

# Attempts to photostabilize paper made from high-yield pulp by application of UV screens and control of pH

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## Abstract

Paper made from bleached chemithermomechanical pulp (CTMP) was treated with UV absorbers, e.g. 2,4-dihydroxybenzophenone and a 2-(2-hydroxyphenyl)benzotriazole derivative (Tinuvin 1130) to reduce the tendency of the paper to undergo photoyellowing. Whilst some of the UV absorbers offer some protection, their effect can be enhanced by use in conjunction with a reducing agent (sodium hypophosphite) and by lowering the pH of the paper by application of potassium dihydrogen phosphate. The best effect was obtained by using Tinuvin 1130 in combination with both a reducing agent and potassium dihydrogen phosphate. The use of hindered phenols in both the presence and absence of thiols offered little protection to the paper.

**Keywords:** Photostabilize; High-yield pulp; UV screens; pH

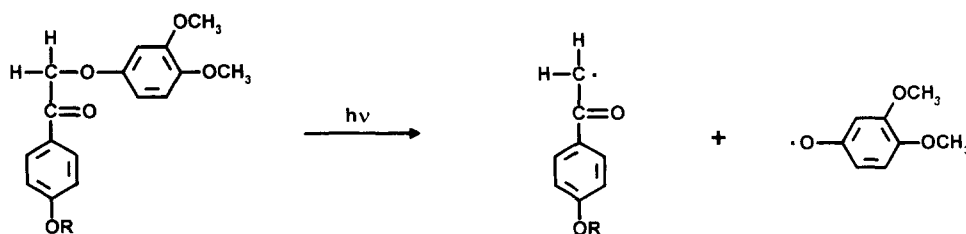
## 1. Introduction

Papers made from high-yield pulps exhibit intense colour reversion when exposed to daylight. The lignin content appears to be responsible for most of the observed effect [1]. Shorter wavelengths (less than 400 nm) cause the papers to yellow, whereas longer wavelengths cause bleaching [2]. The origin of the formation of coloured species has been the subject of much research. Lignin contains free carbonyl groups, including  $\beta$ -O-4 residues [3] and quinones [4]. On irradiation, the  $\beta$ -O-4 residues undergo rapid scission from the excited singlet and triplet states generating phenoxy radicals [5] (Scheme 1). The reduction of  $\beta$ -O-4 residues

gives ketyl radicals which can also be generated in other ways, and these also fragment to give phenoxy radicals [6].

Phenoxy radicals react with both ground state oxygen and peroxy radicals to give a variety of coloured oxidation products which include quinones [4a,7]. Phenoxy radicals can also be generated thermally and photochemically from phenols both in their neutral and ionized forms [8]. Another source of phenoxy radicals is undoubtedly the photoreaction of quinones with phenols [9] with the possibility of charge transfer complexes as intermediates [10].

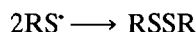
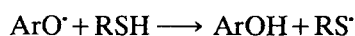
Given that phenoxy radicals play a crucial role in the yellowing process, we have attempted to mitigate their effect by reducing their efficiency of photogeneration by application of UV screens and by adjusting



Scheme 1.

the pH of the paper, so that they are only present in their unionized forms. We have also applied reducing agents to the paper with the aim of converting the phenoxyl radicals to phenoxide ions and of reducing any hydroperoxides to harmless products.

Another classical method which has been used previously to retard oxidative degradation has been to include hindered phenols, which act as chain breakers, in formulations [11]. Such compounds have been applied to paper in both the presence and absence of thiols with the latter serving to regenerate phenols from phenoxyl radicals generated either from the lignin or the hindered phenols.



