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Photochemistry of Lignocellulosic Materials

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Foreword

THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of this series is to publish comprehensive books developed from symposia, which are usually “snapshots in time” of the current research being done on a topic, plus some review material on the topic. For this reason, it is necessary that the papers be published as quickly as possible.

Before a symposium-based book is put under contract, the proposed table of contents is reviewed for appropriateness to the topic and for comprehensiveness of the collection. Some papers are excluded at this point, and others are added to round out the scope of the volume. In addition, a draft of each paper is peer-reviewed prior to final acceptance or rejection. This anonymous review process is supervised by the organizer(s) of the symposium, who become the editor(s) of the book. The authors then revise their papers according to the recommendations of both the reviewers and the editors, prepare camera-ready copy, and submit the final papers to the editors, who check that all necessary revisions have been made.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

M. Joan Comstock
Series Editor

Preface

OUR UNDERSTANDING OF THE PHOTOCHEMICAL PROCESSES responsible for the photoyellowing of lignocellulosic materials has seen much progress during the past few years. The time was appropriate to bring together a group of prominent researchers of diverse backgrounds to discuss recent advances in this area and to promote an open exchange of ideas. This book provides up-to-date information on the status of the field and reports on many new advances not yet available in the current literature.

The symposium on which this book is based was organized as part of a concerted effort to address some of the fundamental problems related to the useful life of lignin-containing pulp and paper products. Photoinduced degradation of these products leads to the formation of yellow chromophores. The formation of these chromophores limits the applications and value of products manufactured from lignin-containing mechanical and ultrahigh-yield pulps. Understanding the details of the chemistry underlying these changes will aid the development of lignin-containing pulps with stable brightness and color suitable for the manufacture of many types of white, value-added paper products with high brightness.

This book is published approximately four years after an ACS book entitled *Lignin: Properties and Materials* (ACS Symposium Series 397), edited by Wolfgang G. Glasser and Simo Sarkanen. In their preface, Glasser and Sarkanen pointed out that 23 years had elapsed since the previous ACS publication on the subject. We hope that this increased pace in updating reflects increased interest in the field and will lead to faster progress as well.

The symposium had international representation. We are grateful to the participants for their willingness to travel to San Francisco to attend the symposium and to contribute to this book; the high quality of their work has made our job a pleasant one. Additional thanks go to Barbara C. Tansill and Paula M. Bérard for serving as most helpful acquisition and production editors. We two editors and several other contributors are participants in the Mechanical and Chemimechanical Wood-Pulps Network, which is part of Canada's program of Networks of Centres of Excellence. The support received under this program is gratefully acknowledged.

One prominent scientist was absent from this symposium. Professor Kyosti Sarkanen died in December 1990, and with his death a career devoted to excellence in research has ended. He leaves behind a legacy of research that has advanced our knowledge of pulping, bleaching, and pollution abatement. Kyosti started his career in photochemistry by studying the flash photolysis of chlorophyll with Professor Linschitz of Syracuse University. During the next 30 years he devoted his research efforts to the chemistry of lignin. In 1987, he published his first paper on the inhibition of light-induced yellowing with thiols and thioethers. This paper was the first systematic study of a group of inhibitors of light-induced yellowing. Other scientists will continue this research, but Kyosti's intelligence and devotion to excellence will be missed. We dedicate this book in honor of his contributions to lignin chemistry.

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April 15, 1993

Chapter 1

Light-Induced Yellowing of Wood-Containing Papers

An Evolution of the Mechanism

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Fifty years of research has shown that light-induced yellowing of mechanical and ultra-high yield pulps proceeds through a photooxidative discolouration of lignin in the fibre wall. At least four reaction pathways were identified: (1) direct absorption of uv light by conjugated phenolic groups to form the phenoxy free-radical, (2) abstraction of phenolic hydroxyl hydrogen as a result of aromatic carbonyl triplet excitation to produce a ketyl and phenoxy free-radical, (3) cleavage of non-phenolic phenacyl- α -O-arylethers to phenacyl-phenoxy free radical pairs, and (4) abstraction of the benzylic hydrogen of the guaiacylglycerol- β -arylether group to form the ketyl free-radical which in turn undergoes cleavage of the β -O-4 aryl ether bond to produce an enol and phenoxy free radical. Alkoxy and peroxy free-radicals produced from the reaction of oxygen and lignin free-radicals react with the phenoxy free-radical formed to produce the quinonoid coloured chromophore.

Over the last ten years the production of thermomechanical pulp, TMP, and chemithermomechanical pulp, CTMP, in Canada has more than tripled. Since 1982, the increase in refiner pulp production has been due to an increase in CTMP capacity, which has doubled in the last four years. TMP and CTMP are used primarily for the production of newsprint, advertising inserts, directory paper and some catalog papers - all short life products. Both of these pulps can be bleached to ISO brightness levels of about 80 per cent. At these levels of brightness TMP and CTMP can be used in furnishes for the manufacture of long life papers such as business forms, copy and reprographic papers, tablet and writing papers and high grade publication papers for books. However, all TMP and CTMP, unbleached and bleached, tend to turn yellow during use because of the high lignin content. This restricts use of these pulps to short life papers such as newsprint. In a recent paper presented at the 1989 International Mechanical Pulping Conference (1), Cockram suggested that if the time taken for light-induced yellowing of these papers were increased by three to 36 months the potential market for bleached CTMP would be

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expanded by 0.6 to 2.2 million tonnes per year. If this tendency to yellow - called brightness reversion - could be stopped, bleached TMP and CTMP could successfully be included in furnishes used to manufacture high brightness papers. The potential market for these pulps would be enlarged by 2.6 million tonnes per year.

Brightness reversion may occur through one of two mechanisms:-

* Thermal, oxidative discolouration through long storage time at ambient temperature. Thermal reversion results in losses of 2-5 points in brightness, depending on temperature and humidity.

* Photochemical, oxidative discolouration through exposure of paper to daylight. Photochemical reversion or light-induced yellowing of paper containing mechanical or ultra-high yield pulp can cause more than 30 points in brightness decrease in a short time. Under identical conditions, light-induced yellowing of bleached kraft pulp causes only about three points loss in brightness. Therefore, this pulp is used in the production of long-life paper products. Yellowing of groundwood-based papers has been observed for as long as 90 years (2). It was in these early studies that thermal and light-induced yellowing were attributed to changes in lignin. Further progress in elucidating the reaction pathway was hampered by lack of knowledge about the structure of lignin.

Effect of Environment

The first definitive experiments were conducted on wood and unbleached mechanical pulps and describe the role of lignin and the effects of ambient oxygen, temperature and humidity. The chemical changes in lignin associated with light-induced yellowing were first described by Forman of the Institute of Paper Chemistry (3). He showed that irradiating sprucewood meal with near ultraviolet light ($\lambda = 300$ to 400 nm) for about 15 hours lowered the brightness, from 50% to 29%. Only a small decrease in brightness was observed after irradiating the wood meal for a further 155 hours. Similar results were obtained for newsprint sheets by Leary (4) 17 years later, except that the change in colour stopped after 200 hours of irradiation. The different times for complete yellowing observed by Forman (3) and Leary (4) may be explained in terms of the different sources of material used, wood meal versus newsprint, and the strength of the uv source.

Forman found that extraction of the sprucewood meal with a series of organic solvents decreased the lignin content from 27.5 to 18 per cent when sprucewood meal had been irradiated for 170 hours (3). Therefore, it appears that lignin degradation caused by irradiation of milled sprucewood sheets with near uv light is associated in part with colour formation. Forman found that the methoxyl content of lignin in groundwood decreased continuously with increasing time of irradiation (3). As with the lignin content, both Forman (3) and Leary (4) observed that decreases in methoxyl content are associated with decreases in brightness.

The uv absorption spectra of several types of isolated lignins were compared with the extent of yellowing of groundwood pulp as a function of the wavelength of the incident light (5). The degree of yellowing is highest when lignin is irradiated with

uv light absorbed by lignin chromophores. That is, the higher the absorption of light by lignin the greater the degree of yellowing. This experiment shows that the absorption of light by lignin is responsible for most of light-induced yellowing of groundwood. Since exposure of paper made from bleached kraft pulp causes a small decrease in brightness (three to four points after 24 hours irradiation with uv light), there is also a small contribution to yellowing from cellulose and/or residual hemicellulose.

Both Van den Akker et al. (5) and Leary (6) found that the presence of oxygen effects the light-induced yellowing of wood fibre. However, there were some differences observed in the effect of atmospheric oxygen on light-induced yellowing. Van den Akker et al. (5) found that for a given uv irradiation of groundwood pulp, the brightness loss was 6.8 points in N₂ compared to 10.1 points in air. Leary (6), however, found that irradiation of newsprint in a vacuum, or in the presence of nitrogen or carbon dioxide, did not cause any significant yellowing after irradiation for up to 500 hours. The diminished yellowing observed by Van den Akker may be attributed to either incomplete removal of oxygen from the wood fibre or to the formation of chromophores via reaction pathways not involving oxygen.

Lin and Kringstad (7) confirmed Leary's results in an experiment with a solution of milled wood lignin (MWL) in methylcellulose:water. Irradiation of this solution in a vacuum produced no colour. This solution, opened to air and irradiated, produced the same amount of colour as a solution of milled wood lignin initially irradiated in air. The effect of oxygen on light-induced yellowing of newsprint is further illustrated by the accompanying effect on methoxyl content. Leary found that the methoxyl content of newsprint after irradiation in a vacuum decreased by only 0.1% whereas the same irradiation in air decreased the methoxyl content by 0.4% (6).

The effect of humidity is small but significant (5). The light-induced brightness decrease in moist air was 10.9 points versus eight points in dry air. Increasing the temperature during uv irradiation from $\approx 25^\circ\text{C}$ to 100°C increased the brightness loss from 10.9 to 14 points (5). A similar increase in temperature in the dark decreased the brightness by only 0.5 points. Therefore light-induced yellowing is accelerated by increased temperature.

The early work on light-induced yellowing clearly demonstrates the roles of lignin, oxygen, humidity, and temperature on light-induced yellowing of groundwood-based paper. That is, light-induced yellowing of groundwood-based paper is a photooxidation of the lignin in paper that produces chromophores that absorb visible light.

Chromophore Formation

Light-Induced Yellowing of Unbleached Mechanical Pulp. Most of the early research on light-induced yellowing of groundwood based papers used some measure of reflectance or brightness at a single wavelength. To elucidate the reaction pathways leading to yellowing, the effect of near uv irradiation on the uv-visible spectrum of lignin-rich paper is required.

Claesson, Olson and Wennerblom (8) carried out the earliest studies on the effect of near-uv irradiation on the uv-visible reflectance spectra of high-yield spruce bisulphite liner and newsprint. In this work, the relative reflectivity (equation 1) of samples was plotted against wavelengths in the range 300 to 600 nm (8).

$$\text{Relative reflectivity} = R(\text{irradiated})/R(\text{initial}) \times 100. \quad (1)$$

Yellowing of bisulphite liner is manifested by a broad minimum in the relative reflectivity at wavelengths between 450 and 500 nm. As the time of irradiation is increased from zero to 60 minutes, the relative reflectivity at 470 nm decreases to about 73 per cent, and does not change after irradiation for two hours.

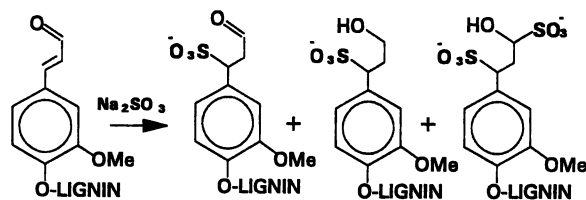
The uv-visible difference spectra of newsprint and wood irradiated at 365 nm are quite different from those of high-yield bisulphite liner. The relative reflectivity of newsprint and wood increases at about 360 nm and decreases at about 430 nm. After 1 hour irradiation, the relative reflectivity of newsprint at 430 nm does not decrease further.

Leary (6) found similar results when he irradiated newsprint with near ultraviolet light. He observed the same decrease in reflectance at 430 nm and increase in reflectance near 350 nm as did Claesson et al. The time of irradiation is much higher than that observed by Claesson and may be accounted for by the different amount of uv light emitted by the lamps.

The changes in the reflectance of paper observed by Claesson et al. and Leary are attributed to absorption of light by the chromophores formed during the exposure of paper to uv light. These results raise the critical question of the structure of the chromophores that cause a minimum in the reflectance spectrum of bisulphite liner at 470 nm, and that cause a maximum at 350 nm and a minimum at 430 nm in the reflectance spectra of newsprint and wood. Both Claesson and Leary have observed the increased reflectance of irradiated newsprint at 350 nm. However, Claesson found no such increase in reflectance for high yield bisulphite liner. This difference in response of high-yield bisulphite liner and newsprint to irradiation with uv light is due to the reaction of bisulphite with the coniferaldehyde group in lignin.

In his study of the chemistry of lignin sulphonation, Gellerstedt (9) has shown that sodium sulphite and sodium bisulphite add across the carbon - carbon double bond of the coniferaldehyde end group of lignin, as seen in Scheme 1. This reaction decreases the degree of conjugation and shifts the absorption maximum from 350 to about 280 nm. The effect of the addition of sulphite to the coniferaldehyde group on the difference absorption spectrum of black spruce CTMP is shown in Figure 1. Treatment of black spruce wood with sodium bisulphite decreases the light absorption (or increases reflectance) at 350 nm (10).

The light-induced increase in reflectance of newsprint at 350 nm can be attributed to photooxidative cleavage of the coniferaldehyde carbon-carbon double bond in the lignin of newsprint to produce a vanillin type group, as shown in Scheme 2. This reaction shifts the absorption maximum from 350 to 280 nm. Irradiation of bisulphite liner with uv light does not increase the reflectance at 350 nm, because the coniferaldehyde moiety has been previously consumed by treatment with bisulphite.



Scheme 1

Sodium sulphite adds to the double bonds of coniferaldehyde (9).

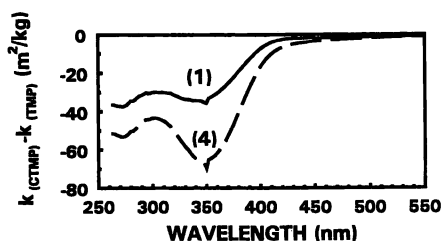
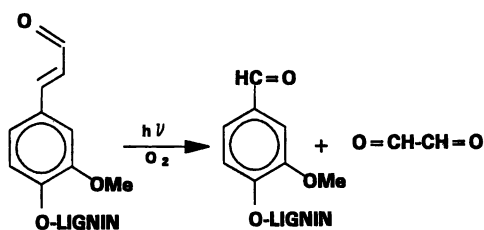


Figure 1. Treatment of black spruce chips with sodium sulphite decreases the light absorption at 350 nm of the CTMP produced due to lower coniferaldehyde end-group content. The numbers in brackets denote the per cent sodium sulphite charge on wood (Adapted from ref. 10).



Scheme 2

The Photooxidation of the coniferaldehyde group.

Based on his observation of demethoxylation during light-induced yellowing, Leary (13) was the first to propose the quinone group as the yellow product of the photooxidation of lignin in paper. However, Lin and Kringstad (7) were the first to provide some evidence for the formation of o-quinones in lignin models. They observed that the reduction difference spectrum of vanillin treated with sodium periodate and that of vanillin irradiated with near ultraviolet light were nearly identical. Since vanillin is oxidized by sodium periodate to produce an o-quinone and methanol, this experiment suggests that photooxidation of vanillin produces a quinone similar to that produced by sodium periodate oxidation.

More direct evidence for the formation of o-quinones in light-induced yellowing was presented by Lebo et al. (14). They found that trimethyl phosphite reacts with o-quinones to produce oxyphosphoranes, which in turn, react with water to form cyclic phosphate triesters, as shown in Scheme 3. Treatment of yellowed refiner mechanical pulp with trimethyl phosphite decreased the light absorption at 457 nm, as seen in Table I. Similar decreases in specific absorption were observed at 415 and 520 nm. Solid state ^{31}P nmr analysis of pulp treated with trimethyl phosphite was consistent with the formation of the cyclic phosphate triesters.

TABLE I
The Effect of Trimethyl Phosphite Treatment on
the Specific Absorption of White Spruce RMP

Sample	Specific Absorption at 457 nm (cm^2/g)
Untreated RMP	49
Trimethyl Phosphite Treated RMP	13
Irradiated RMP	186
Irradiated and Trimethyl phosphite Treated RMP	42

SOURCE: Data are from reference 14.

Light-Induced Yellowing of Bleached Mechanical Pulp. Much of the early research on light-induced yellowing of lignin-rich papers was on unbleached mechanical pulps. Figure 2 shows the effect of near-uv irradiation of bleached TMP for one-half to 24 hours (10,15). The shoulder at 420 nm is consistent with results obtained on unbleached mechanical pulp. However, at a wavelength of about 320 - 350 nm the specific absorption increases. In contrast light-induced yellowing of newsprint made from unbleached stone groundwood was characterized by an increase in light absorption at about 420 nm and a decrease in light absorption at 350 nm (6).

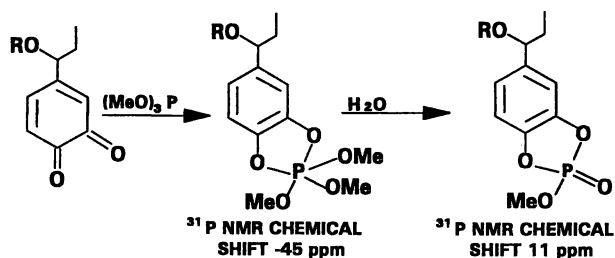
The decrease in light absorption at 350 nm for unbleached mechanical pulps was attributed to oxidation of the coniferaldehyde group in lignin. The light absorption by bleached TMP at 350 nm increases instead of decreasing after exposure to uv light, because fully bleached TMP does not have coniferaldehyde groups. Alkaline hydrogen peroxide cleaves the carbon - carbon double bond of the coniferaldehyde group in lignin (18), as seen in Scheme 4. The effect of alkaline hydrogen peroxide in oxidizing the coniferaldehyde carbon - carbon double bond is shown by the large decrease in absorption at 350 nm by TMP as seen in Figure 3 (10).

The important part of the uv-visible difference spectrum of yellowed bleached TMP is above 400 nm. Absorption in this region is responsible for the yellow colour of paper that has been exposed to ultraviolet light. Similar changes in the absorption spectrum, were observed for irradiated bleached CTMP sheets, except that the increase in the absorption of CTMP at 420 nm was about 30 per cent less than that of TMP (10). This difference in the light-induced yellowing of TMP and CTMP is better illustrated by the lower rate of light-induced yellowing of CTMP compared to that of TMP, attributed to the lower absorption of uv light by CTMP. The effect of the extent of light absorption on the degree of light-induced yellowing was discussed earlier. Absorption of uv light by lignin, promotes the yellowing of lignin.

Another striking change in absorption caused by the uv irradiation of bleached TMP and CTMP occurs at 330 nm (10-12,15) and is shown in Figure 2 for TMP. Figure 4 shows that the treatment of photochemically yellowed, bleached TMP with NaBH_4 decreases the specific absorption above 400 nm to the original value (i.e. $\Delta k = 0$). Also, the absorption is decreased to a minimum centred at 330 nm, because chromophores produced by uv irradiation plus those originally in the pulp were reduced. The absorption maximum at 330 nm has been attributed to aromatic ketones in lignin (16,17)

Light-Induced Transients in Lignin and Paper. The triplet excited state of the aromatic carbonyl group and the phenoxyl free-radical have been proposed as reactive intermediates leading to yellowing of lignin-containing papers. The electron spin resonance (ESR) signal observed after irradiation of vanillyl alcohol, veratraldehyde (19) and α -guaiacoxy-3,4-dimethoxypropiophenone (20) with uv light has been attributed completely or in part to the phenoxyl free-radical. However, the triplet excited state in lignin that has been proposed had not yet been observed.

Neumann and coworkers (21,22) have observed a transient absorption spectrum of dioxane lignin in deaerated 50% dioxane-water solutions with maxima at 410, 460 and 490 nm. Ascorbic acid, a radical scavenger, decreases the transient absorption at wavelengths of 415 to 460 nm. The maxima at 410 and 460 nm were attributed to phenoxyl and ketyl free-radicals, respectively. The addition of oxygen to the solution decreased the intensity of transient absorption spectrum (22). Oxygen quenching of the transient spectrum is attributed to reaction with the phenoxyl free-radical. These transients were attributed to the formation of phenoxyl and ketyl free radicals by hydrogen abstraction of the phenolic hydroxyl group by the carbonyl triplet, as seen in Scheme 5. Phenacyl- α -O-arylether bond cleavage, shown in scheme 6, was not considered by the authors to be a source of free-radicals.



Scheme 3
Derivatization of o-quinone with trimethyl phosphite (14).

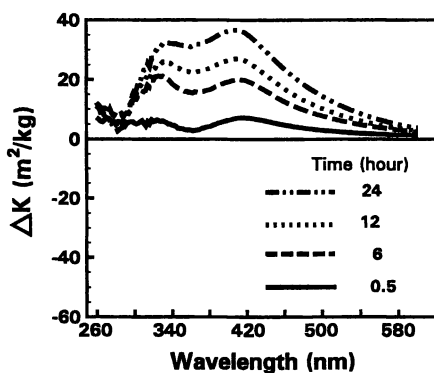
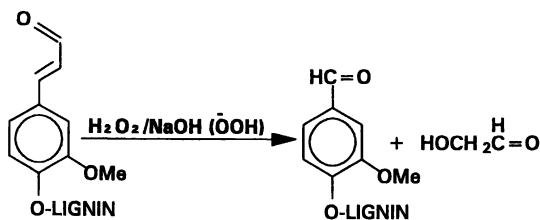


Figure 2. The difference absorption spectrum of bleached TMP has maxima at 350 nm and 420 nm. The specific absorption at these wavelengths increases with increasing time of irradiation shown in brackets as the number of hours (Adapted from ref. 10).



Scheme 4
The reaction of hydroperoxide with the coniferaldehyde double bond (18).

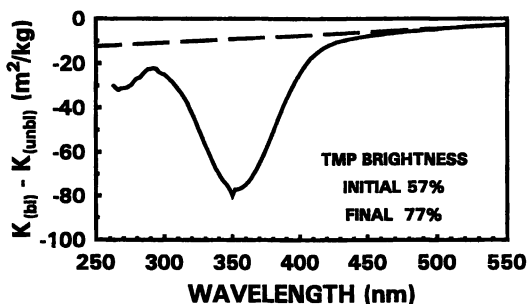


Figure 3. Bleaching TMP with alkaline hydrogen peroxide decreases the specific absorption to a minimum centred at 350 nm (Adapted from ref. 10).

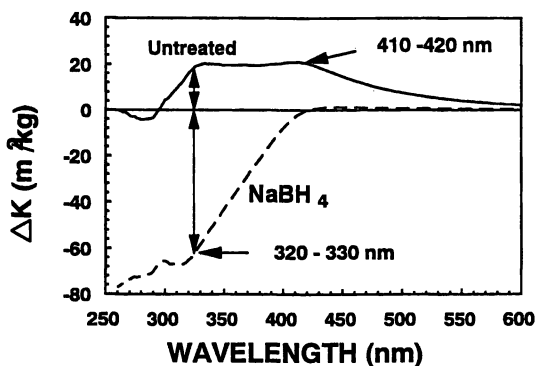
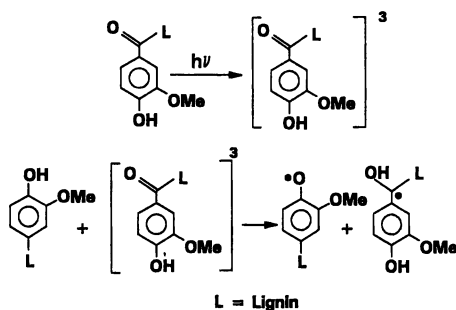


Figure 4. The treatment of photochemically yellowed, bleached TMP reduces the yellow chromophores to colourless groups as seen by the decrease in Δk to zero at wavelengths above 400 nm. Reduction of the carbonyl groups produced by near-uv irradiation plus those native to the pulp fibre decreases Δk at 330 nm to a negative value (Adapted from ref. 15 and 33).



Scheme 5

Hydrogen abstraction of phenolic hydroxyl by aromatic carbonyl triplet.

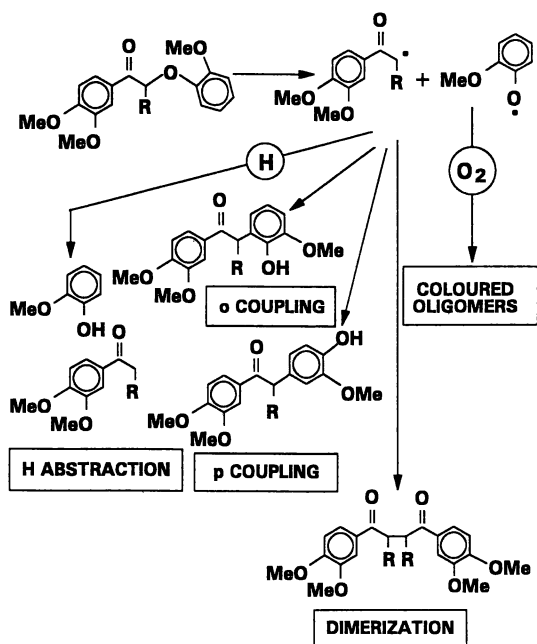
Dioxane lignin in water-dioxane solution is quite different from solid, native lignin in a pulp fibre. In solution, the phenolic hydroxyl groups and carbonyl triplets can diffuse together and react to produce ketyl-phenoxyl free-radical pairs with high efficiency. In pulp fibres, however, diffusion of the components of lignin is severely constrained. Since the molecular dynamics of lignin in solution are intrinsically different from those of lignin in pulp fibres, experiments that can probe mechanical pulp directly are crucial to unravelling the mechanism of light-induced yellowing.

Diffuse-reflectance laser-flash photolysis (DRLFP) allowed direct observation of short-lived chemical species, formed after absorption of light by solid materials. It has been successfully used to detect transient species formed from the photolysis of diverse materials, including dyes adsorbed on fabrics, organic compounds in crystalline and adsorbed phases, and powdered semiconductors (23-25). The first observation of short-lived chemical species during the photolysis of thermomechanical pulp (TMP) (26) shows the transient absorption spectra of both unbleached TMP and TMP bleached with alkaline hydrogen peroxide, as seen in Figure 5. The spectra are characterised by a maximum in the 440 nm region and by a broad, structureless tail extending beyond 700 nm. Except for general changes in intensity, the spectrum observed immediately after the laser flash is identical to that recorded 10 μ s later. In separate experiments, using different time base settings of the digitiser, the same spectrum was observed 500 μ s after the laser flash. The almost identical transient spectra of bleached and unbleached TMP, seen in Figure 5, suggests that the absorption of ultraviolet light by either pulp produces the same transient species. Although the coniferaldehyde moiety absorbs light at 354 nm, it does not appear to contribute to the transient absorption spectrum of unbleached TMP, as indicated by the identical transient spectrum of bleached TMP, which contains a lower amount of coniferaldehyde end-groups.

Methylation of phenolic hydroxyl groups or oxygen removal increased the intensity of the transient spectrum. That is, both oxygen and phenolic hydroxyl groups reduce the detected yield of the transient, due to rapid static quenching. The increase in transient intensity resulting from removal of phenolic hydroxyl groups precluded identification of the transient as a ketyl-phenoxyl radical pair, formed by hydrogen abstraction from the phenolic hydroxyl by the aromatic ketone triplet. If this were the case, the transient intensity should decrease when the phenolic hydroxyl groups are methylated. The triplet excited states of aromatic ketones in fluid solution are characteristically quenched by oxygen and phenols (27, 28). On this basis, the transient absorption was assigned to the lowest triplet state of the aromatic α -carbonyl chromophore in lignin. This assignment is supported by the decrease in transient intensity in bleached TMP, after the carbonyl group has been reduced by NaBH_4 .

Mechanism of Yellowing

The next phase of research focused on the functional groups in lignin that play a role in light-induced yellowing. Carbonyl and phenolic hydroxyl groups have been studied intensively.



Scheme 6

Light-induced cleavage of the phenacyl- α -O-arylether bond (31,37).

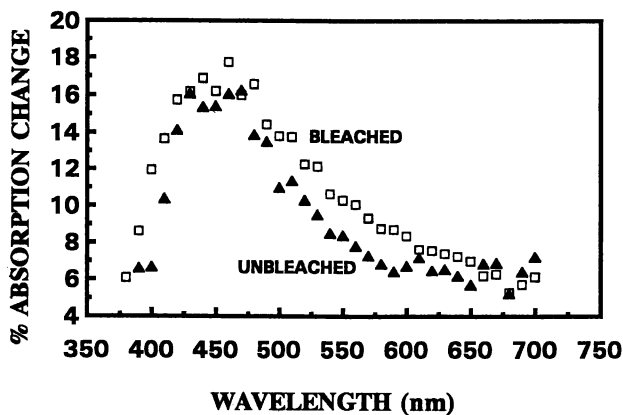


Figure 5. The transient absorption spectra of unbleached TMP and bleached TMP are almost identical (Adapted from ref. 26).

The pioneering work of Singh (29) and Leary (6) on the effect of etherifying or esterifying the phenolic hydroxyl group on light-induced yellowing of newsprint clearly demonstrates the role of the phenolic hydroxyl group. Replacement of the phenolic hydroxyl hydrogen with either a methyl or acetyl group decreased the extent of light-induced yellowing of newsprint. Also, methylation of unbleached and hydrogen peroxide bleached TMP decreased the extent of yellowing by 15 to 20% (8,9), but did not affect the initial rate (12,15). Similar effects were obtained by Lin and Gierer (28) by methylating milled wood lignin. Methylation of milled wood lignin by diazomethane inhibited yellowing, but as with newsprint, did not completely stop it. The fact that etherifying or esterifying phenolic hydroxyl groups does not totally inhibit but only decreases the extent of light-induced yellowing suggests that there is more than one pathway leading to photooxidative discoloration, at least one involving the phenolic hydroxyl group and others involving non-phenolic groups.

Carbonyl groups in lignin-containing paper may be aromatic ketones, aliphatic ketones or quinonoid groups. Treating newsprint with sodium borohydride prior to light-induced yellowing only slows the yellowing reaction and does not decrease the extent of yellowing, as measured by the change in lightness coordinate with time. The lightness coordinate of untreated newsprint is decreased to the minimum value in about 170 hours whereas nearly 1200 hours is required to decrease the lightness coordinate of sodium borohydride treated newsprint to the same value (6). Since NaBH_4 treatment decreases the amount of carbonyl groups in paper, the lower rate after this treatment suggests that carbonyl groups do not directly form yellow chromophores upon exposure of paper to uv light, but they may act as sensitizers to photooxidative discoloration. That is, the amount of precursor to the yellow chromophores is not decreased by sodium borohydride treatment and therefore the ultimate extent of yellowing is the same as that of untreated newsprint.

Sodium borohydride reduction of MWL from untreated wood decreases the rate of yellowing, but does not stop yellowing itself. This result is consistent with that of the yellowing of newsprint. Treatment of MWL solutions with NaBH_4 followed by hydrogenation over a palladium catalyst supported on barium sulphate stopped yellowing of MWL (31). Either the groups that sensitize photooxidative yellowing have been completely removed, or the precursors to the yellow chromophores have been reduced to groups that cannot be photooxidized. Unfortunately heterogeneous catalytic hydrogenation cannot be applied successfully to pulp or paper. As a solid, the Pd/BaSO_4 cannot penetrate wood fibre to the site of hydrogenation. However, this result suggests that homogeneous hydrogenation with the appropriate soluble catalyst might contribute to the stabilization of lignin in paper to photooxidative discoloration.

The effect of sodium borohydride on the light-induced yellowing of hydrogen peroxide bleached TMP is different from that of newsprint made from unbleached mechanical pulp. Treatment of bleached TMP with sodium borohydride does not change the extent or the rate of light-induced yellowing (15).

Tschirmer and Dence (32) have demonstrated the role of both the phenolic hydroxyl and carbonyl groups in light-induced yellowing of spruce TMP. For up to two hours irradiation time, complete reduction of carbonyl groups in TMP

followed by alkylation of phenolic hydroxyl group decreased the extent of light-induced yellowing to levels just above that of bleached kraft pulp. During the initial 2 hours of irradiation, the lowest degree of light-induced yellowing occurred on TMP that had been fully reduced with NaBH_4 , and then completely alkylated with either diazomethane or propylene oxide. Therefore, both carbonyl and phenolic groups play important roles in the initial stages of photooxidative discoloration. However, complete reduction of carbonyl groups followed by complete methylation of phenolic hydroxyl groups in peroxide bleached TMP did not prevent yellowing after uv irradiation for more than 2 hours (32). After the 2-hour induction period, the rate of yellowing was about the same as that of unmodified bleached TMP (32). This result clearly shows that the origins of light-induced yellowing are found in functional groups other than carbonyl or phenolic hydroxyl.

The effect of oxygen removal, carbonyl group reduction and phenolic hydroxyl group alkylation or acetylation on the rate and extent of light-induced yellowing has been explained by several researchers - Leary (6), Kringstad and Lin (7,19) and Gierer and Lin (31) and is shown, in part, in Scheme 5. A reaction pathway of light-induced yellowing is thought to proceed via initial excitation of the carbonyl chromophore and intersystem crossing to the triplet state. The triplet excited state (case 1) abstracts hydrogen from the neighbouring phenolic hydroxyl group to produce a ketyl-phenoxyl free-radical system. Alternatively, singlet oxygen, (case 2) formed by energy transfer from the triplet excited state, abstracts hydrogen from phenolic hydroxyl groups to produce the phenoxyl free-radical. The phenoxyl free-radical is then oxidized to coloured chromophores.

Evidence for the mechanism involving abstraction of hydrogen from the phenolic hydroxyl group was first obtained by Kringstad and Lin (19), primarily through experiments with the appropriate lignin models. ESR spectra, attributed to the appropriate phenoxyl free-radical were observed when solutions containing an aromatic aldehyde (3,4,5-trimethoxybenzaldehyde or veratraldehyde) and a phenolic lignin model compound (syringyl alcohol, vanillyl alcohol, catechol or phenol) were irradiated with near-uv light. Irradiation of the aldehydes or the phenols alone did not produce any free-radicals or yellowing. These phenols did not absorb uv light at the wavelengths used in this experiment (300 to 400 nm). This suggests that phenoxyl free-radicals produced by the abstraction of hydrogen from phenolic end-groups may play an important part in the light-induced yellowing of lignin.

Brunow and Sivonen (34) obtained similar results on a lignin model system, ethylguaiacylcarbinol. This compound did not undergo any oxidation when irradiated with near-uv light until p-methoxyacetophenone, a triplet sensitizer, was added to the solution. As the molar ratio of p-methoxyacetophenone to ethylguaiacylcarbinol was increased to 0.32 the rate of photooxidation of this benzyl alcohol increased. This result is consistent with the mechanism of light-induced yellowing shown in Scheme 5.

The mechanism involving abstraction of phenolic hydrogen by singlet oxygen does not appear to occur during the light-induced yellowing of paper. Exposure of lignin-rich paper (containing mechanical pulp) to singlet oxygen did not cause yellowing (35,36). Indeed, a slight bleaching was observed.

The light-induced yellowing observed for paper containing methylated or acetylated lignin has been attributed to a second reaction pathway that does not involve hydrogen abstraction from phenolic hydroxyl groups. Gierer and Lin (31) have shown that non-phenolic phenacyl- α -O-arylethers, α -guaiacoxyacetoveratrone [1] and α -guaiacoxy-3,4-dimethoxypropiophenone [2] and α -guaiacoxy- β -hydroxy-3,4-dimethoxypropiophenone [3], shown in Figure 6, are rapidly discoloured after irradiation with near-uv light. Irradiation of these lignin models produced the corresponding ketones, acetoveratrone and dimethoxypropiophenone and ketols, α -hydroxyacetoveratrone and α -hydroxydimethoxypropiophenone, from compounds 1 and 2 respectively and in all cases produced guaiacol. These products can only be explained as light-induced cleavage of the β -arylether bond to produce a phenacyl-phenoxy free-radical pair, as seen in Scheme 6. Guaiacol and the ketone are produced via hydrogen abstraction by the guaiacoxy and phenacyl free-radicals and the ketols are formed by reaction of the phenacyl free-radical with ambient oxygen. The corresponding structural isomers, a β -keto- α -O-arylether [4] or an α -keto- β -O-aryl ether [5], shown in Figure 6, are unaffected by irradiation with near uv light. Evidence for the formation of free-radicals from the irradiation α -(*p*-methylguaiacoxy)-3,4-dimethoxypropiophenone is shown by the 5 line signal assigned to the phenacyl free-radical superimposed on the singlet attributed to the phenoxy radical (20).

Vanucci and coworkers (37) have confirmed the formation of guaiacol, ketones and ketols as the monomeric products of light-induced cleavage of the α -arylether bond of phenacyl- α -O-arylethers in solution and adsorbed on cellulose. In addition, some dimeric products of the light-induced cleavage of the α -arylether bond of compound 1 were identified as the structural isomers 3,4-dimethoxy- α -(3'-methoxy-4'-hydroxyphenyl)acetophenone and 3,4-dimethoxy- α -(2'-hydroxy-3'-methoxyphenyl)-acetophenone. The formation of these 2 structural isomers of 1 was attributed to combination of the phenacyl radical with the guaiacoxy radical at the reactive carbon atoms ortho and para to the phenoxy oxygen. Similar results were obtained by Scaiano and Netto-Ferreira for α -phenoxyacetophenone (37) and α -phenoxy-*p*-methoxyacetophenone (39).

Since light-induced cleavage of the α -arylether bond of the keto arylether moiety of lignin is a pathway to paper yellowing, it is essential to understand the effects of chemical and physical environment on the extent of bond cleavage and the relationship of bond cleavage to yellowing. The quantum yield of α -arylether bond cleavage, Φ_d of α -guaiacoxyacetoveratrone in ethanol was double that of the same reaction in benzene (37). The increase of Φ_d in alcohols is accompanied by the increase in triplet lifetime as observed by Netto-Ferreira and Scaiano (38,39). These solvent effects of alcohols may be due to increases in solvent polarity and/or to hydrogen bonding.

Figure 7 shows the degradation quantum yield, Φ_d of α -guaiacoxyacetoveratrone in 7 deaerated solvents: acetonitrile (ACN), dioxane (DIOX), 1,2-dimethoxyethane (DME), methanol (MeOH), ethanol (EtOH), isopropanol (iPrOH) and ethoxyethanol (EtOEtOH) (40,41). The Φ_d was significantly larger in alcohols, 0.34 to 0.52, than in pure aprotic solvents, < 0.1. There was very little difference in Φ_d in polar aprotic solvents, 0.08 in acetonitrile, compared to that in non-polar aprotic solvents,

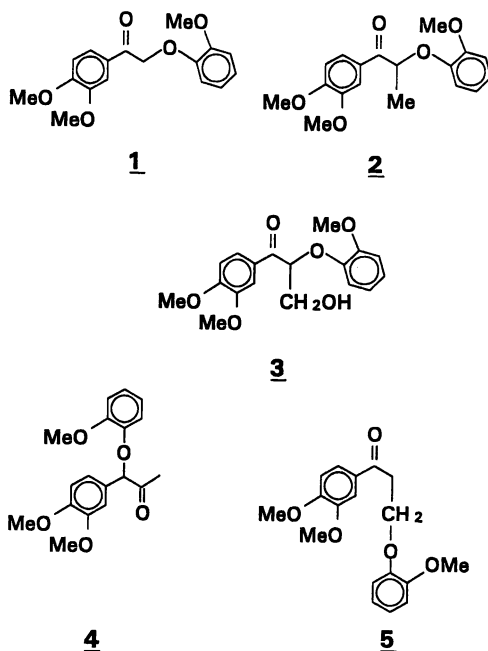
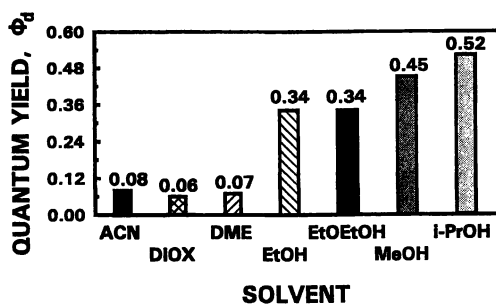


Figure 6. Lignin model ketones (31).

