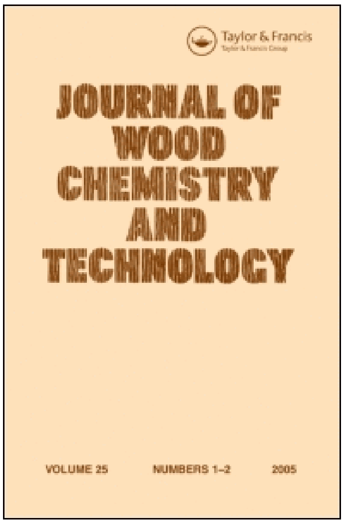

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R. S. Davidson[a]; L. A. Dunn[a]; A. Castellan[b]; N. Colombo[b]; A. Nourmamode[b]; J. H. Zhu[b]
[a] Department of Chemistry, City University, London, UK [b] Laboratoire de Photochimie Organique CNRS UA 348, Photophysique et Photochimie Moleculaire, Universite de Bordeaux I, Talence Cedex, FRANCE

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A STUDY OF THE PHOTOYELLOWING OF PAPER MADE FROM BLEACHED CTMP

R S Davidson[1] and L A Dunn[1]
A Castellan[2], N Colombo[2], A Nourmamode[2], J H Zhu[2]

[1]Department of Chemistry, City University, Northampton Square, London EC1V 0HB, UK.

[2]Laboratoire de Photochimie Organique, CNRS UA 348, Photophysique et Photochimie Moleculaire, Universite de Bordeaux I, 351 Cours de la Liberation, F 33405 Talence Cedex, FRANCE

ABSTRACT

The photoyellowing of papers produced from bleached CTMP is retarded when these papers are irradiated in aqueous solutions containing reducing agents such as Rongalit C and Blankit D. Papers impregnated with the reducing agents showed some photostability when irradiated in the dry state but not when irradiated in aqueous solution. The reducing agents present in these papers also failed to significantly retard the photoyellowing under natural lighting conditions and under simulated solar irradiation. It is concluded that the migratability of the reducing agents is important if photoprotection is to be achieved and that the latter is caused by the reagents bleaching the yellow photodegradation products as well as destroying prodegradent species such as hydroperoxides.

INTRODUCTION

Pulps containing lignin (high yield pulp, HYP) such as CTMP have a yellow-brown colour, and therefore, to enhance their utility the material is bleached[1]. Conventionally high yield pulp is bleached by the action of hydrogen peroxide in basic medium. The use of this reagent raises the spectre of groups such as the hydroperoxyl group (via hydroxyl-radical attack upon the sugar residues followed by autooxidation) and other prodegradent species being introduced into the pulp eg. quinones. If iron (II) is present, even in trace amounts, treatment with hydrogen peroxide will lead to production of hydroxyl radicals and thereby, by reaction with the benzenic ring, increase the phenolic content of the lignin[2] and also promote oxidative degradation processes. It is therefore remarkable that this reagent leads to a whitening of the pulp but this has been shown to be due in part to the peroxide generating structures which act as fluorescent whitening agents ie absorb radiation of 350-400 nm and re-emit the energy as fluorescence in the 400-450 nm region [3].

We now report upon a study of the effect of irradiating paper produced from CTMP in solutions of reducing agents and the effect of impregnating papers with reducing agents and subsequently exposing them to light. In concomitant studies[4] we showed that lignin model compounds did not photoyellow on irradiation in the presence of reducing agents [4]. Also, we have shown that irradiation of wool, which is composed of 80% protein (containing some aromatic amino acid residues), in solutions of reducing agents, led to either bleaching or retardation of the photoyellowing[5].