## 2. Experimental details

### 2.1. Materials

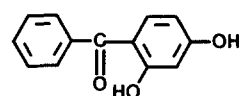
The papers used in the experiments described in Tables 1–5 (see later) were made from stoneground wood pulp and those described in Figs. 1–7 (see later) were made from an industrial bleached chemithermomechanical pulp (CTMP). Both pulps were kindly provided by Dr D. Lachenal (Centre Technique du Papier, Grenoble). Reagents, unless otherwise stated, were supplied by Aldrich Chemical Company and were used without further purification. CL Bafast W (2-(2'-hydroxy-3'-tert-butylbenzene-5'-sulphonic acid)benzotriazole) was kindly supplied by the International Wool Secretariat (Ilkley, UK). Tinuvin 1130 (polyethylene glycol molecular weight (MW) 300) ester of 3-[(2'-benzotriazinyl)-4'-hydroxy-5'-tert-butylphenyl]propionic acid and Tinuvin 326 (2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl)benzotriazole) were kindly supplied by Ciba Geigy Ltd. (Macclesfield, UK). Rongalit C (sodium formaldehyde sulphonylate was a sample kindly supplied by BASF (Cheshire, UK) (see Scheme 2 for formulae).

### 2.2. Irradiation conditions

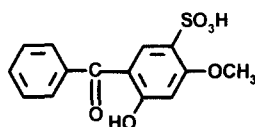
For the results reported in Tables 1–3 (see later), the illumination conditions described in an earlier publication were used [12]. The results shown in the figures were obtained using another previously described system which employs a medium-pressure mercury lamp surrounded by a Pyrex filter [13].

### 2.3. Colour measurement

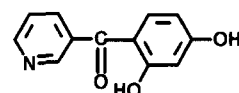
The brightness indices of the paper samples were determined using a Zeiss Elrepho 2000 reflectometer operating at 457 nm.



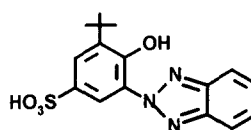
DHB



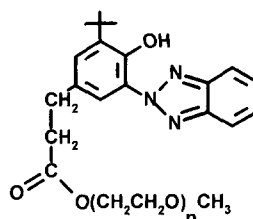
UVINOL MS40



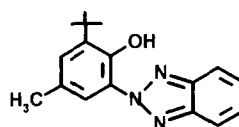
DHBP



CL Bafast W



Tinuvin 1130



Tinuvin 326

Scheme 2. Formulae of the UV absorbers used in this study.

### 2.4. Application of reagents to paper

For reagents that were insoluble in water, ethanolic solutions were applied to preweighed paper samples by means of a syringe. The papers were dried and reweighed. A similar procedure was adopted for the application of water-soluble reagents.

### 2.5. Synthesis of 3-(2',4'-dihydroxybenzoyl)pyridine (DHBP)

This compound was obtained by reacting the acid chloride of nicotinic acid and resorcinol in the presence

of aluminium(III) chloride. Anhydrous aluminium(III) chloride (8 g) was added with stirring to nitrobenzene (100 ml) at room temperature. After 20 min, resorcinol (6.55 g) was added. The suspension was stirred and then heated to 80 °C. The acid chloride of nicotinic acid (11 g) was added dropwise to the mixture over a period of 1 h. After 3 h, aqueous dilute hydrochloric acid (2 M, 100 ml) was added. The nitrobenzene layer was washed with water, dried and the solvent was evaporated to give the crude product as an oil. The product was purified by column chromatography on silica (eluent, diethyl ether–methylene chloride (3:7, v/v) to give the product (8.9 g), melting point. (m.p.) 196 °C (190 °C [14]). Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) ( $\text{CD}_3\text{COCD}_3$ )  $\delta$ : 6.25 (m, 3H), 7.0–7.85 (m, 4H). IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3600–3100, 2900, 1580, 1440, 1400, 1330, 1250, 1110, 1040, 1020, 910, 830, 700. Mass spectrum (MS): 215 ( $\text{M}^+$ , 100%). UV (methanol)  $\lambda_{\text{max}}$ : 331 nm ( $\epsilon_{\text{max}}$ : 9340 l mol $^{-1}$  cm $^{-1}$ ).

### 3. Results

Many synthetic polymers can be protected from photodegradation by the use of hindered phenols, with the performance of the latter being improved by the addition of thiols [11]. A number of hindered phenols in the presence and absence of thiols were applied to paper and the papers were exposed to simulated sunlight. Following irradiation, the brightness index of the papers was measured (Table 1). The thiol compounds improved the performance of the phenols, but there were no cases where the stabilization could be considered as effective.

