria, M.C. Foces-Foces, F.H. Cano, J. Elguero and R. Sastre, *J. Am. Chem. Soc.*, *112* (1990) 747.

[18] J. Catalan and J.C. Del Valle, *J. Am. Chem. Soc.*, *115* (1993) 4321.

[19] C.M. Carr and I.H. Leaver, *J. Appl. Polym. Sci.*, *33* (1987) 2087.