RESULTS

Sheets of paper formed from bleached CTMP in aqueous solutions of a variety of reducing agents were immersed and irradiated. After irradiation, the Brightness Index (BI), uv/visible absorption spectra and infrared spectra of the samples were recorded. From the BI values shown in Table 1 it can be seen that Blankit D, Rongalit C (both of which photobleach wool[5,6]) and potassium metabisulphite bleached the paper and that the other reagents retarded the photoyellowing. These effects are shown by the uv/visible spectra for paper irradiated in the presence of reducing agents (eg. Rongalit C Fig 1) in which it can be seen that there is diminished absorption between 300-500 nm. The infrared spectra showed that in general the reducing

TABLE 1

Effect of Reducing in Solutin Upon the Photoyellowing of Paper Containing Lignin

Reagent	Brightness Index Irradiation Times 8 hr	24 hr[cd]	120 hr[c]
Control (no reagent)		60.8	
Rongalit C[a]		75.8	
Blankit D[a]		76.6	45.3
Sodium hypophosphite[a]	70.5	68.3	
Thiourea dioxide[b]		71.5	
Thioglycerol[ad]	73.5	70.4	
n-Butylthioglycollic acid[ad]		61.0	
THPC Tetrkis(hydroxy-methyl) phosphonium chloride[a]		72.3	(100 hr) 65.0
Potassium metabisulphite	78.1	78.4	

a 2% solutions
b 1% solution (poor solubility of thiourea dioxide dicatated strength
c non irradiated bleached CTMP BI of 75.0
d irradiated under glass BI of 60.8

It can be seen that the beneficial effects of the reducing agents were more marked when the dry papers were irradiated. Presumably the papers examined contained in their macro structure some of the reducing agents which were able to exert a positive effect in the dry state, whereas in aqueous solution they were leached out. To corroborate these results the paper was impregnated with the reducing agents and then subjected to irradiation. The BI values of the papers so obtained are shown in Table 3.

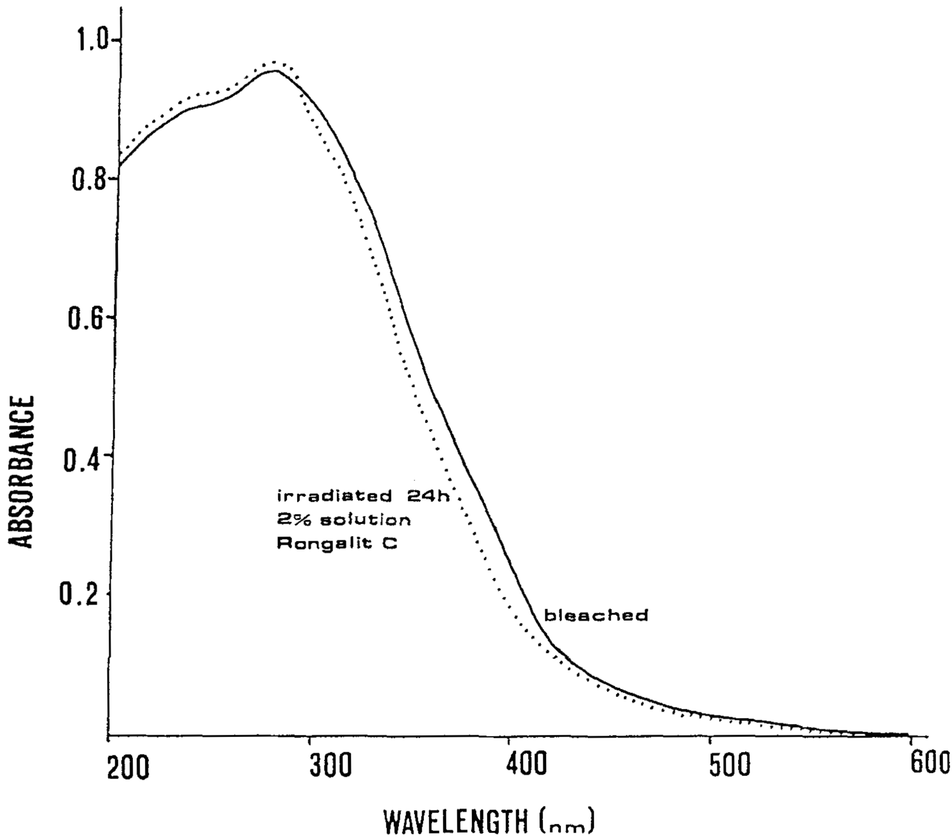


Figure 1 UV/visible diffuse reflectance of CTMP paper bleached with hydrogen peroxide, and of bleached CTMP paper following irradiation for 24 hours in a 2% solution of Rongalit C.