Attention was therefore turned to the use of UV screens. Compounds based on 2-hydroxybenzophenone (e.g. 2,4-dihydroxybenzophenone, 2-methoxy-4-hydroxy-5-benzoylbenzenesulphonic acid and 3-(2',4'-dihydroxybenzoyl)pyridine) were applied and tested in a similar fashion to the hindered phenols (Table 2). Another class of UV screen is based on the benzotriazole nucleus. Two such compounds were tested. The polyethylene oxide ester of 3-[(2"-benzotriazinyl)-4'-hydroxy-5'-tert-butylphenyl]propionic acid, because of its limited solubility in common solvents, was applied to the paper dissolved in butylcarbitol (2-(2-butoxyethoxy)ethanol). From Table 2, it can be seen that good stabilization was achieved. To check that this stabilization was produced by the benzotriazole nucleus and not by the polyethylene glycol (a known stabilizer of paper [15]) or butylcarbitol, polyethylene and polypropylene glycols and butylcarbitol were applied to paper and the papers were irradiated (Table 3). The influence of the glycols on the performance of the UV screens was also checked, e.g. CL Bafast W (Table 2). Since all the tests were carried out using simulated daylight, it was thought wise to check the performance of the best material (Tinuvin 1130) in sunlight (Table 4). Since reducing agents are known to affect the stabilization of paper [12], Tinuvin 1130 was also tested in the presence of Rongalit C (sodium formaldehyde sulphonylate) and sodium hypophosphite (Table 4). From Tables 2–4, it can be seen that the loading of the UV screens and reducing agents is high, and if such materials are to be of any practical use they would have to be used at much lower loadings.

A factor which undoubtedly affects the photolability of lignin is the pH of the paper, with a high pH leading

Table 1  
Effect of hindered phenols on the retardation of the photoyellowing of paper containing lignin

Material applied	% owp <sup>a</sup>	Brightness index after 8 h irradiation	Brightness index after 24 h irradiation
4-Methoxy-2,6-diphenylphenol	4.6	48.8	38.1
4-Methoxy-2,6-diphenylphenol + <i>n</i> -butylthioglycolic acid (1:1 w/w mixture)	8.6	56.9	45.0
4-Methoxy-2,6-diphenylphenol + dimethyl-3,3'-dithiopropionate (1:1 w/w mixture)	3.4	55.2	41.4
2,6-Diphenyl-4-stearyloxyphenol	4.4	60.4	47.2
2,6-Diphenyl-4-stearyloxyphenol + <i>n</i> -butylthioglycolic acid (1:1 w/w mixture)	9.1	61.6	48.1
2,6-Diphenyl-4-stearyloxyphenol + dimethyl-3,3'-dithiopropionate (1:1 w/w mixture)	3.1	62.5	54.1
Control		56.9	46.3

<sup>a</sup>owp, on the weight of paper.

Table 2

Effect of additives in preventing the photoyellowing of papers made from high-yield pulp

Entry	Material applied	% owp	Brightness index after 8 h irradiation	Brightness index after 24 h irradiation
1	2,4-Dihydroxybenzophenone (DBH)	6.0	67.1	61.2
2	DHB + polyethylene glycol (MW 300 (1:1 w/w mixture)	5.4	64.7	57.4
3	DHB + polypropylene glycol (MW 425) (1:1 w/w mixture)	3.7	66.3	56.7
4	2-Methoxy-4-hydroxy-5-benzoylbenzenesulphonic acid (Uvinol MS 40)	8.2	64.3	54
5	3-(2',4'-Dihydroxybenzoyl)pyridine (DHBP)	5.1	62.7	55.6
6	(2-(2'-Hydroxy-3'-tert-butylbenzene-5'-sulphonic acid)benzotriazole (CL Bafast W)	9.7	69.8	67.2
		4.4	65	55.4
7	(2-(2'-Hydroxy-3'-tert-butyl-5'-methylphenyl)benzotriazole (Tinuvin 326)	3.5	59.3	48.8
8	Polyethylene glycol (MW 300) + CL Bafast W (1:1 w/w mixture)	6.0	64.2	54.7
9	Polypropylene glycol (MW 425) + CL Bafast W (1:1 w/w mixture)	3.4	65.7	54.7
10	3-[2''-Benzotriazinyl]-4'-hydroxy-5'-tert-butylphenyl]propionic acid (Tinuvin 1130, Tin 1130)	4.2	65	57.5
11	Tin 1130 + 9.5% butylcarbitol (2-(2'-butoxyethoxy)ethanol)	13.8 <sup>a</sup>	71	65.5
12	Tin 1130 + 9.5% butylcarbitol	11.9 <sup>a</sup>	73	64
13	Tin 1130 + 9.5% butylcarbitol	27.7 <sup>a</sup>	67.6	67.2
14	Tin 1130 + 9.5% butylcarbitol	6.0	73.7	60.5
15	Tin 1130 + 2% butylcarbitol	4.7	71.5	65.2
16	Tin 1130 + 2% butylcarbitol	10.9	72.8	66.7
17	Tin 1130 + Rongalit C (1:1 w/w mixture)	5.8	72	64
18	Tin 1130 + sodium hypophosphite (1:1 w/w mixture)	5.1	69.0	61.9
19	Control		56.9	46.3