Figure 7. The degradation quantum yield, Φ_d of α -guaiacoxyacetoveratrone increases in protic solvents (Adapted from ref. 40).

0.06 in dioxane. Therefore, solvent polarity does not appear to have much influence on Φ_a .

It has been assumed that the photodegradation of phenacyl aryl ethers such as α -guaiacoxycetoveratrone arises almost exclusively from the lowest triplet state (34-39). However, Figure 8 shows that the addition of 0.1 mol/L 1,3-cyclohexadiene, an effective triplet quencher, has essentially no effect on the Φ_a of α -guaiacoxycetoveratrone in acetonitrile or dioxane. The Φ_a is decreased from 0.34 to 0.1 in ethanol. Flash photolysis experiments confirm the formation of triplet excited states in all three solvents that are 99% quenched by 1,3-cyclohexadiene (40,41).

These results suggest that the photodegradation of α -guaiacoxycetoveratrone proceeds only via the singlet excited state in aprotic solvents. In protic solvents, about 1/3 of this photodegradation proceeds through the singlet state and 2/3 via the triplet state.

Palm and Dreeskamp (42,43) recently reported a CIDNP (Chemically Induced Dynamic Nuclear Polarization) study of the photolysis of α -(3,5-dimethoxyphenoxy)-acetophenone. From the polarization of the methylene protons they concluded that at least two of the products (diphenyl-1,4-butadiene and α -(3,5-dimethoxy-4-hydroxyphenyl)-acetophenone) are formed from the singlet excited state.

The triplet lifetime of α -guaiacoxycetoveratrone is higher in protic solvents than in aprotic solvents as seen in Figure 9. This result, although consistent with the observations of Netto-Ferreira and Scaiano (39), is surprising considering the fact that the reactivity of the triplet excited state is induced by protic solvents. This reactivity would tend to decrease instead of increase triplet lifetime. However, there are other factors that can explain increased triplet lifetime in protic solvents. Besides cleavage of the arylether bond, triplet energy dissipation can also occur via rotation of the α -carbon oxygen (guaiacoxy, phenacyl) bond to bring the guaiacoxy group close to the excited carbonyl group. Triplet energy is dissipated by energy transfer to the guaiacoxy group to regenerate the ground state (38) by a process called β -phenyl quenching. Equation 2 shows the contributions of the rate of β -phenyl quenching k_1 and of bond cleavage k_2 to the triplet lifetime. Protic solvents may increase triplet lifetime by hydrogen bonding to the carbonyl group, thus sterically hindering any rotation about the α -carbon oxygen bond to decrease k_1 . Therefore, it appears that the effect of triplet reactivity in protic solvents caused by hydrogen bonding in decreasing triplet lifetimes is offset by the steric hinderance caused by hydrogen bonding to decrease β -phenyl quenching and increase triplet lifetime.

$$\tau = (k_1 + k_2)^{-1} \quad (2)$$

Castellan and co-workers have observed that the benzyl-O-aryl bond, another interunit linkage in lignin, underwent cleavage to produce benzyl and guaiacoxy free-radicals when irradiated with uv light at wavelengths in the range 220 to 400 nm (42,43). Coloured chromophores were then formed, probably via oxidation of the guaiacoxy radical. This range of wavelengths is not characteristic of those in daylight. However, the benzyl-O-aryl group in the lignin macromolecule does not absorb uv light at $\lambda > 300$ nm and would not be expected to form coloured chromophores when irradiated with the uv component of daylight. It is expected

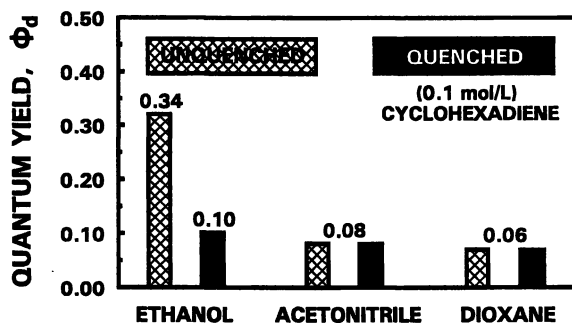


Figure 8. The addition of 0.1 mol/L cyclohexadiene has no effect on the Φ_d in aprotic solvents but partially decreases Φ_d in protic solvents (Adapted from ref. 40 and 41).

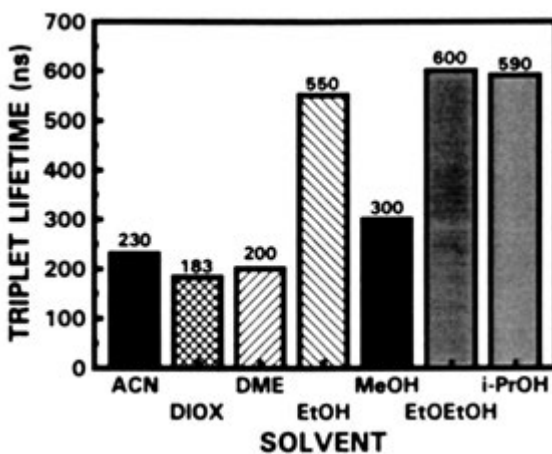


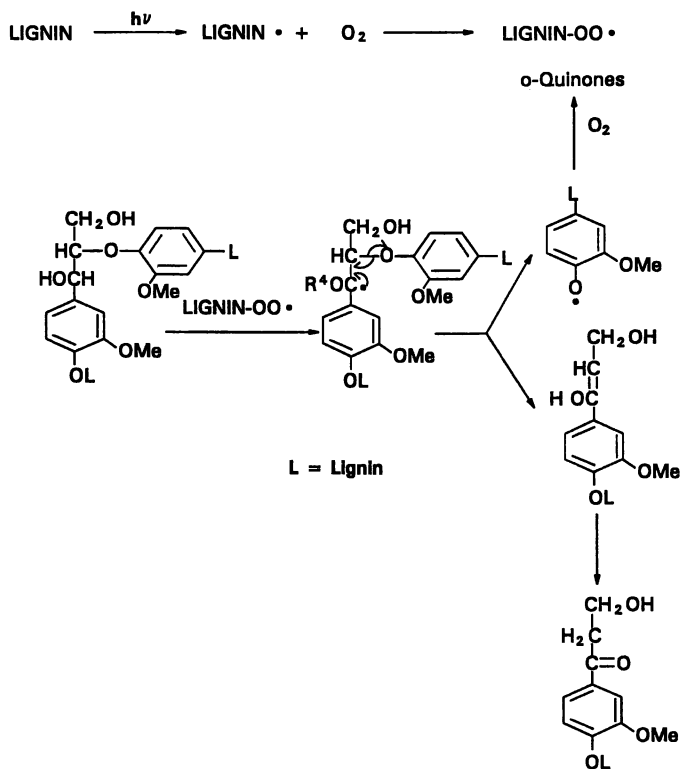
Figure 9. The lifetime of the triplet excited state of α -guaiacoxy-acetoveratrone is higher in protic solvents than in aprotic solvents (Adapted from ref. 41).

that light-induced cleavage of the benzyl-O-aryl bond and the accompanying colour formation in daylight ($\lambda > 300$ nm) would be negligible. This rationale is supported by the delay in the yellowing of TMP where the carbonyl and phenolic hydroxyl groups were completely removed by reduction with sodium borohydride followed by hydroxyalkylation with propylene oxide (32,33). Such treatments were found to delay the yellowing of TMP after 1.5 to 2 hours of exposure to near uv light. Benzyl-O-aryl groups in TMP do not react with sodium borohydride and propylene oxide. Therefore, these results suggest that the presence of benzyl-O-aryl groups have very little effect on the initial stages of light-induced yellowing when TMP is exposed to uv light at wavelengths above 300 nm. If wavelengths lower than those of sunlight (wavelength < 300 nm) are used, then cleavage of the benzyl-O-aryl group could lead to yellowing as was observed by Castellan et al. (44,45).

Reduction of carbonyl groups by NaBH_4 does not prevent light-induced yellowing (6,15,30). This result indicates phenolic groups in lignin absorb uv light at wavelengths > 300 nm to produce the phenoxyl free-radical that in turn produces yellow chromophores. Although monomeric phenols have very low light absorption above 300 nm, conjugated phenols do absorb a moderate amount of uv light in the range 300 to 330 nm (46). Conjugated lignin model phenols, such as 1-hydroxy-1',2,2'-trimethoxy-4,4'-di-n-propylbiphenyl adsorbed on cellulose paper yellowed when exposed to uv light at wavelength > 300 nm (46). These type of biphenols have been shown to occur in lignin and are proposed as a product of the reaction of light-induced phenoxyl free-radical with neighbouring aromatic groups (47).

Recently, it was shown that the mechanical pulping process can be a source of precursors to light-induced yellowing. Lignin contains at least 18 phenylcoumaran units per 100 phenylpropane units (48,49). Disc refining of pulp samples impregnated with phenylcoumaran models produces the corresponding diguaiacylstilbene compounds (50). It was shown that diphenolic diguaiacylstilbenes and phenolic guaiacylveratrylstilbenes adsorbed on cellulose paper underwent rapid light-induced yellowing (46). The degree of yellowing of diveratrylstilbenes is less than that of phenolic stilbenes.

The yellowing of reduced and methylated bleached TMP after 2 hours uv irradiation (33) suggests that there are functional groups in lignin that eventually produce coloured chromophores that are not associated with aromatic carbonyl and phenolic hydroxyl groups. Reaction pathways leading to yellow chromophores first involve the formation of a peroxy free-radical from the combination of a carbon centred lignin free-radical and oxygen. This is a typical first stage in oxidative degradation of polymeric materials. The peroxy radical then abstracts benzylic hydrogen from a guaiacylglycerol- β -arylether group to form a ketyl free-radical and the hydroperoxide. Enol and phenoxy free-radical are formed by cleavage of the β -aryl ether bond of the ketyl free-radical. The enol then tautomerizes to the ketone. This reaction pathway, shown in scheme 7, explains the light-induced formation of aromatic carbonyl groups that cause an increase in specific absorption at 330 nm for both untreated bleached TMP and bleached TMP that was extensively reduced with sodium borohydride (15,33). Also, analysis of the photodegradation products of mechanical pulp indicates the production of β -hydroxypropionguaiacone that is an expected product of β -O-4-aryl ether cleavage (51). The formation of ketyl free-



Scheme 7
The major reaction pathway via the ketyl free-radical

radicals via abstraction of hydrogen from a benzylic alcohol group followed by β -O-4-aryl ether bond cleavage is supported by the results obtained by Scaiano (52). He has shown in a recent publication that the t-butoxy free-radical generated by the photolysis of t-butyl peroxide abstracts the benzylic hydrogen of 1-phenyl-2-phenoxy glycol to produce the ketyl free-radical which in turn undergoes β -aryl ether cleavage to give acetophenone and phenol via the enol and phenoxy free-radical. Evidence for the light-induced degradation of β -O-4-guaiacyl ether bonds is provided by the effect of uv irradiation on the phenolic hydroxyl content of reduced plus methylated bleached TMP. Thirty hours of uv irradiation of methylated bleached TMP increased the phenolic hydroxyl content from about 0.58% to 2.13%. The same irradiation of methylated and reduced bleached TMP increased phenolic hydroxide from 0.66% to 1.59% (Schmidt, J.A. and Heitner, C., *J. Wood Chem. Technol.* in press). This is consistent with the cleavage of β -O-4 ether bonds to release phenolic groups. The absolute values of phenolic hydroxyl content are affected by the fact that light induced yellowing involves some oxidative demethylation of phenols, which decreases the phenolic hydroxyl content. That is, some proportion of the phenolic hydroxyl groups released during uv irradiation are consumed by the light-induced yellowing.

In addition, further evidence for the cleavage of β -O-4-aryl ether bonds of lignin moieties containing the benzylic alcohol group is provided by the results of Pan, Lachenal, Lapiere and Monties (53). Irradiation of bleached TMP for 24 hours decreased the content of β -O-4 linked guaiacyl units from 1003 to 149 $\mu\text{mol/g}$ of lignin, a decrease by one order of magnitude. Since the carbonyl content represents only about 400 $\mu\text{mol/g}$ of lignin, the cleavage of the phenacyl aryl ether bonds cannot account for such a large loss of β -O-4 linked guaiacyl units observed.

Three concurrent chemical changes in the composition of lignin in yellowed bleached TMP should be observed to satisfy the proposed mechanism. (1) A net increase in aromatic carbonyl groups - this has been observed during light-induced yellowing of untreated bleached TMP, sodium borohydride reduced bleached TMP and reduced and methylated bleached TMP; (2) increase in phenolic hydroxyl content, although phenolic hydroxyl groups are oxidized during yellowing, a threefold increase in phenolic hydroxyl groups was found on uv irradiated bleached TMP that was reduced and methylated; (3) near-uv irradiation of bleached TMP for 24 hours decreased the β -O-4 linked guaiacyl groups by an order of magnitude. It can be concluded that, light-induced yellowing of etherified phenolic groups in lignin proceeds via abstraction of hydrogen from a benzyl alcohol group to produce a ketyl free-radical which in turn undergoes cleavage of the β -O-4 aryl ether bond forming aryl carbonyl and phenolic hydroxyl groups.

It is generally believed that during the initial stages of light-induced yellowing, *o*-quinone is the coloured chromophore formed. However, very little is known about the reaction leading to *o*-quinones. Recently, the reaction of guaiacoxyl free-radicals with ambient oxygen was studied (54). It was found that the formation of yellow chromophores could only occur in the presence of carbon-centred free-radicals, molecular oxygen and phenoxy free-radicals. Yellowing did not occur when any of the aforementioned components were absent.

Summary

In almost fifty years research has shown that light-induced yellowing of mechanical and ultra-high yield pulps occurs by photooxidation of lignin in the fibre wall. The phenoxyl free-radical believed to be the precursor to light-induced yellowing occurs through at least four reaction pathways. The first is absorption of uv light by conjugated phenolic groups, the second is abstraction of hydrogen from the neighbouring phenolic hydroxyl group by the aromatic carbonyl triplet excited state and the third is cleavage of non-phenolic phenacyl- α -O-arylethers. Light-induced yellowing of mechanical and ultra-high yield pulps has been delayed for about 2 hours by the complete reduction of carbonyl groups by sodium borohydride followed by alkylation of phenolic hydroxyl groups. After 2 hours, a fourth reaction pathway occurs through abstraction of benzylic hydrogen by oxygen based free-radicals such as peroxy and alkoxy to produce ketyl free-radicals that undergo facile β -O-4-aryl ether cleavage to phenoxy radicals and the corresponding guaiacyl-1-propanone.

There is general agreement that the phenoxyl free radical reacts with oxygen and/or with functional groups in the fibre wall to form quinones, the coloured chromophores. Although there has been much progress both in elucidating the reaction pathways leading to yellowing of bleached mechanical and ultra-high yield pulps, and in identifying the coloured chromophores, more needs to be known about the key oxidation step of phenoxyl free-radicals to quinones.

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Chapter 2

Raman Spectroscopic Evidence for Coniferyl Alcohol Structures in Bleached and Sulfonated Mechanical Pulps

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Light-induced brightness reversion (photoyellowing) is a major drawback in the use of mechanical pulps. Mechanical pulp would otherwise be a desirable substitute for chemical pulp. Photoyellowing processes in high-yield mechanical pulps would be better understood if the identities of light-sensitive units in lignin were known because the interaction of light with lignin is assumed to be the major cause of photoyellowing. The objective of this study was to identify structures that may be responsible for photoyellowing by investigating the nature of lignin in bleached mechanical and sulfonated chemithermomechanical pulps using Raman spectroscopy, which is particularly well suited to the studies of molecular structures that contain aromatic-ring-conjugated bonds, such as lignin. In this study on the Raman spectra of mechanical pulps, a band at approximately 1654 cm^{-1} was found to be associated with both the α, β C=C bond of coniferyl alcohol and the γ C=O bond of coniferaldehyde structural units in lignin. In pulp and wood samples, the 1654 cm^{-1} band intensity varied depending on whether a sample was bleached, sulfonated, or acetylated. The band persisted, with reduced intensity, after most coniferaldehyde units were removed or modified and, therefore, represented contributions from coniferyl alcohol units alone. The 1654 cm^{-1} band intensity data indicated that the high-yield sulfite pulp had the least aromatic-ring-conjugated double bonds. But even in this case, the residual amount of coniferyl alcohol structures was significant enough to play an important role in the photoyellowing processes. This study showed that the Raman technique is particularly useful in studies of ring-conjugated double bonds in lignocellulosics.

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Lignin-rich high-yield pulps can be produced at less than half the cost of low-yield chemical pulps. Not only do these high-yield pulps have good optical and strength properties, but the mechanical processes associated with their production generally produce less environmentally troublesome effluents. Therefore, substitution of mechanical pulps for chemical pulps is desirable. However, the problem of light-induced brightness reversion (photoyellowing) associated with their use continues to be a major impediment to progress towards this goal. For several decades, researchers have studied various aspects of this phenomenon. Yet the photoyellowing process remains poorly understood.

Cellulose and hemicellulose, constituents of mechanical pulps, do not appear to directly participate in photoyellowing. It is generally agreed that the interaction of light with lignin is the major cause of photoyellowing [1-3]. Lignin has many aromatic structures. Because some of them are modified to varying degrees during bleaching, it is difficult to ascertain which structures are important in photoyellowing. Additional complexity arises from the possibility that native structures may be modified by the processes of mechanical pulping. Mechanochemical effects are known to occur in lignin models [4-6]. Furthermore, for unbleached pulps, the role of native chromophores should also be taken into account. In reality, such chromophores are never completely removed with bleaching, but their concentration is significantly reduced (or structures significantly altered) so that the photoyellowing of a bleached pulp is considered to arise primarily from photo-initiated changes in lignin.

The purpose of this work was to investigate the nature of lignin in bleached mechanical pulp and sulfonated chemithermomechanical pulp (CTMP). Specifically, the purpose was to identify structures that may be responsible for photoyellowing.

Since there are numerous types of structural units in lignin, it is highly unlikely that a single technique will be sensitive to all of them. In addition to the standard analytical techniques, we have been applying Raman spectroscopy to the studies of lignin in pulps. This report focuses primarily on Raman spectroscopic studies of mechanical pulps. Previously, we applied this technique to the studies of celluloses, chemical pulps, and wood.

Although both the Raman and the infrared (IR) techniques provide information on vibrational modes in molecules, the two techniques are complementary. In a molecular system, the vibrational modes that are weak in IR are generally strong in Raman and vice versa. Moreover, fewer bands are active in Raman spectra, which is advantageous in the studies of complex systems.

In a chemical system, Raman scattering coefficients depend on, among other things, the pi electron conjugation [7]. In lignin, a number of structural components contain bonds conjugated to the aromatic ring. These bonds are expected to contribute strongly and would be detected at low concentrations. Further information on Raman spectroscopy can be found elsewhere [8,9].

In addition to mechanical pulps, selected wood samples and lignin models were studied. Wood samples were used to study the effect of mechanical pulping, whereas lignin models were used in the band assignment work. Assignments of certain lignin bands became necessary because previously only band positions were identified [10].

Experimental

Raman Spectroscopy. Raman spectra were acquired using an Instruments SA Ramanor HG2S spectrometer. This is a computer-controlled scanning instrument and has a photomultiplier tube as a detector. The spectra were obtained using either the 514.5-nm line of an argon ion laser or the 647.1-nm line of a krypton ion laser. The laser power at the sample was kept constant by operating the lasers in the light control mode. Samples were irradiated with 100 mW of laser power. Spectral resolution was set for 8 cm^{-1} . The band positions were accurate to 2 cm^{-1} . In most cases, sampling for the Raman experiments was carried out in the traditional 90° scattering configuration. The spectra were recorded in the 250 to 3700 cm^{-1} spectral region. With the exception of sample 3 (Table I), wood samples were air dried and sandwiched between two thin coverslips. Sample 3 was studied using a Raman microprobe. The microprobe consisted of the Ramanor HG2S spectrometer coupled with a modified Natchet NS 400 optical microscope. The Raman spectrum obtained from sample 3 represented a small area of the secondary wall in the woody tissue (S_2 cell wall area). Pulps were studied as handsheets. Ball-milled enzyme lignin and hydrogenated pulp were studied as thin pellets. Lignin models and other compounds were studied either in glass capillaries or as thin films on coverslips. Wood and pulp samples were irradiated in the presence of molecular oxygen in order to quench the sample-generated fluorescence [11]. In most cases, 10 to 15 scans were added to increase the signal-to-noise ratio in the spectrum. Often, an averaged acquired-spectrum contained a significant contribution from fluorescence. This contribution to the background was broad and was removed by subtracting a mathematically generated curve that paralleled the fluorescence spectrum. Most background-subtracted spectra were smoothed once using a 7-point Savitsky-Golay algorithm [12].

Other Instrumentation. Brightness of pulp handsheets was measured with a Technibrite TB-1 instrument using Tappi Standard T525 om-86 [13]. Diffuse reflectance as well as transmission FT-IR spectra were obtained on a Nicolet 6000c spectrophotometer.

Samples. All samples that were studied are listed in Table I; each sample is assigned a number and identified. Molecular structures of the compounds listed are given in Figure 1.

Wood. Wood samples were from black spruce (*Picea Mariana* (Mill.) B.S.P.; samples 1 to 3 and 29 to 31). A small piece of wood was microtomed to obtain approximately 8- by 4-mm, 30- μm -thick transverse sections that were first extracted in toluene/ethanol and then solvent exchanged to methanol. The sections were stored in methanol in the dark.

A few wood sections were delignified using the acid chlorite method [14] (sample 2). In order to obtain sample 3, a 1.6- μm spot in the S_2 cell wall of a cross section was laser-delignified (514.5-nm line) by exposing it in a Raman microprobe experiment [15]. In our laboratory, it has been observed that the

Table I. Presence or Absence of Band in 1645 to 1654 cm⁻¹ Region (~1650 cm⁻¹ Band) in Wood, Mechanical Pulps, and Lignin Models

Sample number	Sample description	~1650 cm ⁻¹ band		
		Present	Absent	Comments
Wood and pulp samples				
1	Spruce wood	X		Band at 1654 cm ⁻¹
2	Acid-chlorite-delignified 1		X	No C=O, C=C bands
3	Laser-delignified 1		X	No C=O, C=C bands
4	Unbleached spruce mechanical pulp	X		Brightness 52.8
5	Sodium-borohydride-treated 4	X		Brightness 66.2
6	Peroxide-hydrosulfite-treated 4	X		Brightness 65.9
7	Sodium-borohydride-treated 6	X		Brightness 76.9
8	Unbleached spruce sulfite	X		Brightness 66.3
9	Hydrogen-peroxide-bleached sulfite	X		Brightness 64.9
10	Hydrosulfite-bleached sulfite	X		Brightness 64.3
11	Unbleached stone groundwood pulp	X		Brightness 58.2
12	Hydrogen-peroxide-bleached 11	X		Brightness 72.4
13	Hydrosulfite-bleached 11	X		Brightness 63.4
Lignin models and other compounds				
14	Coniferyl alcohol	X		Band at 1650 cm ⁻¹
15	Isoeugenol methyl ether		X	Band at 1643 cm ⁻¹
16	Eugenol		X	Band at 1634 cm ⁻¹
17	Coniferaldehyde	X		Bands at 1652 and 1628 cm ⁻¹
18	Trans-Ferulic acid		X	Band at 1628 cm ⁻¹ In methanol also at 1670 cm ⁻¹
19	Dehydro diisoeugenol	X		Band at 1648 cm ⁻¹
20	Dihydro dehydro diisoeugenol		X	No C=C band
21	Alpha-Guaiacoxy propiovavanillone		X	Band at 1670 cm ⁻¹
22	4,4' Dipropyl 6,6' biguaiacol		X	Band at 1604 cm ⁻¹
23	3-methoxy-ortho-benzoquinone		X	Not seen with 514.5-nm excitation
24	2-methoxy-para-benzoquinone		X	Not seen with 514.5-nm excitation
25	Stilbene		X	Band at 1638 cm ⁻¹
26	Pinosylvin mono methyl ether		X	Band at 1635 cm ⁻¹
27	1,3-bis(3-methoxy-4-benzyloxy-phenyl) prop-2-ene-1-one	X		Very weak feature
28	Coniferin	X		Band at 1650 cm ⁻¹
Additional samples				
29	Sodium-borohydride-treated black spruce	X		Band at 1652 cm ⁻¹
30	Acetylated black spruce		X	1650-1665 cm ⁻¹
31	Hydrogen-peroxide-treated black spruce	X		Band at 1654 cm ⁻¹
32	Ball-milled enzyme lignin	X		1652 cm ⁻¹
33	Hydrogenated (Pd-C ^a 5%) pulp 7	X		Band at 1650 cm ⁻¹

^aPalladium-on-activated carbon.

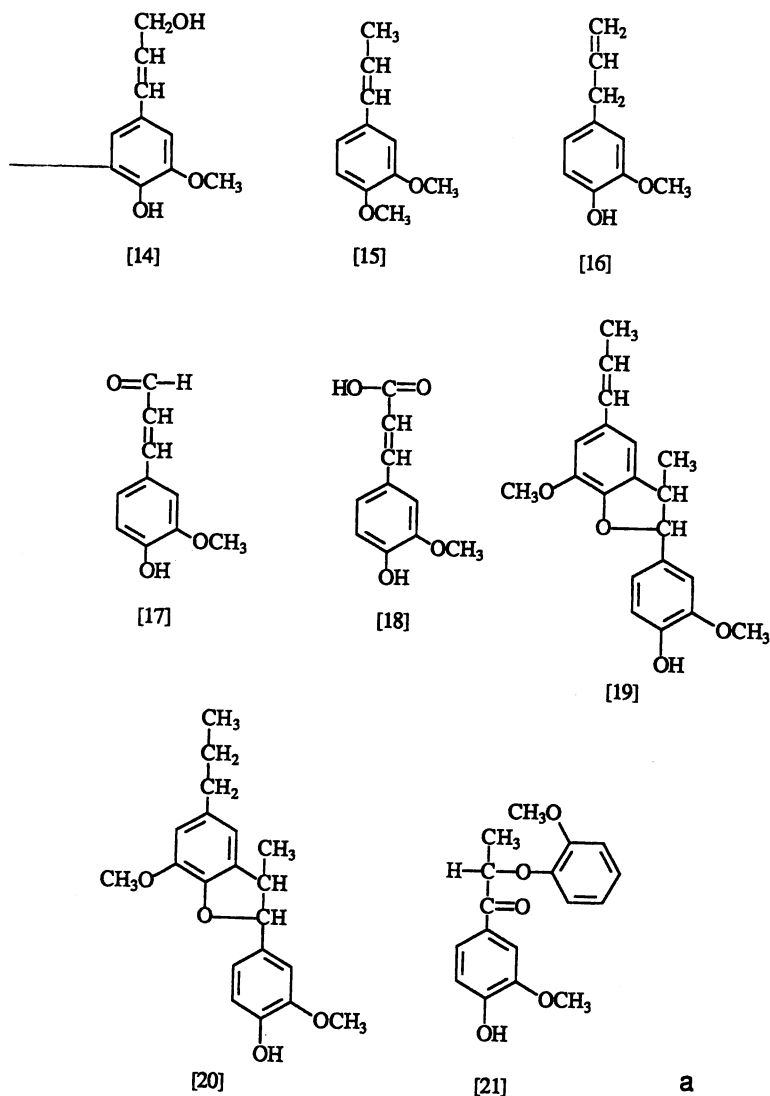
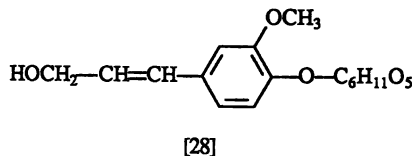
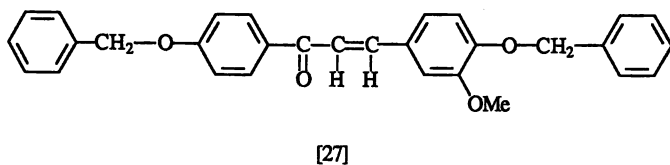
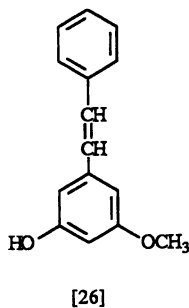
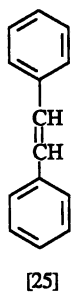
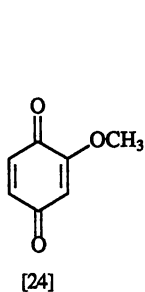
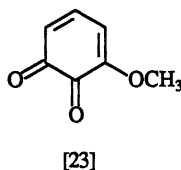
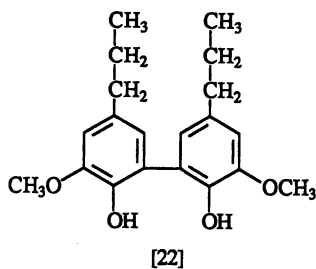


Figure 1. (a) Molecular structures: coniferyl alcohol [14], isoegenol methyl ether [15], Eugenol [16], coniferaldehyde [17], trans-ferulic acid [18], dehydro diisoeugenol [19], dihydro dehydro diisoeugenol [20], alpha-guaiacoxy propiovanillone [21]; (b) Molecular structures: 4,4'-dipropyl 6,6'-biguaiacol [22], 3-methoxy-ortho-benzoquinone [23], 2-methoxy-para-benzoquinone [24], stilbene [25], pinosylvin mono methyl ether [26], 1,3-bis(3-methoxy-4-benzyloxy-phenyl) prop-2-ene-1-one [27], coniferin [28].



b

Figure 1. Continued.

extended high-density laser irradiation of a small water-immersed cell wall area leads to complete lignin removal. Once a satisfactory stage of lignin decay was achieved, an *in situ* micro Raman spectrum was obtained. In order to completely exclude scattering from regions outside the focused spot, a pinhole was inserted in the back image plane of the microscope objective. Sample 3 is the only sample whose Raman spectrum was obtained using the Raman microprobe. The other samples were studied in the macro sampling mode, and therefore, their spectra provide vibrational information that is representative of the sample as a whole.

A few of the transverse sections were treated with sodium borohydride to remove contributions from chromophores and aromatic carbonyls (sample 29). The sections were treated with 0.5 M NaBH₄ in water for 6 days at room temperature. At the end of the treatment, the sections were washed with bisulfite and distilled water. Acetylation of black spruce samples was carried out for 1 week in pyridine using acetic anhydride (1:1) as the acetylating agent [16] (sample 30). In wood, the reaction acetylates both the alcoholic groups in carbohydrates and the phenolic hydroxyls in lignin. Acetylation using acetic anhydride was the preferred method since no additional chromophores were generated in the process. In conventional Raman, chromophores are often the cause of the problematic fluorescence signal that can mask Raman scattering. Hydrogen peroxide was used to carry out oxidative bleaching of a few additional wood sections (sample 31, Table I). We used 8% H₂O₂ at room temperature in this method [16].

Pulps. The spruce thermomechanical pulp (TMP) was obtained from Consolidated Papers Inc., Wisconsin Rapids, Wisconsin. This pulp is sample 4 in Table I. Samples 5, 6, and 7 were the results of various bleaching treatments.

A sample of unbleached TMP was reductively bleached with 0.5 M NaBH₄ for 4 days (sample 5). Another amount of sample 4 was bleached in two stages. In the first stage, it was treated with 8% H₂O₂ (on pulp) in aqueous alkali for 4 h at 40°C in the presence of sodium silicate and magnesium sulfate; the pH of the liquor was 10.5. After treatment, the pulp was washed with distilled water until all the alkali was removed. In the second stage, the peroxide-bleached pulp was treated with a 2% hydrosulfite solution at 70°C for 1 h. This pulp was thoroughly washed and became sample 6 in Table I. Some of the two-stage bleached pulp was further treated in the third stage in a 0.5 M NaBH₄ solution for 4 days (sample 7).

The hydrogenated pulp, sample 33, was obtained by hydrogenating sample 7 in the presence of a solid catalyst, palladium-on-activated carbon (5%) [16].

The rest of the pulp samples listed in Table I (8 to 13) were provided by Dr. C.-H. Tay of Abitibi-Price Inc., Mississauga, Ontario, Canada. These samples were in the form of handsheets and were stored in the dark in a freezer at -18°C until used.

Lignin, lignin models, and other compounds. Ball-milled enzyme lignin, sample 32 in Table I, was provided by Dr. H. Chum of the Natural Renewable Energy Laboratory, Golden, Colorado. It was produced by ball milling cottonwood followed by enzyme hydrolysis.

With the exception of stilbene, all organic compounds listed in Table I (samples 14 to 28) were either obtained commercially or prepared by scientists at the USDA Forest Service, Forest Products Laboratory using well-established methods. Purchased chemicals were from both Aldrich Chemical Co., Milwaukee, Wisconsin, and Fluka Chemical Corporation, Ronkonkoma, New York. The Raman data for stilbene were taken from the literature [17]. Whenever the purity of a compound was in doubt, it was checked by gas chromatography-mass spectrometry. The Raman spectra reported here are from compounds that were more than 99% pure.

Most compounds were studied as liquids or solids, depending on their state at ambient conditions. However, a few that were either available in very small quantities or difficult to study were analyzed in solutions. Others were studied both as solids and in solution to determine if any changes occurred in their spectral features upon dissolution. Coniferaldehyde and trans-ferulic acid (samples 17 and 18, respectively) were studied as solids and in solution in methanol. 3-methoxy-*o*-benzoquinone and 2-methoxy-*p*-benzoquinone (samples 23 and 24) were studied as solutions in benzene.

Results and Discussion

Raman spectra obtained from pulp samples 4 to 13 are shown in Figures 2 to 4. For these samples, pulping and bleaching processes produced changes in the 850 to 1850 cm^{-1} spectral region. The features in these spectra are typical of lignocellulosic materials (authors' unpublished work).

Table II lists the Raman peak positions for samples 4 and 11, which are typical of unbleached lignin-rich wood pulps. These peaks have been assigned in terms of contributions by cellulose and lignin. Raman contributions from hemicelluloses were expected to be broad and to occur at wavenumbers where cellulose contributions were detected. In Table II, certain bands are assigned to specific chemical-group vibrations. The assignment of bands to various groups in cellulose was based on literature [18]. The lignin-related assignments are based on the work described in this paper and the authors' unpublished work.

None of the bands in the region 1500 to 1800 cm^{-1} was assigned to cellulose or hemicelluloses. Assignments in this region were made on the basis of the spectra shown in Figure 5. Figure 5A shows spectra of a black spruce section; Figure 5B shows an acid-chlorite-delignified section; Figure 5C shows a small laser-delignified S_2 cell wall area. Because no Raman bands were observed in the spectra of the latter two samples in the region 1500 to 1800 cm^{-1} , the spectral contributions at approximately 1595, 1620, and 1654 cm^{-1} arose from lignin and chromophores in the woody tissue. In Figure 5A, the sharp feature at 1550 cm^{-1} is from molecular oxygen.

Spruce Mechanical Pulps and Treatments. When spruce pulp sample 4 was treated with borohydride, the pulp became brighter (Table I). In the Raman spectrum of the bleached pulp, bands at 1620 and 1654 cm^{-1} declined in intensity (Table III). These changes were probably caused by the removal or modification, or both, of chromophores and aromatic carbonyl groups. It is known that

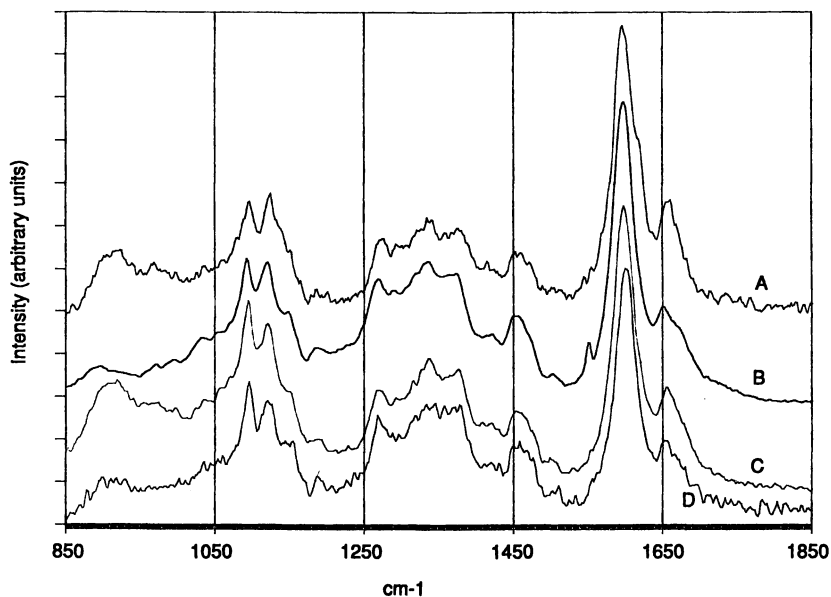


Figure 2. Raman spectra in spectral region 850 to 1850 cm^{-1} ; A, unbleached spruce mechanical pulp; B, borohydride-treated; C, peroxide-hydrosulfite-treated; D, peroxide-hydrosulfite-borohydride-treated. Peak at 1550 cm^{-1} in B is due to molecular oxygen.

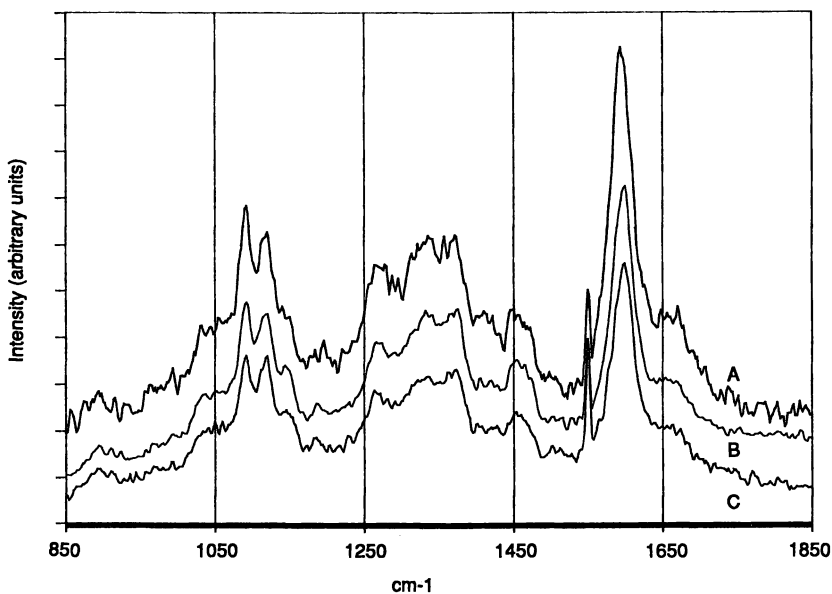


Figure 3. Raman spectra in spectral region 850 to 1850 cm^{-1} ; A, unbleached spruce sulfite pulp; B, peroxide-bleached; C, hydrosulfite-bleached. Band at 1550 cm^{-1} in all three spectra is due to molecular oxygen.

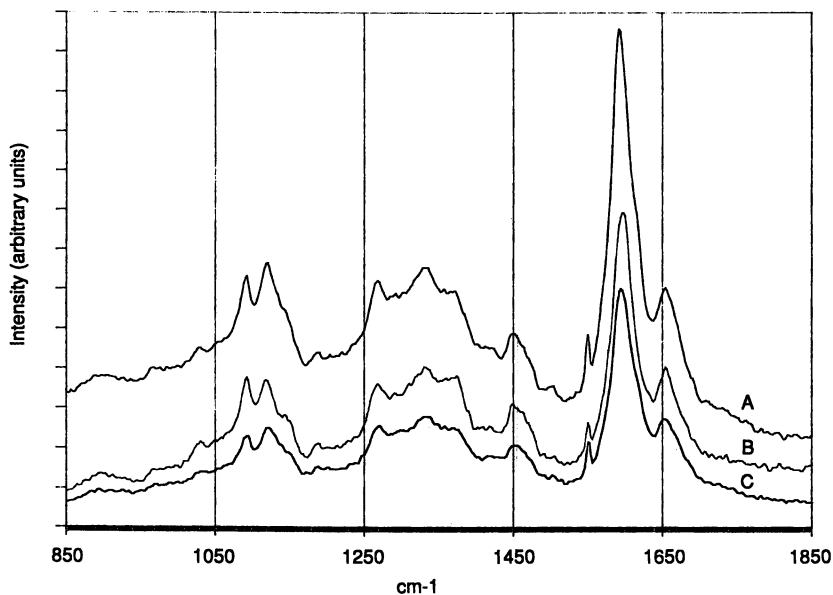


Figure 4. Raman spectra in spectral region 850 to 1850 cm^{-1} ; A, unbleached stone groundwood pulp; B, peroxide-bleached; C, hydrosulfite-bleached. Sharp band at 1550 cm^{-1} is due to molecular oxygen.

