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The action of phloroglucinol in the presence of hydrochloric acid on photoaged, totally-chlorine-free, bleached chemical pulps

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Abstract

UV-Vis diffuse reflectance spectrometry has been used to monitor the reaction of phloroglucinol (in the presence of hydrochloric acid) with totally-chlorine-free (TCF) bleached softwood bisulfite chemical pulps. Pulps (1–4) bleached via various sequences, which include ozone and hydrogen peroxide processes, were studied. The unirradiated pulps show a very small absorption band with a maximum at about 460 nm when the phloroglucinol test was performed. Pulp 3, which was bleached only with peroxide and contains the higher amount of lignin (Kappa number, 4), displays, after ageing with UV light and after the phloroglucinol test, a broad absorption band with a maximum at 560 nm, similar in behaviour to photodiscoloured lignin-rich pulps. Pulp 2, bleached by one ozone stage followed by a peroxide stage (Kappa number, 1.7) displays the same trend (broad band centred at 560 nm) although the lignin content was lower. This indicates that the phloroglucinol test is very sensitive to oxidized lignin. Pulps 1 and 4, which were fully bleached (Kappa number, 0.5 or less), still present a narrow absorption band around 555 nm after irradiation with UV light. The origin of this band remains uncertain. *ortho*-Quinone models adsorbed on cellulose paper appear to be insensitive to the phloroglucinol test, in contrast to 2-methoxy-*para*-quinone and coniferaldehyde. Such chromophores are probably formed by UV irradiation of the TCF pulps.

Keywords: Phloroglucinol; Totally-chlorine-free bleaching; Photoaging; UV-Vis diffuse reflectance spectroscopy

1. Introduction

White chemical pulps used in the manufacture of high-quality writing and printing papers have been conventionally bleached with elemental chlorine. Nowadays, the bleaching sequences generally accepted are elemental chlorine free (ECF) using chlorine dioxide. Nevertheless, environmental concerns have led to the development of totally-chlorine-free (TCF) bleaching sequences combining the use of oxygen, hydrogen peroxide and, more recently, ozone [1–3]. The light-induced discolouration of lignin-rich pulps, which is more intense than that of chemical pulps, has been thoroughly studied [4]. This is in contrast to TCF pulps, which display a sensitivity to light that is not very well known. In a previous study [5], it has been shown by diffuse reflectance spectroscopic and fluorescence emission measurements on softwood chemical pulps (bisulfite, maritime pine) previously bleached with TCF (using oxygen, ozone and hydrogen peroxide, or oxygen and hydrogen peroxide without ozone) or ECF (using oxygen and chlorine dioxide) sequences as a reference, that the treatment with hydrogen peroxide was a source of light sensitivity, reminiscent of the behaviour of lignin-rich pulps. Ozone appeared to be a very good bleaching agent, even if this leads to some slight thermal instability. In other respects, a colour test for lignin based on phloroglucinol in the presence of acid (Wiesner reaction) was used to study the photodegradation of high-yield pulps [6]. The irradiated papers display, after treatment with phloroglucinol (PG) and hydrochloric acid, a strong absorption at 560 nm attributable to coniferaldehyde residues. Also, using morphological fractions of poplar, it was shown that such a colour test was not quantitative [6]. We exploited the knowledge that the Wiesner test is very sensitive, using it to characterize some chromophores formed during the photodegradation of bisulfite maritime pine TCF pulps. Reference models related to quinoid compounds and coniferaldehyde were used in this study.

2. Experimental

The bleaching sequences of pulps 1–4, the photoageing conditions of the four papers and the physical methods (dif-

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fuse reflectance spectroscopy and Kubelka–Munk calculations) have been reported in Ref. [5]. The application conditions of the phloroglucinol stain on the TCF pulp were the same as previously used on stone-ground pulp [6]. The 2-methoxy-*p*-quinone (MPBQ) was prepared according to Ref. [7]. The synthesis of the *o*-quinone BPOQ was reported in Ref. [8]. Coniferaldehyde and the *o*-quinone DtBuOQ were purchased from Aldrich. The different models dissolved in tetrahydrofuran were applied on filter paper at a concentration of about 0.5% by weight.