<sup>a</sup>These values are far higher than the calculated values and may indicate substantial water absorption or incorporation of butylcarbitol into the paper.

Table 3

Effect of added ethers on the photoyellowing of paper containing lignin

Material applied	% owp	Brightness index after 8 h irradiation	Brightness index after 24 h irradiation
Polyethylene glycol (MW 300)	7.2	61.1	49.7
Polyethylene glycol (MW 3400)	9.1	60.5	49.5
Polypropylene glycol (MW 425)	6.9	61.1	54.2
Butylcarbitol	36.5	66.5	59
Control		56.9	46.3

to the formation of phenoxide anions which are readily oxidized by atmospheric oxygen to give phenoxy radicals, which may then undergo coupling or further oxidation to give quinones.

Various phosphates were therefore applied to the paper to see if they led to an increase in photostability (Table 5). The best result was obtained with potassium

dihydrogen phosphate. The sodium salt behaves in a similar fashion and paper to which this material had been applied was subjected to a more severe weathering test (Fig. 1). Using this test method, the efficiency of 2,4-dihydroxybenzophenone (DHB) alone, in the presence of the hypophosphite and sodium dihydrogen phosphate was ascertained (Fig. 2). 3-(2',4'-Dihydrox-

Table 4

Effect of UV screens and reducing agents on paper containing lignin when exposed to direct and indirect sunlight

Material applied	% owp	Brightness index 1 week direct sunlight	Brightness index 1 week indirect sunlight <sup>b</sup>	Brightness index 2 weeks direct sunlight	Brightness index 2 weeks indirect sunlight <sup>b</sup>
Tin 1130+3% butylcarbitol	14.8	70.6	71.0	63.5	71
Tin 1130	4.3	69.5	74.5	64.3	74.4
Tin 1130+Rongalit C (1:1 w/w mixture)	7.2	74.6	77.5	68.0	78.0
Tin 1130+sodium hypophosphite (1:1 w/w mixture)	6.4	69.8	75.5	63.5	74.9
Control <sup>a</sup>		56.9	74	50.7	74.0

<sup>a</sup>Before irradiation the brightness index of the control was 75.0.<sup>b</sup>Exposed to north light, i.e. the paper was never exposed directly to the sun.

Table 5

Effect of pH on the photoyellowing of CTMP<sup>a</sup>

Reagent	pH of solution	Brightness index after 8 h irradiation	Brightness index after 24 h irradiation
Disodium hydrogen phosphate	≈ 9	57.8	51.0
Potassium dihydrogen phosphate	≈ 7	62.7	58.7
Sodium dihydrogen phosphate	≈ 7	59.7	51
Formic acid	≈ 3	62.9	48.6 <sup>b</sup>
Calcium phosphate (Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O)	≈ 1	55.5	47.3