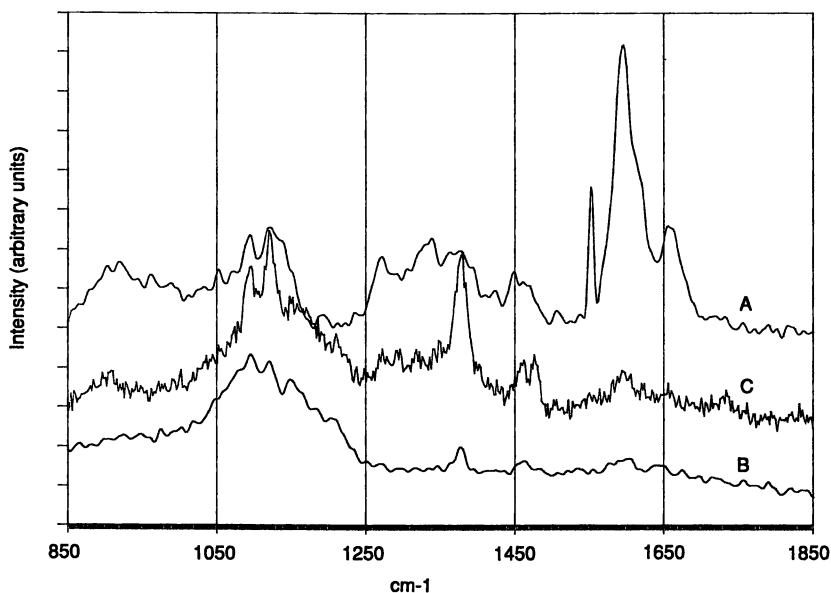


Figure 5. Raman spectra in spectral region 850 to 1850 cm^{-1} ; A, spruce wood; B, acid-chlorite-delignified; C, laser-delignified spot in S_2 layer of cell wall. Band at 1550 cm^{-1} in A is due to molecular oxygen.

Table II. Contributions From Cellulose and Lignin in the Raman Spectra (850 to 1850 cm⁻¹) of Unbleached Mechanical Pulps^a

Band position (cm ⁻¹)	Contributors and chemical group
895	Cellulose, HCC and HCO bending at C ₆
1000	Cellulose, C-C and C-O stretching
1035	Cellulose, C-C and C-O stretching
1065	Cellulose, C-C and C-O stretching
1098	Cellulose, C-C and C-O stretching
1120	Cellulose, C-C and C-O stretching; lignin
1150	Cellulose, heavy atom stretching and HCC and HCO bending
1275	Cellulose, HCC and HCO bending; lignin
1290	Cellulose, HCC and HCO bending
1335	Cellulose, HCC, HCO and HOC bending; lignin
1375	Cellulose, HCC, HCO and HOC bending; lignin
1380	Cellulose, HCC, HCO and HOC bending; lignin
1410	Cellulose, HCC, HCO and HOC bending
1460	Cellulose, HCH and HOC bending; lignin
1595	Lignin, phenyl group
1620	Lignin, ethylenic C=C in coniferaldehyde
1654	Lignin, ethylenic C=C in coniferyl alcohol, C=O in coniferaldehyde

^aCellulose assignments are from Reference 18.

Table III. Relative Band Intensities for 1620 and 1654 cm⁻¹ Raman Features in Spruce Mechanical Pulps^a

Sample	I ₁₆₂₀	I ₁₆₅₄	Intensity remaining in 1654 cm ⁻¹ band(%)
4 Spruce TMP	1.64	1.00	100
5 Sodium-borohydride-treated 4	0.80	0.80	80
6 Peroxide-hydrosulfite-treated 4	0.93	0.71	71
7 Sodium-borohydride-treated 6	0.90	0.71	71

^aIntensities relative to the 1098 cm⁻¹ band of cellulose.

borohydride attacks both chromophores and aromatic carbonyls [19]. The Raman spectroscopic data support the expectation that chromophores were being attacked by borohydride, since the pulp chromophores contributed at 1620 and 1654 cm⁻¹ [20].

To find out if carbonyls were being attacked, we first determined the wavenumber positions where the carbonyls were likely to contribute. To obtain this information, lignin models containing appropriate carbonyl groups were

studied (Table I, Fig. 1) (samples 17 and 21). Raman spectra of these samples in the 1500 to 1800 cm^{-1} region are shown in Figure 6 along with other models.

As Figures 6D and 6G and Table I (band positions for C=O and C=C) show, coniferaldehyde contributed weakly around 1654 cm^{-1} . The other type of aromatic carbonyl structure found in lignin and thought to be important in its photochemistry is the α C=O in β -O-4 linked lignin units, which was found to contribute at 1670 cm^{-1} (sample 21) rather than at 1654 cm^{-1} . The coniferaldehyde structure had an additional band at 1628 cm^{-1} (Table I) from the α, β C=C bond. Hence, when pulp was reductively bleached, contributions from coniferaldehyde structures at both these wavenumbers were removed. Therefore, the Raman spectral observations were consistent with the expectation that both the chromophores and the coniferaldehyde structures were attacked during borohydride bleaching. The technique appears to be effective in studying such changes in pulps. It is difficult to comment on the effect of borohydride on the α C=O β -O-4 type carbonyls because there was no significant intensity at 1670 cm^{-1} even for the unbleached pulp. Perhaps the concentration of such groups is very low in pulps or their contribution is present within the decaying wing of the band at 1654 cm^{-1} . To address this question, IR spectroscopy was used to study these pulps in the carbonyl-bond stretching region. However, the 1640 to 1670 cm^{-1} region was found to have contributions from not only the stretching modes of the C=C and C=O bonds in lignocellulosics, but also from the bending mode of water. The IR technique is especially sensitive to moisture in the samples. In view of this, carbonyl-related changes were difficult to measure quantitatively.

Even after 4 days of bleaching by sodium borohydride, significant intensity (80% of that in sample 4 (Table III)) remained in the 1654 cm^{-1} band. To determine what other structures may have contributed at 1654 cm^{-1} , lignin models containing ethylenic double bonds were studied. These were samples 14 to 16, 18, 19, and 25 to 28 (Table I, Fig. 1). From the spectra in Figure 6 and data in Table I, it is clear that a very strong band existed near 1650 cm^{-1} in coniferyl alcohol (sample 14), isoeugenol methyl ether (sample 15), dehydro diisoeugenol (sample 19), and coniferin (sample 28). All these structures had an α, β C=C bond attached to one aromatic ring. Moreover, in the case of model 19, this band completely disappeared after hydrogenation, as is noted in the spectrum of dihydro dehydro diisoeugenol (sample 20) (Table I, Fig. 6F). These observations clearly indicate that the band under consideration is associated with the C=C bond conjugated to the aromatic ring. Furthermore, other than coniferaldehyde, which had a C=C band at 1628 cm^{-1} , coniferyl alcohol structures are the only structures in lignin likely to have α, β C=C bonds. Therefore, we assigned a portion of the 1654 cm^{-1} band intensity to coniferyl alcohol structures in pulps. Chemical modification of the phenolic hydroxyl to an ether bond did not result in any significant shift of the C=C vibrational frequency. This was obvious when data for the C=C stretching mode were compared for coniferyl alcohol (sample 14) and coniferin (sample 28) (Table I). The latter is the paralogoside of coniferyl alcohol. Such an assignment of the residual band at 1654 cm^{-1} is also supported by the fact that borohydride is not expected to attack coniferyl alcohol groups [19, 21].

Once again, after sample 4 was bleached with peroxide and hydrosulfite, the features at approximately 1620 and 1654 cm^{-1} were reduced in intensity. This observation can be explained by the fact that coniferaldehyde and chromophores were removed by the bleaching sequence. When a pulp sample was further treated by sodium borohydride for 4 days, it was brightened considerably (Table I), but no additional changes were seen in the Raman spectrum of this treated pulp (Table III and Fig. 2D). The increased brightness resulted from the fact that the third stage extended borohydride bleaching effectively removed pulp chromophores that were either not completely removed or were perhaps even generated in the previous two-stage sequence. The band at approximately 1654 cm^{-1} remained and supported the notion that coniferyl alcohol groups remained unattacked.

Spruce Sulfite Pulps and Treatments. Sulfonated CTMP (sulfite) pulps are usually brighter than unbleached mechanical pulps. It is generally accepted that the process of sulfonation attacks chromophore, coniferaldehyde, and coniferyl alcohol structures [22-29]. The Raman spectroscopic observations in Figure 3 and Table IV seem to support such results. Attack on both the chromophore and coniferaldehyde structures resulted in near disappearance of the shoulder at 1620 cm^{-1} and reduced intensity at 1654 cm^{-1} . Moreover, support for attack on coniferyl alcohol structures is seen when one compares data for samples 7 and 8 (Tables III and IV). Sample 8 was the unbleached spruce sulfite pulp. In this pulp, the additional 30% reduction in the intensity of the 1654 cm^{-1} band was caused by the removal of some coniferyl alcohol structures. However, from Figure 3A, it is clear that there was still significant intensity left in this band. The intensity of the band remained more or less unchanged when sample 8 was bleached (Table IV). We interpreted this result in terms of residual coniferyl alcohol structures. Since such structures survive both oxidative and reductive bleaching, further significant decline in the 1654 cm^{-1} band was not observed.

Stone Groundwood Pulps and Treatments. Raman spectra of another set of mill pulps are shown in Figure 4. As expected, the unbleached stone groundwood pulp (sample 11) shows the 1620 and 1654 cm^{-1} features. As a result of bleaching, these bands were reduced to varying degrees (Table V). The 1654 cm^{-1} band intensity did not change significantly as is obvious from the relative band intensity data in Table V. The difference between this observation and the approximately 20% to 30% intensity reduction seen earlier in black spruce pulps (samples 4 to 7) could have been caused by conditions of bleaching and the nature of pulps. In the case of stone groundwood pulp, the wood species used are not known. Moreover, since bleaching was carried out in a pulp production facility, it may not have been as thorough as was the case for samples 4 to 7.

Other Structures. From the results on the pulps studied here, it appears that coniferyl alcohol structures survive bleaching and sulfonation treatments. As alternative causes of residual intensity at 1654 cm^{-1} , we have considered quinone and stilbene structures. Stilbene structures (samples 25 and 26) give a Raman band around 1635 cm^{-1} (Table I, Fig. 6I,J). Such structures have not been

Table IV. Relative Band Intensities for 1620 and 1654 cm⁻¹ Raman features in black spruce and sulfonated chemithermomechanical pulps^a

Sample	I ₁₆₂₀	I ₁₆₅₄	Intensity remaining in 1654 cm ⁻¹ band (%)
1 Spruce wood	1.81	1.21	100
8 Spruce sulfite	0.78	0.50	41
9 Hydrogen-peroxide-bleached 8	0.76	0.39	32
10 Hydrosulfite-bleached 8	0.78	0.44	37

^aIntensities relative to the 1098 cm⁻¹ band of cellulose.

Table V. Relative Band Intensities for 1620 and 1654 cm⁻¹ Raman features of stone groundwood pulps^a

Sample	I ₁₆₂₀	I ₁₆₅₄	Intensity remaining in 1654 cm ⁻¹ band (%)
11 Stone groundwood	1.79	1.25	100
12 Hydrogen-peroxide-bleached 11	1.23	1.11	89
13 Hydrosulfite-bleached 11	1.90	1.30	104

^aIntensities relative to the 1098 cm⁻¹ band of cellulose.

shown to be present in wood. Furthermore, the possibility of stilbene structures being produced during pulping does not explain the fact that the band also survives in wood samples (Table I, Fig. 7). Figure 7 is a bar chart of the 1654 cm⁻¹ band intensity data for both wood and pulp samples.

It has been suggested that quinones are present in milled wood lignins [30]. However, their occurrence in wood and pulps is doubtful. The quinone models studied, 3-methoxy-*o*-benzoquinone (sample 23) and 2-methoxy-*p*-benzoquinone (sample 24), did not show any Raman bands when studied using 514.5-nm laser excitation. These compounds were fluorescent and degraded in the laser beam. Nevertheless, such structures, if present, are not expected to survive various bleaching treatments. Quinones are easily attacked chemically and probably do not survive peroxide and borohydride bleaching [19, 31, 32].

Hydrogenated Pulp. In an earlier study, Tschirner and Dence [16] concluded that aromatic-ring-conjugated double bonds are not very important in photoyellowing. That conclusion was based on the fact that the mechanical pulp subjected to hydrogenation still yellowed. However, no evidence was produced that hydrogenation of ethylenic C=C bonds did indeed occur in the pulp. We have subjected a bleached pulp (sample 7) to hydrogenation under conditions similar to those used in one of the methods in the study by Tschirner and Dence. When such a pulp was analyzed using Raman spectroscopy, the band at 1654 cm⁻¹ was still present (Fig. 8A). Although the spectrum of the hydrogenated pulp was noisier, there was no doubt that the band intensity was similar to

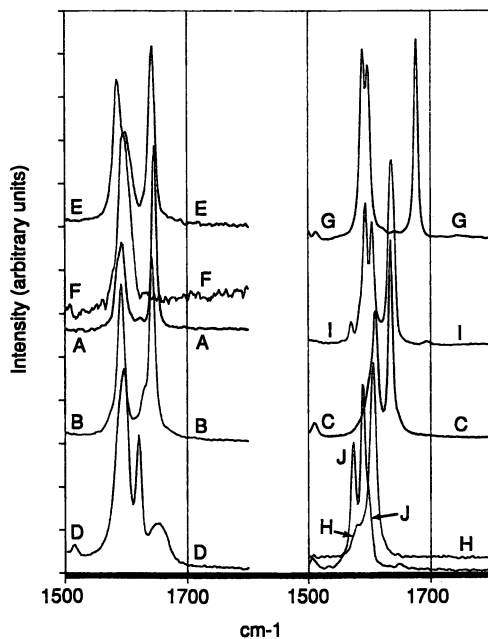


Figure 6. Raman spectra in spectral region 1500 to 1800 cm^{-1} . Sample numbers: A, 14; B, 15; C, 16; D, 17; E, 19; F, 20; G, 21; H, 22; I, 26; J, 27. Samples are identified in Table I and Figure 1.

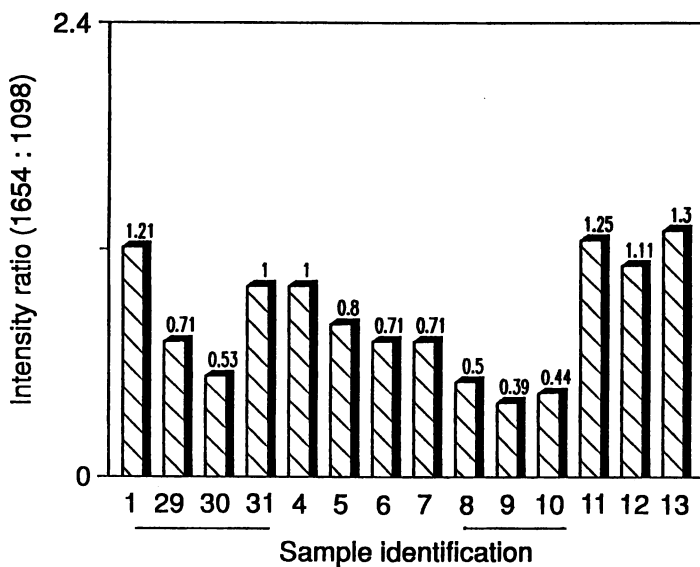


Figure 7. Relative band intensity of 1654 cm^{-1} Raman band in various wood and pulp samples. Samples are identified in Table I.

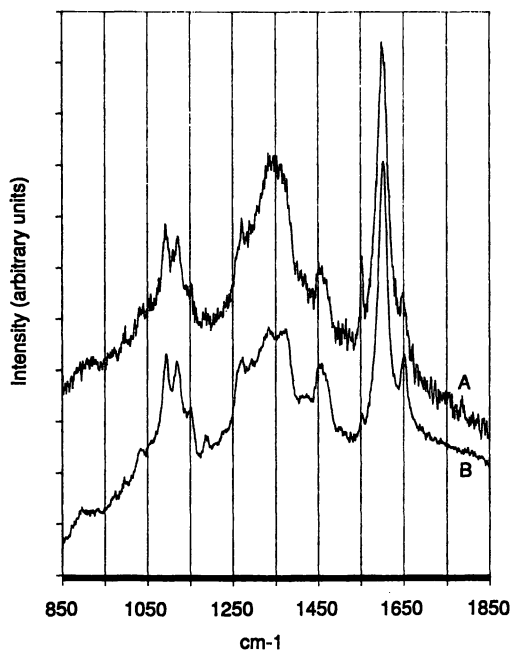


Figure 8. Raman spectra in spectral region 850 to 1850 cm^{-1} for A, hydrogenated bleached pulp, and B, control pulp. Band at 1550 cm^{-1} in both spectra is due to molecular oxygen.

that in the unhydrogenated pulp (Fig. 8B). The data imply that the treatment did not reduce conjugated double bonds in the pulp. Further experiments are planned to study the behavior of pulps under various hydrogenation conditions.

The relevance of aromatic-ring-conjugated double bonds to the photoyellowing processes was highlighted by studies of a ball-milled lignin sample [33]. Lin and Kringstad showed unequivocally that unless such bonds were hydrogenated, the lignin continued to photoyellow. We believe that in the pulp the hydrogenation reaction failed for reasons of heterogeneity and accessibility.

Implications to Photoyellowing. On the basis of the Raman spectral results, survival of coniferyl alcohol structures (this includes both phenolics and those etherified at the para-position) in bleached and sulfite pulps would seem to be a major reason why pulps yellow in daylight. Such groups are expected to participate in the primary photochemical events that lead to yellowing. Thus, in pulps, coniferyl alcohol structures would act as leucochromophores. Photoyellowing of coniferyl alcohol structures has been evaluated [34], and it has been reported that the free phenolic structure contributes much more to yellowing than does the para-etherified unit.

Figure 7 shows the samples with the lowest intensity for the 1654 cm^{-1} band were 8, 9, 10, and 30. These were unbleached sulfite pulp, peroxide-bleached sulfite pulp, hydrosulfite-bleached sulfite pulp, and acetylated wood section, re-

spectively. The three pulp samples were expected to show reduced yellowing because the concentrations of coniferyl alcohol structures were lowest in these pulps. In fact, sulfonated pulps yellow to a lesser degree than do unsulfonated pulps [22, 23]. It is not clear if the intensity reduction in the acetylated wood section was due to more complete removal of chromophores or coniferylaldehyde structures or to modification of the Raman scattering coefficients of coniferyl alcohol structures. Since pulp acetylation was not expected to attack the coniferyl alcohol double bonds, reduction in the number of such bonds is not likely to be a cause for the reduced Raman intensity at 1654 cm^{-1} . Whatever the case, acetylation was expected to reduce the electronic absorption coefficient of such units in the 300- to 400-nm region [35, 36]. As a result, the sample was expected to show limited absorption and, hence, limited yellowing. Another way pulp acetylation can affect photoyellowing is through altering the mechanisms of yellowing, since photogeneration of phenoxy radicals would be modified. Such expectations are supported by reports in the literature that acetylation of lignin significantly reduces photoyellowing [37].

Raman Sensitivity to Conjugated Structures. Certain Raman bands show enhanced intensities when aromatic ring conjugation is present [7, 38-40]. In the case of lignin models, both coniferyl alcohol and coniferaldehyde structures showed conjugation enhancements [41, 42]. This is the primary reason why such structures are easily detected in Raman spectroscopy. Since the concentrations of both the coniferyl alcohol and coniferaldehyde structures are low in wood [43] (and are not expected to change considerably with mechanical pulping), characteristic C=C bands in IR spectroscopy are expected to be weak. For coniferyl alcohol, this becomes obvious when IR and Raman intensities (authors' unpublished data) are compared for the band associated with the ring-conjugated C=C bond. In Raman, the relative intensity (relative to the 1595 cm^{-1} benzene ring mode) is approximately 16 times higher than in IR. Moreover, when the 2935 cm^{-1} band was chosen as an internal standard in both IR and Raman, the latter technique was found to be even more sensitive (30 times as opposed to 16). This reference-band-dependent sensitivity difference between the two techniques can be accounted for by considering that in the Raman spectrum of coniferyl alcohol, the scattering coefficient for the 1595 cm^{-1} band is enhanced by conjugation effects. (In Raman spectroscopy, the scattering coefficients depend on the excitation frequency and the Raman shifts. In conventional laser Raman (excitation in visible), intensity differences caused by differences in Raman shifts are not significant. Therefore, such a dependence is not the cause for the difference between the intensity ratios when the 1595 and 2935 cm^{-1} Raman bands are chosen as internal standards.) Including this information in our discussion, the two techniques are better compared when the 2935 cm^{-1} band is used as an internal standard. This suggests that previous IR studies of mechanical pulps [3] would not have been sensitive to the changes in the amounts of coniferyl alcohol structures.

Concluding Remarks

Raman spectroscopic studies of mechanical pulps indicated that coniferyl alcohol structures are present in bleached and sulfonated pulps. The concentrations of such structures were found to be lowest in pulps that were produced by the chemithermomechanical process involving sulfonation. These findings were supported by studies of lignin models and other samples. In the case of a bleached mechanical pulp, hydrogenation (palladium-on-activated carbon) apparently did not reduce the aromatic-ring-conjugated C=C bonds. Coniferyl alcohol structures, by virtue of being precursors of yellowed products, are implicated in the photoyellowing of pulps. In the studies of aromatic-ring-conjugated structures, Raman spectroscopy was found to be much more sensitive than infrared spectroscopy.

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Chapter 3

Action Spectra in the UV and Visible Region of Light-Induced Changes of Various Refiner Pulps

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Various chemimechanical refiner pulps (unbleached, peroxide-bleached and pre-yellowed) were irradiated with monochromatic light at selected wavelengths. The change in reflectance at 457 and 557 nm was monitored using UV-VIS reflectance spectroscopy and post-color values were calculated from the reflectance changes. Photoyellowing and photobleaching were observed. Unit yellowing was subsequently obtained using experimentally derived kinetic curves for the reflectance versus exposure dose at a certain wavelength. The action spectra for the photoyellowing were obtained by plotting the reciprocal of the exposure dose necessary to produce a certain change versus wavelength. A different set of action spectra for both photoyellowing and photobleaching was constructed by keeping the exposure time constant and plotting the ratio of the photoyellowing or photobleaching to the light intensity at a certain wavelength against wavelength. The action spectra obtained with the two methods are similar in shape, suggesting that the observed changes are linearly dependent on the light intensity. Photoyellowing was found to be most extensive with light of wavelength 310-320 nm. For strongly pre-yellowed pulp, photobleaching with a maximum effect at 430-450 nm was observed to be the major process on irradiation. The implications of the action spectra for the different pulps are discussed.

In spite of numerous efforts and considerable progress the detailed mechanism of the photoyellowing of high-yield pulps is still unsettled. The inherent chromophores in the wood and fresh pulps, their modification during manufacturing and subsequent reactions during aging or/and photo-oxidation are indeed difficult to establish and further work is required to reach a full understanding of the process.

The biological effects of ultraviolet exposure of human skin have been studied extensively because of the growing general awareness of the risks of solar ultraviolet exposure [1]. A further spur to research has come from the benefits of ultraviolet radiation, the ultimate goal being to develop new phototherapy and other methods. In that context the limits of safe exposure to long wavelength ultraviolet radiation have been estimated and different techniques for their assessment have evolved. High-

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intensity sources of monochromatic light of various wavelengths are now available for basic research and ingenious detection systems have been developed to measure the human skin response. The knowledge obtained in these studies should be equally applicable to radiation studies of other biological materials such as wood and wood products.

The light-induced yellowing or color reversion of high-yield pulps can in some respects be compared to the photochemical ultraviolet-induced formation of erythema (redness) of the skin. One important advantage for the pulp researcher, however, is the fact that delayed biochemical reactions, often referred to as sunburn in case of skin, are absent. Only in fresh wood material is there any biochemical activity that might cause discoloration on storage [2]. Enzymes are readily inactivated by the heat used in manufacturing pulps from wood logs or chips.

Nevertheless, delayed photochemical reactions after the end of the exposure are likely in both systems. For wood pulps, the outcome is strongly influenced by factors such as the increased lifetime and much retarded transport rate due to the trapping of intermediates and photoproducts in the solid matrices. This has to be taken into account when designing experiments. The main color changes caused by light in mechanical pulps are fairly rapid, which enables accurate measurements to be made either directly after the irradiation or after a certain delay. Thermal reactions, e.g. hydrolysis and oxidation, which also occur in the pulps, can be prevented by keeping the pulps in a freezer before analysis.

Most photobiological responses follow the reciprocity law, which states that a given exposure dose yields a constant biological response. This means that constant quantities of some photochemical reaction products are produced per absorbed photon at given wavelengths and that these products yield a constant biological response [1]. This should certainly be true also for light-induced changes in pulps.

Action Spectra

The method used in the present work to obtain action spectra of wood pulps is analogous to that developed to construct the erythema action spectrum for human skin [1]. In order to evaluate the action spectra for the photochemical discoloration of the pulps, the spectral irradiance at the sample position must be measured and the response of the exposure, e.g. in terms of the reflectance at 457 nm, has to be analyzed. Thus, an action spectrum takes into account both the exposure dose and the character of the chromophores that are photoactive in the pulp. The action spectrum for the yellowing is then obtained by plotting the reciprocal of the exposure dose necessary to produce a certain predetermined degree of yellowness versus wavelength.

In principle, a carefully constructed action spectrum may be used to identify the absorbing chromophore. This is possible at least when the action spectrum corresponds closely to the absorption spectrum of a molecule that can be shown to react photochemically in the wavelength region studied [3]. The success of this approach decreases rapidly as the number of different reacting chromophores increases. In such cases the action spectrum becomes complex and difficult to interpret. When a large and varied number of chromophores are involved, some of them may only act as intermediates in conveying the incident energy to important sites in the material [3], making the interpretation of the action spectrum even more complicated. Further difficulties are shifts in the absorption spectra caused by solvent changes and different states of aggregation.

The situation is also complicated by the fact that the response, e.g. the yellowing, in reality is not a function of a single radiation wavelength, a fact that has led to the construction of polychromatic action spectra [3]. Nevertheless, the polychromatic action spectra become very complex and may obscure the individual chromophores.

The wavelength dependence of the photoyellowing and photobleaching of

groundwood was studied by Nolan et al. [4] and van den Akker et al. [5] more than forty years ago. The latter authors presented a relative spectral sensitivity curve over the wavelength region 250-385 nm for eastern spruce groundwood together with spectral absorption coefficient curves of native lignin and lignin derivatives. Based on their results, the authors stated that lignin is mainly responsible for the yellowing and darkening of the color caused by light [5]. Later Leary [6] and Claesson et al. [7] studied the yellowing and bleaching of newsprint and mechanical pulps using light at different wavelengths. Recently, the same phenomena have been investigated either with filter combination systems [8] or using monochromatic illumination [9-11]. Summarizing the results, yellowing or discoloration was found to occur at 360-395 nm [6], at 290-390 nm [8], at 255-346 nm with the maximum effect at 310-328 nm [9], at 340 nm (maximum effect) [10] or at 310-320 nm (maximum effect) [11] and bleaching or brightening, often of a pre-yellowed sample, at 410-520 nm [6], 396-420 nm and 420-470 nm [8], at 420-500 nm [9] and at 420-430 nm (maximum effect) [11]. Considerable variations with tree species were found.

A study of the wavelength sensitivity of the light-induced yellowing of newsprint containing thermomechanical pulp (TMP) made from unbleached loblolly pine has recently been published [12] in which some action spectral data in the region 280-600 nm are presented. As far as we are aware, no action spectra for the light-induced changes of untreated and treated (bleached or pre-yellowed) chemimechanical and chemithermomechanical pulps made from spruce have been published.

Experimental

Outline of Methods Used to Obtain Action Spectra. One problem encountered in wood photochemistry is that it is difficult to irradiate pulp sheets to a certain predetermined level of yellowness with the equipment usually available for response detection, the reflectance spectrometer. The exposure dose required for unit yellowing, which for a given area equals the product of irradiance and exposure time ($H=E \cdot t$, where H is the exposure dose, often expressed in J/cm^2 , E is the irradiance, expressed in W/cm^2 , and t is the radiation time in seconds), is different for different radiation wavelengths and has to be evaluated. This problem was solved in an empirical way. In method 1 experimentally derived kinetic curves for the various pulps were obtained by plotting the yellowing versus the exposure dose. The measurements were made at certain wavelength intervals. From these curves the exposure dose required for unit yellowing was obtained graphically. The kinetic curves change slowly with the radiation wavelength and no sudden discontinuity could be found. In the vicinity of the most effective wavelengths the kinetic curves were measured at shorter wavelength intervals.

In part of this work, method 2, the radiation time was kept constant for all selected wavelengths, 2h for unbleached and bleached chemimechanical pulps (CMP and CMPB), and 7h for an untreated (CTMP) and a pre-yellowed (CTMP-Y) chemithermomechanical pulp. The action spectra of the pulps were then constructed by plotting the ratio of the degree of yellowing in PC units to the number of quanta/cm² provided by the light source - monochromator combination at the various wavelengths as a function of the radiation wavelength.

Pulps. Chemimechanical pulp (CMP) was made from fresh spruce chips on a laboratory scale and the pulp was bleached with 4% hydrogen peroxide as previously reported [11]. Chemithermomechanical pulp (CTMP) was made in a full-scale refiner (at KCL) after pretreatment of industrial spruce chips (*Picea abies*) with sodium sulfite solution (30 g/l) at 130°C for 5-10 min, followed by pressurized refining.

Thick sheets (ca. 400g/m²) were made from all pulps. The sheets were stored in the freezer before being irradiated.

Irradiation experiments. Pre-irradiation of the CTMP pulp for 90 h was performed at 23°C and 50% RH in a Xenotest 150 S (Hereaus Hanau) apparatus equipped with a 1.3 kW xenon lamp and with IR and glass filters (UV cut-off at 310 nm). The irradiation caused strong yellowing of the pulp and the reflectance measured at 457 nm decreased from 64.3% to 29.9% and that at 557 nm from 77.2% to 58.4%.

Irradiations with monochromatic light were carried out with an Applied Photophysics Model 5350 photo-irradiator, equipped with a 900 W short arc high pressure xenon lamp, a *f*/3.4 monochromator and an exit lens of quartz providing illumination over an area of 1.3 by 2.4 cm at a distance of 16 cm from the lens. The entrance slit of the monochromator was kept at 5 nm and the exit slit at 10 nm to secure a sufficiently high output energy. Irradiations were performed at ambient temperatures (ca. 23°C) in air. The light source - monochromator combination was calibrated with an Applied Photophysics precalibrated thermopile coupled to a voltmeter. The active area of the thermopile was 10 mm². Several points over the illuminated area were measured and a small decrease towards the edges was found. However, the central area which was analyzed using reflectance spectroscopy was much smaller (0.8 by 1.7 cm) and over this area the illumination was uniform. The spectral irradiance measured for the xenon arc - monochromator assembly is shown in Figure 1.

UV-VIS reflectance spectra of the pulps were recorded directly after irradiation in the wavelength range 250-750 nm on a Perkin-Elmer Lambda 15 spectrophotometer equipped with an integrating sphere. The reflectance values (R_{∞} , strictly speaking the reflectivity of an infinitely thick specimen) at 457 and 557 nm were taken from the reflectance curves. Difference spectra were calculated by subtracting the spectrum of the irradiated pulp from the spectrum of the unirradiated one. The post-color values (PC) were calculated as previously [13] according to Giertz [14] using the equation:

$$PC = 100(k_1/s_1 - k_0/s_0) \quad (1)$$

where k_i/s_i is obtained from the Kubelka-Munk relationship:

$$k_i/s_i = (1 - 0.01R_i)^2 / 0.02R_i \quad (i = 0 \text{ or } 1) \quad (2)$$

where R_i =reflectance (%), k_i = specific absorption coefficient (m²kg⁻¹) and s_i =specific scattering coefficient (m²kg⁻¹). Index $i=0$ refers to the unirradiated sample and $i=1$ to the irradiated sample.

Results and Discussion

Irradiation of the Pulps by Monochromatic Light.

UV-VIS Reflectance Values. The reflectance (R_{∞}) values at 457 nm measured from the reflectance spectrum of untreated CTMP (initial R_{∞} = 63.0%) after irradiation at selected wavelengths for seven hours were plotted against radiation wavelength (Figure 2). The curve is very similar to the corresponding curves for CMP (initial R_{∞} =73.9%) and CMPB (initial R_{∞} =82.8%) shown in Figures 1 and 2 of ref. [11] although the irradiation times were different (7 and 2 h). The curve in Figure 2

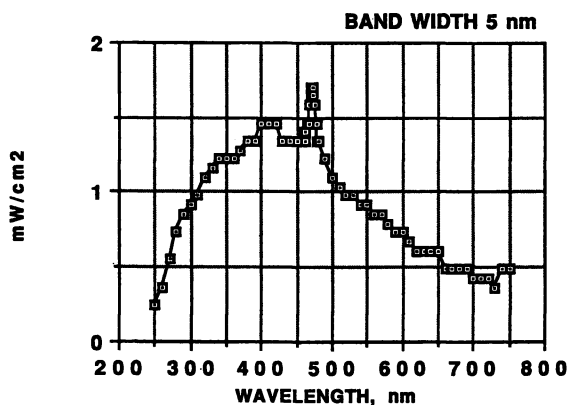


Figure 1. Spectral irradiance at the sample site of the xenon arc - monochromator assembly.

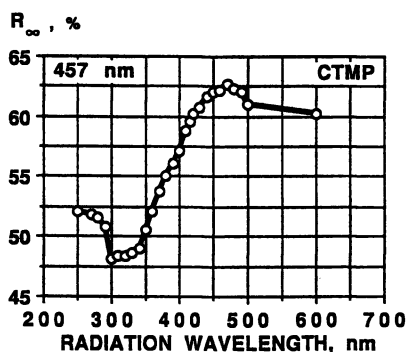


Figure 2. Reflectance (R_{∞}) measured at 457 nm of untreated chemithermo-mechanical pulp (CTMP) irradiated for 7 h with light at selected wavelengths.

(present work) also displays a deep minimum for radiation wavelengths of 300-320 nm and a maximum for wavelengths of 450-500 nm.

Difference Reflectance Spectra. UV-VIS difference reflectance spectra (ΔR_{∞} , unirradiated minus irradiated) of the CMP and CMPB pulps irradiated at wavelengths of 280, 320, 350, 370, 390, 410 and 480 nm for two hours are shown in Figures 3 and 4, respectively. Irradiation of both pulps resulted in two maxima or in a minimum and a maximum, depending upon the irradiation wavelength selected [11]. Both pulps were most sensitive to yellowing or color reversion when irradiated at 320 nm, but the intensity (ΔR_{∞}) for the bleached pulp was markedly higher than for the unbleached pulp. Further comparison of the pulps reveals that the intensity order was reversed on irradiation at 280 nm and 350 nm. For CMP the more efficient wavelength in terms of yellowing measured at 457 nm was 280 nm and for CMPB 350 nm, see Figures 3 and 4.

The corresponding difference reflectance spectra for the untreated and pre-yellowed CTMP pulps irradiated at different wavelengths for seven hours are shown in Figures 5 and 6. The figures show considerable differences, a fact that reflects the great change in chromophore content of the CTMP pulp caused by the pre-irradiation for 90 h in the Xenotest apparatus. Comparing the spectra for the untreated CMP pulp (Figure 3) with the spectra for the untreated CTMP pulp (Figure 5) reveals that the content of the chromophores giving rise to the maximum at around 370-380 nm (irradiation wavelength 280-350 nm) in relation to the content of compounds causing the maximum at 430 nm is much smaller for the CTMP pulp. Apart from the difference in the manufacturing process, the difference in the degree of sulfonation of the two pulps was pronounced; the sulfur content of the CMP pulp was 90 mmol/kg and of the CTMP pulp 69 mmol/kg.

For pre-yellowed CTMP, irradiation at long wavelengths (450-550 nm) caused strong photobleaching of about three units (Figure 6), whereas only a very weak photobleaching was observed for the untreated CTMP on irradiation at around 450 nm. The amount of photoyellowing of the pre-yellowed CTMP caused by radiation wavelengths below 410 nm was of the same magnitude as the amount of photobleaching. The overall changes in intensity for the pre-yellowed pulp caused by irradiation at selected wavelengths were small (about 6 units, Figure 6) compared with those for the untreated CTMP (about 18 units).

Post-Color (PC) Values of Irradiated Pulps. The PC values at 457 nm and 557 nm were calculated for the irradiated pulps and plotted as a function of the radiation wavelength. The results are shown for the untreated CTMP in Figure 7 and for the pre-yellowed CTMP in Figure 8. Very similar curves were obtained for CTMP (Figure 7) and for CMP and CMPB (figures not shown), whereas the curve for pre-yellowed pulp, CTMP-Y (Figure 8) was very different. For the first three pulps the most efficient wavelength causing yellowing was around 310-320 nm. This region was somewhat broader when the response of the irradiation was measured at 557 nm. In terms of the PC values, bleaching the pulps did not seem to change the situation at all: the unbleached and the bleached pulps yellow to about the same extent.

For CTMP-Y, there occurs a small decrease in reflectance, expressed as PC at 457 nm, at short radiation wavelengths (around 270 nm), an increase in reflectance at 290-340, a sudden decrease in reflectance at 350 nm and a pronounced brightening of the pulp by wavelengths in the region from 360 nm to at least 550 nm. The somewhat surprising variation in positive and negative PC values in this curve for different radiation wavelengths is supported by the curve generated using the measurements at 557 nm. In the latter curve the increase in reflectance at around 350 nm extends over a

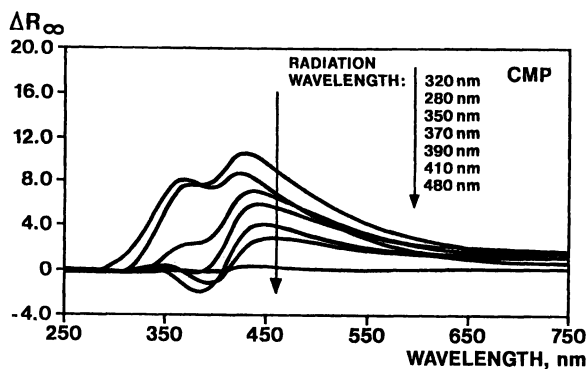


Figure 3. UV-VIS difference reflectance spectra (unirradiated minus irradiated) of untreated chemimechanical pulp (CMP) after irradiation with light at selected wavelengths.

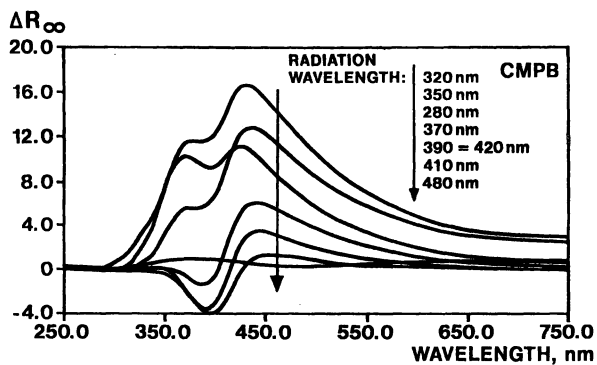


Figure 4. UV-VIS difference reflectance spectra (unirradiated minus irradiated) of peroxide-bleached pulp (CMPB) after irradiation with light at selected wavelengths.