reagents suppressed the formation of ketonic compounds, that there was a decrease in the absorptions ascribed[7] to quinones 1660-1670 cm^{-1} (Fig 2) and that usually the formation of carboxyl groups could be observed (1700-1750 cm^{-1}).

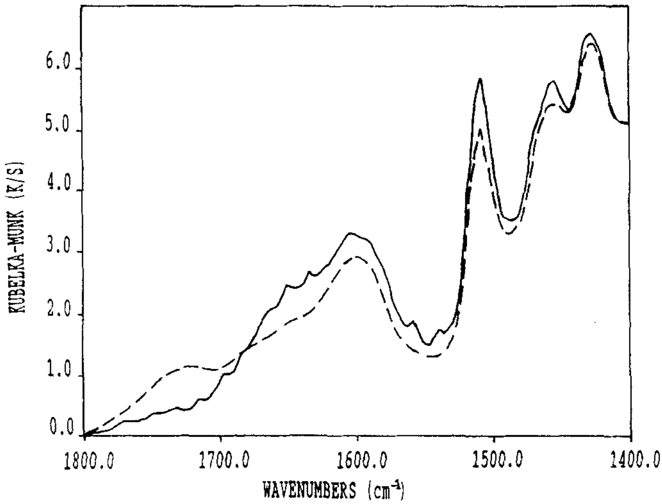


Figure 2 FTIR diffuse reflectance spectra of bleached CTMP before irradiation and after irradiation for 24 hours in a 2% solution of Rongalit C.

The papers subjected to irradiation in solutions of reducing agents for 24 hrs were subsequently irradiated in (a) water and (b) in the dry state. BI values were measured for all the samples and these are shown in Table 2.

The rate of yellowing (as measured by BI values) as a function of time was determined for a number of compounds, the results are shown in Fig 3 and 4. The extent to which the reducing agents retard the yellowing is, not surprisingly, dependent upon the amount of reducing agent applied to the paper.

TABLE 2

Brightness Index of Papers Irradiated in Solution of Reducing Agents and Then Irradiated (8 hr) Under Water and Also in the Dry State

Reagent	Brightness Index Start	Wet	Dry
Rongalit C	75.8	62.5	64.6
Blankit D	76.6	55.1	73.5 (1 hr)
Sodium hypophosphite	68.3	58.8	66.7
Thiourea dioxide	71.5	57.5	63.9
Potassium metabisulphite	78.4	62.6	60.9
Thioglycerol	70.4	62.3	67.3
n-Butylthioglycollic acid	61.0	46.5	56.6
THPC	72.3	60.9	65.2

TABLE 3

Effect of Irradiation Upon Papers in the Dry State Which Have Been Impregnated With Various Reducing Agents

Reducing Agent	%[a] owp	Brightness Index Irradiation Times 8 hr[bc]	24 hr[bd]
Control (no reagent)		56.9	46.3
Rongalit C	8.0	64.5	50.1
Sodium hypophosphite	2.9	57.3	45.5
" "	7.7	65.3	51.2
Thiourea dioxide	2.9	60.4	46.3
" "	7.7	65.3	51.2
Potassium metabisulphite	4.8	56.6	49.3
" "	7.6	58.4	49.5
Tetrakis(hydroxymethyl) phosphonium chloride	8.0	59.4	47.9
Thioglycerol	4.5	67.8	56.0
"	7.8	70.2	61.6