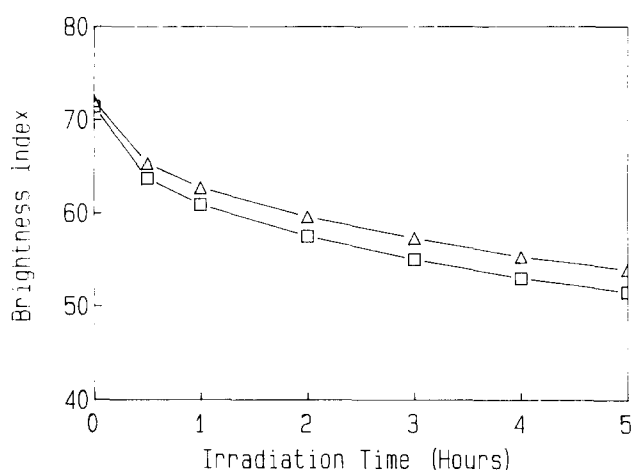
<sup>a</sup>Solutions (5 ml, ≈0.15 mol l<sup>-1</sup>) were applied to paper (0.6–0.7 g) and then dried prior to irradiation.<sup>b</sup>We assume that this low value is due to some of the formic acid evaporating from the paper during this longer irradiation period.

Fig. 1. Photoyellowing of softwood bleached high-yield pulp (CTMP): Δ, impregnated with sodium dihydrogen phosphate (2%); □, control.

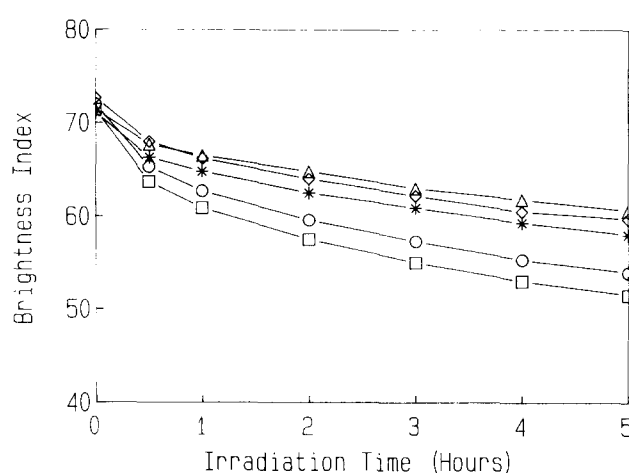


Fig. 2. Photoyellowing of softwood bleached high-yield pulp (CTMP): Δ, impregnated with DHB (2%); ○, sodium hypophosphite (2%); \*, DHB (1%) + sodium hypophosphite (1%); ◇, DHB (1%) + sodium hypophosphite (1%) + sodium dihydrogen phosphate (2%); □, control.

ybenzoyl)pyridine was tested in a similar way and in this case a reduction in pH had a deleterious effect (Fig. 3). 2,4-Dihydroxybenzophenone and Tinuvin 1130 at a loading of 2% led to a similar degree of stabilization (Fig. 4) and a similar result was obtained when the two UV screens were used at the 0.5% level in the presence of 1% sodium dihydrogen phosphate (Fig. 5). The performance of Tinuvin 1130 was improved by the

presence of sodium hypophosphite (Fig. 6) and sodium dihydrogen phosphate (Fig. 7).

#### 4. Discussion

The application of hindered phenols in the presence and absence of thiols failed to alleviate the photo-

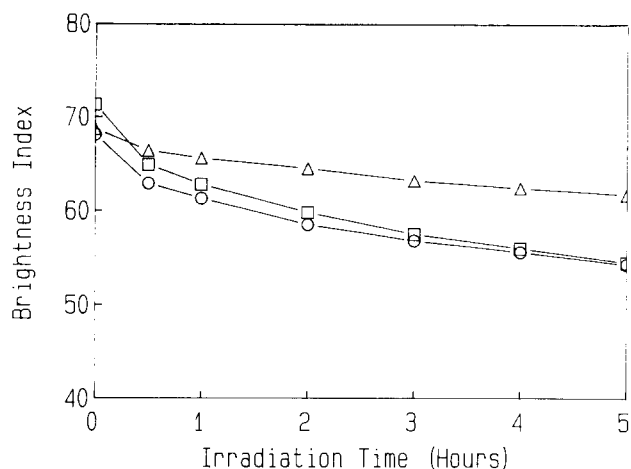


Fig. 3. Photoyellowing of softwood bleached high-yield pulp (CTMP) impregnated with DHP (2%): Δ, neutral pH; ○, pH ≈ 3.5; □, control.