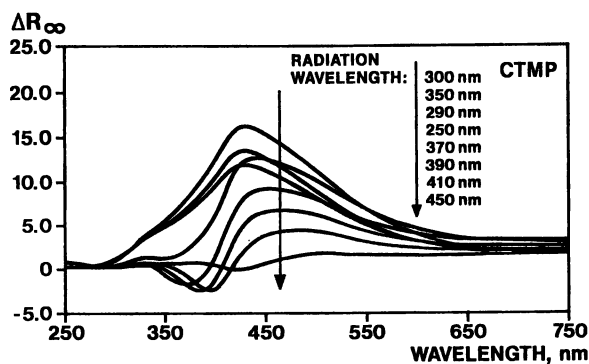


Figure 5. UV-VIS difference reflectance spectra (unirradiated minus irradiated) of untreated chemithermomechanical pulp (CTMP) after irradiation with light at selected wavelengths.

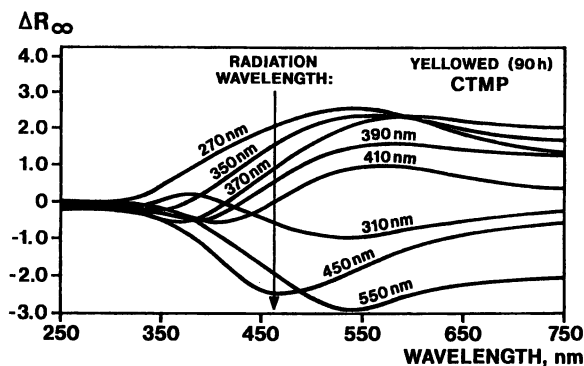


Figure 6. UV-VIS difference reflectance spectra (unirradiated minus irradiated) of pre-yellowed chemithermomechanical pulp (CTMP-Y) after irradiation with light at selected wavelengths.

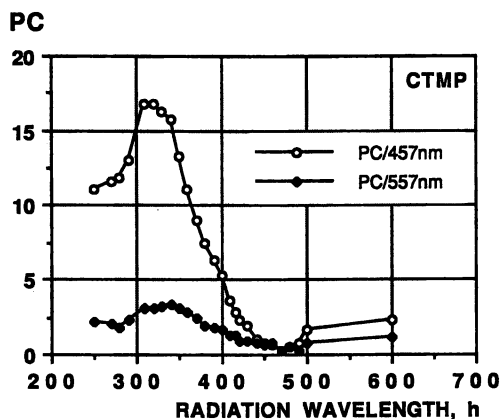


Figure 7. Post-color values (PC) of untreated chemimechanical pulp (CTMP), measured at 457 and 557 nm after irradiation for 7 h with light at selected wavelengths, as a function of wavelength.

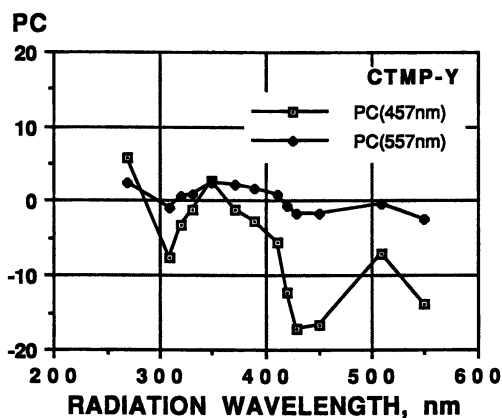


Figure 8. Post-color values (PC) of pre-yellowed chemithermomechanical pulp (CTMP-Y), measured at 457 and 557 nm after irradiation for 7 h with light at selected wavelengths, as a function of wavelength.

longer wavelength range and the brightening in the 450 nm region is diminished, but the overall changes in the curve are similar.

The PC value of an irradiated pulp depends on both the initial and the final reflectances of the pulp. If the samples can be considered homogeneous, pulps exhibiting different initial reflectance values can conveniently be compared in terms of their PC values. In homogeneous samples the changes in PC values are proportional to changes in specific light absorption coefficient provided that the specific scattering coefficient does not change. Neither of these two assumptions, homogeneity and a constant scattering coefficient is true for irradiated samples. In fact, when the change in R_{∞} is less than 10% and the concentration of the chromophores declines exponentially from the sample surface, it is the differences in the value of R_{∞} which may be proportional to chromophore concentration [15]. Furthermore, the idea that the specific scattering coefficient remains constant during the irradiation and ageing of wood pulps has been around for a long time [16,17]. Recent studies [18,19] have indicated that in many cases this is not completely true. However, if the specific absorption coefficient (k) is not determined after irradiation for every wavelength studied and the effect of the eventual change in scattering is not evaluated, the use of PC values appears to be a reasonable choice for measuring the degree of yellowing.

Action Spectra for CMPB Generated Using Method 1. The kinetics of the yellowing of CMPB monitored at 457 and 557 nm are shown in Figures 9 and 10, respectively, for radiation wavelengths from 270 to 450 nm. Above 450 nm, CMPB undergoes no further yellowing. The PC values were calculated for different time intervals according to Figures 9 and 10, and the unit yellowing (one PC unit for 457 nm and half a PC unit for 557 nm) was obtained graphically from plots of the PC values versus irradiation time. Taking into account the measured spectral irradiance values (Figure 1), action spectra for the yellowing of CMPB were then evaluated, Figure 11 (457 nm), and Figure 12 (557 nm). Both action spectra display maxima at 300-325 nm, but the maximum for the former curve is significantly broader, also showing a marked tailing, possibly from a hidden maximum around 350 nm. Subtracting the 557 nm action spectrum (by doubling the response, which compensates for the difference in unit yellowing) from the 457 nm action spectrum in the region 330-400 nm reveals the position of the curve maximum actually to be situated near 350 nm. The action spectra show clearly that the yellowing response observed at 557 nm is a result of the changes of fewer chromophores or possibly a distribution of chromophores other than the yellowing response observed at 457 nm (the wavelength where brightness is usually measured). Not only is the 457 nm action spectrum broader at longer radiation wavelengths, it is also considerably broader in the 280-320 nm region, where the 557 nm action spectrum falls off very rapidly. For both spectra the ordinate value increases for shorter radiation wavelengths (270 nm). This behavior is in agreement with the early results by Van den Akker et al. [5] showing the relative spectral sensitivity curve obtained for groundwood in the region 250-385 nm [5], although the maxima of the action spectra of CMPB in the present work are shifted to longer wavelengths.

Action Spectra for CMP, CMPB, CTMP and CTMP-Y Generated Using Method 2. In method 2 the experimentally derived degree of yellowing was determined after a constant exposure time. By plotting the PC values divided by the number of light quanta of a specific wavelength hitting the target pulp surface during the time observed as a function of the radiation wavelength, another set of action spectra can be constructed. In the present work, the PC values calculated from the R_{∞} values at 457 nm obtained from the spectra recorded before and after irradiation were used. The result for CMP and CMPB after an exposure time of two hours is shown in

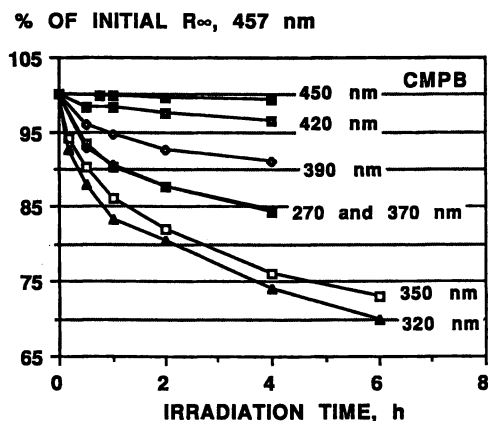


Figure 9. Kinetics of irradiation of peroxide-bleached chemimechanical pulp (CMPB) at selected wavelengths analyzed by measuring the reflectance at 457 nm.

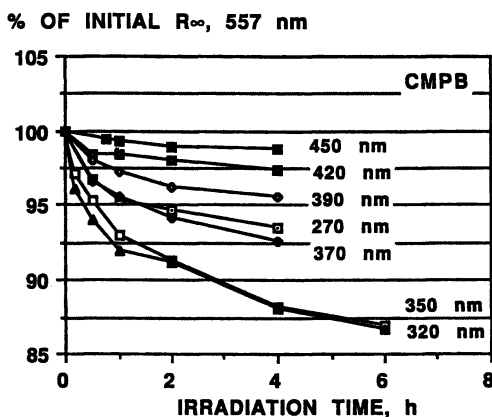


Figure 10. Kinetics of irradiation of peroxide-bleached chemimechanical pulp (CMPB) at selected wavelengths analyzed by measuring the reflectance at 557 nm.

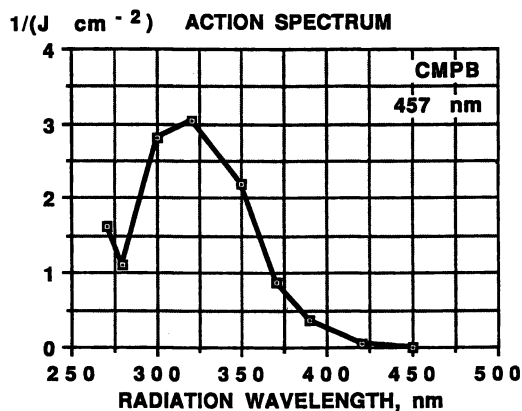


Figure 11. Action spectrum for the photoyellowing of peroxide-bleached chemimechanical pulp (CMPB) constructed after irradiation at selected wavelengths producing yellowing of one PC unit at 457 nm.

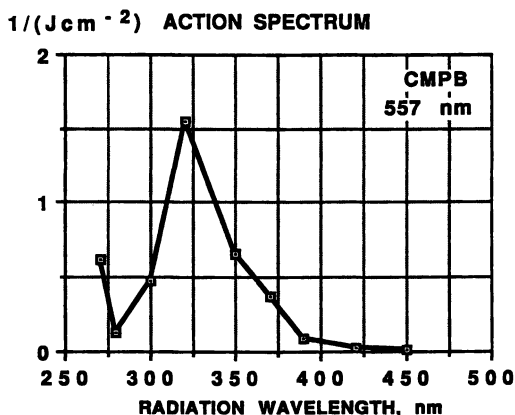


Figure 12. Action spectrum for the photoyellowing of peroxide-bleached chemimechanical pulp (CMPB) constructed after irradiation at selected wavelengths producing yellowing of half a PC unit at 557 nm.

Figure 13. The two action spectra are fairly similar, and the band maxima observed for both pulps are located at 310 nm and coincide completely. The ordinate value of both curves decreases significantly at shorter wave-lengths and a minimum in both curves is displayed around 280 nm. Both curves show increasing ordinate values again at shorter wavelengths. For wavelengths longer than about 320 nm a slight divergence is observed between the two curves; the curves intersect at about 340 nm and the greatest difference in ordinate value between the curves is found at 370-380 nm, at which position one of the bands in the difference reflectance curves is situated, see Figures 3 and 4. The intensity of the action spectrum for CMPB is considerably weaker in this region compared with that of CMP. Recent studies indicate that some coniferaldehyde groups may survive sulphonation [20] and that coniferaldehyde structures also may be formed during irradiation [21]. Bleaching CMP is known to cause a marked decrease in the chromophore content at 370-380 nm due to the disappearance of coniferaldehyde type structures, quinone and other conjugated carbonyl structures [20, 22]. From the action spectra in Figure 13 it can be deduced that the most efficient wavelengths causing photoyellowing of chemimechanical pulps are around 310 nm. The same conclusion can be drawn from the action spectra for the same pulps evaluated using method 1, see Figures 11 and 12.

Action spectra using method 2 were also constructed for CTMP and for pre-yellowed pulp (CTMP-Y) based on an exposure time of seven hours. These action spectra are shown in Figure 14. If the spectrum of CTMP is superposed on the spectrum of CMP in Figure 13, the spectra coincide within the limits of experimental error. The difference in the manufacturing processes for unbleached CMP and CTMP pulps produces no change in the action spectrum. On the other hand, as seen in Figure 13, the bleaching process seems to shift the action spectrum to lower ordinate values in the radiation wavelength region from 320 to at least 450 nm. For CTMP the strong increase in ordinate value at short wavelengths was confirmed, as one measurement was also performed using irradiation at 250 nm. The ordinate value for this point was $14.4 \cdot 10^{-19}$ while that obtained at 270 nm was only $6.2 \cdot 10^{-19}$. In the action spectrum of CTMP-Y the photobleaching effect caused by radiation wavelengths longer than 370 nm is clearly observed. This spectrum is again remarkably similar to the spectrum shown in Figure 8, in which PC was plotted against radiation wavelength.

Conclusions

The present investigation of the action spectra of different chemimechanical pulps confirms our previous results concerning the most efficient wavelengths causing photoyellowing and photobleaching. The strongest effect of photoyellowing occurs on irradiation with light of wavelength 310-320 nm, while the extent of photobleaching and the wavelengths that cause this change depend on whether the pulp has been pre-irradiated and, if so, also on the amount of radiation the sample has received. Although untreated chemimechanical and chemithermomechanical pulps displayed no photobleaching effect regardless of radiation wavelength, a minimum in the curve for PC value versus radiation wavelength (corresponding to a maximum in the reflectance) in the vicinity of the normal photobleaching region (ca. 470 nm) was still observed. The bleached pulp displayed no such minimum or maximum in the corresponding region. For a strongly pre-yellowed pulp, photobleaching is a major reaction in simulated sunlight, and only a narrow portion of the spectrum at around 350 nm is able to cause further discoloration of the pulp as measured at 457 nm. In this case, photobleaching starts at 370 nm and continues throughout the whole visible region, being most efficient at 430-450 nm. When measured at 557 nm, this active region is wider, extending from 320 to 410 nm.

Action spectra are used to throw more light upon the nature of the chromophores responsible for the photochemical changes; in certain situations they

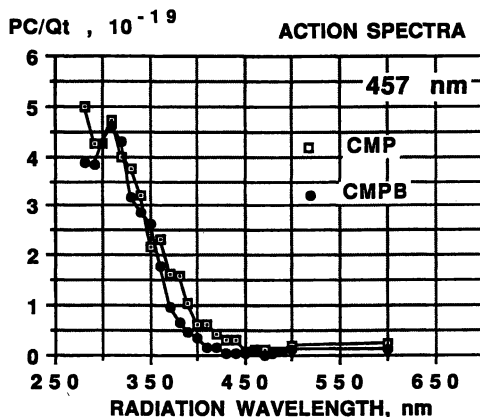


Figure 13. Action spectra for the photoyellowing measured at 457 nm of untreated (CMP) and peroxide-bleached (CMPB) chemi-mechanical pulp constructed after irradiation at selected wavelengths for 2 h.

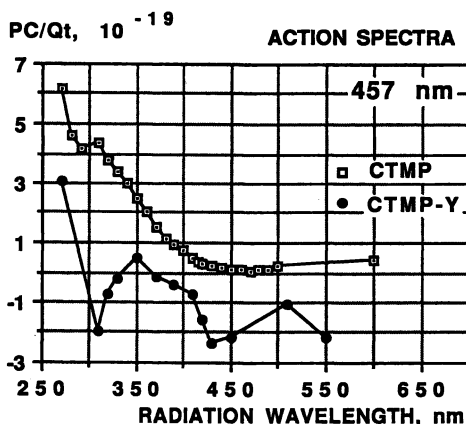


Figure 14. Action spectra for the photoyellowing or photobleaching measured at 457 nm of untreated (CTMP) and pre-yellowed (CTMP-Y) chemithermo-mechanical pulp constructed after irradiation at selected wavelengths for 7 h.

may even make it possible to identify the chromophores by comparison with their absorption spectra. This is a challenge in the case of wood pulps, too. However, this will require an extensive series of model studies with suitable samples. This seems to be particularly important since lignin model compounds have been found to display very different reflectance spectra in different pulps. Therefore, the direct use of the solution absorption spectra does not appear to be appropriate. Before more detailed conclusions can be made concerning the active chromophores based on the action spectra presented in this study, an investigation of the behavior of lignin model compounds and their intermediates in different pulps is needed. An investigation to this end is already in progress.

Acknowledgments

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Chapter 4

Photochemistry of Quinones and Hydroquinones in Solid 2-Hydroxypropylcellulose Films and on Filter Paper

UV-Visible Absorption and Diffuse Reflectance Spectroscopy

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UV/Vis absorption spectroscopy was used to study the photochemical behaviour of quinones and hydroquinones incorporated in solid 2-hydroxypropylcellulose (HPC) films. 2-methoxyhydroquinone **A** which displays significant absorption at wavelengths above 300 nm, where the sunlight is efficient, undergoes more severe yellowing than 4-methylcatechol **B** and 2-hydroxy-2',3,3'-trimethoxy-5,5'-di-n-propylbiphenyl **C**. A very rapid photoreduction of methoxy-p-benzoquinone **D** is seen, followed by discolouration of the film. 4,4'-Dimethoxybiphenyl-2,5,2',5'-bisquinone **E** in HPC film displays bleaching in the visible region and yellowing in the blue visible part of the spectrum. 8-Hydroxy-3,7-dimethoxydibenzofuran-1,4-quinone **F** displays an intense red colour, which is bleached by irradiation. 2,5-Dihydroxy-2',3,3'-trimethoxy-5'-hydroxymethylbiphenyl in presence of the related p-quinone **H** (86/14% mixture) is at first bleached and then discoloured as for **A** and **D** mixture. GPC analysis of the irradiated HPC film containing hydroquinone **A**, reveals a cross-linking of the yellow photoproducts with the solid matrix. Under irradiation hydroquinone **A** adsorbed on filter paper (FP) is partly consumed and a drastic decrease in the reflectance of the paper is observed in the visible region. Extraction with solvents of the irradiated paper restores the reflectance only to a very little extent. Apart from unreacted compound **A**, the amount of compounds released from the impregnated and irradiated FP by extraction is very low. The degree of discolouration after irradiation caused by the methoxyquinone **D** on filter paper is even worse than that of hydroquinone **A**. The general behaviour of the quinone/hydroquinone couple in solid carbohydrate matrix on irradiation is a very rapid

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photoreduction of the quinone followed by discolouration of the hydroquinone via further photo-chemical pathways involving the carbohydrate framework.

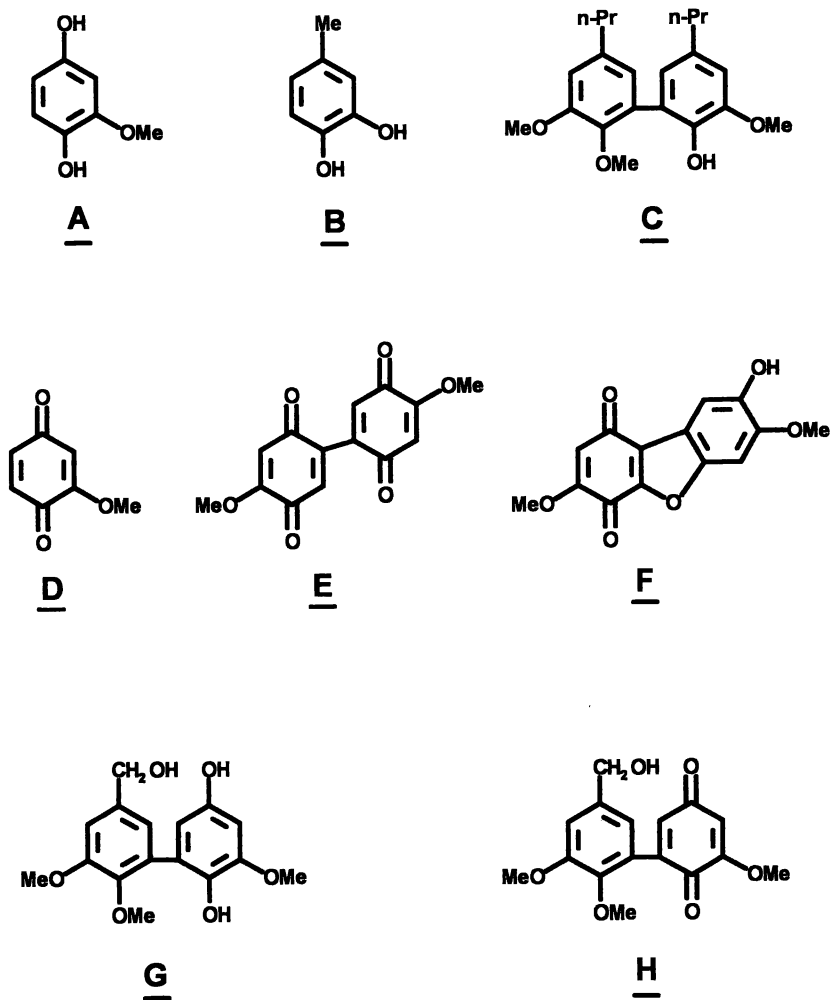
Lignin is largely responsible for the light-induced yellowing of high-yield pulps (HYP) [1]. Although numerous studies have been devoted to the subject, the mechanism of photodiscolouration is not completely understood [2]. Most mechanisms propose that aromatic ketones absorb solar radiation (> 300 nm) and subsequently sensitise oxidation of phenolic species [2]. In addition photocleavage reactions generating radicals were shown to be important in α -carbonyl β -O-4 and β -1 structures [3]. Of particular significance are the reactions leading to crosslinking or reactions with oxygen to give highly coloured products many of which are oligomeric [3]. The photochemistry of light-absorbing phenols has been somewhat neglected but it appears to be of major significance [4]. Ortho and para quinones also contribute significantly to the photochemical and thermal yellowing of high-yield pulps [5-9]. It has been shown that small amounts of monomer and dimer quinones of the methoxy-p-benzoquinone type, in either their oxidized or reduced form can cause strong discolouration of lignocellulosic pulps on irradiation [5]. Dimerization and cyclization to a dibenzofuran-1,4-quinone are also among the major modes of photochemical reaction of these monomers. Moreover, difference reflectance spectra obtained after application of quinone to the pulp showed that the matrix influences the position of the bands [5].

Recently, 2-hydroxypropyl cellulose (HPC) was demonstrated to be a very suitable matrix for UV/Vis absorption study of photoyellowing of milled-wood lignin in the solid state [10] where clean kinetics of discolouration were established after different chemical treatments of the lignin in solution. This indicates the importance in the discolouration process of phenolic structures without carbonyl groups and conjugated double bonds. The present communication describes a similar photochemical study on quinones and hydroquinones incorporated in HPC films under comparative concentrations ($\approx 6.5 \times 10^{-5}$ mol/g HPC). For comparison, we also use UV/Vis reflectance spectroscopy to examine the behaviour of these compounds adsorbed on filter paper after light-exposure.

Experimental

Compounds

The compounds studied were 2-methoxyhydroquinone **A**, 4-methylcatechol **B**, 2-hydroxy-2',3,3'-trimethoxy-5,5'-di-n-propylbiphenyl **C**, methoxy-p-benzoquinone **D**, 4,4'-dimethoxybiphenyl-2,5,2',5'-bisquinone **E**, 8-hydroxy-3,7-dimethoxydibenzofuran-1,4-quinone **F**, 2,5-dihydroxy-2',3,3'-trimethoxy-5'-hydroxymethylbiphenyl **G**, and the related p-quinone **H** (scheme 1). Compounds **A**, **D**, **E**, and **F** were synthesized according to ref. [9], and compound **G**, was prepared from 2-hydroxy-2',3,3'-trimethoxy-5-formyl-5'-hydroxymethyldiphenyl by Dakin reaction using the same procedure as for compound **A**. Compound **G** was isolated in presence of the corresponding p-quinone **H**. Titration of **H** was performed by



Scheme 1: Formulae of the compounds involved in the study.

capillary GC-MS on the silylated mixture (TMS). Compound **B** is from Aldrich, and the synthesis of the biphenyl **C** was previously described [4]

Films

The compounds (2-5 mg) were dissolved in 2.5 mL of THF (Aldrich, spectrophotometric grade) and 0.25 mL of water. 2-Hydroxypropylcellulose (Hercules, Klucel E 60,000; 200mg) was then added and the mixture was shaken until the HPC dissolved completely. The solution was then placed in an open quartz cell (1mm deep) and evaporated in a circulating air oven (35°C) to dryness leaving a transparent film suitable for absorption measurements. Irradiation of the films was performed with the set-up described previously [11] using a medium pressure mercury lamp and a borosilicate glass filter to eliminate wavelengths below 300 nm.

Papers

The filter paper, FP (Stora, Munktel; 90 g m⁻²) was impregnated with a solution of the compound (7.1×10^{-3} mol L⁻¹) in diethyloxide for 5 min and dried. The approximate concentration of the compound on paper (5.7×10^{-6} mol/g FP) was evaluated by determining the amount of diethyloxide adsorbed by the filter paper (0.57 g/ g FP). The impregnated paper was irradiated for 5 hours with a Suntest CPS apparatus (Heraeus Hanau) and then extracted (0.5 h in a shaker) with 40 mL of dichloromethane-ethylacetate mixture (1V/1V). Spectra were obtained from the unirradiated, the irradiated, the unirradiated and extracted, the irradiated and extracted papers and from the extract solution. In order to get a sample infinitely thick, 8 papers were treated and the reflectance (R_{∞}) was measured of the whole pack of papers. In another experiment thick filter paper (Tervakoski rag paper, 250 g m⁻²) was impregnated with a solution of the compound (3.6×10^{-3} mol L⁻¹) and treated as above. Only one paper was treated in this case because the paper was thick enough for the R_{∞} measurements. The irradiation was performed in a Xenotest apparatus (Heraeus Hanau) for 3 h. Irradiation for 3 h in the Xenotest apparatus corresponded to about 5 h in the Suntest apparatus. Both devices were equipped with Xenon arcs.

General methods

Absorption spectra of the films were measured on a Cary 219 spectrometer connected to a PC to analyse the data. Rigorously reproducible positioning of the films in the optical compartment was essential for a good comparison of the spectra. Spectra on paper were obtained with a Perkin-Elmer lambda 15 spectrometer equipped with an optical reflectance unit.

Gel permeation chromatography on dissolved irradiated and non-irradiated films (THF/water 99V/1V) was performed on a Waters HPLC apparatus equipped with both UV (280 nm) and refractive index detectors and with 4 microstyragel columns (10⁵, 10⁴, 10³, 500). THF was used as eluent. The elution time was calibrated with polystyrene standards. The same concentrations were employed for

both solutions which were filtered over a glass wool membrane (0.2 μm) before injection.

Results and Discussion

Compounds in HPC films

2-Methoxyhydroquinone **A** displays significant absorption at wavelengths above 300 nm where sunlight is efficient (Figure 1). In contrast, 4-methylcatechol **B** which was chosen to mimic catechol structures in lignin, presents very little absorption above 300 nm (Figure 2). The fact that the electron donating effect on the benzenic ring of the third oxygen in **A** is stronger than that of the alkyl substituent in compound **B** explains the bathochromic shift in hydroquinone **A**, and could be a very important cause of discolouration of HYP.

Compound **A** under near-UV irradiation undergoes severe yellowing (Figure 1) with a small induction period (30 min.). The band in the visible region is broad and structureless and is indicative of the formation of a series of colored species. The decrease in the absorption band at 290 nm when the compound **A** is irradiated is similar to the behaviour of MWL in HPC films under similar conditions [10].

Catechol **B** displays weak discolouration under our experimental conditions (Figure 2) as already observed for this compound when it was adsorbed on bleached chemical bisulfite pulp [4]. The low absorption above 300 nm is presumably the cause of this low reactivity.

The phenolic biphenyl **C** which was shown to undergo photoyellowing on carbohydrate fibers [4] presents in HPC films (Figure 3) a reactivity weaker than that of methoxyhydroquinone **A** despite its stronger absorption above 300 nm.

The photoreactivity of the compounds was also appraised by plotting the differential absorbance at 390 nm where differences are larger and more accurate than those measured at 457 nm, the usual wavelength for brightness index measurements. Nevertheless, the same trend is observed for these two wavelengths. The kinetics established for **A**, **B**, and **C**, shown in figure 4, reveal an induction period for the hydroquinones and a regular increase for **C**, indicating that different mechanisms of photoyellowing might be involved for these compounds.

In solid HPC film methoxy-p-benzoquinone **D** shows absorption maximum at 352 nm (figure 5) ascribable to a $\pi\pi^*$ transition [12]. The weak band observed at 530 nm is likely due to the dibenzofurane-1,4-quinone **E** formed in small yield during the preparation of the film. After 30 min irradiation, the bands of the quinone chromophore disappear completely (Figure 5) giving rise to absorption similar to that of hydroquinone **A** irradiated for one hour (Figure 1). Such behaviour is also observed, as is shown below, when **D** is adsorbed on filter paper.

To investigate the influence of the presence of quantities of quinone with the hydroquinone, a mixture of **A** (90%) and **D** (10%) was irradiated and the

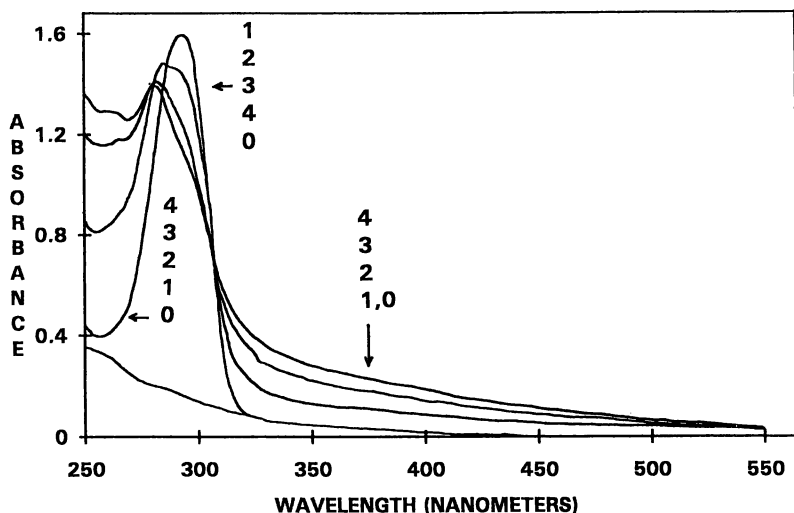


Figure 1. Absorption spectra of A in HPC film (6.40×10^{-5} mol/ g HPC) after irradiation under UV light ($\lambda > 300$ nm). 0: HPC film before irradiation; 1: A in HPC film before irradiation; 2: 1h; 3: 3h; 4: 5h.

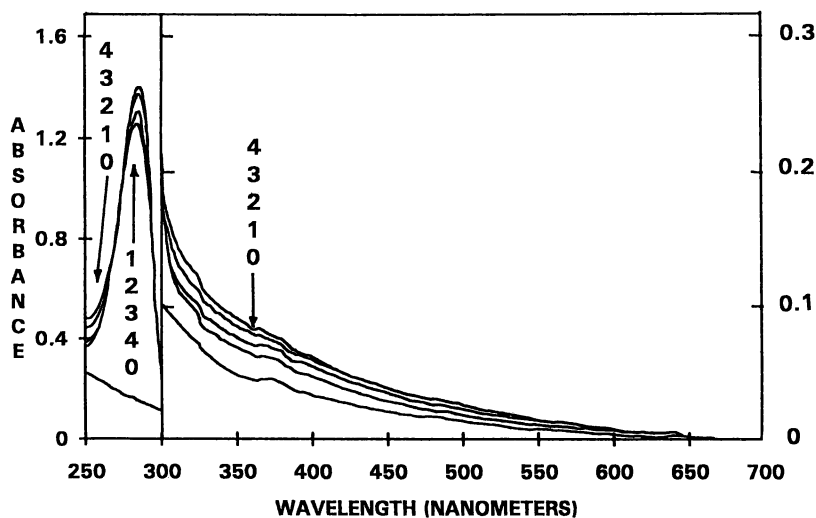


Figure 2. Absorption spectra of 4-methylcatechol B (6.35×10^{-5} mol/ g HPC) after irradiation. 0: HPC film before irradiation; 1: B in HPC film before irradiation; 2: 1h; 3: 3h; 4: 5h.

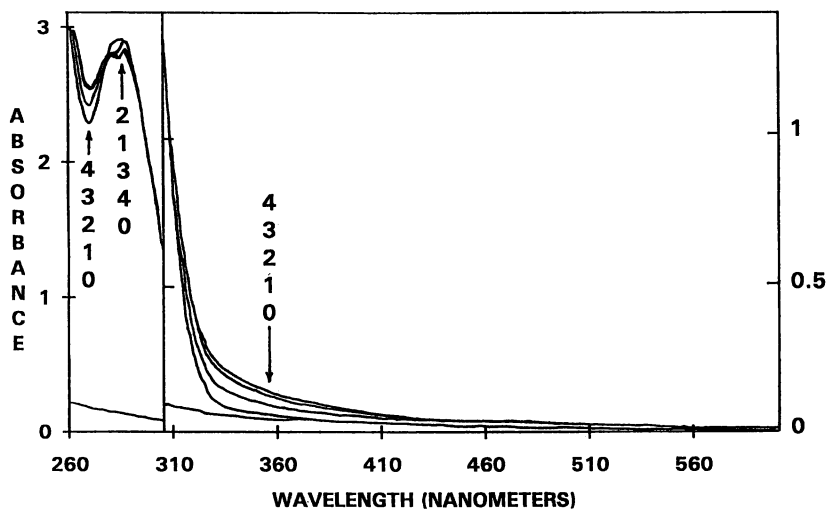


Figure 3. Absorption spectra of 2-hydroxy-2',3,3'-trimethoxy-5,5'-di-n-propyl diphenyl **C** (6.44×10^{-5} mol/ g HPC) after irradiation. 0: HPC film before irradiation; 1: **C** in HPC film before irradiation; 2: 1h; 3: 3h; 4: 5h.

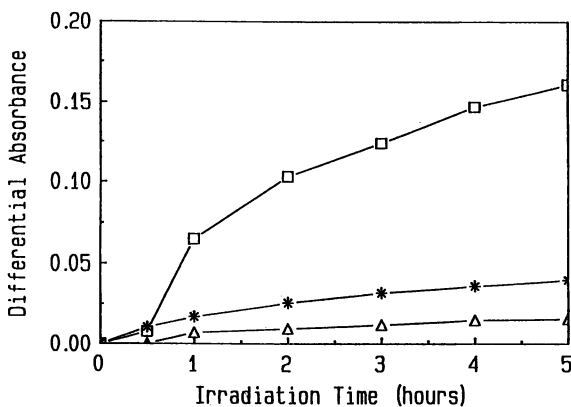


Figure 4. Kinetics of photoreactivity expressed using the differential absorbance measured at 390 nm in figures 1-3 for **A**: □ ; **B**: Δ ; **C**:*

spectra recorded (Figure 6). It is noticeable that no dramatic changes due to quinhydrone formation [13] occur in the absorption spectrum before irradiation with respect to the one of each monomer. The absorption curves at different irradiation times look very much like those presented for **A** in figure 1 emphasizing the importance of the role played by hydroquinones as major chromophores in the discolouration process even in presence of quinones.

In contrast to what was observed on lignin rich paper [5], the bisquinone **E** in HPC film displays bleaching in the 500 nm region and yellowing in the blue part of the spectrum near 420 nm. Apparently the very sensitive compound **E** reacted at least partially already during the film formation giving rise to benzofuran-1,4-quinone **F** (Figure 7). The changes observed in the UV part of the spectra under irradiation are similar to the photoreduction noticed for quinone **D**. This mechanism therefore also applies to compound **E**.

The behaviour of compound **F** in HPC (Figure 8) parallels the observations made when it is adsorbed on paper where bleaching of the intense red colour was seen [5]. Some photoreduction of the quinone part may therefore be involved during the bleaching.

To assess the general role played by hydroquinones in the yellowing process, compound **G** was prepared, and isolated in the presence of some quantities of quinone **H** (14%). The spectra are shown in figure 9 and indicate that the **G** - **H** mixture behaves as an **A** - **C** mixture i.e. bleaching followed by discolouration.

The kinetics of photoreactivity measured at 390 nm for compounds **A**, **D**, **E**, and **A** - **D** and **G** - **H** mixtures are reported in figure 10. The main features are the negative values associated with the photoreduction of quinones and the large reactivity in HPC films of the methoxyhydroquinone **A**.

Analysis of the irradiated HPC film which contains hydroquinone **A** by GPC after dissolution in THF and filtration over a glass-wool membrane (0.2 μm) reveals a cross-linking of the yellow products with the HPC matrix since the amount of residual hydroquinone is only 49% (Figure 11). Cross-linked HPC is retained on the glass-wool membrane during the filtration and does not contribute to the GPC chromatogram. This observation is in accordance with what was observed on HYP and, as is shown below, with the behaviour of **A** adsorbed on filter paper.

Compounds adsorbed on filter paper

During irradiation of compound **A** on filter paper the hydroquinone is partly consumed and simultaneously a drastic decrease in the reflectance of the paper is observed in the visible region (Figures 12 and 13).

Extraction of the irradiated paper restores the reflectance only to very little extent; the curves 4 and 5 in figure 12 are very similar. The difference spectrum, figure 13, showing the change upon extraction, reveals a band minimum at 500-550 nm with low intensity. The absorption spectra from the extract solutions (not

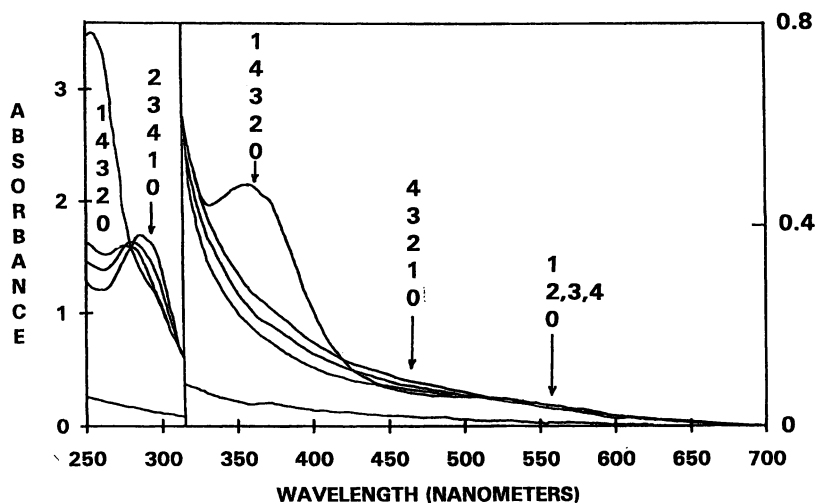


Figure 5. Absorption spectra of 2-methoxyquinone D (6.38×10^{-5} mol/ g HPC) after irradiation. 0: HPC film before irradiation; 1: D in HPC film before irradiation; 2: 0.5h; 3: 3h; 4: 5h.

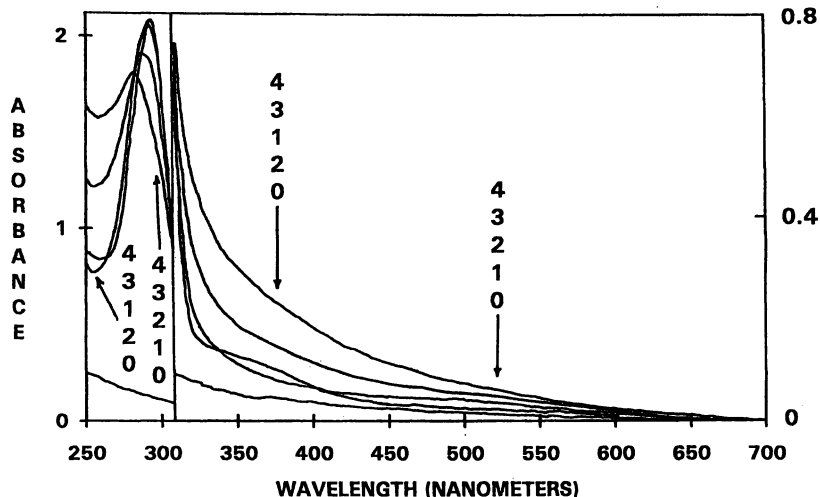


Figure 6. Absorption spectra of a mixture of A (6.57×10^{-5} mol/ g HPC) and D (0.65×10^{-5} mol/ g HPC) in HPC film after irradiation. 0: HPC film before irradiation; 1: A and D mixture in HPC film before irradiation; 2: 0.5h; 3: 2h; 4: 5h.