3. Results and discussion

The four TCF pulps previously studied by UV-Vis diffuse reflectance spectroscopy and fluorescence spectroscopy [5] were examined further. Pulp 1, after oxygen delignification, was bleached with two ozone stages and, in between, with a peroxide-reinforced oxygen sequence. The bleaching sequences used for pulp 2 were very similar to those of pulp 1, except that the last ozone stage was replaced by a peroxide sequence. Pulp 3 is typical of a peroxide- bleached TCF pulp without any ozone treatment. Pulp 4 was chosen as an example of an ECF bleached bisulfite pulp. The bleaching sequences and the lignin content (Kappa number) are reported in Table 1. Phloroglucinol in the presence of hydrochloric acid was applied to the TCF pulps 1–4 before and after light exposure (UV light: medium pressure mercury lamp, $\lambda > 300$ nm; temperature, about 30°C) in the dry state for 2, 4 and 6 h irradiation periods. Using diffuse reflectance spectroscopy, the effect on the papers, backed with white and black backgrounds, was measured. This allows the calculation of the absorption coefficient (K) and the scattering coefficient (S) according to the Kulbelka–Munk formalism [5]. The absorption coefficient versus wavelength for the pulps 1–4 are presented in Fig. 4. The scattered light response, as already observed [5], was not very sensitive to UV irradiation and is not presented.

Table 1
Bleaching sequence and lignin content of the studied pulps

Pulp	Bleaching sequence[a]	Kappa number[b]
1	OAZ(EOP)Z	0.5
2	OAZ(EOP)AP	1.7
3	(OP)A(OP)AP	4
4	OD(EO)D	<0.5

[a] O, oxygen delignification; A, acid wash; Z, ozone delignification; (EOP), alkaline extraction in the presence of oxygen and hydrogen peroxide; (EO), alkaline extraction in the presence of oxygen; (OP), hydrogen peroxide delignification in the presence of oxygen; P, hydrogen peroxide delignification; D, chlorine dioxide delignification.

[b] The content of lignin (expressed as Klason lignin (KL)) may be evaluated approximately by the formula %KL = KN × 0.15.

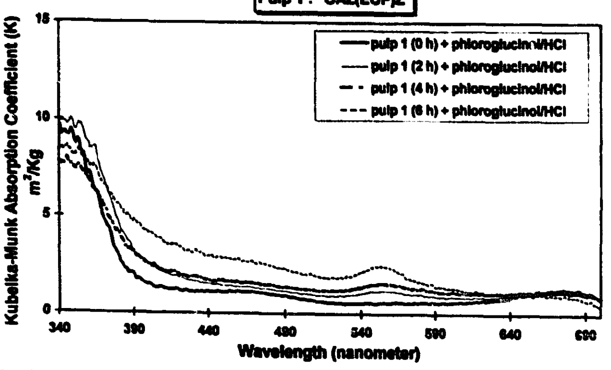


Fig. 1. Action of phloroglucinol in the presence of hydrochloric acid on pulp 1 after UV irradiation, studied by UV-Vis diffuse reflectance spectroscopy.

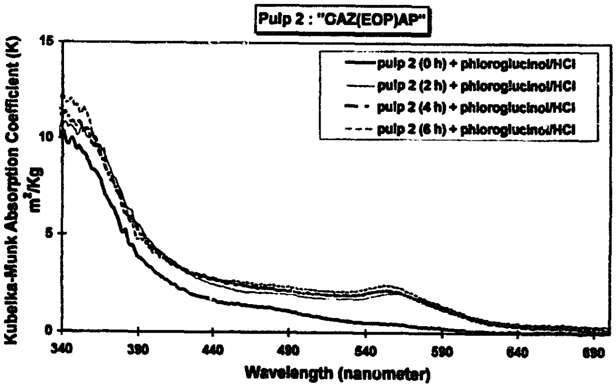


Fig. 2. Pulp 2 (see Figs. 1, 2 and 1).

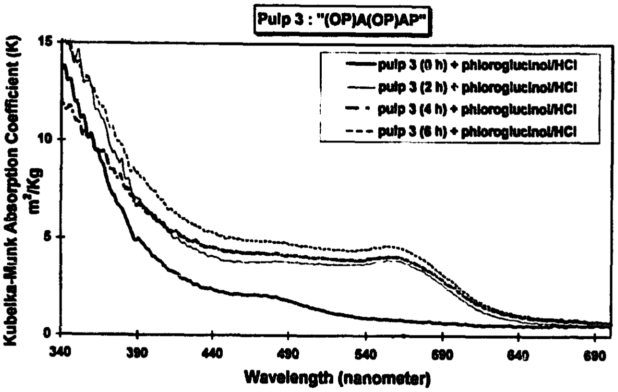


Fig. 3. Pulp 3 (see Figs. 3 and 1).