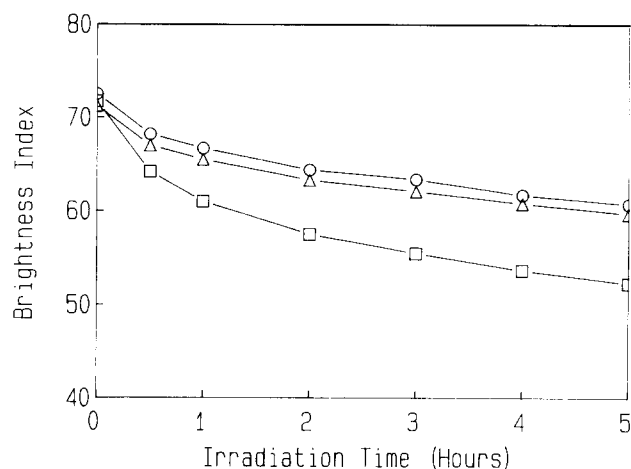


Fig. 6. Photoyellowing of softwood bleached high-yield pulp (CTMP): Δ, impregnated with Tin 1130 (2%); ○, Tin 1130 (1%)+sodium hypophosphite (1%); □, control.

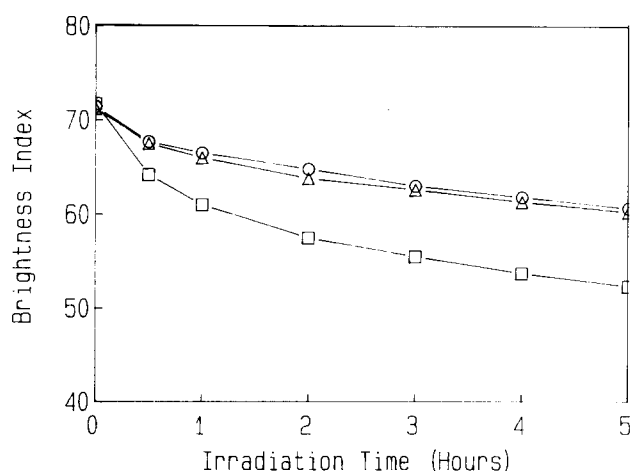


Fig. 4. Photoyellowing of softwood bleached high-yield pulp (CTMP): Δ, impregnated with Tin 1130 (2%); ○, DHB (2%); □, control.

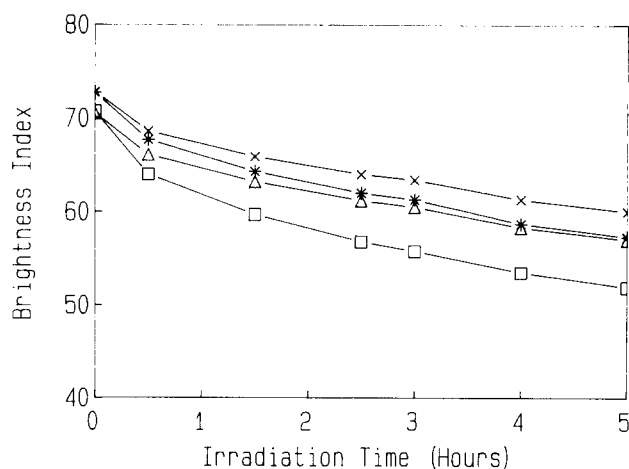


Fig. 7. Photoyellowing of softwood bleached high-yield pulp (CTMP): Δ, impregnated with Tin 1130 (1%); \*, Tin 1130 (0.5%)+sodium dihydrogen phosphate (1%); ×, Tin 1130 (1%)+sodium dihydrogen phosphate (1%); □, control.

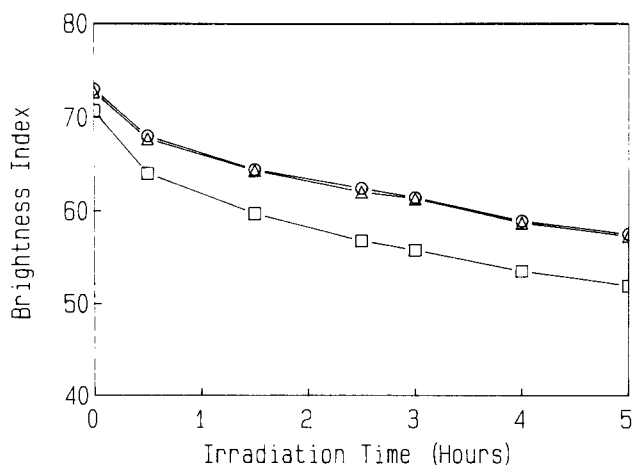


Fig. 5. Photoyellowing of softwood bleached high-yield pulp (CTMP): Δ, impregnated with Tin 1130 (0.5%)+sodium dihydrogen phosphate (1%); ○, DHB (0.5%)+sodium dihydrogen phosphate (1%); □, control.