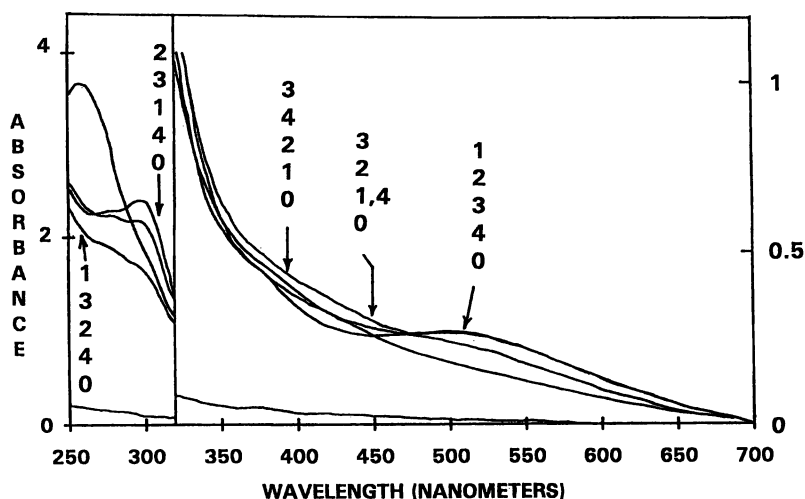


Figure 7. Absorption spectra of 4,4'-dimethoxybiphenyl-2,5,2',5'-bisquinone E in HPC film (6.76×10^{-5} mol/ g HPC) after irradiation. 0: HPC film before irradiation; 1: E in HPC film before irradiation; 2: 0.5h; 3: 2h; 4: 5h.

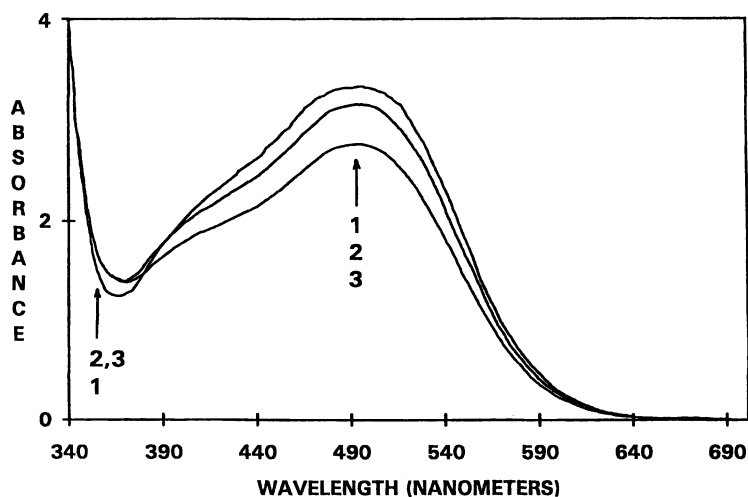


Figure 8. Absorption spectra of 8-hydroxy-3,7-dimethoxydibenzofuran-1,4-quinone F in HPC film (6.47×10^{-5} mol/ g HPC) after irradiation. 1: F in HPC film before irradiation; 2: 2h; 3: 5h.

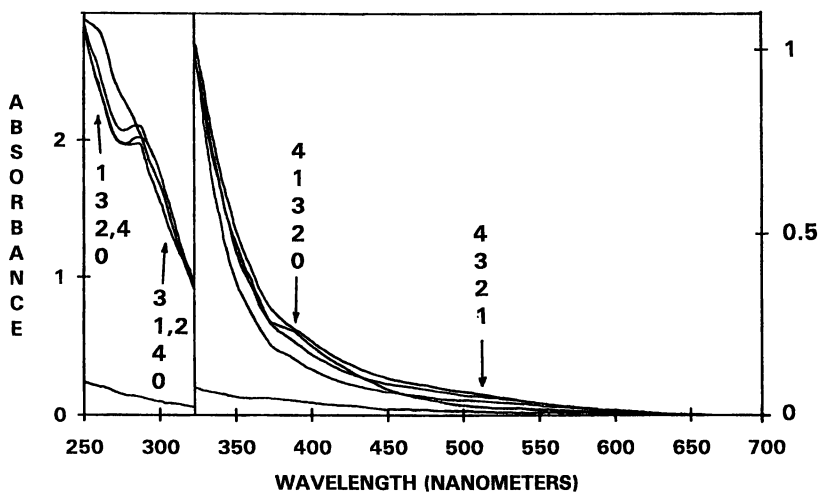


Figure 9. Absorption spectra of a mixture of 2,5-dihydroxy-2',3,3'-trimethoxy-5'-hydroxymethylbiphenyl G (5.58×10^{-5} mol/ g HPC) and 2',3'-dimethoxy-5'-hydroxymethylbiphenyl-2,5-quinone H (0.91×10^{-5} mol/ g HPC) in HPC film after irradiation. 0: HPC film before irradiation; 1: G and H mixture in HPC film before irradiation; 2: 0.5h; 3: 3h; 4: 5h

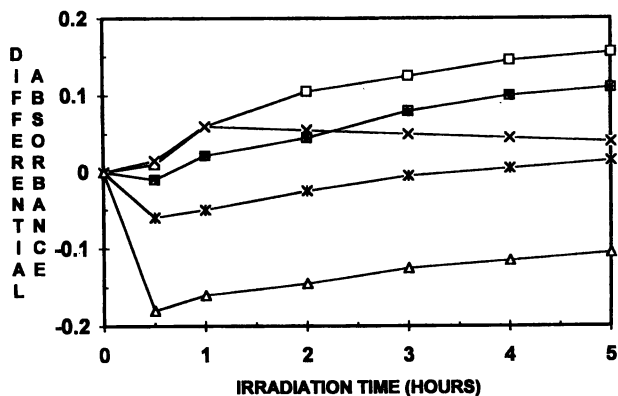


Figure 10. Kinetics of photoreactivity expressed using the differential absorbance measured at 390 nm for A: \square ; D: \triangle ; E: \times and A - D mixture \otimes (see figure 6), and for G - H mixture $*$ (see figure 9).

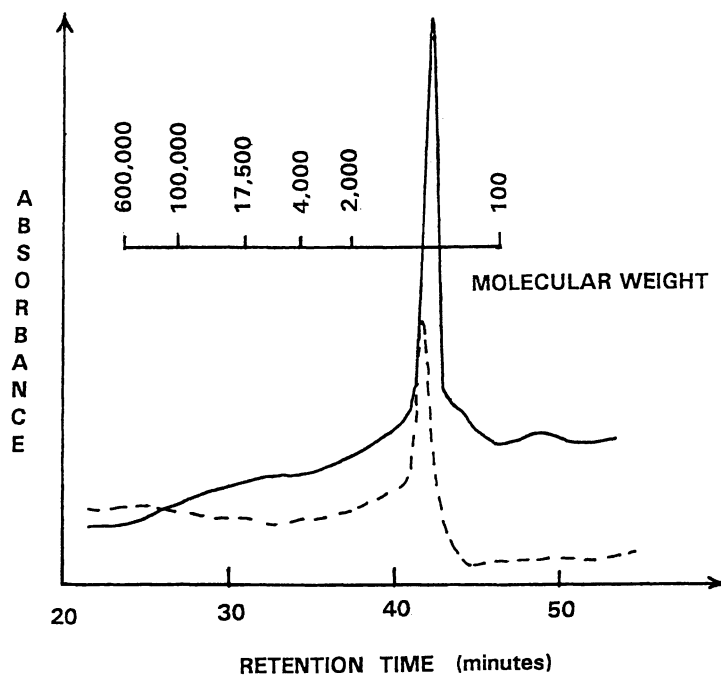


Figure 11. Gel permeation chromatography traces of compound **A** in HPC film (5.43×10^{-5} mol/ g HPC) dissolved in THF/water (99V/1V). (—): non-irradiated film; (---): film irradiated for 5h. The same concentrations were used for both solutions which were filtrated over a glass wool membrane (0.2 μ m) before injection (UV wavelength detection: 280 nm).

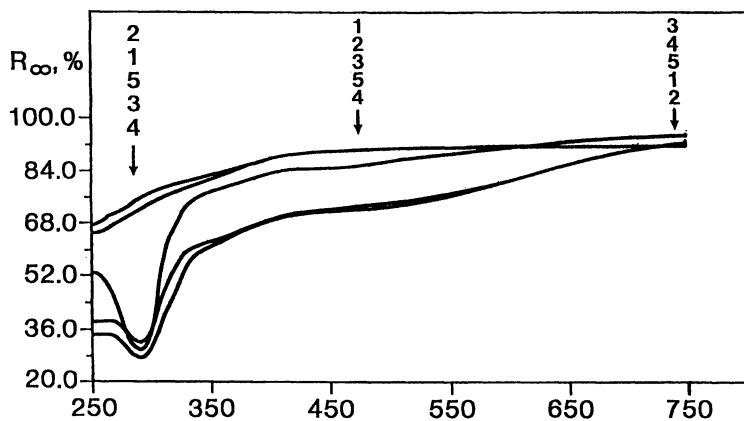


Figure 12. UV/Vis reflectance spectra of 2-methoxyhydroquinone **A** after irradiation on filter paper (FP) in a Suntest apparatus for 5 h. 1: Unirradiated FP; 2: irradiated FP; 3: unirradiated FP impregnated with **A** (FP+A); 4: irradiated (FP+A), and 5: extracted, irradiated (FP+A).

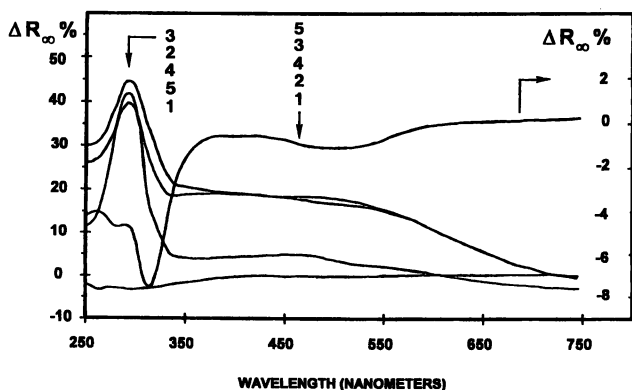


Figure 13. Difference reflectance spectra from the papers obtained from the curves in figure 12. 1: Unirradiated (FP) minus irradiated FP; 2: FP minus (FP+A); 3: FP minus irradiated (FP+A); 4: FP minus extracted, irradiated (FP+A), and 5: irradiated (FP+A) minus extracted, irradiated (FP+A), note the difference in scale.

represented) show the band caused by residual compound A but also a weak and broad absorption in the visible region. Apart from unreacted hydroquinone A, the amounts of compounds released from the impregnated and irradiated filter paper by extraction are very low.

The degree of discolouration caused by the hydroquinone A and the methoxyquinone D on filter paper was compared after irradiation. Both compounds gave a reddish hue to the filter paper after exposure. The discolouration caused by hydroquinone A was pronounced but that of quinone D was even worse (Figures 13 and 14). Despite the fact, that the yellow quinone D decreased the reflectance at 450 nm of the paper significantly already after impregnation, the light-induced color formation in the presence of D is nevertheless even larger than for hydroquinone A. This behaviour on filter paper differs somewhat from that displayed by the compounds in HPC films, where the absorbance at 450 nm of the film initially doped with hydroquinone A after irradiation for 5 h was a little higher than that doped with compound D (figures 1 and 5). The shape of curve 2 in figure 15 indicates that photoreduction of the quinone D to hydroquinone A had occurred. The same reaction has recently been demonstrated to occur in solution [14]. Moreover, the lack of the deep minimum in curve 2 compared to curve 4 displays the rapid consumption of quinone D on irradiation. In addition to the study on HPC films, the experiments on paper show clearly the importance of both hydroquinone and quinone structures, e.g. A and D, in the discolouration processes on solid matrices, as has been observed previously [5].

The photochemistry of the methoxyhydroquinone A / methoxyquinone D couple in solution was extensively studied in our laboratories [14]. It involves, as for the reactivity of other simple quinones [12, 15], the formation of a neutral semiquinone radical which is able, in the low viscosity medium, such as fluid

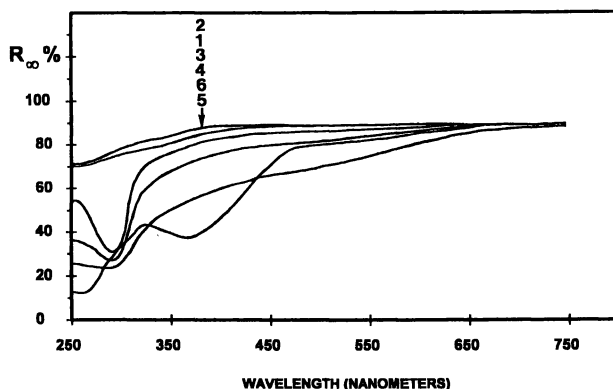


Figure 14. UV/Vis reflectance spectra of 2-methoxyhydroquinone **A** and methoxy-*p*-benzoquinone **D** after irradiation on filter paper (FP) for 3 h in a Xenotest apparatus. 1: Unirradiated FP; 2: irradiated FP; 3: Unirradiated (FP+**A**); 4: irradiated (FP+**A**); 5: Unirradiated (FP+**D**), and 6: irradiated (FP+**D**).

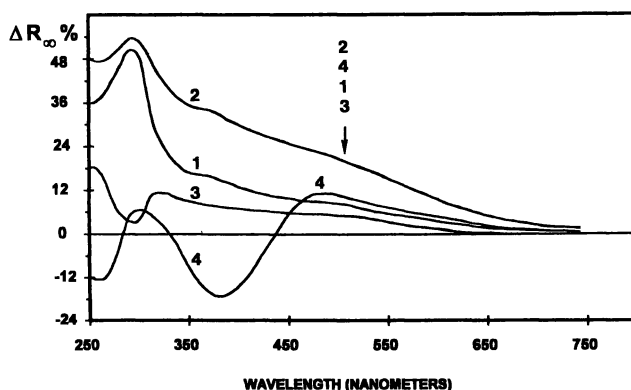
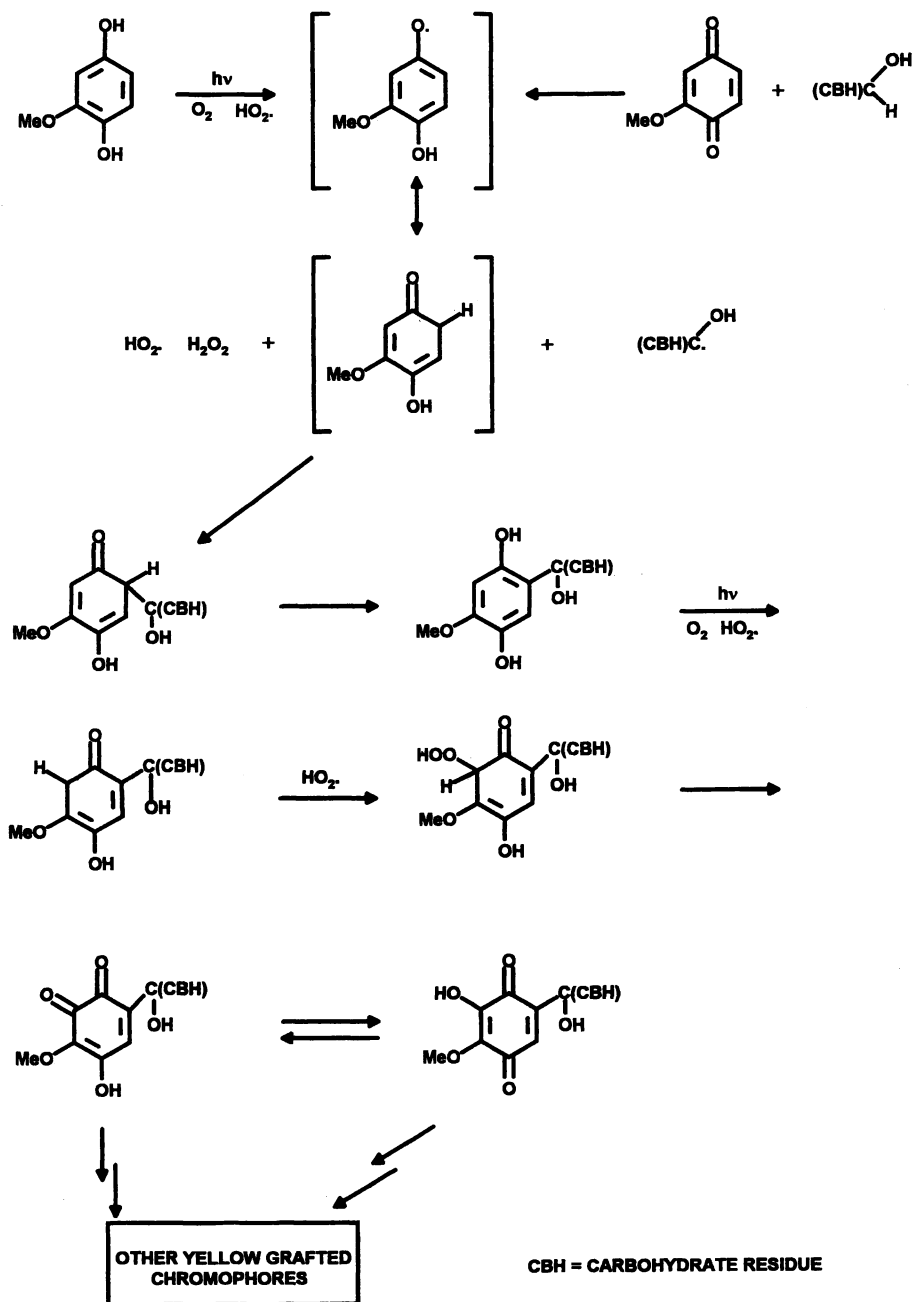


Figure 15. Difference reflectance spectra from the papers obtained from the curves in figure 14. 1: Irradiated FP minus irradiated (FP+**A**); 2: irradiated FP minus irradiated (FP+**D**); 3: unirradiated (FP+**A**) minus irradiated (FP+**A**), and 4: unirradiated (FP+**D**) minus irradiated (FP+**D**)



Scheme 2: Tentative rationalization of the production of cross-linked yellow chromophores by near-UV irradiation of quinol **A** and quinone **D** couple in solid carbohydrate matrix.

solution, to dimerise. and ultimately to conduce to the dibenzofuran-1,4-quinone **F**. In the solid state (HPC film and filter paper) the mobility is reduced and the semiquinone radical is probably now able to couple with other radicals generated in the carbohydrate framework, giving *inter-alia* cross-linking and production of coloured elements linked to the matrix. A tentative rationalization for the cross-linking with the carbohydrate matrix is given in scheme 2.

Conclusion

Our study of the photoreactivity of hydroquinone and quinone lignin models in solid carbohydrate matrix has revealed the key role probably played by hydroquinones and the solid carbohydrate framework in the discolouration process of high-yield pulps. For bleached pulps, the rapid yellowing step is probably correlated with the amount of methoxyhydroquinone type structures that are produced during the peroxide bleaching, which are not eliminated when sodium borohydride reduction and catalytic hydrogenation are performed on lignin. Interconversion between both forms of these types of redox pairs in oxygen-containing media is very easy and the redox state of the medium determines the balance between the oxidized and the reduced forms. Irradiation changes at least partly this balance, which is observed by photoreduction of quinone generating hydroquinone. Other compounds, both organic and inorganic such as degraded carbohydrates and metal ions can react similarly. The involvement in the discolouration process of carbohydrates, probably hemicelluloses which are non-crystalline and strongly linked to lignin, is consistent with the huge amounts of alkylating agents needed to stabilize bleached high-yield pulps [16, 17]. Further studies are being pursued in our groups for a better understanding of the brigtness reversion mechanism of high-yield pulps.

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Chapter 5

Photoreactivity of Ligninlike Quinoid Structures

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Simple lignin-like *para*- and *ortho*-quinoid structures were impregnated onto cellulose and mechanical pulp and photolyzed with a xenon lamp. The photo-reversion properties of these impregnated pulp samples were monitored as a function of time. The results of these studies indicate that in general not all quinoid type structures contribute to further photo-yellowing of mechanical pulp.

Advances in mechanical pulping and bleaching have provided the means of manufacturing ultra high-yield pulps that have a Tappi brightness above 80% (1). At these levels of brightness, mechanical pulps could potentially be employed in high-value paper products, such as business forms, reprographic papers, and writing papers. However, the rapid light-induced yellowing of these brightened pulps restricts their use as furnishes for low-value or short-life paper products. It has been suggested that if the relative rate of light-induced yellowing could be reduced from three months to thirty six months then the potential market for bleached chemithermal mechanical pulp (BCTMP) would increase fourfold (2).

Clearly, there is an increasing need to investigate the fundamental chemical reactions which are initiated when high-yield pulps are photolyzed, and to apply this knowledge to halt or significantly retard the yellowing process. Although the photooxidation mechanisms have not been fully elucidated, significant advances have been made in understanding brightness reversion. It is now well-recognized that extended conjugated structures present in lignin absorb near-UV light ($\lambda=300-400$ nm) and that in the excited state these structures can react to produce radicals (3). Regardless of the exact mechanism responsible for generating the proposed radicals, it is generally

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accepted that these radical intermediates lead to the oxidative formation of *ortho*- and *para*-quinones (4). The presence of quinoid-like structures in photo-aged mechanical pulp has been detected spectroscopically (5), and these structures are believed to be one of the principle components contributing to the yellowing of mechanical pulp.

Results and Discussion

The photo-formation of *ortho*- and *para*-quinones during brightness reversion has frequently been suggested to contribute to the photo-yellowing of mechanical pulp. Although a variety of spectral techniques have been employed to characterize the nature of the chromophoric structures present in photo-aged mechanical pulp, it is only recently that the presence of *ortho*-quinones have been conclusively established (6). Several recent publications have suggested that quinones formed during brightness reversion contribute to subsequent photochemical reactions which further darken irradiated mechanical pulp (7). If this suggestion were found to be generally true, new mechanisms for photo-stabilizing mechanical pulp could be designed.

To examine the photo-reactivity of lignin-like quinonoid structures in mechanical pulp, we selected several model compounds which are representative of quinone structures that could be formed during brightness reversion. The compounds studied are summarized in Figure 1. Model compounds 1 and 2 are representative of hydroxy *para*-quinones which have been proposed to be formed during the manufacturing and bleaching of mechanical pulp (8). Structures 3 to 6 are model compounds of lignin-derived quinone structures which could be formed during the photo-oxidation of lignin.

Brightness pads of BCTMP and cotton linters were impregnated with the model compounds and irradiated with a xenon arc light source to study the photo-reactivity of compounds 1 to 6 under the brightness reversion conditions. Our initial studies focused on examining the photo-reactivity of the quinones adsorbed onto cellulose handsheets. It was anticipated that by employing cotton linter sheets we could decipher the fundamental photochemical behavior of these model compounds unencumbered by photochemical changes occurring with the solid support matrix.

The results of irradiating the *para*-quinoid structures (compounds 1-4) adsorbed onto cellulose sheets are summarized in Figure 2. Examination of the photolysis data indicates that with the notable exception of 2-methoxy-1,4-benzoquinone the remaining *para*-quinone model compounds did not cause any further darkening of the handsheets during irradiation. Indeed, several of the quinones exhibit a minor brightening response upon photolysis which could be attributed to a photo-bleaching effect, but the lack of a complete mass balance makes this conclusion tenuous.

The decrease in reflectance for irradiated 2-methoxy-1,4-benzoquinone impregnated cellulose and mechanical pulp handsheets has been previously reported by Forsskahl (10). We have further explored this phenomenon and have examined the rate of reversion. As summarized in Figure 2, the rates of

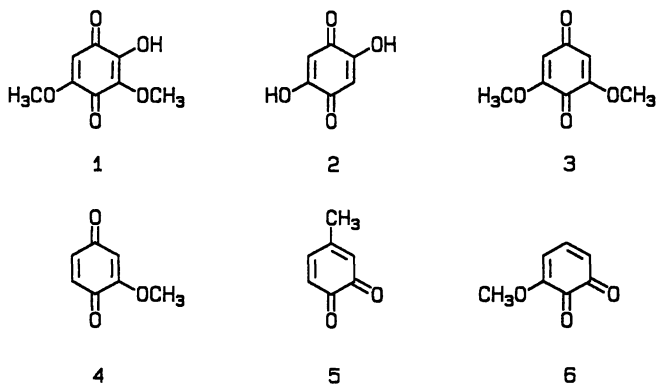


Figure 1: Model Compounds Employed in Photo-Reversion Studies

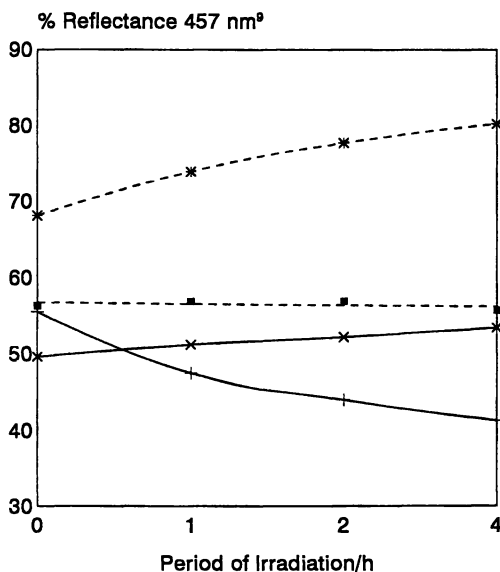


Figure 2: Brightness Changes Incurred During the Photolysis of *Para*-Quinones Impregnated on Cellulose Handsheets^a

- ✱ 2,6-Dimethoxy-1,4-benzoquinone (0.0034 g/g Cellulose)^b
- + 2-Methoxy-1,4-benzoquinone (0.0022 g/g Cellulose)^b
- ✱ 2-Hydroxy-3,5-dimethoxy-1,4-benzoquinone (0.0056 g/g Cellulose)^b
- 2,5-Dihydroxy-1,4-benzoquinone (0.0012 g/g Cellulose)^b

^aemployed an Oriel 100 Watt Solar Simulator for photo-aging studies, see experimental section for complete experimental procedure; ^b mass of quinone applied/mass of handsheet.

reversion are sensitive to the period of irradiation, and the greatest loss in % reflectance occurs during the first hour of irradiation. The photolyzed cotton linter/2-methoxy-1,4-benzoquinone handsheets were extracted and the extracts were examined by GC/MS. The principle product detected from these photolysis experiments was 2-methoxyhydroquinone. The hydroquinone was presumably formed by photo-reduction of 2-methoxy-1,4-benzoquinone, analogous photo-reductions have been reported to occur for several benzo-1,4-quinones in alcoholic solutions (11).

Serendipitously, we have also found that 2-methoxy-1,4-benzoquinone impregnated cotton linter sheets undergo a slow thermal reversion process. The results of the thermal reversion data are summarized in Table 1.

Table 1. Brightness Changes Incurred During Thermal-Aging of 2-Methoxy-1,4-Benzoquinone Impregnated Cellulose^a/BCTMP^b Handsheets

Storage Period/day	% Reflectance ⁹	
	2-Methoxy-1,4-Benzoquinone	
	Cellulose ^c	BCTMP ^d
0	64.8	50.6
1	62.5	-
2	60.7	44.6
3	54.7	44.2
4	51.2	44.0
6	49.5	43.7
8	47.0	-
10	45.0	42.8

^aapplied 0.03 g of 2-methoxy-1,4-benzoquinone on 1.98 g of cellulose; ^bapplied 0.02 g of 2-methoxy-1,4-benzoquinone on 1.09 g of BCTMP; ^ccontrol handsheets of cellulose exhibit no loss of brightness during the ten days of storage; ^dcontrol handsheets of BCTMP exhibited a 0.9% loss of brightness (87.2-->86.4) during the ten days of storage, handsheets were prepared according to Tappi standard procedures T-452 and/or T-534.

Although the rate of thermal reversion is much slower than the photo-reversion, the values are clearly significant and result in a 30% drop in brightness over ten days. Research efforts have also examined the thermal reversion properties of BCTMP brightness pads impregnated with 2-methoxy-1,4-benzoquinone. These impregnated sheets also undergo a slow thermal reversion process resulting in a 16% decrease in brightness over ten days. In comparison, control BCTMP sheets virtually maintain their original brightness levels over the same time period. These results serve to emphasize the need for monitoring both photo and thermal reversion properties of model compounds employed in the study of brightness reversion. The slow thermal reversion process noted for 2-methoxy-1,4-benzoquinone impregnated handsheets could also be relevant to the continued reversion of post-irradiated mechanical pulp handsheets previously noted by Gratzl (12).

The rates of photo-reversion for BCTMP brightness pads impregnated with quinones 1 to 4 are summarized in Figure 3. The observed changes in brightness for the BCTMP/*para*-quinone impregnated handsheets are due to both the photoreactivity of the applied quinones and the photo-reversion properties of the BCTMP handsheets. A review of this data will indicate that only 2-methoxy-1,4-benzoquinone impregnated handsheets exhibited significant photo-reversion properties. The remaining quinones failed to exhibit significant brightness reversion properties under the experimental conditions employed.

The two *ortho*-quinone model compounds were applied onto cellulose sheets following the same general experimental procedure. Application of either 3-methoxy-1,2-benzoquinone or 4-methyl-1,2-benzoquinone onto cellulose brightness pads led to a significant drop in the initial brightness of the impregnated handsheets. As summarized in Figure 4, irradiation of these samples with the xenon arc lamp resulted in a minor brightness gain which was tentatively attributed to a photo-bleaching effect.

Repeating these reactions with BCTMP brightness pads yielded a more complex response as the impregnated brightness pads initially experience a brightness gain followed by a brightness loss. These results, summarized in Figure 4, have been attributed to two competing processes, the brightness reversion of the handsheet itself and a photo-bleaching effect of the quinones. Of greater significance is the general observation that with the exception of 2-methoxy-1,4-benzoquinone all other structures did not accelerate brightness reversion of the treated handsheets. Based upon these observations, it is our hypothesis, that in general, not all quinoid structures are involved in intermolecular photochemical-initiated reactions which further darken mechanical pulp.

Since all of the model compounds examined were monomeric lignin-like structures, our current studies do not address the possibility of an intramolecular photochemical initiated reaction contributing to brightness reversion. Investigations directed at examining this latter issue are ongoing.

Experimental Reagents. 2,6-Dimethoxy-1,4-benzoquinone was prepared following Matsumoto's procedure (13). 2-Methoxy-1,4-benzoquinone, 3-methoxy-1,2-benzoquinone, and 4-methyl-1,2-benzoquinone were synthesized from the corresponding hydroquinones by oxidation with (diacetoxyiodo)benzene following the procedure described by Ando (14). 2-Hydroxy-3,5-dimethoxy-1,4-benzoquinone was provided by Dr. Sumimoto, and 2,5-dihydroxy-1,4-benzoquinone is commercially available.

General Procedures. Optical brightness pads of hardwood BCTMP and cellulose were prepared following TAPPI procedures (15). All handsheets were extracted with methanol followed by dichloromethane, vacuum dried, and stored at below 0° C prior to use. Cotton linter handsheets had an average Tappi brightness value of 86.5 ± 0.1 and the BCTMP

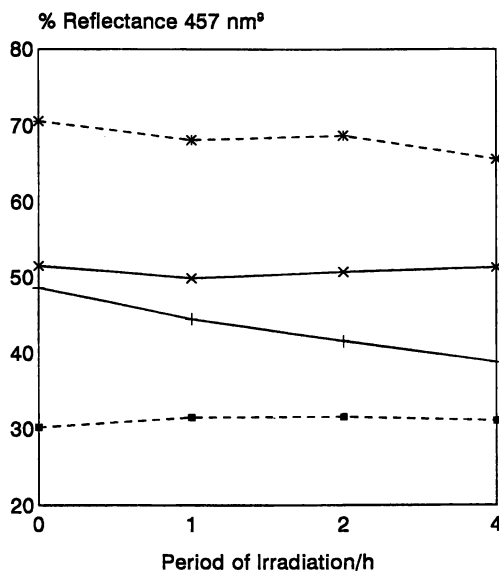


Figure 3: Brightness Changes Incurred During the Photolysis of *Para*-Quinones Impregnated on BCTMP Handsheets^a

- ✱ 2,6-Dimethoxy-1,4-benzoquinone (0.0008 g/g BCTMP)^b
- + 2-Methoxy-1,4-benzoquinone (0.0084 g/g BCTMP)^b
- ✱ 2-Hydroxy-3,5-dimethoxy-1,4-benzoquinone (0.0120 g/g BCTMP)^b
- 2,5-Dihydroxy-1,4-benzoquinone (0.0084 g/g BCTMP)^b

^aemployed an Oriel 100 Watt Solar Simulator for photo-aging studies, see experimental section for complete experimental procedure;

^b mass of quinone applied/mass of handsheet.

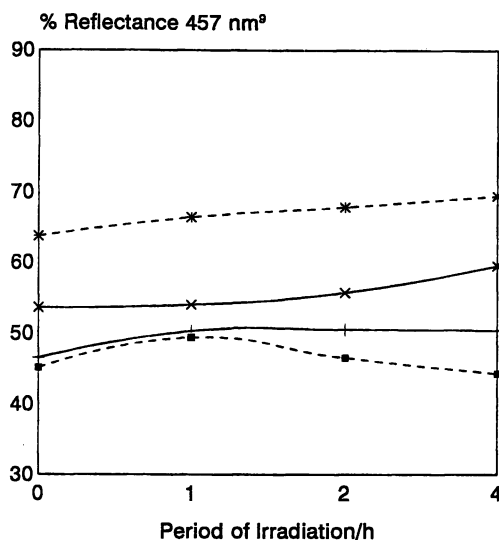


Figure 4: Brightness Changes Incurred During the Photolysis of *Ortho*-Quinones Impregnated on Cellulose and BCTMP Handsheets^a

- x— 3-Methoxy-1,2-benzoquinone/Cellulose
- * 4-Methyl-1,2-benzoquinone/Cellulose
- + 3-Methoxy-1,2-benzoquinone/BCTMP
- 4-Methyl-1,2-benzoquinone/BCTMP

^aemployed an Oriel 100 Watt Solar Simulator for photo-aging studies, see experimental section for complete experimental description.

handsheets had brightness values of 86.6 ± 0.3 . All quinones except 2,5-dihydroxy-1,4-benzoquinone were applied onto the handsheets in a solution of dichloromethane. Due to solubility problems, 2,5-dihydroxy-1,4-benzoquinone was applied onto brightness pads with 1:8 mixture of methanol and dichloromethane. The handsheets were immersed in the quinone/dichloromethane solution for 1/2 h, and the resulting doped handsheets were then dried under a high vacuum for 2 to 6 hr. The impregnated brightness pads were protected from light at all times except during the photolysis experiments.

The handsheets impregnated with quinone model compounds were photolyzed in an Oriel 1000 W Solar Simulator. The Solar Simulator uses a xenon arc lamp to simulate the solar spectrum and was fitted with an air mass 1.5 global filter to model the average wavelength distribution of solar irradiation in the continental United States. An exhaust fan provided air circulation to minimize heating of the sample. The spectral distribution of the solar simulator is approximately equivalent to natural sunlight.

Optical measurements were carried out using a Technidyne S-4 Brightness Tester and Colorimeter. GC\MS studies were performed employing a HP 5890 Series II GC and a HP 5971A Mass Selective Detector.

Irradiation and Extraction of 2-Methoxy-1,4-Benzoquinone Impregnated Handsheets. Previously extracted cotton linter handsheets (10.0163 g) were placed in a saturated solution of 2-methoxy-1,4-benzoquinone/dichloromethane (250 ml). After remaining in the solution for 1/2 h (shielded from light), the handsheets were air and vacuum dried, as described above. The impregnated handsheets (0.1035 g 2-methoxy-1,4-benzoquinone/10.0163 g cotton linters) were then irradiated for 4 hours in a Rayonet RPR-100 merry-go-round photochemical reactor. The lamps contained a blacklight phosphor, which has roughly a Gaussian spectral distribution between 300 and 400 nm and a maximum output at ca. 350 nm. After photolysis the handsheets were extracted with dichloromethane (3 * 250 ml), followed by methanol (1 * 250 ml). Removal of the solvent yielded a 77% mass recovery (0.0792 g), which by GC analysis consisted of 90% 2-methoxy-1,4-benzoquinone, 9% 2-methoxyhydroquinone (parent peak, $M=140$), and several unidentified trace components. The identity of 2-methoxyhydroquinone was confirmed by comparison with reported fragmentation patterns for the hydroquinone (16) and by co-injection with a commercial source of 2-methoxyhydroquinone.

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Chapter 6

Diffuse Reflectance Laser Flash Photolysis of Thermomechanical Pulp

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A comparative study of the photochemical properties of aromatic α -carbonyl groups found in the lignin part of thermomechanical pulp (TMP) with those of an α -carbonyl lignin model compound 3,4-dimethoxyacetophenone has been undertaken with a view to gaining insight into the photoyellowing mechanisms of TMP. The technique of diffuse reflectance laser flash photolysis has been used to investigate transient reflectance changes observed following pulsed excitation of TMP samples. Chemically modified TMP with reduced phenolic hydroxyl content within the lignin part of the pulp shows a 29% increase in the size of the transient signal upon reducing the phenolic hydroxyl content from 0.128 to 0.0091 phenolic hydroxyl units per C_9 lignin unit. Upon excitation of TMP samples under an atmosphere of oxygen we were able to see dynamic quenching of the transient signal relative to a sample with all oxygen removed. Studies with the lignin model compound 3,4-dimethoxyacetophenone in benzene solution demonstrate that triplet states of carbonyl groups α to an aromatic ring are quenched efficiently by phenolic hydroxyl groups ($k_Q = 6.3 \times 10^9 \text{ l.mol}^{-1} \text{ s}^{-1}$) and can also be quenched by methoxyl moieties ($k_Q = 2.6 \times 10^6 \text{ l.mol}^{-1} \text{ s}^{-1}$ for methoxybenzene) present in the lignin structure.

Mechanistic photochemical investigation in heterogeneous systems such as lignocellulosic materials constitutes a considerable challenge. Heterogeneity makes the analysis of photochemical and photophysical data much more complicated than in homogeneous media but the technological and commercial importance justifies efforts which are made to cope with the inherent complexities. Recently we have extended to heterogeneous opaque and often highly scattering systems, the advantages of being able to subject them to flash photolysis investigation by monitoring changes in diffusely reflected light rather than in transmitted light. This has allowed probing of transient events on timescales extending from several seconds to picoseconds(1, 2).

Laser induced transient spectra and decay kinetics have been observed from a wide variety of samples including fractions of monolayers of organic molecules adsorbed on catalytic metal oxide surfaces(3, 4), and included within zeolites(5), from

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semiconductor powders(6), and porous electrodes doped and undoped(7), from ruthenium (II) complexes within ion exchange resins(8), from organic microcrystals(9) and from organic dyes adsorbed on microcrystalline cellulose(10, 11), on fabrics and chemically bound to polymers(12, 13) and from paper pulp(14, 15).

Since the α -carbonyl group is the primary photochemical absorber in the near U.V. part of the electromagnetic spectrum leading to photoyellowing (brightness reversion) of high yield thermomechanical pulp (TMP), we investigate in this paper the excitation of carbonyl groups within lignin using laser flash photolysis in diffuse reflectance mode and compare this with results from an α -carbonyl lignin model compound studied by transmission laser flash photolysis in dilute solution and by diffuse reflectance laser flash photolysis when adsorbed onto microcrystalline cellulose. The effects of methoxylation of phenolic hydroxyl groups within pulp samples, and the presence of moisture and oxygen on both spectral and kinetic observations, were also investigated with regard to the photoyellowing process.

Experimental

Materials. All solvents were spectrophotometric grade (Aldrich) and were used without purification. Microcrystalline cellulose (Aldrich, 20 micron mean particle size) was used as supplied. 3,4-dimethoxyacetophenone (Aldrich) was purified by sublimation under vacuum at a pressure of 5×10^{-4} mBar at 40°C, purity being checked by melting point, UV-Visible and N.M.R. Spectroscopy. Phenol (Aldrich) and methoxybenzene (Aldrich) were used without further purification.

Preparation Of TMP Samples. All experiments with pulp samples were performed using black spruce thermomechanical pulp (TMP) which had been bleached to an ISO brightness of 75% by 4% hydrogen peroxide at 60°C for approximately two hours. With the exception of the data presented in Figure 2 where optically thick pulp sheets were used, all investigations involving TMP were performed using powdered samples. Samples used to investigate the effect of varying phenolic hydroxyl content, the effect of oxygen and the effect of water were ground to a 40 mesh powder in a Wiley mill and packed into quartz cuvettes prior to investigation. Sufficient pathlengths and packing densities were used to ensure that samples were optically thick at both excitation and analysing wavelengths. Pulp samples were dried under a vacuum of 2×10^{-5} mbar for 1 hour prior to introduction of either dry nitrogen or oxygen. Pulp samples used to investigate the effect of water on the observed transient kinetics were saturated with water following packing into the sample cuvette.