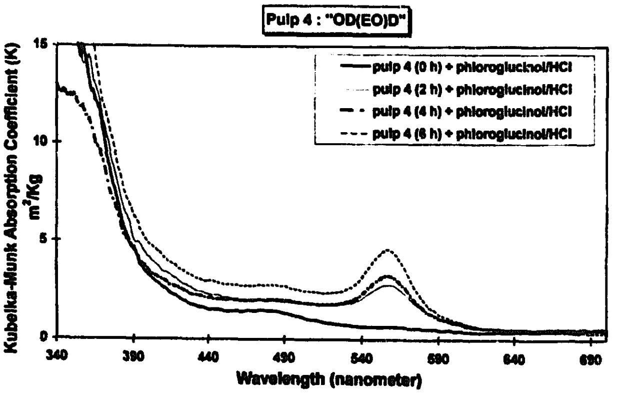
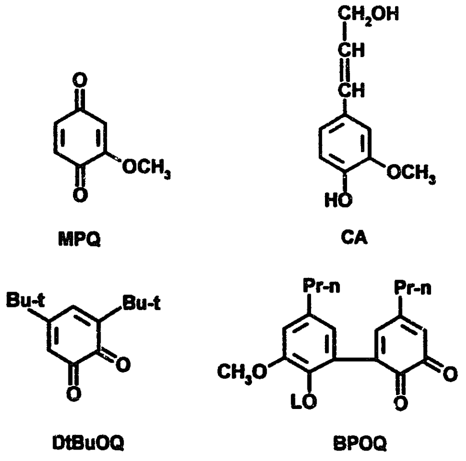


Fig. 4. Pulp 4 (see Fig. 1).

Pulp 1, bleached twice with ozone and therefore containing little lignin (Kappa number, less than 0.5), when subjected to the Wiesner test displays a very small absorption near 460 nm (Fig. 1). When the sample is subjected to UV irradiation followed by the application of acidified phloroglucinol, absorption over the spectral range studied, with a new band centred at 555 nm, is observed (Fig. 1). Similar observations are made for pulp 4, which was bleached with a conventional ECF sequence using chlorine dioxide. The intensity of the band at 555 nm observed for the irradiated sample is even more pronounced and remarkably sharp for pulp 4 (Fig. 4). The origin (lignin or polysaccharide) of this band is uncertain. Pulps 1 and 4 exhibit small peaks at 460 nm and at 475 nm, respectively, before irradiation whereas cotton and filter paper give rise to an absorption band at 450 nm [6]. The origin of these bands is unclear. Similar bands are also exhibited by pulps 2 and 3, and this suggests that they may be due to oxidation products of phloroglucinol (oxidation is likely to be rapid due to the ease of access of oxygen to the phenol since the latter is thinly spread on the surface of the fibres [6]).

Pulp 3, solely bleached with hydrogen peroxide, a reagent which is not strongly delignifying, gives a paper having a higher lignin content (0.6%) than pulps 1 and 4. This pulp does not give a strong positive response to the Wiesner test (Fig. 3). According to results obtained on sodium-borohydride-reduced stone-ground wood pulp [6], one may conclude that the residual lignin in pulp 3 contains relatively few enones such as coniferaldehyde residues. Weathering pulp 3 with UV light, followed by treatment with PG–HCl, leads to material which exhibits a broad envelope of absorption bands with a maximum at 560 nm. This absorption maximum is characteristic for samples containing lignin (Fig. 3). This result is similar to that obtained for lignin-rich bleached pulps. A similar behaviour is observed for pulp 2 but to a lesser extent (Fig. 2). This is to be expected since its lignin content (0.26%) is lower.