yellowing of paper (Table 1). The addition of thiols did improve the performance of the phenols, but not to a satisfactory extent. It is probable that the phenols undergo oxidative degradation in much the same way as the phenolic groups in lignin. This degradation may be due to ionization of the phenols to give phenolate ions or their reaction with quinone residues in the lignin.

Other phenols which offer protection to polymers are the UV screens based on 2-hydroxybenzophenone and 2-(2'-hydroxyphenyl)benzotriazole. From Table 2 (entry 1), it can be seen that 2,4-dihydroxybenzophenone affords some protection to the paper when used at a fairly high loading (6% on the weight of paper, owp). When applied in the presence of polyethylene glycol and polypropylene glycol (entries 2 and 3 respectively), protection at lower levels of application of the UV screen can be obtained. From Table 3, which shows

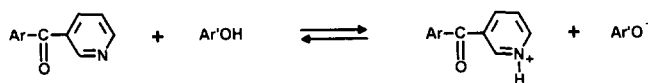
that these glycols when applied at very high loading afford little protection, it can be concluded that it is the dihydroxybenzophenone which affords the real protection. It seems that the glycols improve the efficiency of dihydroxybenzophenone.

The two other hydroxybenzophenones tested (Table 2, entries 4 and 5) showed no improvement in performance compared with dihydroxybenzophenone. It was hoped that the pyridine derivative (entry 5) would show an improvement due to the basic pyridine group which should lead to the location of the absorber in the lignin-rich areas via interaction with the phenoxyl groups (Scheme 3). This beneficial effect may have been offset by an increase in the concentration of phenolate ions in the paper. From Fig. 3 it can be seen that an increase in the acidity of the paper led to a disastrous performance of this UV screen, which could have been caused via ionization of the phenolic hydroxyl groups present in the UV screen (Scheme 4).

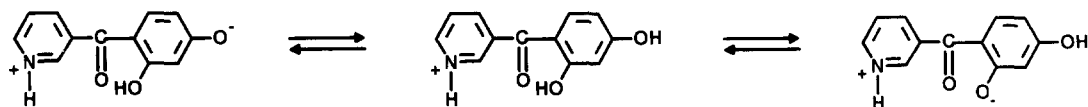
The use of some 2-hydroxyphenylbenzotriazoles proved disappointing (Table 2, entries 6 and 7), and this agrees with a previously reported result [16]. Once again it was found that the use of a UV screen mixed with polyethyleneglycol or polypropyleneglycol led to some improvement in performance (Table 2, entries 8 and 9), thereby enabling the loading of the triazole to be reduced without sacrificing the stabilization effect. Tinuvin 1130 (Table 2, entries 10–16) gave some positive results (e.g. entry 10). The concentration of the 2-hydroxyphenylbenzotriazole group in this compound is (as determined by UV spectroscopy) around 50% which suggests that this group is a highly effective UV screen. Clearly the polyethylene oxide chain present in the absorber increases the efficiency of the UV absorber. Thus from entry 10, a 2% owp concentration of the 2-hydroxyphenylbenzotriazole group gives slightly better stabilization than the benzotriazole applied at 4.4% owp (entry 6) and the triazole applied at 3.5% owp (entry 7). Polyethylene and polypropylene glycol do undoubtedly afford some protection (Table 3), but their effect on the performance of Tinuvin 1130 and 2,4-dihydroxybenzophenone (Table 2, entries 3 and 4) suggests that they are aiding the action of the UV screens. We suggest that the compatibility of these polymers with the UV screens and with water aids the

transport of the UV screens within the paper. This will ensure that the UV screens are evenly distributed in the paper. It is also possible that the UV screens act as radical scavengers since they are phenols and, in the case of the 2-hydroxyphenylbenzotriazoles, hindered phenols. If these compounds act in this way, aiding their transport within the paper will help their migration to sites where radical formation has occurred leading to damage limitation. Such action would lead to the consumption of the UV screens. Therefore it is essential to be able to regenerate the UV screen. This can be done by incorporating a reducing agent into the paper, and this was found to be highly effective (Table 2, entries 17 and 18). Gratifyingly, these beneficial effects were observed when Tinuvin 1130 was tested in sunlight (Table 4).