a = on the weight of paper
b = non irradiated bleached CTMP has BI of 75.0

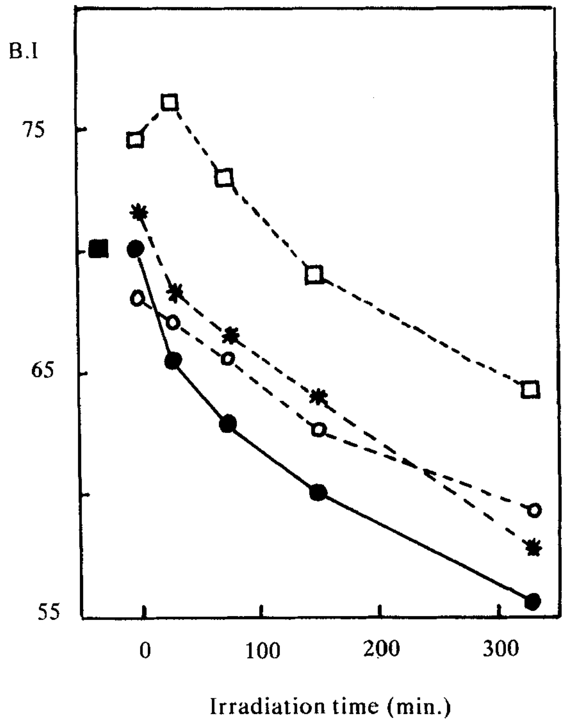


Figure 3 Change in brightness index of bleached mechanical pulp impregnated with reducing agent and irradiated in the dry state. The numbers in parenthesis are the percentages of additive relative to dry pulp.

■ non irradiated paper, ● control

□ Rongalit C (6.3%), ○ Blankit D (6%),

✱ Thiourea dioxide (6.3%).

Given that the reducing agents are able to retard the photoyellowing when the paper is in the dry state it would seem that they are transported through the paper structure via the residual water. This process is very

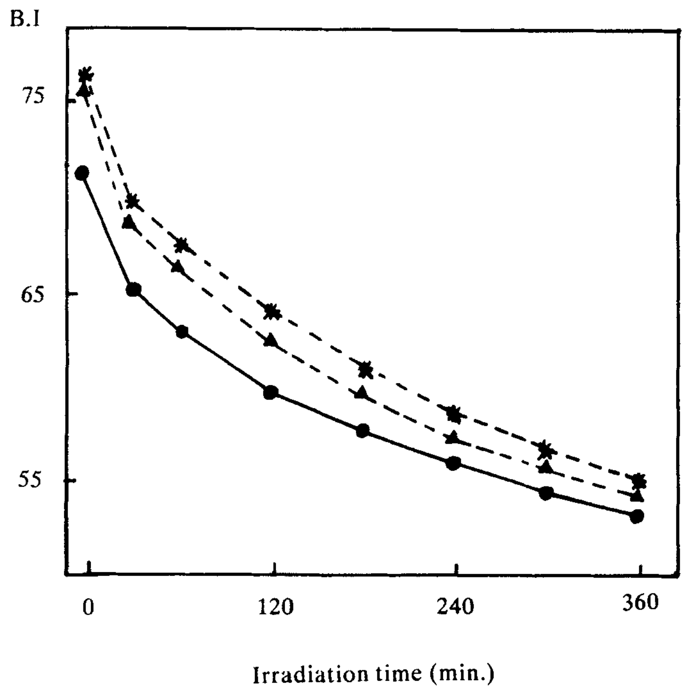


Figure 4 Change in brightness index of bleached CTMP impregnated with THPC and irradiated in the dry state. Numbers in parenthesis are the percentages of a additive relative to dry pulp.

● control, ▲ THPC (2%), ✱ THPC (6.4%).

slow and therefore as the weathering conditions are increased in severity by increasing the light intensity, the possibility arises that the initially coloured photodegradation products are further photolysed giving an increase in discolouration before the reducing agents can exert their beneficial effect.

Paper impregnated with Rongalit C and another impregnated with sodium hypophosphite was therefore exposed to daylight (far lower light intensity than in the artificial weathering conditions). Brightness Indices following the exposures were determined and are shown in Table 4.