In order to obtain more information concerning the structures of the chromophores formed by UV irradiation of pulps 2 and 3, two *o*-quinones, DTBuOQ and BPOQ, the 2-methoxy-*p*-benzoquinone (MPQ) and coniferaldehyde (CA) (see Scheme 1) were adsorbed onto filter paper and the samples so obtained treated with the PG–HCl mixture. The 2-methoxy-*p*-quinone is very sensitive to the presence of hydrochloric acid which catalyzes the dehydrodimerization and ultimately the formation of coloured dibenzofuran-1,4-quinone [7]. For this reason, it was necessary to run some control samples. The papers impregnated with DTBuOQ and MPQ were treated with hydrochloric acid, and the diffuse reflectance spectra recorded. Since the base-weight of the filter paper was too high for correct calculations of K, the reflectance axis was converted to log $(1/R)$ which is not a true absorbance. The spectra are presented in Figs. 5–8.



Scheme 1.

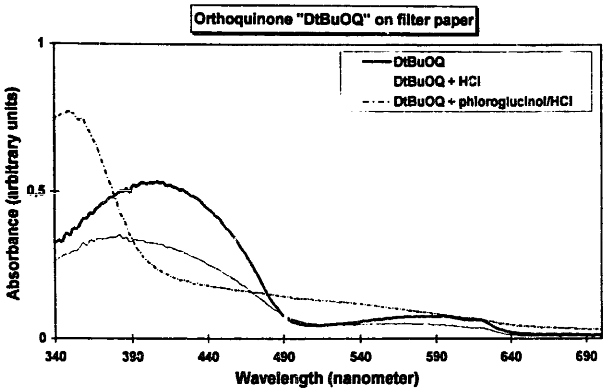


Fig. 5. Action of phloroglucinol in the presence of hydrochloric acid on DtBuOQ adsorbed on filter paper, studied by UV-Vis diffuse reflectance spectroscopy (the absorbance is log$(1/R)$, and R is the diffuse reflectance intensity normalized to $BaSO_4$).

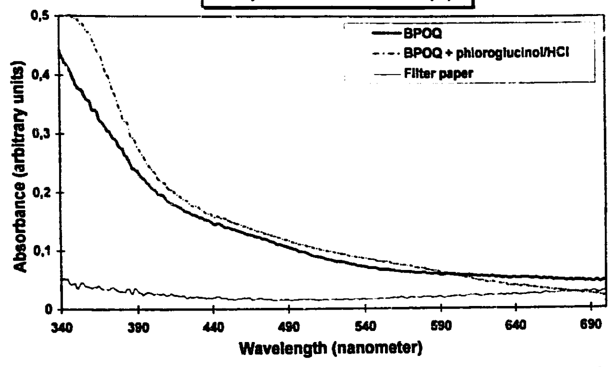


Fig. 6. Action of phloroglucinol in the presence of hydrochloric acid on BPOQ adsorbed on filter paper.

The *ortho*-quinone DtBuOQ adsorbed on filter paper exhibits the characteristic electronic absorption band of *o*-quinones at 400 nm and 600 nm, respectively, due to n,π^* and π,π^* transitions. The addition of hydrochloric acid leads to the disappearance of the quinoid structure by the formation of chlorocatechol [9]. When phloroglucinol is added in the presence of HCl, the spectrum is converted into a continuous absorption without any maximum. The same trend was observed for the quinone BPOQ although its concentration on filter paper was lower. In contrast, 2-methoxy-*p*-quinone in the presence of HCl reveals a very broad absorption band characteristic of the formation of the dehydro dimer and of the dibenzofuran-1,4-quinone [9,10]. In the presence of

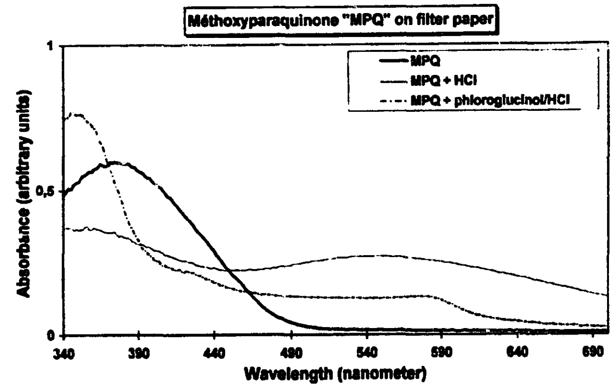


Fig. 7. Action of phloroglucinol in the presence of hydrochloric acid on MPQ adsorbed on filter paper.