Methoxylation of TMP samples was achieved by heating pulp fibres together with appropriate amounts of dimethyl sulphate in an equivolume solvent of water, ethanol and dimethoxyethane(14), methoxyl content of the pulp fibres being controlled by the amount of dimethyl sulphate added (Schmidt, J.A.; Heitner, C. *J. Wood Chem. Chem. Technol.*, In Press). Samples were analysed for methoxyl content by Scharzskopf Microanalytical Laboratories, Woodside, New York. Analysis of the TMP samples for phenolic hydroxyl content was according to the method of Gellerstedt and Lindfors(16).

All ground state diffuse reflectance spectra were recorded using a Phillips PU8800 UV-Visible spectrophotometer equipped with an integrating sphere, interfaced to an Elonex PC-386SX computer. These ground state diffuse reflectance spectra were measured relative to a BaSO₄ white reflectance standard (Eastman Kodak Ltd.).

Preparation Of Samples Adsorbed On Microcrystalline Cellulose. The cellulose powder was dried under vacuum (65 mBar) at 70°C overnight prior to use. A known mass of ca. 2g was weighed into a 100 ml beaker and immediately submerged under the appropriate solvent (in this case benzene) to avoid moisture uptake. To this

mixture was added a solution of 3,4-dimethoxyacetophenone to give a surface concentration of ca. 10^{-6} moles of ketone per gram of cellulose powder. The sample was then magnetically stirred allowing slow solvent evaporation until only residual solvent remained and then dried in a vacuum oven (65 mBar) at 30°C overnight.

Solution Phase Studies. Freshly prepared solutions were used for all experiments. All solution phase studies were carried out using samples which had been thoroughly de-gassed using a minimum of three freeze-pump-thaw cycles for each sample. The final pressure above the sample was in all cases less than 5×10^{-4} mBar. Laser energy densities of less than 2.5 mJ cm^{-2} were used such that sample degradation was kept to a minimum.

The rate constants for quenching of the triplet state of 3,4-dimethoxyacetophenone by methoxybenzene or phenol in benzene solution were determined using samples of 3,4-dimethoxyacetophenone with an absorbance of 0.1 (ca. $2 \times 10^{-3} \text{ mol.l}^{-1}$) at the laser excitation wavelength (354.7 nm) in the presence and absence of the quenchers. Neither phenol nor methoxybenzene absorb at the laser excitation wavelength.

Nanosecond Flash Photolysis. Diffuse reflectance flash photolysis studies were carried out using the apparatus and optical geometry illustrated in Figure 1. The timing of events in the system is controlled by an analogue delay unit, data acquisition being controlled via a microcomputer (Elonex PC286S-10) using software written specifically for the purpose at Loughborough. The excitation source is a Q-switched hyperYAG HY-200 Nd:YAG laser (Lumonics). The analysing source is a 250W xenon arc lamp (Optical Radiation Corporation), which may be pulsed to provide an approximately ten-fold intensity increase for a period of 0.5 ms using an arc lamp pulsing unit (Applied Photophysics). Diffusely reflected light from the sample is collected by a lens system and focussed onto the slit of an $f/3.4$ grating monochromator (Applied Photophysics). The selected wavelength is detected by an R928 side-window photomultiplier tube (Hamamatsu). The time evolution of the laser induced transient reflectance change is captured by a 2432A digital oscilloscope (Tektronix) and transferred to the microcomputer via an IEEE-488 interface bus. Samples were contained within cylindrical quartz cuvettes of 2 cm diameter and 1 cm pathlength.

The observable parameter in diffuse reflectance laser flash photolysis experiments is the fractional reflectance change $\Delta J(t)/J_0$ defined as in Equation 1.

$$\frac{\Delta J(t)}{J_0} = \frac{R_b - R(t)}{R_b} \quad (1)$$

Here, R_b is the sample reflectance before exposure to the laser pulse and $R(t)$ the reflectance at time t after the laser pulse.

Transmission flash photolysis studies were carried out using a similar system to that used for diffuse reflectance studies. In this case the excitation source was a JK2000 Q-switched Nd:YAG laser (Lumonics), the transient events being captured by a 7612AD transient digitiser with a 7A12 differential plug-in amplifier (Tektronix). For these experiments conventional flash photolysis geometry (ie. perpendicular excitation and analysing beams) was employed. The samples were contained within 1 cm x 1 cm quartz cuvettes.

Results

Effect of Oxygen Concentration on the TMP Transient. Samples of high yield thermomechanical pulp (TMP), when subjected to laser photolysis, show a transient reflectance change which decays by complex kinetics. With these samples substantial fluorescence renders transient absorption measurements unreliable at times less than ~ 150 ns. The difference spectrum of this transient exhibits a peak at approximately 450 nm, the shape of the spectrum being independent of the time delay after the excitation pulse to within experimental error (Figure 2). For dry TMP, the kinetics of the transient decay are seen to be slightly faster in the presence of oxygen than in an atmosphere of pure nitrogen, suggesting some dynamic quenching and thus measurable oxygen mobility in dry pulp (Figures 3a and 3b), although whether this implies penetration of oxygen into the lignin polymer itself or simply interaction with exposed surface groups has not been established. The transient decays in dry pulp are non-exponential and can be characterised by first empirical half lives of 4.5 ± 0.3 and 5.8 ± 0.3 microseconds for oxygen and nitrogen saturated samples, respectively. However, oxygen concentration had no effect on the size of the initial transient reflectance change, suggesting that static quenching of the transient or its precursor by oxygen is not significant in this system.

Following saturation with water, the observed first empirical half life of the transient for a TMP sample which had been bubbled with nitrogen overnight was reduced to 0.90 ± 0.2 microseconds. The first empirical half life for an oxygen saturated wet TMP sample was found to be 0.65 ± 0.2 microseconds. As with dry TMP samples, second and subsequent empirical half lives for water saturated samples were also found to be oxygen sensitive. Given that the first empirical half lives for nitrogen and oxygen saturated dry TMP samples were found to be 5.8 ± 0.3 and 4.5 ± 0.3 microseconds, the large decreases in first empirical half lives upon addition of water may be explained by either water quenching the carbonyl triplet states or, water swelling of the pulp fibres allowing for greater mobility of functional groups within the pulp fibres resulting in more rapid triplet carbonyl decay. We interpret the small decrease in first empirical half lives for wet samples with increasing oxygen concentration as being due to greater oxygen mobility resulting in more rapid quenching of the carbonyl triplet states within the lignin.

Treatment of TMP with sodium borohydride reduces the absorption by the pulp sheet in the 330nm region and decreases the size of the laser induced transient reflectance change in proportion (Schmidt, J.A.; Heitner, C. *J. Wood Chem. Chem. Technol.*, In Press). Absorption by the pulp in this spectral region has been attributed to the presence of aromatic carbonyl functionality. This and the fact that the transient signal is seen to be dynamically quenched by oxygen is consistent with the observed transient being assigned as the lowest lying triplet state of the aromatic carbonyl groups present in the pulp(14,15).

Effect of Methoxylation of Phenolic Hydroxyl Groups. Methylation of the phenolic hydroxyl groups in the lignin by treatment with dimethyl sulphate has no measurable effect on the ground state diffuse reflectance spectrum of the TMP. Increasing methylation does, however, result in an increase in the size of the transient reflectance change observed upon laser photolysis but does not, to within the error of the experiment, affect the spectral shape thereof (Figure 4). In addition, there is no effect of methoxyl content on the kinetics of decay of the laser induced transient reflectance change.

In going from no methoxylation (0.128 phenolic hydroxyl groups per C_9 unit) to a high proportion of methoxylation (0.0091 phenolic hydroxyl groups per C_9 unit) there is an increase in the size of the transient reflectance change of some 29% (Table I).

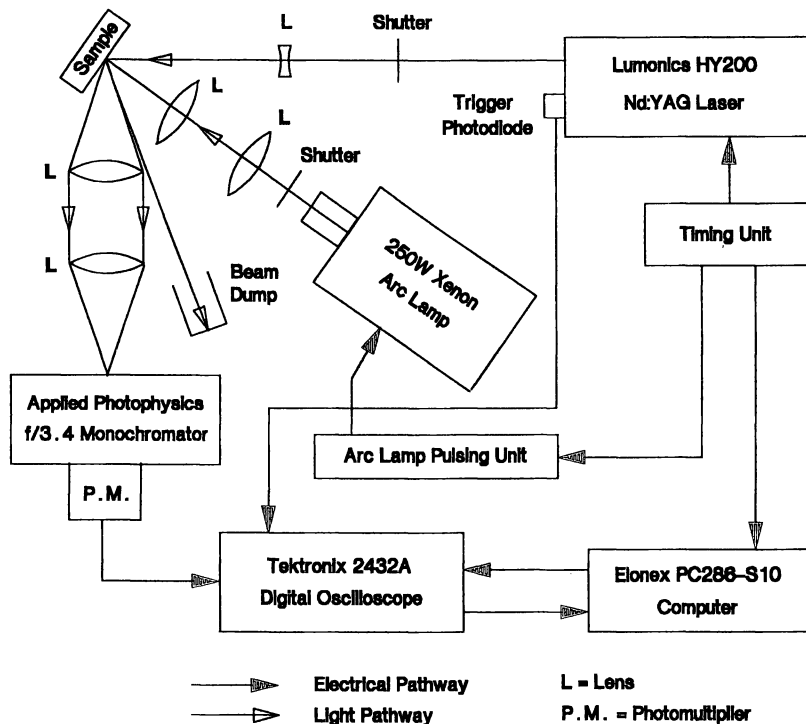


Figure 1. Schematic Diagram of the Apparatus and Optical Arrangement used for Diffuse Reflectance Laser Flash Photolysis Experiments.

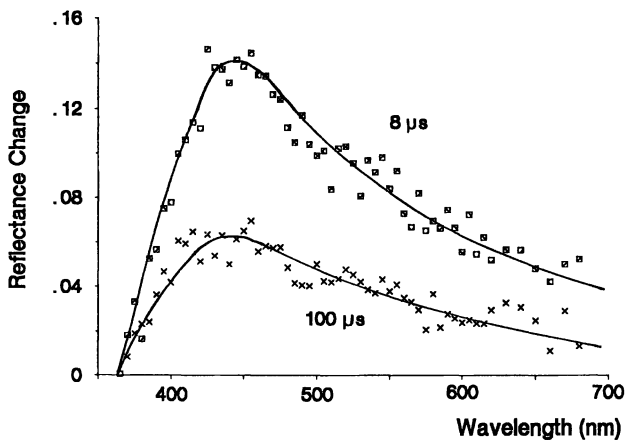


Figure 2. Transient Difference Spectrum Observed from a Sample of TMP at Two Delays Following the Laser Excitation Pulse.

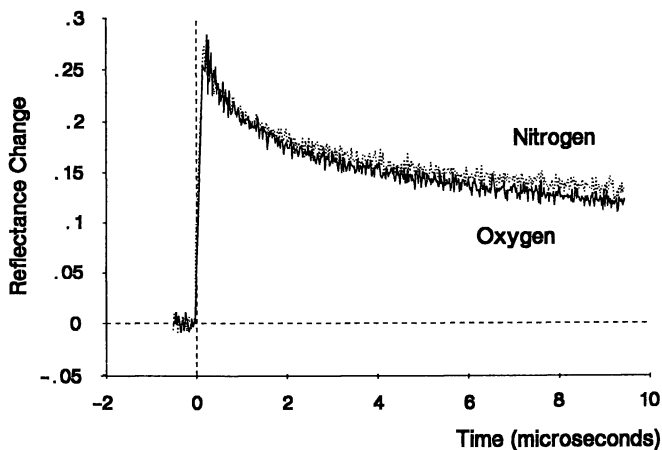


Figure 3a. Transient Decay Following Laser Excitation Analysing at 450 nm for Dry Samples of TMP under Atmospheres of Oxygen and Nitrogen over a 10 μ s Time Sweep.

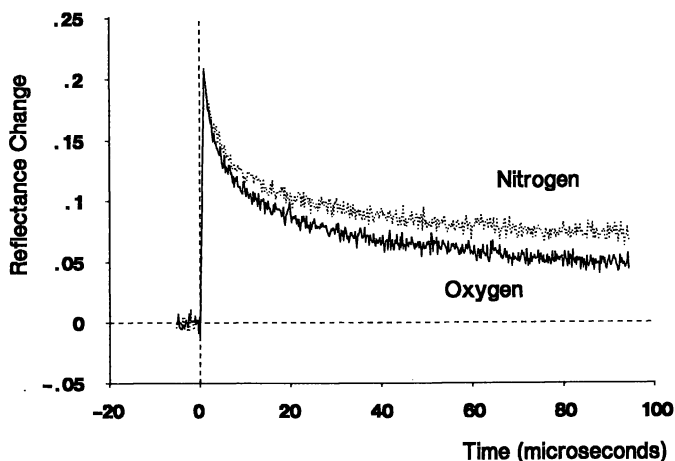


Figure 3b. Transient Decay Following Laser Excitation Analysing at 450 nm for Dry Samples of TMP under Atmospheres of Oxygen and Nitrogen over a 100 μ s Time Sweep.

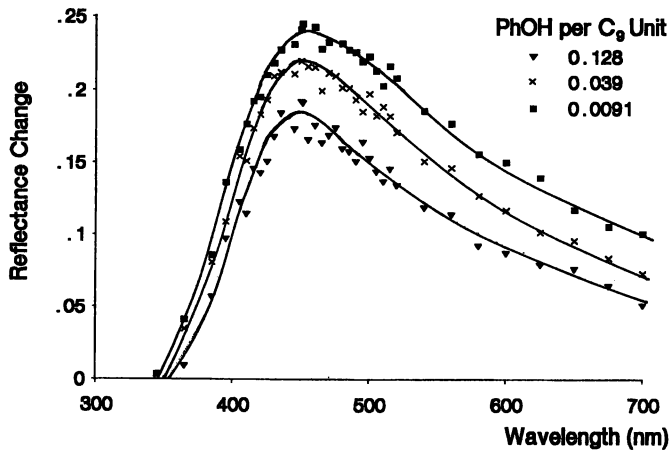


Figure 4. Transient Difference Spectra Recorded 3 μ s after the Laser Pulse For TMP Samples with Various Degrees of Methoxylation.

Table I. Relative Transient Reflectance Change ($\Delta J(0)/J_0$) Observed Immediately Following Laser Photolysis ($t = 0$) For TMP Samples Of Varying Phenolic Hydroxyl Content.

Phenolic Hydroxyl Content per C ₉ Lignin Unit	Methoxyl Content (% by Mass)	Relative $\Delta J(0)/J_0$ at 450 nm
0.128	4.4%	1.00
0.039	7.23%	1.19
0.0091	8.13%	1.29

This observation confirms the results obtained in previous studies, where for total methoxylation an increase in signal of 30% was reported(14). If the observed transient is due to absorption by the lowest triplet states of the aromatic carbonyl groups within the lignin, then the predominant triplet state deactivation pathway will be intersystem crossing to the ground state. From our measurements, phosphorescence emission as a mode of triplet state deactivation is a minor pathway relative to the intersystem crossing. The increased transient reflectance change from detected triplet carbonyls with increasing methoxylation of the substrate and no change in the observed deactivation kinetics may be explained in two ways;

(i) Reduction in the number of -OH groups leads to less quenching of the precursor of the triplet carbonyls leading to a greater population of the carbonyl triplet state.

(ii) Hydroxyl groups within the lignin structure may quench triplet carbonyls by a static mechanism which is too fast to be detected within the time resolution of our apparatus (< 20 ns). Fewer hydroxyl groups would lead to more triplet carbonyls having a lifetime sufficiently long to be detected.

Given that in TMP which has not had any phenolic hydroxyl groups replaced by methoxyl groups there are approximately 0.07 α -carbonyl groups and 0.128 phenolic hydroxyl groups per C₉ lignin phenylpropane unit(17), the magnitude of the increase in transient signal with increasing methoxylation suggests that phenolic hydroxyl groups are not distributed randomly with respect to the carbonyl moieties, perhaps as a result of the biochemical reaction mechanisms leading to lignin formation.

Studies Involving Lignin Model Compounds. Acetophenone derivatives with methoxyl and/or hydroxyl substitution patterns in the 3,4 and 5 positions of the aromatic ring have been suggested as appropriate model compounds for the carbonyl functionality present in the lignin structure(18). Consequently, studies involving the lignin model compound 3,4-dimethoxyacetophenone have been conducted to characterise its photochemical and photophysical properties. Upon flash excitation of a solution of 3,4-dimethoxyacetophenone, a transient absorption is seen which displays a solvent dependent λ_{max} and lifetime; these are tabulated in Table II. The transient absorption is assigned as triplet-triplet absorption from the first triplet state on the basis of energy transfer studies to perylene and naphthalene. The triplet yield was determined as unity on the basis of energy transfer studies with naphthalene as the acceptor.

Inspection of the data in Table II reveals a bathochromic shift of the λ_{max} of the triplet-triplet absorption with increasing solvent polarity, with a further bathochromic shift when the compound is adsorbed on microcrystalline cellulose. No phosphorescence emission in solution is seen from this compound at room temperature, indicating that the radiative lifetime of this triplet state is long. This is consistent with the lowest energy excited triplet state having predominantly (π , π^*) character. The shape of the triplet-triplet absorption spectrum also suggests that this is the case(20).

Table II Triplet-Triplet Absorption Maxima (λ_{\max}), Extinction Coefficient (ϵ_{\max}) and Triplet Lifetime (τ_T) for 3,4 dimethoxyacetophenone in a Variety of Environments

Solvent/Support	Excitation Wavelength/nm	λ_{\max}/nm	ϵ_{\max}	Triplet Lifetime
			$\text{l.mol.}^{-1}\text{cm.}^{-1}$	$\tau_T/\mu\text{s}$
Benzene	354.7	365	12400 ^a	39 ^b
Acetonitrile	354.7	385		15 ^b
Cellulose	266	400		4000 ^c

^a relative to triplet benzophenone in benzene ($\epsilon_{\max} = 7220 \text{ l.mol.}^{-1} \text{ cm.}^{-1}$)(19)

^b first order decay ($\tau_T = 1/k_d$)

^c first empirical half life

The excited triplet state of 3,4-dimethoxyacetophenone is quenched by both phenolic hydroxyl and methoxyl functionalities. The rate constant for decay of the 3,4-dimethoxyacetophenone triplet state k' , in the presence of a quencher Q is related to the rate of triplet state decay in the absence of quencher k_d , the quenching rate constant k_Q and the quencher concentration according to Equation 2.

$$k' = k_d + k_Q[Q] \quad (2)$$

Hence, a plot of k' as a function of $[Q]$ will be linear with slope equal to k_Q and intercept k_d . Triplet decay constants k' were obtained by simultaneously fitting four kinetic traces obtained for each sample with a first order function of the form (Equation 3):

$$A(t) = A(0) \exp -(k't) + C \quad (3)$$

where $A(t)$ is the laser induced change in absorbance at the analysing wavelength at time t after the laser pulse and $A(0)$ is the change in absorbance at the analysing wavelength immediately following the laser pulse. The term C accounts for a small amount of residual absorbance observed due to formation of the ketyl radical of the 3,4-dimethoxyacetophenone. The yield of the ketyl radical in the presence of phenol is, as anticipated, significantly increased relative to a sample of the ketone alone. In addition, absorption by the phenoxy free radical also contributes to the overall residual absorption following complete triplet state deactivation(21).

Plots of k' as a function of quencher are shown in Figures 5a and 5b. The rate constant for quenching by phenol in benzene is determined as $6.3 \times 10^9 \text{ l.mol.}^{-1} \text{ s.}^{-1}$ (Figure 5 a). This is in good agreement with other authors who demonstrated that the quenching of predominantly (π, π^*) character aromatic carbonyl triplet states with phenols is an efficient process(22). Figure 5b demonstrates that the triplet state of 3,4-dimethoxyacetophenone is also quenched by methoxyl containing moieties, although at a considerably slower rate relative to that observed with phenol as the quencher. The quenching constant for methoxybenzene in benzene was determined as $2.6 \times 10^6 \text{ l.mol.}^{-1} \text{ s.}^{-1}$.

The high value for the quenching of 3,4-dimethoxyacetophenone by phenol suggests that it is probable that within the lignin structure hydroxyl groups are able to quench carbonyls by a static mechanism to yield phenoxy-ketyl radical pairs which decay on a timescales faster than the time resolution of our laser flash photolysis apparatus. Intersystem crossing rate constants for triplet radical pairs in the restricted environments of micelles have been demonstrated to be of the order of $2 - 5 \times 10^6 \text{ s}^{-1}$ (23, 24). However, in the lignin matrix where diffusional processes are likely to be

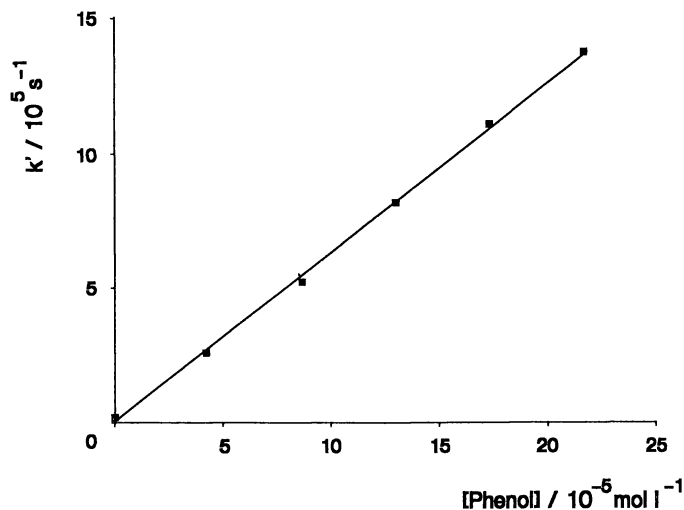


Figure 5a. A Plot of the Pseudo First Order Rate Constant k' as a Function of Quencher Concentration $[Q]$ for 3,4-dimethoxyacetophenone in Benzene Quenched by Phenol.

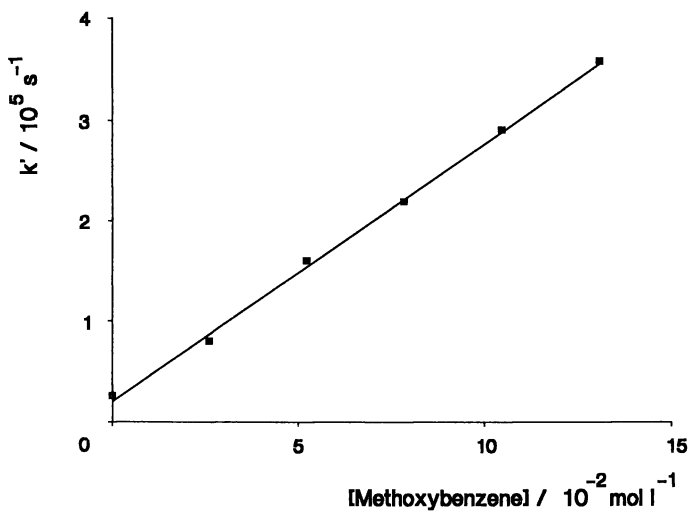


Figure 5b. A Plot of the Pseudo First Order Rate Constant k' as a Function of Quencher Concentration $[Q]$ for 3,4-dimethoxyacetophenone in Benzene Quenched by Methoxybenzene.

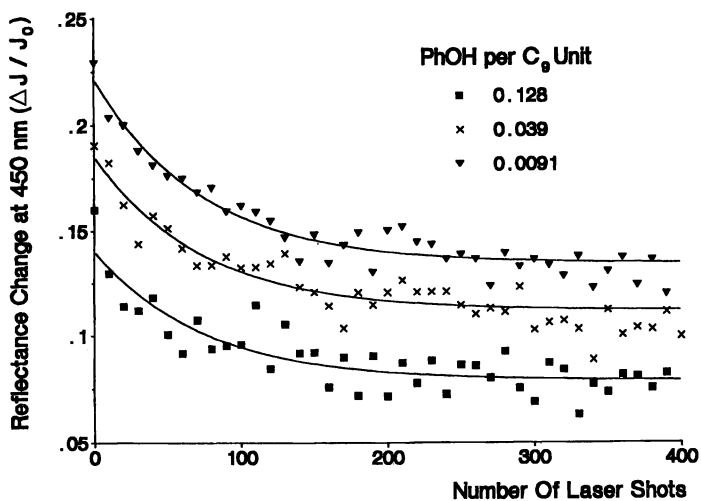


Figure 6. Transient Difference Signal Analysing at 450 nm for Samples of TMP with Varying Degrees of Methoxylation as a Function of Laser Shot Exposure Recorded 4 μ s after the Laser Pulse.

even more restricted, rate constants for intersystem crossing of triplet radical pairs are likely to be greater than those observed for micellar environments, leading to much faster radical pair decay which we are unlikely to detect.

Photoyellowing of TMP. The transient absorption signal ($\Delta J(t)/J_0$) observed from TMP at 450 nm is seen to decrease with increasing number of laser shots to which it is exposed as photoyellowing of the sample proceeds (Figure 6). Following exposure to several hundred laser shots, changes in ($\Delta J(t)/J_0$) with further exposure are virtually zero. This may be attributed in the main to consumption of the aromatic carbonyl groups and to the production of products which absorb at 354.7 nm, since there is a decrease in ground state reflectance at 354.7 nm of only 3% following irradiation due to lignin photodegradation and product build-up. Assuming that photodegradation products are formed below the surface with the same distribution as the carbonyl moieties within the pulp, the magnitude of this decrease in reflectance at 354.7 nm is not sufficient to explain the above observation as purely an inner filter effect. If the coloured products are generated preferentially at the front surface, perhaps as a consequence of oxygen availability, then filtering of the exciting light by a product would have a greater effect on the observed transient signal than the magnitude of the absorption at 354.7 nm would suggest. However, even allowing for this effect, we calculate some destruction of the carbonyl functionality must also be taking place.

Measurement of the ground state diffuse reflectance spectra of these samples before and after exposure to many laser pulses showed that increasing methoxylation decreases the amount of photoyellowing which occurs, an observation in agreement with those of Schmidt and Heitner (Schmidt, J.A.; Heitner, C. *J. Wood Chem. Chem. Technol.*, In Press) obtained under conditions of steady state irradiation. Additionally, the quantum yield of photoyellowing decreases with increasing irradiation time, which may again be attributed to both an inner filter effect and destruction of the aromatic carbonyl groups. Hence on the grounds of these studies both aromatic carbonyls and phenolic hydroxyl groups are implicated in the photoyellowing mechanism.

Conclusions

We have provided experimental evidence demonstrating the very different behaviour of triplet states of aromatic carbonyls in lignin and in dilute solution. These differences result, we believe, from the very restricted motion within the lignin structure relative to fluid solution. By using oxygen saturated samples rather than air saturated samples, we have been able to establish for the first time that dynamic quenching by oxygen occurs within TMP.

We have also confirmed our previous results on the effect of methoxylation of phenolic hydroxyl groups within lignin. On the basis of our model studies, we suggest that the most likely explanation for this is that triplet carbonyl groups are quenched statically by hydroxyl groups within the lignin structure on timescales less than 20 ns thus reducing the amount of transient detected in our laser photolysis experiments.

Acknowledgements

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Chapter 7

Primary Photophysical and Photochemical Processes of α -Guaiacoxyacetoveratrone

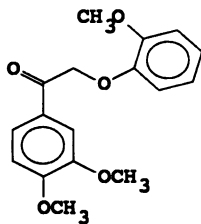
Time-Resolved Chemically Induced Dynamic Electron Polarization and Optical Emission Studies

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Time-resolved CIDEP and optical emission studies provide further definitive characterization of the triplet and excited singlet states followed by their primary photochemical reactions producing transient radicals in individual mechanistic steps in the photolysis of α -guaiacoxylacetoveratrone. Both fluorescence and phosphorescence are observed and CIDEP measurements confirm the mainly π, π^* character of the lowest triplet state. The results indicate a photo triplet mechanism involving the formation of the ketyl radical prior to the β -ether cleavage to form phenacyl radicals and phenols. Indirect evidence of excited singlet photo decomposition mechanism is observed in the photolysis at 77 K.

In order to prevent the light-induced yellowing processes of TMP (thermal mechanical pulp) paper a better understanding of the photochemistry of lignins is paramount. In recent years this significant objective has stimulated much interest in the fundamental study of the photophysical as well as the photochemical processes of some lignin model compounds, such as the α -guaiacoxylacetoveratrone (GAV). Basically there are three



(GAV)

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common major categories of techniques in photochemistry. The most important one is the product analysis that clearly defines the overall chemistry of the photochemical system. It also includes the task of quantum yield measurements and recent mechanistic tools such as nmr-CIDNP (chemically induced nuclear polarization) analysis of products. The remaining two categories arbitrarily deal with optical and electron spin spectroscopic techniques in various forms, including the time-resolved dynamic studies of transient reaction intermediates such as triplet states and radicals. Analogous to the fable of three blind persons examining the elephant, no single physical or chemical technique, however powerful, is able to give a complete true picture of the photochemistry of an enormously complex system such as lignin. In this paper we combine the time-resolved CIDEP (chemically induced dynamic electron polarization) and optical emission techniques in the laser photolysis study of GAV to provide a further definitive characterization of the triplet and excited singlet states and their subsequent primary photochemical reactions leading to transient radicals in individual mechanistic steps. Much of the conventional wisdom and documented results from other laboratories around the world have been taken into account in the formulation of our work and to which we gratefully acknowledge.

It was exactly 20 years ago when we first discovered the photo triplet mechanism in solution CIDEP systems (1). Together with the preceding elegant Radical-Pair mechanism an overall understanding of the CIDEP phenomenon in photochemical systems began to emerge and it has now formed the foundation of a popular technique for photophysical and photochemical studies (2-5). In the photo triplet CIDEP mechanism the electron polarization is initially evolved from the symmetry-governed intersystem crossing (6) from the excited singlet to the sublevels of the triplet. While the polarized triplet is not observable in liquid solution due to relaxation and anisotropy, it is sometimes observed in solids at 77 K. This phenomenon becomes a salient feature in comparing the flash optical study and CIDEP study in solution. In flash optical study transient absorption of both triplet and free radicals are observable and sometimes they can overlap. For CIDEP in solution only the radicals are observed. However, the CIDEP measurement of the triplet in solids provides a simple confirmation of the electronic nature of the triplet states, such as distinctions between π, π^* and n, π^* characters.

Aromatic carbonyl compounds generally yield an emissively (E) polarized triplet state following intersystem crossing. Before the electron polarization decays via spin-lattice relaxation (usually within 10^{-7} s) the triplet may react to produce a pair of primary radicals with both radicals being emissively (E) polarized. This conservation of spin memory from triplet to doublet radicals is a powerful finger-printing of the primary triplet reaction mechanism. As well, the triplet spin-lattice relaxation rate serves as an internal clock to set the lower limit of the triplet reaction rates. Furthermore, primary polarized radicals may undergo secondary reactions to yield new radicals with "secondary polarization" of varying magnitudes depending on both the radical spin-lattice relaxation rates and the secondary reaction rates. Thus a careful study of time-evolution profiles of the polarization of various radicals can map the sequence of the chemical events. Obviously, radicals produced by excited singlet state reactions do not contain such finger-printing information.

The elegant Radical-Pair theory on the other hand, deals with both singlet and triplet reactions. Here it is not required that the radicals contain any initial polarization at birth and thus they can be stable radicals or transient radicals. However, in most cases simple rules have emerged from this sophisticated theory ($S-T_0$ mixing) for geminate pairs (spin correlated pairs such as those produced by singlet reactions) and for random pairs (such as pairs produced by triplet reactions). For most common cases in liquid solution, symmetrical E/A polarization (low-field emission, E and high-field absorptive, A) is exhibited in the hyperfine pattern of triplet-pair radicals and an analogous A/E pattern for the singlet-pair radical. It is significant to note here that under these mechanisms the radical-pair polarization of the central hyperfine line is zero and thus not observed in pure radical-pair CIDEP spectra.

Although we classify the two entirely different origins of the polarization phenomenon, nature very seldom obliges. In most photochemical systems simultaneous contributions from both mechanisms often occur and it is the experimentalist's chore to sort them out before one interprets the results. Despite the great potential of the time-resolved CIDEP technique, there are a few severe restrictions we must clearly understand. Non-radical reactions and thermal continuous reactions cannot be studied by CIDEP, nor triplet and radical reactions which occur significantly slower than their respective relaxation rates. Typically, time-resolution and spectral sensitivity are fundamentally inferior to flash optical techniques. While the absorption or emission intensity of an optical transition normally follows Beer's Law, the polarization magnitude of an ESR hyperfine line cannot be simply related directly to its parent-radical concentration. In order to improve the time-resolution and the sensitivity of the CIDEP experiments (or flash optical experiments), high-power short-duration pulse lasers are normally employed as the light source. This may lead to double-photon phenomena and other unusual optical conditions which are not typical of common photolysis systems employing conventional light sources, including the sun. A more serious implication is that when such a high density of energy is instantly deposited within a very small reaction zone, the transient temperature in this zone may be substantially higher than the ambient temperature. This condition in turn will affect all the thermal activation parameters for both primary and secondary reactions. One does need to exercise caution when transferring results from laser experiments to the real-world situation.

In this article we characterize the mechanisms of the triplet photodecomposition of a model lignin α -guaiacoxylacetoveratrone in solution, and in low temperature solid matrix. Most experiments were carried out within the ESR cavity of a modified spectrometer which permits simultaneous detection of free radicals by 100 kHz modulation (thermalized radicals), time-resolved CIDEP (DC detection) and time-resolved fluorescence and phosphorescence. The conventional and time-resolved ESR results establish a phototriplet mechanism involving the formation of the ketyl radical of the aryloxy phenoxy model compounds prior to cleavage of the β -ether linkage to form phenacyl radicals and substituted phenols. Both time-resolved phosphorescence and solid state CIDEP measurements confirm that the lowest triplet state of the model lignin is mainly π, π^* in character. Solution fluorescence, together with solid state photolysis of the model lignin at 77 K suggest indirect evidence of the β -ether cleavage from the excited singlet state. In addition, the reduced form and the methyl ether

derivatives of GAV were shown to yield the same ketyl radicals when reacted with another triplet ketone such as benzophenone. However, in the methyl ether derivative no rearrangement to form a phenacyl radical and phenol would be possible and indeed such a process was not observed. The reduced form of GAV on the other hand will lead to similar chemistry yielding phenols which can subsequently be oxidized to colored compounds. These results account for the fact that light-induced yellowing still occurs even when most of the carbonyl groups in lignin samples have been chemically reduced.

As we establish the triplet photoreduction mechanism in which the primary ketyl radicals rearrange via a cleavage of the ether link to form phenacyl radicals and diamagnetic phenols, it is obvious that the overall light-induced yellowing processes would also involve at some stages photooxidation of the methoxy substituted phenols. We have therefore studied the involvement of free radicals and the roles of molecular oxygen in the photooxidation of various methoxy substituted phenols in separate series of experiments and under various conditions. The findings which strongly indicate the roles of peroxy and alkoxy radicals in initiating the oxidation processes, may help to resolve some of the previous inconsistent results regarding the effect of molecular oxygen in the photooxidation of lignins.

EXPERIMENTAL

The lignin model compounds and their derivatives used in this study were custom synthesized at Queen's University by Dr. R. Bowers (Colour Your Enzyme). CIDEP and conventional ESR experiments were conducted using either a Varian E-104 spectrometer or a customized Bruker X-band spectrometer, modified similarly as previously described (7). The light source used for *in situ* irradiation was either a super high pressure 200 W mercury lamp, a Lambda-Physik EMG101-MSX XeCl excimer laser at 308 nm., or a Quanta-Ray GCR-11 Nd:YAG solid state laser equipped for all four harmonic generations.

Solutions were flowed through a suprasil flat cell (0.1 mm thickness) at rates between 0.1 - 5.0 mL/min in order to minimize any interference from signals produced by secondary photolysis of products. Time-resolved polarization evolution profiles for the formation and relaxation of the polarized radicals were measured at a constant magnetic field and monitored by both a Hitachi 40 MHz digital oscilloscope and a Stanford Research Systems gated integrator/boxcar averager at 5 ns resolution, and both coupled to a 486 PC desk-top microcomputer for analysis.

Modifications to the experimental set-up for the acquisition of fluorescence spectra from samples within the ESR microwave cavity are described in previous work (8). Further improvements using a fast photomultiplier/photon counting technique were made in an attempt to determine the radiative fluorescence lifetime in solution. Phosphorescence at 77 K was measured both by a conventional Varian spectrofluorimeter and a pulsed laser/cooled diode array imaging device. Radiative phosphorescence lifetimes were measured by the photon counting technique, using the Stanford Research System SR400 gated photon counter.

RESULTS AND DISCUSSION

Fluorescence and Phosphorescence. Fluorescence spectra using the diode array linear imaging apparatus were obtained for GAV in benzene and in isopropanol at ambient temperatures. The fluorescence and absorption spectra are characterized by absorption λ_{max} (abs) = 280 nm and 230 nm, and a λ_{max} (emission) = 368 nm in fluorescence. The radiative fluorescence lifetime is apparently shorter than the laser pulse envelope of 5 ns and the best estimate from the photon counting experiments indicates a lifetime of about 2 ns.

Phosphorescence of a solid solution of GAV in benzene or in acetonitrile at 77 K was readily observable with a λ_{max} at 530 nm in a cw (continuous wave) fluorimeter. However, it has been demonstrated that cw irradiation of the solid sample at 77 K led to some yellowing and care must be taken to eliminate the possibility of phosphorescence deriving from the colored products. The definitive observations therefore were made with the pulse laser/diode array using only a single laser pulse. The single laser-shot phosphorescence so obtained is given in Figure 1. The radiative lifetime of the triplet is measured at 300 ms in both solvents. The long phosphorescence lifetime is typical of a π, π^* triplet and this is further confirmed by the time-resolved ESR characterization given below.

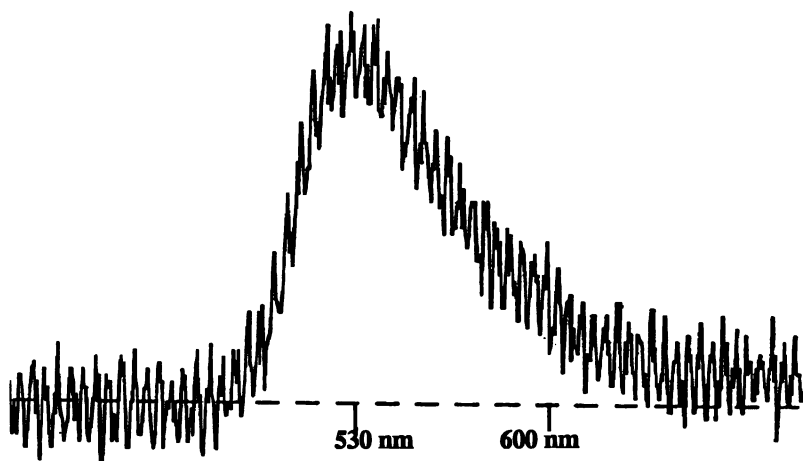


Figure 1. The diode array linear imaging of the phosphorescence of GAV in benzene at 77 K, produced by a single laser pulse of 5 ns width.

Time-Resolved Triplet CIDEP Spectra at 77 K. The time-resolved CIDEP spectra of the triplet state of GAV in a solid solution at 77 K are given in Figure 2.

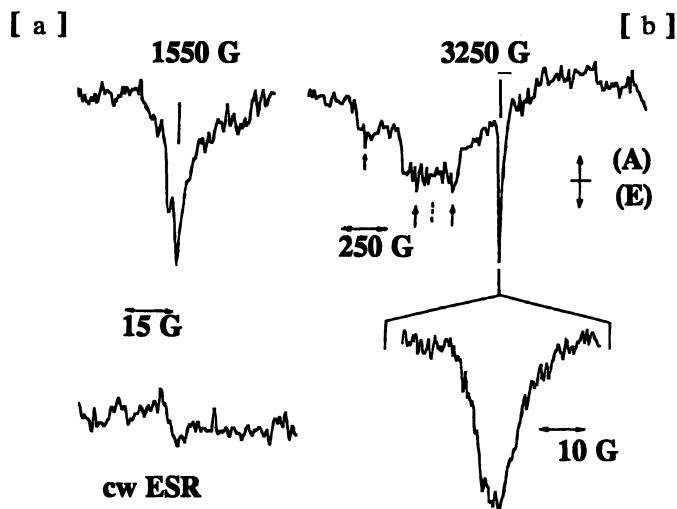


Figure 2. Time-resolved CIDEP spectrum of the lowest triplet of GAV at 77 K. a, $\Delta m = 2$ transitions at half field. b, $\Delta m = 1$ transition at the canonical orientations. The strong emissive signal at $g = 2$ is due to phenoxy radicals.