Having established that certain UV screens reduced the photoyellowing of paper and that further benefits could be obtained by increasing the mobility of the screens in the paper and by incorporating reducing agents, we examined the possibility of increasing the stability of the paper and UV screens by a change in pH. Undoubtedly one of the main causes of the photoinstability of lignin is due to the ionization of phenolic groups. When these groups are blocked by methylation, the paper is stabilized to a measurable extent, but because of the heterogeneous nature of paper and pulp, such chemical treatments are difficult to carry out. We therefore sought to stabilize the phenol groups by lowering the pH of the paper (the paper employed has a pH of 7). Table 5 shows that the use of potassium dihydrogen phosphate is advantageous. Further detailed experiments were carried out with 2,4-dihydroxybenzophenone and Tinuvin 1130 in the presence or absence of reducing agents and dihydrogen phosphate in the hope of reducing the amount of UV screen required to achieve satisfactory stabilization. Fig. 1 shows that the application of sodium dihydrogen phosphate alone reduces the rate of photoyellowing to a measurable degree and confirms the conclusion reached from the results shown in Table 5. Fig. 2 shows that the hypophosphite affords some stabilization. Furthermore, by using 2,4-dihydroxybenzophenone in combination with phosphite and phosphate, stabilization can be achieved to a similar degree at half the concentration of the UV screen when used alone. Fig. 4 shows that dihydroxybenzophenone and Tinuvin, when used at similar concentration, afford the same degree of protection. This result is quite impressive when we consider the UV-visible absorption properties of the two com-



Scheme 3.



Scheme 4.

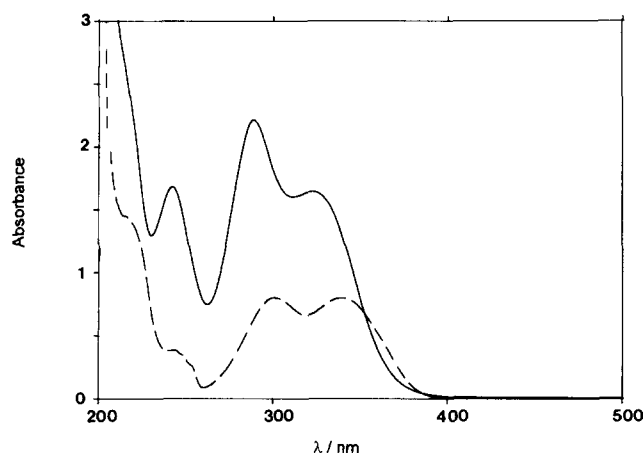


Fig. 8. Comparative absorption spectra of Tinuvin 1130 (---) and DHB (—) on a weight basis (1.85 mg in 50 ml of methanol).

pounds (Fig. 8). Tinuvin 1130 is a much weaker absorber than the benzophenone, but it does absorb slightly further into the red. It is perhaps this extra absorption that increases the efficiency of Tinuvin. The use of these two screens at the same loading and in the presence of the same amount of sodium dihydrogen phosphate leads to a similar degree of stabilization (Fig. 5). The beneficial effect of using hypophosphite with Tinuvin is demonstrated by the results shown in Fig. 6, where it can be seen that stabilization is achieved with a reduced level of loading of the UV screen. In Fig. 7 the beneficial effect of adding the phosphate can be seen and further improvement is realized when this is used in conjunction with a reducing agent.

## 5. Conclusions

By reducing the tendency of the phenolic groups in lignin to ionize and by the coapplication of UV screens and reducing agents, a measurable level of protection to paper can be obtained. These effects are also aided by the presence of groups and additives which help the even distribution and mobility of the UV screen within the paper.

## References

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