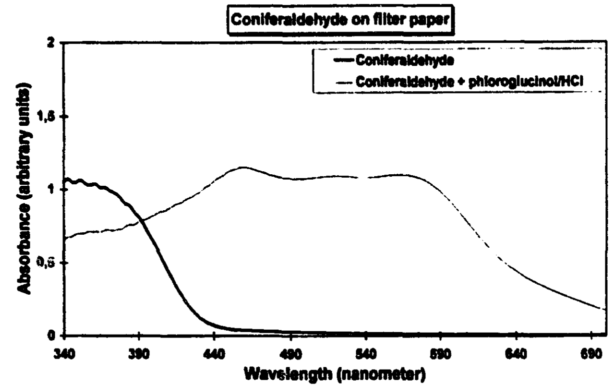


Fig. 8. Action of phloroglucinol in the presence of hydrochloric acid on CA adsorbed on filter paper.

phloroglucinol, the spectrum, which is very different, exhibits an absorption maximum at 585 nm. Coniferaldehyde on filter paper gives the usual positive test with a maximum at 575 nm and another maximum at 450 nm which is probably due to the oxidation of phloroglucinol [6].

From a comparison of the PG–HCl action on photoaged pulps 2 and 3, and on 2-methoxy-*p*-benzoquinone and coniferaldehyde, it is obvious that the maxima of the absorption bands exhibited by the different samples are not the same, the differences being 15 nm for CA and 25 nm for MPQ. Some of these differences may stem from the fact that the model compounds have been applied at a concentration that will lead to a chromophore concentration that is much higher than that found in the paper samples. Futhermore, the model compounds used in this study may not be the best due to the lack of knowledge of the true chemical structure of the residual lignin. It is quite reasonable to attribute these absorption bands to the formation of enones, e.g. coniferaldehyde residues. *p*-Quinones, unlike *o*-quinones, give a positive reaction with phloroglucinol in the presence of acid. This positive colour test for the *p*-quinones is probably due to the quinones undergoing an acid-catalyzed condensation reaction with phloroglucinol. Given that the phloroglucinol is an electron-rich aromatic compound, one might have expected it to give coloured species with both types of quinone, due to the formation of charge- transfer complexes.

Complementary experiments, based on the thioacidolysis of pulp 3, did not reveal the presence of any coniferaldehyde-like structures after photoweathering. This experiment demonstrates that the Wiesner test is sensitive and able to detect some enone (*p*-quinone and/or coniferaldehyde) structures formed after the UV irradiation of low- lignin-content bleached TCF chemical pulp.

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References

[1] J.S. Gratzl, *Papier, 41* (1987) 120.
[2] N. Liebergott, B. Van Lierop and A. Skothos, *Tappi J., 75*(1) (1992) 145.
[3] C. Chirat, M.T. Viardin and D. Lachenal, *Pap. Puu, 75* (1993) 338.
[4] (a) R.S. Davidson and A. Castellan, *Paper, 10* (1991) 24. (b) C. Heitner, ACS Symp. Ser. 531, American Chemical Society, Washington, DC, 1993, p. 2. (c) A. Castellan, *Actual. Chim., 7*(suppl.), 1994 148. (d) G.J. Leary, J. Pulp Pap. Sci., 20 (1994) J154.
[5] A Castellan, V. Trichet, J.C. Pommier, A. Siohan and S. Armagnacq, *J. Pulp Pap. Sci., 21* (1995) J291.
[6] R.S. Davidson, H. Choudhury, S. Origgi, A. Castellan, V. Trichet and G. Capretti, *J. Photochem. Photobiol. A: Chem., 91* (1995) 87.
[7] I. Forsskåhl, J. Gustafsson and A. Nyberg, Acta Chem. Scand., *35 (1981) 389.*
[8] A. Castellan, N. Colombo, A. Nourmamode, J.H. Zhu, D. Lachenal, R.S. Davidson and L. Dunn, J. Wood Chem. Technol., *10 (1990) 461.*
[9] K.T. Finley, in S. Patai (Ed.), *The Chemistry of Quinoid Compounds*, John Wiley, London, 1974, p. 877.
[10] A. Castellan, A. Nourmamode, C. Jaeger and I. Forsskåhl, ACS Symp. Ser. 531, American Chemical Society, Washington, DC, 1993, p. 60.