Figure 2a shows the $\Delta m = \pm 2$ transition and 2b, the low-field components at the canonical orientations of the $\Delta m = \pm 1$ transitions. Note the large polarized signal (due to phenoxy radicals) at the field $g=2$, which we shall discuss later. From this partially resolved spectrum we calculated the zero-field splitting parameters of the lowest triplet state to be $D=0.10 \text{ cm}^{-1}$ and $E=0.0082 \text{ cm}^{-1}$. These values are typical of a π, π^* carbonyl triplet of low symmetry. From both the phosphorescence and time-resolved CIDEP results we can conclude that the lowest triplet state of GAV is predominantly π, π^* in character. The long phosphorescence lifetime suggests that any chemical reactivity of the lowest triplet at 77 K is not significant. The fact that continuous irradiation of the solid solution at 77 K induces yellowing is most likely due to the direct cleavage reactions of the excited singlet state (S_1) which competes with the relatively fast intersystem crossing process. The observation of phenoxy radicals formed at 77 K gives indirect evidence of the excited singlet cleavage reaction, since at that temperature triplet chemical reactivity is insignificant. As singlet reactions do not produce totally emissive (E) ESR signals the observed polarization of the phenoxy

radicals at 77 K is rather surprising and interesting. The unusual optical conditions created by high-power laser pulses may facilitate the polarization transfer mechanism from the polarized triplet to the "stabilized" and "thermalized" phenoxy radicals trapped in the solid matrix. Such a mechanism has indeed been observed and proposed by Obi and coworkers (10).

Solution ESR and Time-Resolved CIDEP Studies.

Photolysis of GAV. A typical CIDEP spectrum of the laser photolysis of a static solution of GAV in a 1:3 ethanol / benzene solvent is shown in Figure 3a. The

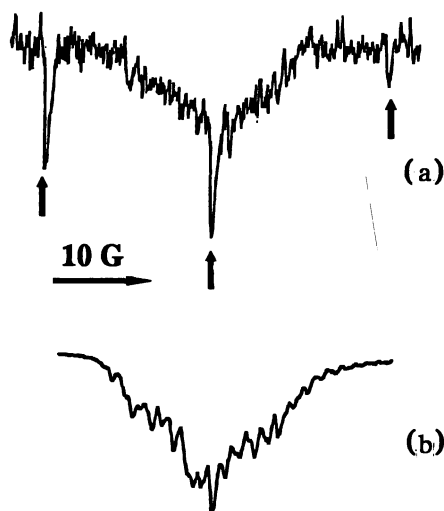


Figure 3. a, Emissive CIDEP spectrum observed during the photolysis of GAV in ethanol/benzene solution. b, The comparative CIDEP spectrum of the photolysis of 2-methoxy phenol and benzophenone.

spectrum contains two superimposed components. The well resolved 3-line component with a typical methylene proton hyperfine splitting of 18 gauss (G) is assigned to the phenacyl radicals and the underlying broad component is attributed to the methoxy phenoxy radicals, as confirmed by a comparative, separate experiment in which polarized methoxy phenoxy radicals were produced by the triplet benzophenone reaction with methoxy phenol (Figure 3b). The phenacyl radical polarization is readily accounted for by superimposition of both the all emissive (E) triplet polarization and the minor contribution from the symmetrical Radical-Pair (E/A) polarization. The results unambiguously establish that both the phenacyl and the phenoxy radicals are

produced by a phototriplet reaction mechanism. It is thus tempting at first thought to assign the CIDEP observations to the direct β -cleavage of the ether link from the triplet state (11-13). However, a closer and systematic examination of the photolysis in a flow system (to minimize secondary radical productions) and an individual monitoring of the time-resolved polarization evolution profiles of each of the components in the CIDEP spectra reveals more interesting and definitive information on the primary triplet photochemical mechanisms of GAV.

Figure 4a shows the CIDEP spectrum of the laser photolysis of GAV in the same solvent but at a very fast flow rate of 5 mL/min. As the reaction cell is only 0.1 mm thick and the incident laser beam is approximately 7 mm in diameter, this represents a very high space velocity. The overall CIDEP observation is indeed dependent upon flow rates. There are at least two major different features between the static system in Figure 3a and the fastest flow system in Figure 4a.

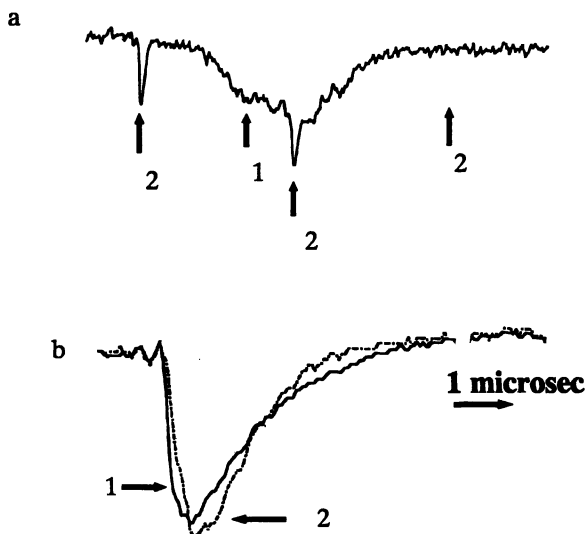


Figure 4. a, CIDEP spectrum observed during the photolysis of a flowing GAV solution (flow rate at 5 mL/min). b, The time-resolved polarization profiles monitored at selected magnetic fields: 1, ketyl radicals and 2, phenacyl radicals.

First, the polarization pattern of the 3-line phenacyl radicals appeared very different. Actually the difference is only due to the increased contribution of the E/A Radical-Pair polarization which now increases the relative emissive intensity of the low-field hyperfine line and essentially cancels the high-field line. As mentioned earlier E/A Radical-Pair polarization has no effect on the centre line. The relative Radical-Pair

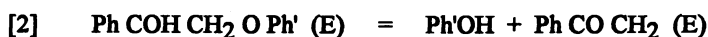
polarization of the phenacyl radicals can further be enhanced by increasing the viscosity of the medium to a point that the high-field line is observed in the absorptive (A) mode. The second feature in Figure 4a is that the underlying broad component is now shifted to lower field indicating that in addition to the phenoxy radicals there are new radicals with a higher *g*-factor involved. The relative intensity of this "new" radical is also dependent upon flow rate and hardly observable in a static system.

Further revealing information is obtained from individual monitoring of the polarization evolution profiles of the separate components of the CIDEP spectrum. These are given in Figure 4b. The results clearly indicate that the "new" radical is the primary intermediate, formed before the phenacyl radical. Furthermore, the relative relaxation rate of the spin polarization of the phenacyl radical is faster than that of the "new" radical. A final critical experiment is that when very dry acetonitrile was used as solvent, no CIDEP observations could be obtained for any radicals. From all these observations we are now ready to formulate the primary phototriplet reactions mechanism to account for all these facts.

The primary photochemical process of the polarized triplet GAV is the photoreduction by solvent molecules to yield the emissive (E) polarized ketyl radical as simplified in the following equation:



In order for the ketyl radical to conserve the spin memory (E) of the triplet, this reaction must proceed at a rate faster than the spin-lattice relaxation rate, usually about 10^7 s^{-1} . In the absence of a hydrogen-donating solvent (such is the case when acetonitrile was used as solvent), this reaction, if it proceeds, would be too slow for CIDEP observation. We note that we have concluded above that the lowest triplet state of GAV is probable an admixture but mainly π, π^* in character and we believe that the abstraction reaction by π, π^* carbonyl triplet is a thermally activated process. Carbonyl triplets such as anthraquinone with predominant π, π^* character is known to abstract a hydrogen atom from suitable donors to produce polarized primary radicals (2). Under the abnormal ambient conditions in the high-power laser flash photolysis, as mentioned earlier, the thermal activation would not have been a barrier within the reaction zone. In the 77 K experiment, it is not expected that such a photoreduction would proceed. In general, the solvent radical X is seldom observed. Two experimental facts also point to the identity of the ketyl being the primary radical: the *g*-factor which is higher than that of the corresponding phenoxy radical; and the apparent slower tumbling rate due to hydrogen-bonding with solvent which leads to a slower relaxation rate than that of the phenacyl radical. As we have established from the time-resolved evolution profiles that the phenacyl radical is a secondary radical, its emissive (E) polarization character must derive from that of the primary ketyl radical, and within the spin relaxation time of the primary radical (10^{-6} - 10^{-5} s). A consistent rearrangement reaction of the ketyl radical is the β -cleavage of the ether link to yield a polarized phenacyl radical and a diamagnetic phenol molecule:



This rearrangement involves considerable molecular flexibility (motions) and thus it is expected that the rate would depend upon the physical properties of the medium, such as the solvent viscosity and solvent interaction. In solid state and at 77 K such a rearrangement would not have been significant. Further design experiments using specific derivatives of GAV as the reactant given in a later section unequivocally confirm this rather unusual radical rearrangement.

With the establishment of the primary phototriplet reduction mechanism we now turn to the explanation for the effect of flow rates and the formation of polarized phenoxy radicals. Since reaction [2] is a relatively fast secondary process it is readily understood that the observation of the primary ketyl radicals will be dependent upon flow rate. The triplet polarization (E) of the secondary phenacyl radical should not have been affected but the increased contribution of the E/A Radical-Pair polarization altered the overall appearance of the polarization pattern. The diffusion model of the Radical-Pair theory relates the E/A polarization magnitude to the radical concentration within the reaction zone. Since the phenacyl radical is considered to be very chemically reactive, and the product phenol "accumulated" within the reaction zone is also a much better hydrogen donor, the following reactions will proceed within the reaction zone:



Both reactions can explain the subsequent formation of the emissive (E) polarized phenoxy radicals and reaction [4] indeed becomes a chain event involving reaction [2] to regenerate the phenol. We believe that this chain event is responsible for most of the polarized phenoxy radicals formed in static systems. The quenching of phenacyl radicals by phenol is more critical to a fast flow system in the CIDEP observation as it amounts to some inhibition of the quenching process within the reaction zone. This in turn maintains a phenacyl radical concentration relatively higher in a fast flow system resulting in a relatively higher contribution of the E/A Radical-Pair polarization. A more subtle and detailed study of the CIDEP phenomenon of GAV in a variety of solvents, including mixed aqueous solutions has been published elsewhere (14) but the results in all systems can be accounted for by the primary phototriplet mechanisms formulated here.

It is not surprising to us that the current CIDEP study was not able to pinpoint the role of the excited singlet reaction. Nevertheless, the results of the solid state experiments at 77 K discussed earlier support the recent CIDNP product analysis of similar lignin model reactions which strongly indicate a primary direct β -cleavage reaction from the excited singlet state (9, 11-12).

Photolysis of GAV and Its Derivatives. Photolysis of GAV together with its reduced analogue GAVH in acetonitrile gave a CIDEP spectrum showing primarily the broad emissive (E) ketyl radical with only a minor component of phenacyl radicals. Since the photolysis of GAV alone in this solvent shows no radical CIDEP the addition of GAVH can be concluded to act as a hydrogen donor in the photoreduction with the resulting formation of two identical ketyl radicals. Furthermore, photolysis of

GAVOMe in which the carbonyl group has been methylated, gave no ESR or CIDEP observations under various conditions. As expected from the above primary triplet photoreduction mechanism, alkylation precludes the photoreduction and the subsequent cleavage rearrangement.

The results from these design experiments firmly establish the nature of the primary triplet photoreduction mechanism of acyloxy ketones such as GAV. The primary triplet photoreduction of aromatic carbonyl compounds such as benzophenone has been very extensively characterized in literature. Our contribution here is the establishment of the more unique rearrangement of the primary ketyl radicals via the β -cleavage of the C-O bond. Even then, our work had been guided and inspired by some of the pioneering observations (11-13) on the photochemistry of aryloxy ketones. Related to the mechanisms of the light-induced yellowing processes of lignin, it is more significant to understand that intermediates such as the acyloxy ketyl radicals can rearrange to give phenols and then phenoxy radicals. There are other thermal and photochemical routes to produce such ketyl radicals even in the initial absence of a carbonyl moiety in the lignin.

The Photo-oxidation of Methoxy Substituted Phenols. As we are now aware of the fact that there are several routes to form phenols in the chemical reactions of lignin, we have looked into the nature of free radical induced photooxidation of phenols (15). There is no doubt that photolysis of methoxy phenols in solutions or in solid state produces yellow products. Molecular oxygen has often been shown to be a necessary reactant in the oxidation, although the radical nature of the mechanism is not understood (16).

In a systematic ESR and CIDEP study of various alkoxy substituted phenols by photochemical reactions with ketones and with organic peroxides, we have shown (15) that molecular oxygen is not the active radical reactant in the oxidation. Rather, molecular oxygen is necessary to produce peroxy and alkoxy radicals, ROO \cdot and RO \cdot which then add onto the phenyl ring to initiate the oxidation processes. The precursor radical R \cdot can be derived from as many ways as one can imagine, both via photo and thermal reactions.

There is no doubt that phenolic groups and methoxy substituted phenoxy radicals play a key role in the light-induced yellowing of TMP. One critical question arises: are there any other components and functional groups in the lignin which can be oxidized to yellow products? One very obvious component which is abundant in lignin is the dimethoxy phenyl group. We have therefore initiated a photo-oxidation study of dimethoxy benzenes as a parallel investigation to the methoxy phenols. While the dimethoxy benzenes do not absorb light longer than 290 nm in wavelengths, in the presence of alkoxy and alkyperoxy radicals the ortho-dimethoxy benzene does produce yellow products which contain carbonyl groups. Further detailed study is now in progress.

In the quest for a better understanding of the light-induced yellowing processes in lignin we must not limit our sight only to the primary photochemistry of lignins and neglect the all important secondary thermal chemistry. As our understanding of this complicated phenomenon is still far from complete, we shall refrain from making any half-hearted conclusions at this time.

Acknowledgments

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Chapter 8

Laser Techniques in the Study of the Photochemistry of Carbonyl Compounds Containing Ligninlike Moieties

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The photochemistry and photophysics of some lignin-related compounds has been studied. The triplet state of these compounds is relatively low at 60 kcal/mol, and is $\pi\text{-}\pi^*$ in nature. The $\pi\text{-}\pi^*$ nature is due to methoxy substitution on the chromophore and results in relatively long triplet lifetimes and low reactivity, compared to $n\text{-}\pi^*$ triplets like that of benzophenone. The α -phenoxy group of α -guaiaicoxyacetoveratrone provides this lignin model compound with a β -phenyl ring for triplet deactivation as well as a source of a phenoxy radical after cleavage. The intersystem crossing quantum yield is significantly less than unity which is consistent with evidence for cleavage from the singlet state.

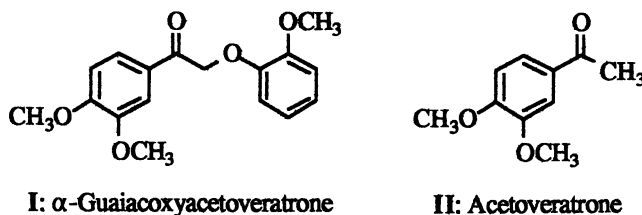
Thermomechanical pulps (TMP) and chemithermomechanical pulps (CTMP) are mainly used today for manufacturing of newsprint, catalog, and directory papers and have the advantage of being produced in high yield from wood. This method of production involves relatively little treatment by harmful chemicals and has become a popular choice as a source of pulp for paper products. TMP and CTMP still contain most of the lignin that was present in the original wood and for this reason they suffer from the limitation that photo-induced yellowing of the products made from these pulps occurs (1). Chemical pulps have most of their lignin removed and, at the cost of wastage of wood and harsh chemical treatment, are more widely produced for long-term usage due to their photostability and higher strength.

It is believed that yellowing occurs predominantly through oxidation of phenoxy radicals supplied by the phenolic hydroxy groups of lignin, although yellowing still occurs to a certain extent with a fully alkylated lignin molecule (2, 3). Hence there must be another source of yellowing in addition to the phenolic hydroxy groups in the natural product. It has been shown that upon irradiation, phenacyl aryl

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ether moieties in the lignin molecule are also an efficient source of phenoxy radicals (4). Studies by Castellan et al. have suggested that α -guaiacoxyacetoveratrone (I) represents a suitable lignin model compound with which to model these phenacyl aryl ether moieties of lignin. (5, 6, 7) While this model compound does not have all the features of lignin, it does contain a carbonyl group, is heavily substituted with methoxy groups, and it contains a guaiacoxy moiety, which upon photodegradation, will produce the corresponding phenoxy radical.

This article presents an account of laser photolysis studies on α -guaiacoxyacetoveratrone (I) and acetoveratrone (II). We summarize our own results and try to place them in the context of our understanding of other substrates which have structural features in common with I and II. We conclude that the products from I arise largely from the singlet manifold and that the decay of its triplet state is dominated by intramolecular interactions involving the guaiacoxy group. Finally, we comment briefly on other, largely heterogeneous systems, where the photochemistry of I may eventually enlighten our understanding of related processes in paper products.



Phosphorescence Studies.

For most carbonyl compounds, we expect to have two near-lying excited states in the triplet manifold, which are either $n-\pi^*$ or $\pi-\pi^*$ in character. The $n-\pi^*$ states frequently show radical-like behavior. Benzophenone is an example of such a molecule which has an $n-\pi^*$ triplet state in which we see occurrences of hydrogen abstraction and very efficient intersystem crossing. When the lowest state is the $\pi-\pi^*$ state, largely centered on the aromatic part of the molecule, as in the case of *p*-methoxyacetophenone, the reactivity decreases significantly (8, 9). With the nature of lignin and the nature of the model we have chosen, we are mostly interested in molecules which have this type of behavior.

The low temperature phosphorescence spectrum of benzophenone (see Figure 1) has a well-resolved structure, in which the splitting corresponds to the carbonyl vibrational frequencies. From this structure, one can determine that the triplet energy of benzophenone is approximately 69 kcal/mol. (10)

By comparison, for triplet states which are $\pi-\pi^*$ in nature, this type of structural resolution is absent from the phosphorescence spectra (Figure 1). Hence for the types of molecules in this study, the exact triplet energy becomes more difficult to determine. The spectra of these molecules are shifted to longer wavelengths and the triplet energy can be estimated at about 60 kcal/mol.

Excited States.

Upon absorption of light by the compounds used in this study, an excited singlet state is formed. Rapid intersystem crossing then takes place into the π - π^* triplet manifold, at about 60-63 kcal/mol. Usually carbonyl compounds will go through chemistry strictly from the triplet state, although in the case of molecules such as I, reaction is also observed from the excited singlet state. In any case, the reactions involve free radicals and we expect that the products formed from the triplet reaction will arise from random encounters by the free radicals. In the case of the singlet, random radical-radical reactions can occur between radicals that have escaped the primary solvent cage, but geminate processes arising from radical pair reactions within the solvent cage are also expected since they are formed with the appropriate electronic spin to directly lead to products.

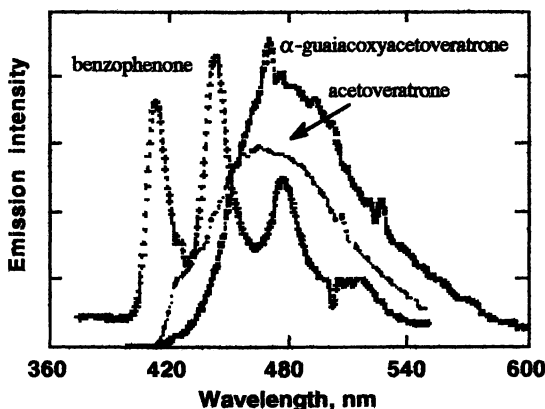


Figure 1: Phosphorescence spectra of benzophenone, α -guaiacoxyacetoveratrone (I), and acetoveratrone (II) in ethanol glass at 77K.

Acetoveratrone Photochemistry.

All of the molecules in this study have triplet states which are easily detectable by the technique of nanosecond transmission laser flash photolysis. (11) The triplet state of acetoveratrone has a lifetime in excess of 15 μ s in ethanol (Figure 2); under conditions of laser excitation the decay involves a mixture of first and second order kinetics, with the latter dominating at high laser powers. This second order decay demonstrates that the triplet state is decaying at least partly by triplet-triplet annihilation.

By contrast, the triplet lifetime of benzophenone in ethanol is <100 ns and decays via hydrogen abstraction (12). Molecules with *p*-methoxy substitution do not abstract hydrogen readily, due to the π - π^* nature of their low-lying triplet state. The long triplet lifetime of acetoveratrone reflects the unreactivity of this molecule towards

ethanol in this case. Similar results were obtained in hydrocarbon solvents such as cyclohexane.

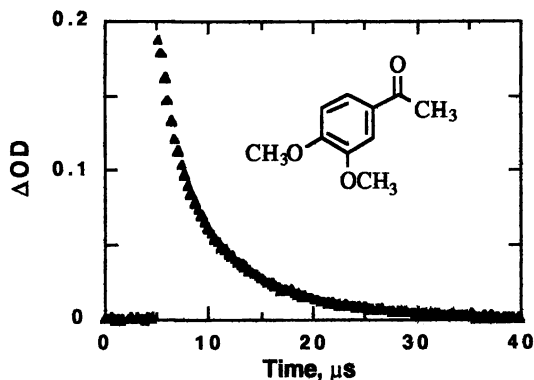


Figure 2: Decay trace of acetoveratrone in ethanol at room temperature monitored at 400 nm after 308 nm laser excitation.

Although acetoveratrone does not react with ethanol, it will readily abstract a hydrogen atom from phenols (Figure 3). This reaction may be important since a large number of phenoxy groups are present in lignin. In the presence of phenol, the acetoveratrone triplet lifetime is shortened. The reaction occurs with a rate constant of $3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile and produces a transient absorption spectrum which can be assigned to the phenoxy radical ($\lambda_{\text{max}} \sim 400 \text{ nm}$) and the ketyl radical of acetoveratrone ($\lambda_{\text{max}} \sim 380 \text{ nm}$).

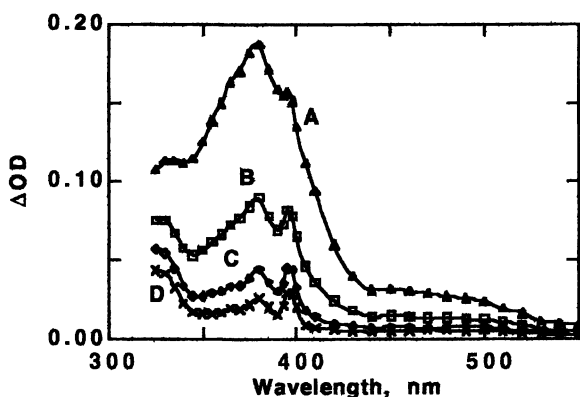
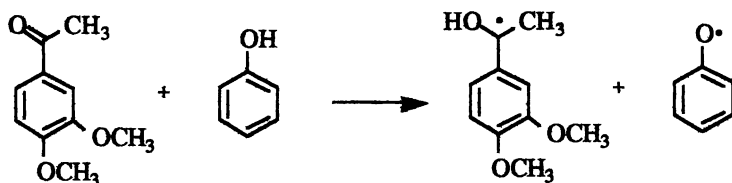


Figure 3: Transient absorption spectra produced from reaction of triplet acetoveratrone with phenol. Spectra recorded 220 ns (A), 700 ns (B), 1.3 μs (C) and 2.3 μs (D) after 308 nm laser excitation.



The transient spectrum of the phenoxy radical can be readily generated by reaction of phenol with *tert*-butoxy radicals, formed by the photodecomposition of di-*tert*-butyl peroxide. This is a very efficient reaction which takes place with a quantum yield of approximately 0.7-0.9 (13, 14). The transient spectra of the phenoxy and guaiacoxyl radicals are shown in Figure 4.

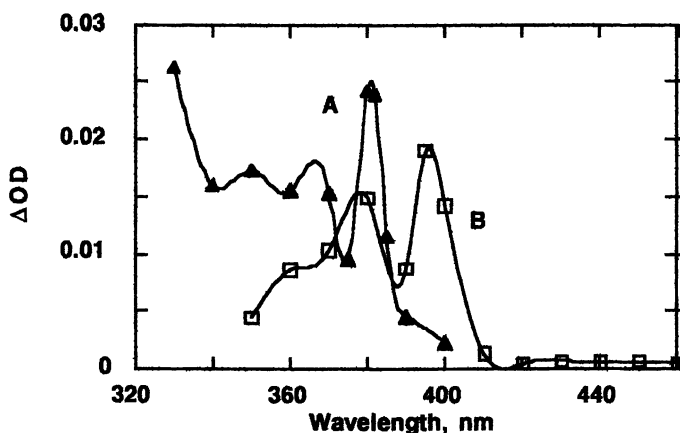
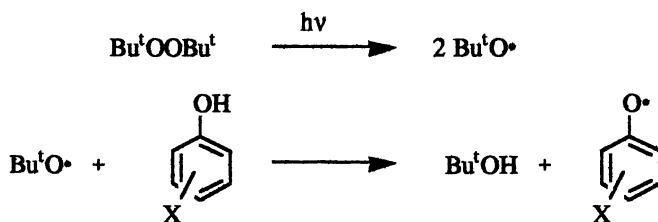


Figure 4: Transient absorption spectra of independently-generated phenoxy and guaiacoxyl radicals, after 308 nm laser excitation of guaiacol (A) and phenol (B) in acetonitrile-di-*tert*-butyl peroxide, monitored at $\lambda < 460$ nm.

The effect of β -phenyl Rings.

α -Guaiacoxyacetoveratrone not only contains the same chromophore as the one present in acetoveratrone, but it also contains an aromatic ring in the beta position. β -phenyl rings are known to greatly affect the photochemistry of these compounds. For example, acetophenone has a triplet lifetime of $\sim 2 \mu\text{s}$ in benzene solution; the triplet lifetime is determined by interactions with the solvent.

β -Phenylpropiophenone which now incorporates a β -phenyl ring, has a triplet lifetime 3 orders of magnitude shorter, Figure 5 (15). Much work has been done on β -phenylpropiophenones and what is known is that a charge transfer interaction will occur between the β -phenyl ring and the carbonyl group, and the β position for the phenyl ring is critical (15, 16). If the ring is in the alpha position the molecules undergo fragmentation, while in the gamma position, the phenyl ring is too far away to induce intramolecular quenching, and this structure leads to a Norrish Type II reaction (17).

Adding a methoxy group to acetophenone (III) to form *p*-methoxyacetophenone (V) lengthens the triplet lifetime with respect to acetophenone since the methoxy group changes the lowest lying triplet state from $n-\pi^*$ to a less reactive $\pi-\pi^*$ state. Adding a β -phenyl ring to give *p*-methoxy- β -phenylpropiophenone (VI) again shortens the lifetime of the triplet (Figure 5) although it is enhanced with respect to the β -phenylpropiophenone (IV) with no methoxy substituent (16). This is true because the mechanism of quenching of the β -phenyl ring probably prefers an $n-\pi^*$ state (15).

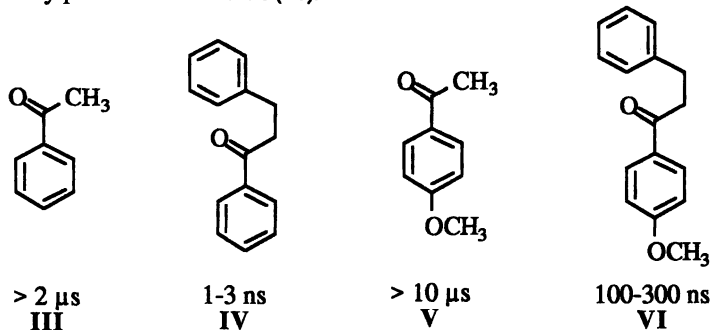


Figure 5: Effect of β -phenyl rings and methoxy substituents on triplet lifetimes.

The presence of an Oxygen Atom in the β Position.

The molecular conformation involved in β -phenyl quenching in β -phenylpropiophenones requires eclipsing the methylene hydrogens on the alpha and beta carbons which is energetically unfavorable (see Figure 6). When the β carbon is

replaced with an oxygen atom, these methylene hydrogens are no longer present and the quenching conformation lies at lower energy. The consequence of this is that the α -phenoxyacetophenones have shorter triplet lifetimes than their β -phenylpropiophenone analogs (18).

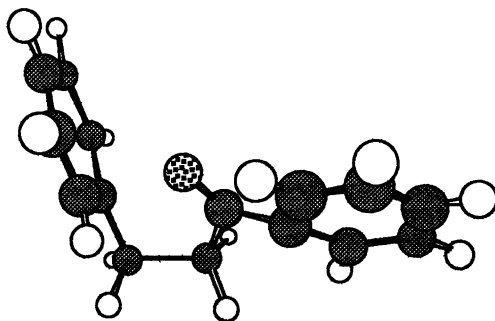


Figure 6: Molecular conformation leading to triplet deactivation via β -phenyl quenching.

The quantum yield of decomposition (Φ_r) for the β -phenylpropiophenone (IV) is essentially zero, but α -phenoxyacetophenone (VII) shows $\Phi_r \sim 0.01$ (18). This quantum yield is not large, but in terms of the decomposition, it is an important reaction. The molecule goes through β -cleavage to produce the phenoxy radical (18) in good *chemical* yields, as shown in Figure 7.

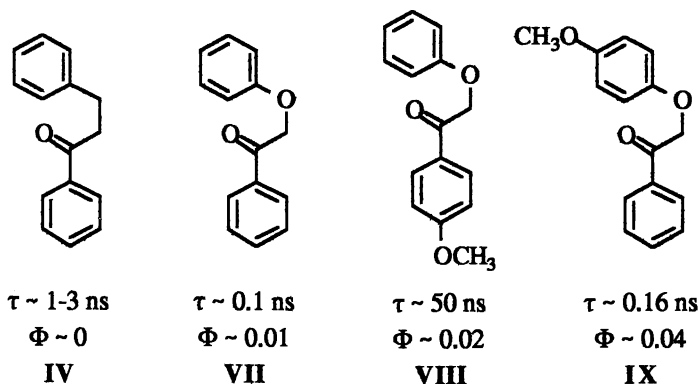


Figure 7: Effect of oxygen atom in β position and methoxy substituents on triplet lifetimes and degradation quantum yields.

As in the case above, adding a methoxy group increases the triplet lifetime since the molecule goes from an $n\text{-}\pi^*$ state to a $\pi\text{-}\pi^*$ state. Φ_r also increases slightly

which perhaps suggests that the inhibiting effect of π, π^* states on the fragmentation reaction is less severe than on intramolecular quenching. Phenoxy radicals are stabilized by methoxy substitution (19). Comparing (VII) and (IX) in Figure 7 shows that the triplet lifetime is not greatly affected, but Φ_T quadruples. In this case, we now produce a more stabilized phenoxy radical. Therefore it can be observed that the presence of an oxygen atom in the β position induces fragmentation.

The triplet-triplet absorption spectra for the molecules shown above are very similar to that recorded for acetoveratrone and related lignin models, in spite of the fact that there are significant differences (almost 10 kcal/mol) in the triplet energies.

Laser Power Effects.

There have been reports in the literature that the lignin model, α -guaiacoxyacetoveratrone, shows wavelength dependent photochemistry (5). However, we have found that these observations arise from the fact that as one changes laser wavelength, one normally changes other experimental parameters. For example, the laser power, laser pulse duration, and substrate concentration are normally changed. Changes in concentration are required to maintain a reasonable absorption at the excitation wavelength. While we reproduced without difficulty the reported wavelength effects, we find that when ground state concentrations and laser energy are kept constant in the different experiments, the rate of decay of the signal due to the transient is independent of the laser wavelength. Using 100% of our laser power at 308 nm (~ 30 mJ/pulse) appears to induce multiphoton chemistry, as we observe some as yet unidentified transients which are very long lived and very easy to misinterpret as triplets of the model compound. This is not believed to be relevant to the lignin modeling system, since it is unlikely that we are dealing with multiphoton processes in the photoreversion of paper. All the transient results reported in this paper are from experiments carried out under flow conditions and in which the laser power and substrate concentration were carefully controlled.

Triplet Quenching Studies.

The triplet state of α -guaiacoxyacetoveratrone is quenched by sorbic acid with a second order rate constant of $2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Sorbic acid is a conjugated diene and is an excellent quencher of the triplet state through energy transfer. It is a very versatile quencher since it has good solubility in a wide range of solvents including alcohols and water. The quenching rate constant quoted above is a bit slower than most triplet-diene quenching constants; this may reflect the fact that the donor triplet has an unusually low triplet energy for a carbonyl compound.

In the absence of quencher, the guaiacoxy group reduces the lifetime of the triplet state from $> 15 \mu\text{s}$ in acetoveratrone to $\sim 500 \text{ ns}$ in the case of α -guaiacoxyacetoveratrone; thus, at least 97% of the triplets must decay by processes (deactivation or cleavage) that involve the guaiacoxy group.

In the presence of 0.016 M sorbic acid, and given the rates of quenching and lifetimes measured, this concentration of diene will quench 96% of the triplets. This implies that the decay of the triplet occurs almost exclusively through energy transfer. (See Figure 8) The surprising result is that in the presence of this large concentration of sorbic acid, the transient absorption spectrum of the guaiacoxyl radical with its characteristic band in the red part of the spectrum is observed. This demonstrates that the guaiacoxyl radical must be produced from the singlet state, since virtually all the triplets have been quenched by the diene.

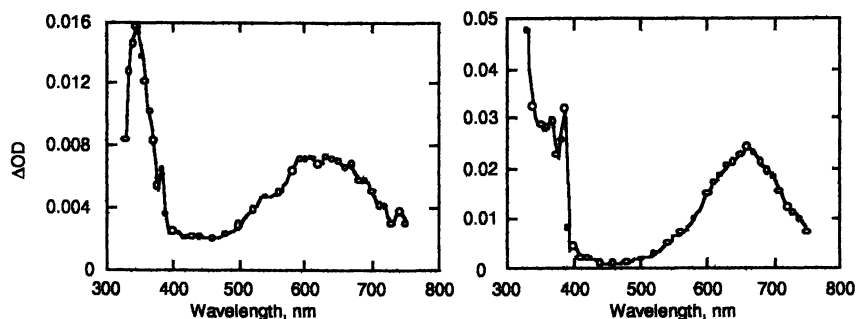


Figure 8: Transient absorption spectra; left: α -guaiacoxylacetoveratrone in ethanol in the presence of 0.016M sorbic acid 0.2 μ s after 337 nm excitation; right: reaction of *tert*-butoxy radicals generated by 308 nm excitation, with guaiacol in acetonitrile leading to guaiacoxyl radical; recorded 450 ns after laser excitation.

In the presence of moderate amounts of sorbic acid (e.g., 0.0015 M), the triplet lifetime of I is shortened by can be readily time-resolved. Under these conditions we find that the characteristic guaiacoxyl radical long-wavelength band is mostly present immediately following the laser pulse as opposed to growing in as the triplet decays.

In order to confirm the identity of the guaiacoxyl radical, we also generated this species by reaction of *tert*-butoxy radicals with the phenol, as indicated above (see Figure 4). These experiments also yield a band in the 600 nm region (Figure 8), therefore supporting the formation of guaiacoxyl radicals in a singlet process from I. Small differences between the two spectra of Figure 8 are presumably due to the presence of other carbon centered radicals produced in the cleavage of α -guaiacoxylacetoveratrone and to differences in the solvent employed.

Intersystem Crossing Quantum Yields.

Carbonyl compounds usually have intersystem crossing quantum yields, Φ_{isc} , of very close to unity. In the case of α -guaiacoxylacetoveratrone, we have shown that some of the chemistry is coming from the singlet state, which necessarily implies that the intersystem crossing quantum yield is no longer 1.

Photoacoustic spectroscopy was used to determine intersystem crossing quantum yields, Φ_{isc} , by a method previously described elsewhere (20). These values of Φ_{isc} show a solvent dependence and are 0.4 in ethanol and 0.6 in dioxane. This is consistent with singlet involvement in the chemistry of α -guaiacoxyacetoveratrone.

Experiments in Solid and Microheterogeneous Systems

Practical applications of the knowledge acquired with model compounds such as α -guaiacoxyacetoveratrone require the understanding of their photochemistry in microheterogeneous environments and in particular solid systems, in which the mobility of the substrates is limited. To this end we have started performing experiments exploring the photochemistry of α -guaiacoxyacetoveratrone incorporated in micelles, in zeolites, as well as in the pure crystalline material. In both, sodium dodecyl sulfate micelles and in the zeolite Na-X the triplet state of this model compound is very long lived (several microseconds). While a decrease in the efficiency of β -aryl quenching may reflect the reduced mobility, it is not clear why the fragmentation reaction does not take over as a dominant triplet decay path. In polycrystalline samples of α -guaiacoxyacetoveratrone all our attempts to detect the triplet state using time resolved diffuse reflectance techniques (21) were unsuccessful. In contrast, for the methoxy derivatives in Figure 5 detection of the triplet state under the same conditions was straightforward. The reasons for these differences are unclear at the present time.

While the results of the paragraph above raise many questions for which no answers are available, they serve to outline some of the challenges that lay ahead on the way to understanding, and hopefully solving, the problem of photoyellowing of pulp and paper products

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Chapter 9

Photodegradation of α -Guaiacoxyacetoveratrone Triplet-State Reactivity Induced by Protic Solvents

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α -Guaiacoxyacetoveratrone, an aromatic ketone and lignin model compound, reacts exclusively from the excited singlet state in aprotic solvents dioxane and acetonitrile, with quantum yields < 0.1 . Addition of a protic co-solvent (water, methanol or ethanol) at 5 mole percent and higher increases the quantum yield of photodegradation to > 0.2 , and increases the triplet lifetime. Most of the enhanced yield can be quenched in the presence of 0.1 M sorbic acid, a triplet quencher. This behaviour, highly unusual for aromatic ketones, can be qualitatively understood as a consequence of hydrogen bonding on the rate of β -phenyl quenching of the triplet state.

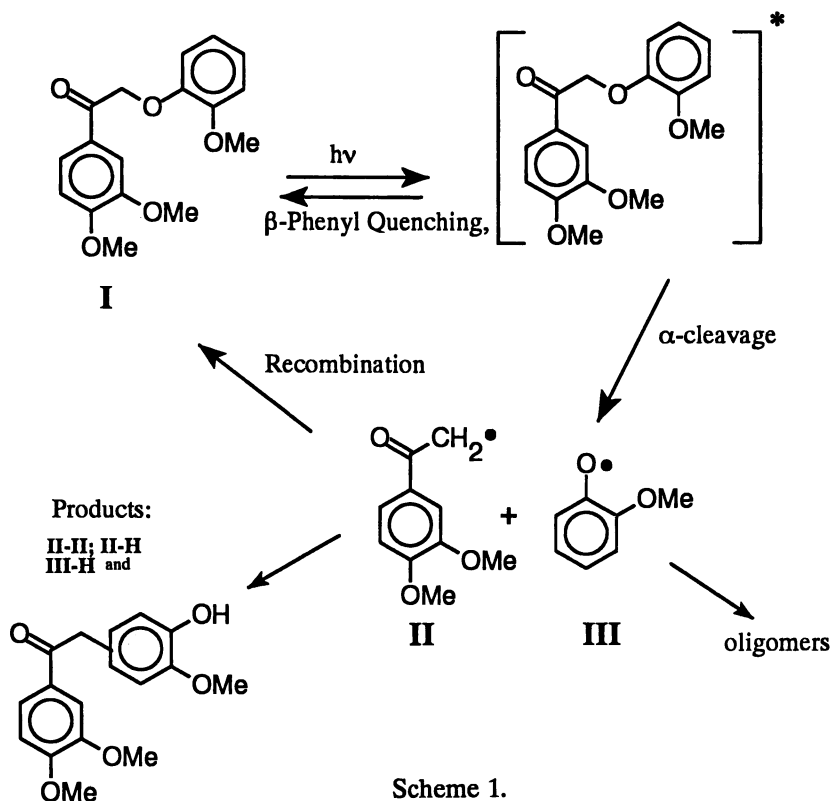
Mechanical and ultra-high yield pulps are used primarily for low-value, short-life grades of paper such as newsprint and advertising, catalog, and directory papers. Their use in more valuable paper products is severely restricted by the rapid yellowing which occurs upon exposure to daylight, a phenomenon which is attributed to the photooxidation of lignin.