An important finding was that paper impregnated with Rongalit C and then irradiated, turned yellow and then apparently reverted to the bleached state when kept in the dark for 2 months. Subsequently, paper produced from bleached CTMP was photo-yellowed by irradiation for 24 hours and then the resultant paper irradiated in a solution of Rongalit C for 24 hours. The paper appeared to be bleached by this post treatment and the solution became yellow in colour. Further experiments with extensively yellowed paper showed that much yellow material (ie. photodegradation products) migrated from the paper into the solution of Rongalit C. An indication that migration is important came from the finding that, on immersion in water for 24 hours, yellowed CTMP showed an increase in the brightness index on both the irradiated (3 units) and non-irradiated (2 units) faces.

TABLE 4

Effect of Direct and Indirect Sunlight Upon Papers in the Dry State Which Have Been Impregnated With Various Reducing Agents

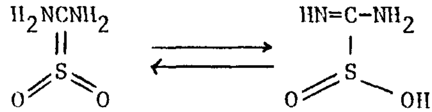
Reducing Agent	%[a] owp	Brightness Index[b]			
		1 week		2 weeks	
		Irradiated Face	Non-irradiated Face	Irradiated Face	Non-irradiated Face
Rongalit C	4.0	59.1	75.1	50.3	74.7
Sodium hypophosphite	4.5	59.5	74.0	52.4	74.7
Control		56.9	74.0	50.7	74.0

a and b as in Table 3.

DISCUSSION

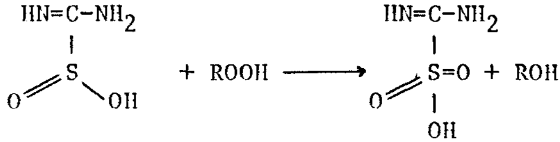
In earlier work we have shown that many reducing agents do not affect the fundamental photochemistry of an o-methylated α-carbonyl β-O-4 dimer chosen to model lignin[4]. It was found that reducing agents prevented the yellowing which accompanies the photolysis of these compounds. In all probability the reducing agents have their most pronounced effect upon the yellowing of oligomers produced in the reactions and also destroy peroxidic species which may lie along the reaction pathways leading to the coloured species.

The reducing agents employed in this study belong to several different classes and therefore play different roles in preventing the photoyellowing. Compounds such as Rongalit C, Blankit D and potassium metabisulphite are in effect sources of sulphur dioxide which is a known reagent for reducing peroxidic species. Thiourea dioxide (formamidine sulphinic acid) is an interesting compound and is known to reduce hydroperoxides and carbonyl compounds.[8]



The reduction of hydroperoxides occurs as follows:

eg



In the case of Rongalit C and Blankit D, reducing agents are produced via decomposition as follows:

$$HOCH_2SO_2 \rightleftharpoons CH_2O + HSO_2^-$$

$$HSO_2^- + RO_2H \longrightarrow HOSO_2^- + ROH$$

(Tetrakishydroxymethyl) phosphonium chloride is a source of a tervalent phosphorus compound which is able to reduce peroxidic species[9].

$$(HOCH_2)_4\overset{+-}{PCl} \longrightarrow CH_2O + HCl + (HOCH_2)_3P$$

The tervalent phosphorus compound can decompose hydroperoxides and peroxides via ionic processes and also reduce alkylperoxy radicals to alkoxyl radicals[10].

$$(HOCH_2)_3P + RO_2H \longrightarrow (HOCH_2)_3\overset{+}{P}OR\ \overset{-}{OH} \longrightarrow (HOCH_2)_3P{=}O + ROH$$

$$(HOCH_2)_3P + R\dot{O}_2 \longrightarrow (HOCH_2)_3\dot{P}OOR \longrightarrow (HOCH_2)_3P{=}O + R\dot{O}$$

Thioglycerol also has two potential roles namely as a hydrogen atom donator (thereby acting as a chain terminator) and as a reducing agent[11].

$$RSH + X\dot{O}_2 \longrightarrow R\dot{S} + XO_2H$$
$$2RS^{\bullet} \longrightarrow RSSR$$

$$RSSR \xrightarrow[\text{or } RO_2H]{RO_2^{\bullet}} R\underset{\underset{O}{\|}}{S}SR$$

$$R\underset{O}{S}SR + H_2O \longrightarrow R\underset{\underset{O}{\|}}{S}OH + RSH$$

$$RSH + XO_2H \longrightarrow RSOH + XOH$$

A great advantage of this type of compound is that many of its degradation products also act as antioxidants eg the disulphide monoxide, sulphinic acid etc.

The experimental results (Table 1) showed that there was a clear advantage in having the reagents in aqueous solution thereby permitting easy access of the reagent to excited states (eg. of the photodegradation products) and in the reactive oxygenated species that they produce.

When the reducing agents are impregnated into the paper one has to rely upon the water present in the paper to transport them to the sites where prodegradent species are being produced, or even to reduce potential prodegradents. Inefficient transport may be caused by a lack of continuity of the structures which leads to islands of water, and in other places where the water is present as a monolayer it lacks the normal water structure and the solvating properties associated with this structure. That reducing agents such as Rongalit C do act slowly within the paper structure and without light activation was shown by the finding that yellowed paper containing Rongalit C bleached when kept in the dark for 2 months. It was also found that some oligomeric degradation products have a degree of water solubility and are leached out into aqueous solution. Thus the bleaching of the paper observed when irradiated in aqueous solution appears to be due to the occurrence of two processes - bleaching of the above products and their removal by leaching. The bleaching process occurs slowly in the dark and is accelerated by light. This point is exemplified by the curve for Rongalit C in Fig 3 in which it can be seen that application of this reagent increased the BI value of the paper from 70 to 74.5 and that irradiation then raised this even further to 76. This corroborates our earlier findings[4] that materials such as Ronglit C promote the photobleaching of the yellow degradation products of oligomers produced by irradiation of model compounds. From this work[4] we can also say that the protective action is unlikely to involve to any substantial extent the quenching of excited states of the carbonyl chromophores within the CTMP.

The influence of light intensity upon the photoyellowing process is quite surprising. From Table 3 it can be seen that 8 hour artificial light irradiation reduces the BI of untreated paper to 56.9 and that this value is reached on exposing the untreated paper to direct light for 1 week (Table 4). Although different weights (expressed as owp in the Table) of reducing agents on paper were used in the two types of experiment it can be concluded that the high light intensities do not diminish the effectiveness of the reducing agents. We conclude from this result that under the artificial irradiation conditions the reducing agent can migrate with an efficiency that allows it to bleach yellowed products before they undergo further photodegradation and also destroy the prodegradent species such as hydroperoxides. If migratability of the reducing agent had been inhibited much more extensive photoyellowing would have been observed on irradiation under artificial irradiation.

EXPERIMENTAL

Softwood CTMP was kindly provided by Prof D Lachenal (CTP Grenoble) and the pulp bleached and converted into paper by previously described methods[12]. Brightness Index measurements were made as previously described[12] with a Zeiss Elrepho Reflectometer. For the experiments shown in Figs 3 and 4 the irradiation equipment previously described[12] was used. In the other experiments the papers were irradiated using 3 x 18 watt 18" (Black Light lamp type TLD 15W/08) housed in a box equipped with a fan. The samples were contained in steel trays which were 12 cms from the light sources. The paper was covered with solutions of the reducing agents (sources given in ref 4) to a depth of 1 cm. Impregnation of the papers was carried out by applying solutions of the reducing agents to the papers with a syringe and then drying with a hot air blower. Irradiation of papers in sunlight was carried out on a north facing window in London during July 1989. Uv/visible diffuse reflectance spectra were recorded on a Perkin Elmer Lambda 5 instrument equipped with an integrating sphere. Infrared spectra were recorded on a Digilab FTS-60 Fourier Transform Infrared Spectrometer equipped with a diffuse reflectance attachment.

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