α -Guaiacoxyacetoveratrone (**I**, SCHEME 1) is a model of one type of photolabile lignin structure: aryloxyacetophenones, which are C_9 units with a carbonyl group adjacent to the aromatic ring, and an O-aryl linkage at the α carbon (throughout this paper we will use the IUPAC nomenclature, which labels atoms as α , β , γ , etc. beginning with the carbon adjacent to the ketone function). In the excited state, the carbon O-aryl bond in **I** is labile, and can cleave to give phenacyl (**II**) and phenoxy (**III**) radicals. These radicals can recombine to form **I**, or to give low-molecular weight degradation products (1,2). In addition, the phenoxy radical can form an oligomeric material (1), which exhibits a strong and stable paramagnetism (Barclay, L.R.C., Mount Allison University, personal communication, 1991).

In an earlier paper (3), we reported that the quantum yield of photodegradation and the triplet state lifetime of **I** are both significantly higher in a protic solvent. As well, we presented evidence that significant reaction can occur from the first excited singlet state of **I**, a phenomenon previously unobserved for aromatic ketones. Here

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we present evidence that the presence of a protic solvent in the range of 5-40 mole percent induces reaction from the triplet state, which is unreactive in aprotic solvents.

Experimental

α -Bromoacetoveratrone was prepared using the procedure of Landucci *et al.* (4), and was then condensed with guaiacol in dry acetone in the presence of K_2CO_3 (5) to give α -guaiacoxyacetoveratrone (I).

The quantum yield of photodegradation, ϕ_d , is defined as follows:

$$\phi_d = \frac{\text{moles of I consumed}}{\text{moles of photons absorbed}}$$

The number of photons absorbed was determined using a commercially-available electronically integrating actinometer (QuantaCount, PTI, Deer Park N.J.), which was calibrated using azoxybenzene (6). Solutions of I (3.0 mL, 0.01 M) were irradiated with monochromatic light (325 nm) in a long-necked quartz cell, 1 x 1 cm². The cells

were sealed with rubber septa and deoxygenated with a stream of nitrogen for about 20 min. before irradiation. Disappearance of I was monitored by HPLC (Varian Vista 5500) using a Whatman Protesil 300 Octyl column, a mobile phase of 40% acetonitrile and 60% acetate buffer (10 mM, pH 4), and UV detection (275 nm). Before analysis, the solutions of I were diluted 1:25, and benzophenone (Aldrich Gold Label) was added as an internal standard. Triplet quenching experiments in aqueous solutions were done by preparing solutions of I containing 100 mM sorbic acid (*trans,trans*-2,4-hexadienoic acid). In non-aqueous solvents naphthalene and cyclohexadiene were also used as triplet quenchers.

Results

Singlet State Participation. Upon absorption of light energy, I is converted from its ground electronic state, S_0 , to its first excited state S_1 . From S_1 , I can cross to the triplet excited state, T_1 , a process known as intersystem crossing. It is well-known that in benzophenone and acetophenone the quantum yield of intersystem crossing, ϕ_{isc} is 1 (7) (*i.e.*, all reactions occur from T_1), and this is often assumed as true for aromatic ketones in general. However, as the results below indicate, this is not the case for I.

TABLE I: Quantum Yield of Photodegradation (ϕ_d) and Triplet Lifetime (τ) for α -Guaiacoxyacetoveratrone

<i>Solvent</i>	ϕ_d (<i>unquenched</i>)	ϕ_d (<i>quenched</i>)	τ (ns) (<i>Ref. 3</i>)
Dioxane	0.06	0.06	183
with 40% water	0.24	0.09	400
Acetonitrile	0.08	0.08	230
with 40% water	0.21	0.13	288
Ethanol	0.34	0.14	550

Table I shows that in either dioxane or acetonitrile the quantum yield for degradation of I, ϕ_d , is unaffected by the presence of 0.1 M of triplet quencher, either sorbic acid, naphthalene or cyclohexadiene. In ethanol, triplet quenchers reduce ϕ_d from 0.34 to 0.14. Quantum yields for intersystem crossing, ϕ_{isc} , as determined by a laser opto-acoustic technique (8), were 0.36 in ethanol and 0.59 in dioxane. These results agree with our earlier report (3), and indicate that significant reactivity occurs from S_1 of I in protic solvents, and that reaction occurs exclusively from S_1 in aprotic solvents. While triplet quenching experiments cannot rigorously exclude participation by short-lived higher triplet states, Palm *et al.* (9) have obtained conclusive evidence from CIDNP experiments for singlet-state participation in a series of aryloxyacetophenones. Note that the triplet state of I is formed in aprotic solvents, and that in deaerated solutions at room temperature it decays by first-order kinetics with a lifetime of ≈ 200 ns (3). Remarkably, despite having lifetimes about 100 times longer than other, differently-substituted, aryloxyacetophenones (the longer lifetimes may

result from the significantly lower triplet energy, ≈ 60 kcal/mol, compared to other aryloxyacetophenones, ≈ 70 kcal/mol) (10), triplet I is apparently unreactive in aprotic solvents.

Effect of Added Protic Solvent. In aqueous dioxane or acetonitrile (40% water by volume) ϕ_d was > 0.2 , compared with values < 0.1 in the pure aprotic solvent (Table I). Most of this additional yield was quenched in the presence of 0.1 M sorbic acid, which suggests that the additional degradation occurs from the triplet state. Thus, addition of a protic co-solvent has apparently caused the triplet state to become reactive.

As Figure 1 shows, in dioxane ϕ_d increased as the mole fraction of added protic solvent, either water, methanol or ethanol, was increased over the range 0.10 - 0.60. Trace amounts of a protic solvent had no effect on ϕ_d . Over the range of concentrations where ϕ_d is increasing with the amount of added protic solvent, water, methanol and ethanol have similar effects; however the maximum value of ϕ_d occurs for addition of ethanol. Photolysis of I in 40% D₂O/dioxane gave $\phi_d = 0.22$, which is indistinguishable from the value obtained in 40% water/dioxane.

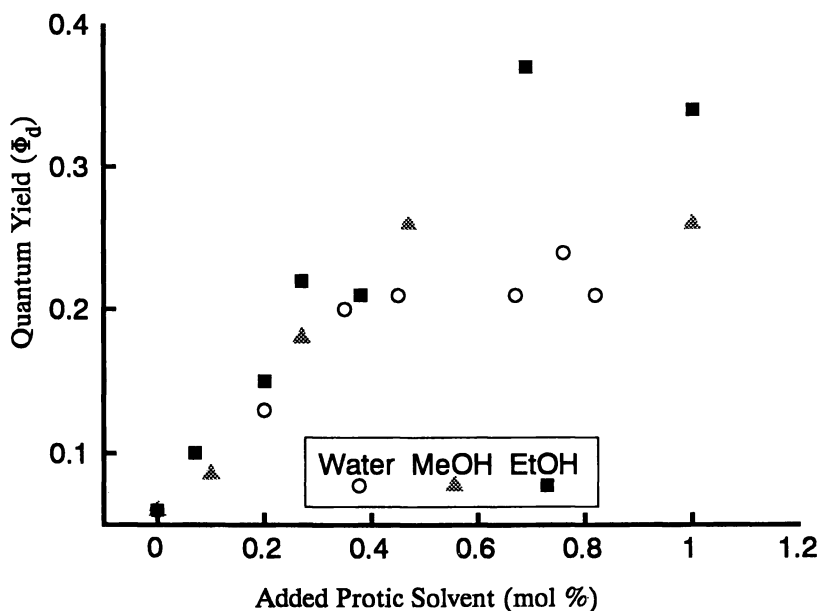


Figure 1: Quantum yield of photodegradation for I in dioxane, as a function of mole fraction of added protic solvent.

The experiments above indicate that the solvent dependence of ϕ_d arises primarily from the solvent dependence of the triplet state reactivity. The absence of a primary deuterium isotope effect makes it unlikely that protic co-solvents affect ϕ_d through a bond-breaking interaction (e.g., photochemical proton transfer). Also, since

ϕ_d shows similar behaviour in acetonitrile and dioxane, and since addition of either water, methanol or ethanol as protic co-solvent have similar effects, solvent polarity or viscosity effects are small.

Discussion

β -Phenyl Quenching. In **I**, as in other aryloxyacetophenones (**10**), the triplet decays predominately through two processes (SCHEME 1): cleavage of the α C-O bond, which generates phenacyl and phenoxy radicals, and β -phenyl quenching, where the ketone triplet is quenched by collision with the attached phenoxy group, after rotation about the α C-O bond has brought it to an appropriate conformation (Figure 2). Bond cleavage can lead to degradation of **I**, while β -phenyl quenching regenerates the ground state of **I**.

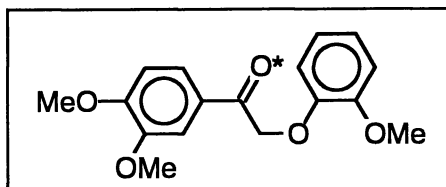


Figure 2: Conformation required for β -phenyl quenching in aryloxyacetophenones.

If the rate constants for β -phenyl quenching and bond cleavage are k_1 and k_2 , respectively, then equation 1 gives the triplet lifetime, τ , and equation 2 gives the maximum quantum yield for degradation from the triplet state, ϕ_{dT} . The actual quantum yield for triplet degradation is less than this, because **II** and **III** can recombine to give the starting material, **I**.

$$\tau = \frac{1}{k_1 + k_2} \quad (1)$$

$$\phi_{dT} = \frac{k_2}{k_1 + k_2} \quad (2)$$

Simultaneous Increase of τ and ϕ_d . The fact that no reaction occurs from the triplet state in either dioxane or acetonitrile implies that $k_2 \ll k_1$ in these aprotic solvents. Equation 1 then gives $\tau = 1/k_1$. The triplet lifetimes in acetonitrile and dioxane are close to 200 ns (3), which gives an estimate for k_1 of about $5 \times 10^6 \text{ s}^{-1}$. If addition of protic solvents simply increases k_2 sufficiently that bond cleavage can compete with β -phenyl quenching, then equation 1 predicts that the triplet lifetime should decrease. However, the opposite occurs for **I**: the conditions which induce reactivity from the triplet state cause an increase in τ (Table I). For example, in dioxane

$$\tau_{\text{protic}} \approx 2\tau_{\text{aprotic}}$$

so that

$$(k_1 + k_2)_{\text{protic}} \approx 1/2(k_1)_{\text{aprotic}}$$

Clearly k_1 , the rate of β -phenyl quenching, has decreased in the presence of the hydroxylic co-solvent. This suggests that the effect of the protic solvent is to decrease k_1 sufficiently that bond cleavage becomes competitive with β -phenyl quenching, allowing a significant fraction of triplets to decay by bond cleavage.

Role of Hydrogen Bonding. Qualitatively, these results can be understood as effects of hydrogen bonding on the triplet-state decay, as explained below. Hydrogen bonding is known to occur at carbonyl triplet states (12), and probably will also occur at the three methoxyl oxygens of I.

The added bulk of hydrogen-bonded groups about I may decrease k_1 by increasing the energy barrier to rotation about the α C-O bond which is necessary for β -phenyl quenching. This hypothesis would also account for another phenomenon which we reported in our earlier paper (3): in 40% aqueous alcoholic solutions of I both ϕ_d and the triplet lifetime decreased, relative to the values observed in the pure alcohol. In alcohol solvents, I reacts from both S_1 and T_1 . Substitution of smaller water molecules for alcohol molecules could reduce the barrier to rotation and increase k_1 , which would decrease the triplet lifetime, and decrease the fraction of triplets which decay by bond cleavage.

These qualitative arguments could be confirmed by explicit calculation of k_1 and k_2 . This has been achieved for other aryloxyacetophenones, by measuring product quantum yields in the presence of thiophenol (10). A good hydrogen donor, thiophenol quantitatively scavenges the phenoxyl and phenacyl radicals formed by bond cleavage, yielding the corresponding acetophenone and phenol. The quantum yield for formation of either acetophenone or phenol is equivalent to ϕ_{dT} and, together with the triplet lifetime τ , allows calculation of k_1 and k_2 . Unfortunately, this experiment was unsuccessful for I because acetoveratrone and guaiacol are formed not only from scavenging of radicals, but also as a result of thiophenol quenching of the long-lived triplet state (3).

Concluding Remarks

The results presented above show clearly that a protic environment is necessary for degradation to occur from the triplet state of I. According to our proposed mechanism, α C-O bond cleavage (and therefore degradation) becomes a viable reaction pathway from the triplet state of I because hydrogen bonding provides steric hindrance to β -phenyl quenching, a competing, non-product forming pathway. In mechanical pulp fibres, the energy barriers to β -phenyl quenching are enormous, because structures such as I are bonded to the rest of the solid lignin polymer. Thus, under the conditions encountered in paper, bond cleavage probably occurs with high efficiency, from both singlet and triplet excited states.

A recent electron paramagnetic resonance study (13) has shown that I also degrades by a photoreduction pathway in the presence of alcohols or water, through the intermediacy of the corresponding ketyl radical. Since corresponding ketyl radicals and triplet states often have overlapping absorption spectra, it is important to emphasize that the transient observed in our optical flash photolysis experiments is the triplet state (not the ketyl radical), the key evidence being that both the yield *and* the lifetime of the transient are decreased by triplet quenchers. An important question

for future research should be to determine the relative yields of photoreduction and α C-O cleavage to the photodegradation of I.

Quantitative assessment of the importance of hydrogen bonding, and the determination of other possible effects of the protic environment on the reaction mechanism, must await the development of an efficient radical scavenger which does not at the same time quench the triplet state.

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Chapter 10

Formation of Leucochromophores during High-Yield Pulping and H₂O₂ Bleaching

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Low molecular weight compounds derived from lignin were released by a mild hydrolysis technique from spruce wood and from unbleached and hydrogen peroxide bleached spruce groundwood (GW) and chemithermomechanical (CTMP) pulps. The major monomeric, dimeric and trimeric structures were isolated and characterized. Quantitative analysis indicated that coniferaldehyde structures, the major leucochromophores originally present in spruce wood lignin, were reduced in quantity during the CTMP process and further eliminated by hydrogen peroxide bleaching. Diarylpropane structures were converted into stilbenes, partly during grinding or disc refining, but mainly during the hydrogen peroxide bleaching process. The contribution of individual structures to photoyellowing was studied by impregnating them on filter paper and irradiating them with simulated sunlight. Of the compounds investigated, diguaiacyl stilbene was found to be the major contributor to color.

The photoyellowing of high yield pulps can generally be considered to be the result of light-induced oxidation of the pulp lignin by air (1). The UV-portion of sunlight in the wavelength range of 300-400 nm has been shown to cause the discoloration (1, 2). Hence, lignin structures capable of absorbing UV-light within this wavelength range are supposed to be responsible for sensitizing or initiating the photo-oxidation reactions.

Little work has been carried out so far to characterize the lignin structures present in various types of high yield pulps. Model compound experiments have shown, however, that α -carbonyl groups (3, 4), biphenyl structures (3, 5), aromatic ring conjugated double bonds (3, 5, 6), phenylcoumarones and stilbenes (5) and ferulic acid (7) can all be excited by sunlight, leading to the formation of color. These observations provide valuable clues to the types of structures which might be responsible for photo-yellowing. It is, however, difficult to draw any firm conclusions about the relative contributions to yellowing of different structural elements based only on the results of model compound experiments, since the natural abundances of these structures in high yield pulps are usually not known.

In the present work, the behaviour of reactive structures present in spruce lignin during high yield pulping and hydrogen peroxide bleaching processes has been studied. Mild hydrolysis was used to release low molecular weight lignin structures bearing intact side chains from spruce wood and also from unbleached and bleached

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CTMP and GW. HPLC techniques combined with GC-MS and 2D-NMR enabled the major monomeric, dimeric and trimeric products to be isolated and unambiguously characterized. Subsequently, these lignols were impregnated onto filter paper sheets and irradiated by simulated sunlight to evaluate their contribution to photoyellowing. Leucochromophores present in native spruce wood lignin as well as those formed in the residual pulp lignin after refining and hydrogen peroxide bleaching are discussed.

Experimental

Materials. Fine shavings of Norwegian spruce wood and samples of commercial unbleached and hydrogen peroxide bleached GW (brightness values: 59 and 78% ISO respectively) and CTMP (brightness values: 59 and 72% ISO respectively) made from Norwegian spruce were extracted with acetone for 48 hours and air dried. A sample of diguaiacyl stilbene was a gift from N-O. Nilvebrant (8). All solvents used in the work-up procedure and in the HPLC separations were distilled before use.

For the hydrolysis, an aqueous buffer solution consisting of sodium acetate (4 grams) dissolved in 2 liter deionized water was used. The solution was adjusted to a pH-value of 4.0 by the addition of 1 M sulfuric acid. This buffer solution was kept in a brown glass bottle and used throughout this work.

Hydrolysis on an analytical scale and work-up procedure. The wood or pulp sample (2.000g), suspended in 100 ml of buffer solution, was refluxed for 19 hours. After being cooled to room temperature, the mixture was filtered through a Buchner funnel. Ethyl acetate (3 × 100ml) was used to wash the solid residue and to extract the aqueous phase. The combined organic extract was dried over anhydrous sodium sulfate and concentrated to a volume of about 1ml. The concentrated solution was added to 200 mg of silica gel (silica gel 60, 70 - 230 mesh, Merck) placed in a pipette with a glass wool stopper and all compounds were eluted by the addition of ethyl acetate (5ml). The eluate was concentrated and adjusted to a volume of 1.00 ml in a volumetric flask and immediately analysed by HPLC.

Analytical HPLC set-up for separation and quantification

Column: 250mm × 4.6mm
Packing: Nucleosil 50-5, 5 μ
Mobile phase: A: Petroleum ether (60 - 70 °C). B: Ethyl acetate
Gradient: Linear; 10% to 100% during 50 min and 15 min at 100%
Flow rate: 1.5 ml/min
Detector: Dual channel UV; 280 nm and 350 nm
Sample volume: 25 μ l

The relative peak heights of coniferaldehyde and diguaiacyl stilbene (eluting as one peak) were determined by collecting the corresponding eluate and carrying out further analysis by reversed phase HPLC in the following way:

Column: 150mm × 4.6mm
Packing: Nucleosil C18, 5 μ
Mobile phase: A: 0.2% acetic acid in water. B: 0.2% acetic acid in acetonitrile
Gradient: Linear; 30% to 100% during 30 min.
Flow rate: 1.0 ml/min
Detector: UV 350 nm
Sample volume: 25 μ l

GC-MS analysis. After the HPLC separation, all peaks were collected and acetylated in the usual way (9) before GC-MS analysis. Conditions were;

Column: 30 m × 0.32 mm ID

Coating: DB-1, 0.1 μm
Injector temp: 280 $^{\circ}\text{C}$
Column temp: 100 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$
Ion energy: 70 eV

MS spectra of the acetylated trimeric lignols were obtained by direct inlet technique.

Hydrolysis on a preparative scale and separation. A sample of spruce wood or pulp (300g), suspended in 6 litres of buffer solution, was refluxed for 19 hours. The resulting aqueous phase was filtered and concentrated to about 200 ml by evaporation at 40 $^{\circ}\text{C}$ under reduced pressure. The concentrated aqueous phase was extracted with ethyl acetate (3 \times 200 ml). Subsequently, the organic extract was dried over sodium sulfate, evaporated to a volume of 50 ml and transferred to a silica gel column (100 mm \times 30 mm, silica gel 60; 70 - 230 mesh). Monomeric and dimeric lignols were eluted from the column with ethyl acetate (200ml) whereas trimeric lignols were subsequently recovered using ethyl acetate containing 5% methanol (200 ml). The mixture of monomeric and dimeric lignols was further separated by HPLC using a semi-preparative column, Polygosil 60-5 (250mm \times 10mm), with petroleum ether/ethyl acetate as solvent (linear gradient from 20% to 100% ethyl acetate during 90 min with a flow-rate of 4 ml/min). Each fraction was acetylated and again separated using the same HPLC system but with a solvent gradient from 10% to 50% ethyl acetate.

The fraction containing trimeric lignols was acetylated and subsequently separated on the semi-preparative HPLC system with a solvent gradient from 50% to 60% ethyl acetate.

NMR analysis. ^1H NMR spectra were collected on a Bruker AC 250 instrument with CDCl_3 as solvent. For structural assignment of dimeric and trimeric lignols, ^{13}C , DEPT, H-H COSY, TOCSY, short range C-H chemical shift correlation and long range C-H chemical shift correlation experiments were performed on Bruker AMX 360 and AM400 instruments using acetone- d_6 as solvent. C-H chemical shift correlation experiments were carried out with inverse detection. Standard pulse sequence programs provided with the instruments were used for all 2-D experiments.

Results and Discussion

Isolation and characterization of lignin structures

Hydrolysis and separation. Mild hydrolysis has previously been used for the structural analysis of both softwood and hardwood lignins (10 - 14). About 20% of the lignin was liberated from spruce wood and 40% of the lignin from beech wood by percolation of finely ground wood meal with water at 100 $^{\circ}\text{C}$ for several weeks (12). Such a mild hydrolytic treatment can be expected to lead to the rupture of only very reactive linkages such as certain α -aryl ether bonds, acetal and hemiacetal linkages. On the other hand, lignin structures bearing intact side chains can be liberated.

In the present work, it was found that buffering the aqueous solution at a pH value of about 4 can accelerate the release of lignols without the danger of changing the structure of the various side chains. In comparison to previous work, a much shorter treatment time (19 hours) was here employed, resulting in the recovery of only about 2% of the total amount of lignin present in the sample. The structures of the major products identified are shown in Figure 1.

The HPLC chromatogram containing monomeric and dimeric lignols from spruce wood can be seen in Figure 2. Dual channel UV-detection was used during the HPLC analysis with one channel set at 280 nm to detect all lignin-related products and the other channel at 350 nm to monitor the presence of leucochromophores. Most

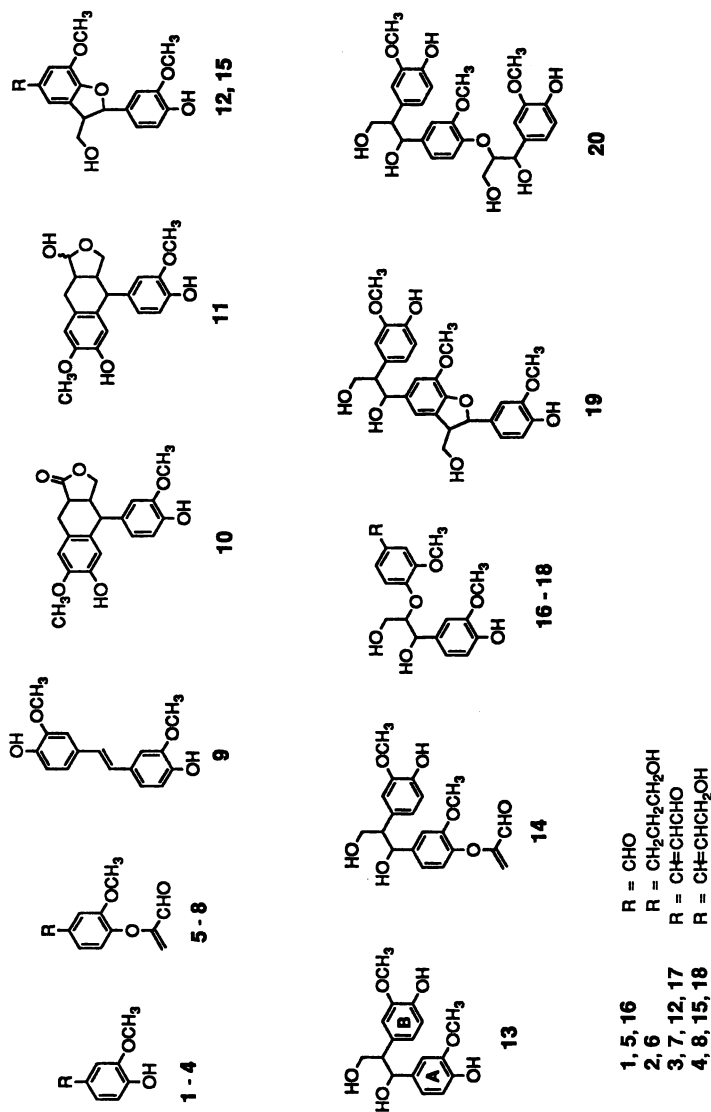


Figure 1. Major low molecular weight lignin products isolated and identified after mild acid hydrolysis of spruce wood and various high yield pulps.

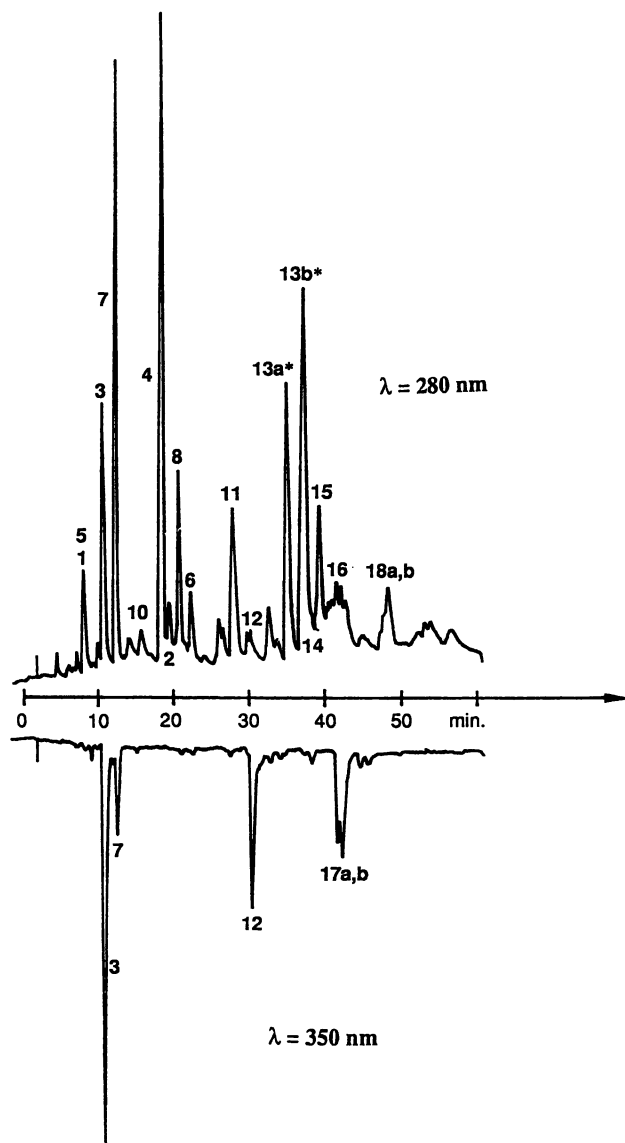


Figure 2. HPLC analysis of low molecular weight lignin products after acid hydrolysis of spruce wood (detector responses at 280 nm, positive curve, and at 350 nm, negative curve). (Two diastereoisomers of compound 13 are present as separate peaks.)

of the major lignin-related low molecular weight products were well resolved and quantified according to their peak heights. It was found, however, that if the ethyl acetate extracts were left to stand for a long time (days) at room temperature or even in the refrigerator, changes occurred in the samples. All extracts were therefore analysed immediately after preparation. The HPLC column used for quantification analysis was reserved solely for these measurements during the whole time-frame of this work, since it was found that contamination of the column by other compounds could change the shape of the peaks. When these precautions were taken, good reproducibility (within 5%) was achieved in the HPLC quantification in this work.

Coniferaldehyde and diguaiacyl stilbene were not resolved during normal phase HPLC separation. The relative peak heights of these two components had to be determined by a second chromatographic separation using reverse phase HPLC. The retention times of coniferaldehyde and diguaiacyl stilbene on a C-18 column were 6.4 min and 14.6 min respectively.

GC-MS and NMR analyses. A large number of lignin-related low molecular weight compounds were present in the ethyl acetate extracts. When such a mixture was acetylated and directly analysed by GC-MS, signal overlapping in the gas chromatogram was a serious problem, resulting in mixed spectra in the MS analysis. However, if the product mixture was first separated with HPLC and each fraction subsequently acetylated, pure mass spectra could be obtained for all the major products present in the various fractions. Mass spectra of the acetylated trimeric lignols were obtained using the direct inlet technique.

In addition to ^1H -NMR and ^{13}C -NMR spectra, modern 2-D NMR techniques were employed to assign structures to the isolated dimeric and trimeric lignols. The characterization of compound **20** by a combination of NMR techniques is here shown as an example. All of the 8 possible isomers were found to be present in compound **20**. These isomers were separated into two groups by HPLC. NMR analysis of one of the fractions containing threo- β -O-4-threo/erythro- β -1 structures (4 isomers) is illustrated here.

The partial long range C-H chemical shift correlation spectrum presented in figure 3 shows signals from the aliphatic side chains of the trimeric compound. This 2-D NMR experiment provides information about the H-C connection 2 to 3 bonds away from the carbon (coupling constants less than 20 Hz). For example, H_α shows correlations with C_β (6.07/80.4, $\alpha\beta$ in Figure 3) and C_γ (6.07/63.4, $\alpha\gamma$ in Figure 3). The H_γ signals, distinguished from those of H_γ by their correlation with C_β (4.00/80.4 and 4.21/80.4, $\gamma\beta$ in Figure 3), indicate the presence of only the threo- β -O-4 structure in this sample (signals from H_γ of the erythro- β -O-4 isomer usually appear at a lower field with δ values of about 4.2 ppm and 4.4 ppm) (18, 19). The presence of both threo- and erythro- β -1 structures in this sample is demonstrated by the correlations of threo- C_β with threo- H_α (6.00/50.4, $\alpha'_t\beta'_t$ in Figure 3) and with threo- H_γ (4.35/50.4 and 4.52/50.4, $\gamma'_t\beta'_t$ in Figure 3) as well as by the correlations of erythro- C_β with erythro- H_α (6.12/50.7, $\alpha'_e\beta'_e$ in Figure 3) and with erythro H_γ (4.17/50.7 and 4.31/50.7, $\gamma'_e\beta'_e$ in Figure 3). These results are in agreement with authentic ^1H NMR chemical shift data on pure threo- and erythro- β -1 structures (20, 21). All the other cross peaks in the spectrum are marked and explained in line with the proposed structure.

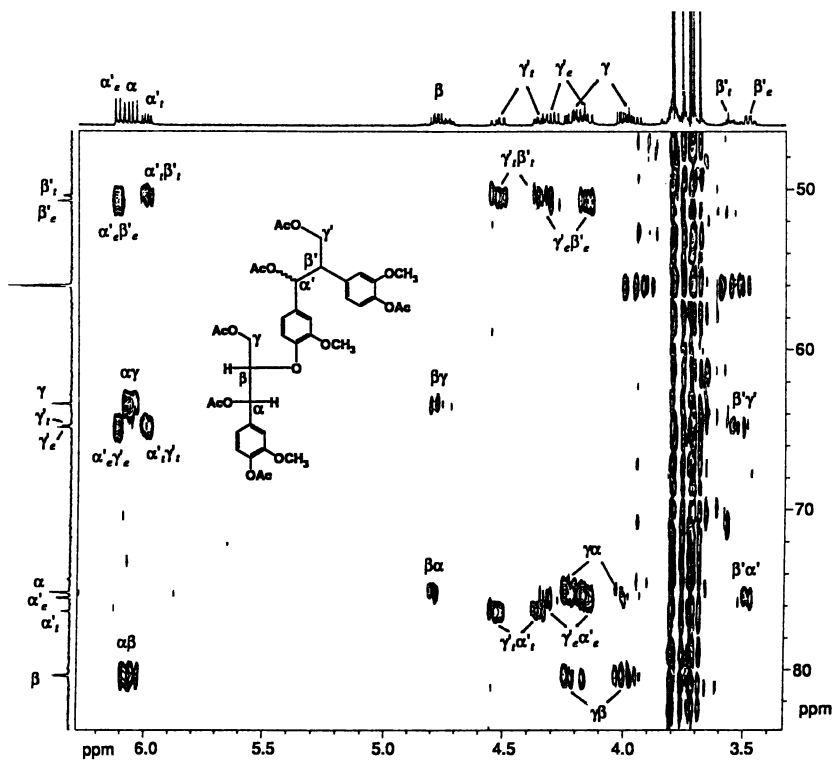


Figure 3. Partial long range C-H chemical shift correlation NMR spectrum of compound 20.

Information about direct C-H couplings (coupling constants between 120 Hz and 170 Hz) can be seen in the spectrum of the short range C-H chemical shift correlation experiment (Figure 4). For instance, H_{β} is seen to be correlated with C_{β} (4.76/80.4, β in Figure 4). All the other cross peaks can also be accurately explained by the proposed structure.

Information about H-H connections within 3 bonds was provided by H-H COSY experiments. TOCSY spectra showed consecutive H-H correlations within the same carbon chain, which proved to be a very powerful tool for structural analysis when several isomers of one compound were present in the same sample. The detailed results of these NMR experiments will be published in a forthcoming paper.

MS and 1-D NMR data for all the identified compounds have been published previously (9, 15 - 17).

Characterization of lignin end groups. The compounds isolated (Figure 1), which are assumed to constitute lignin end groups, include coniferyl alcohol structures (4, 8, 15 and 18), coniferaldehyde structures (3, 7, 12 and 17), detached pyruvaldehyde enol ether side chains (5 - 8, 14), diarylpropane structures (13, 14, 19 and 20), β -aryl ether structures (16 - 18, 20) and phenylcoumaran structures (12, 15 and 19).

Biphenyl structures and α -carbonyl- β -aryl ether structures, which are both assumed to be present in native lignin with a higher abundance than coniferyl alcohol structures (22, 23) and both considered to be important leucochromophores, were not observed among the products, presumably because they are not present in spruce lignin as end groups. Both these types of structures are very stable and unlikely to be structurally changed during mild acid hydrolysis (24).

Coniferaldehyde structures were found to be the only major type of lignin structure present in wood which have a strong UV-absorption around 350 nm (Figure 2). Diguaiacyl stilbene (9) also exhibits a strong UV-absorbance around 350 nm, but this structure cannot be considered to be a main leucochromophore in native wood because of its low abundance (Figure 5). Coniferyl alcohol structures as well as detached pyruvaldehyde enol ether structures and structures derived from vanillin (1, 5 and 16) can absorb UV-light at wavelengths around 315 nm and these structures can therefore also act as sensitizers in photoyellowing reactions (lower wavelength limit around 300 nm).

Structures with saturated side chains such as diarylpropane structures (13), phenylcoumaran structures (19) and β -aryl ether structures (20) do not absorb UV-light above 300 nm and they can thus be considered stable towards sunlight. During high yield pulping and bleaching, a conversion to photosensitive structures may, however, take place. It has been shown by model experiments that phenylcoumarones and stilbenes can be formed from phenylcoumarans during disc refining (25). Stilbenes can also be formed from diarylpropanes during refining (26) and during bleaching with hydrogen peroxide (27). Such lignin structures may absorb daylight and thus serve as substrates for photochemically initiated reactions.

Presence of different structures

Coniferyl alcohol and coniferaldehyde structures. It has been estimated that spruce lignin contains about 6% of coniferyl alcohol units as end groups (28). In previous work, the behaviour of coniferyl alcohol structures during a mild sulfite treatment simulating the chemical pretreatment in a CTMP process was studied (15). It was found that coniferyl alcohol is liberated from spruce wood more rapidly under acidic than under neutral or alkaline conditions. The treatment time needed for complete liberation of coniferyl alcohol structures from wood lignin was, however, found to be more than 100 minutes irrespective of treatment conditions. Considering the short treatment time (5-15 min.) employed in the commercial process, it can

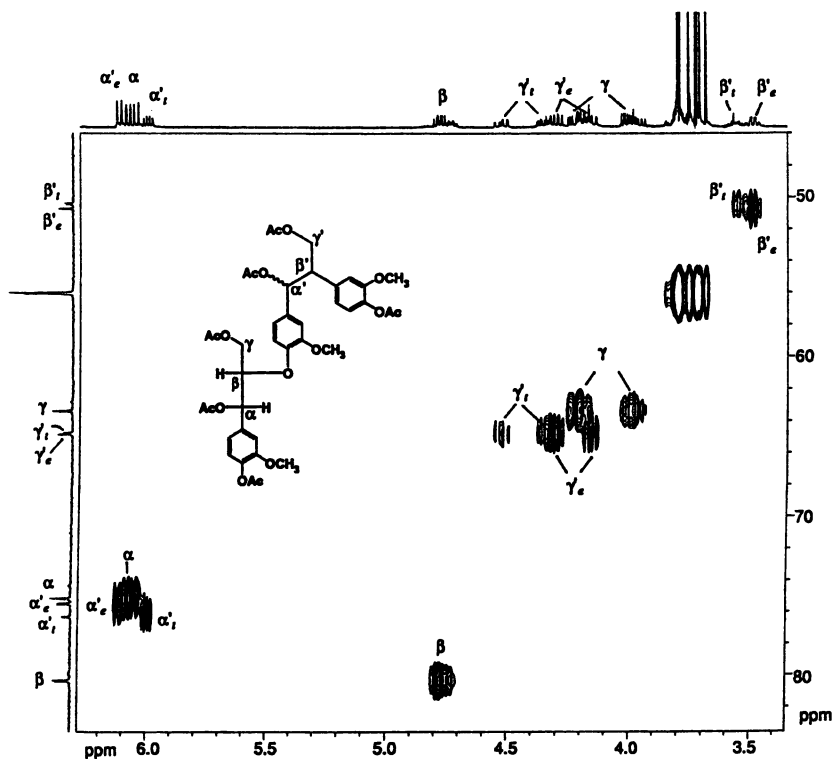


Figure 4. Partial short range C-H chemical shift correlation NMR spectrum of compound 20.

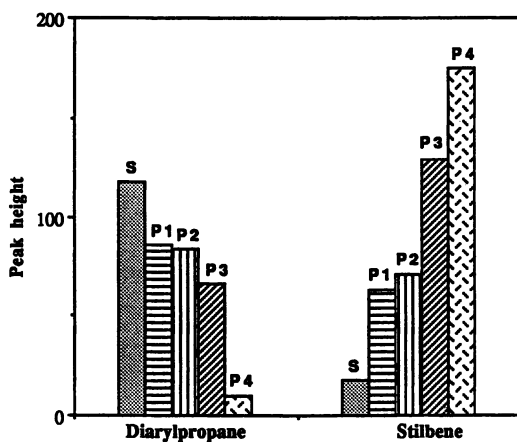


Figure 5. Relative yields (peak heights) of diarylpropane and stilbene structures from spruce wood (S), unbleached GW (P1), unbleached CTMP (P2), hydrogen peroxide bleached GW (P3) and hydrogen peroxide bleached CTMP (P4) after acid hydrolysis.

therefore be assumed that the chemical pretreatment of wood chips with neutral sulfite during CTMP production leads to a dissolution of only a very small portion of the total amount of coniferyl alcohol end groups.

In the present work it was found that coniferyl alcohol end groups are rather stable during high yield pulping and bleaching processes (Figure 6). The GW and CTMP pulping processes may possibly result in a slightly reduced content of such end groups but hydrogen peroxide bleaching seems not to lead to any further reduction. The content of coniferyl alcohol structures from unbleached CTMP should be expected to be at least as high as that from bleached CTMP. The small difference observed may be due e.g. to the liberation of new end groups in lignin accessible to acidic hydrolysis as a result of the treatment with alkaline hydrogen peroxide.

The content of coniferaldehyde end groups in native spruce lignin has been estimated to be 3% (28). In agreement with this, it was found that the hydrolysis extract from spruce wood (Figure 2) contains a considerable amount of coniferaldehyde and its derived structures. This type of structure remains as a major component in unbleached GW (Figure 6) and may therefore play an important role in the photoyellowing of paper products like newsprint containing unbleached mechanical pulp. A mild sulfite treatment, like that in the CTMP process, can lead to a reduction in the coniferaldehyde content in the pulp (29). A further reduction in the content of coniferaldehyde structures can be achieved by hydrogen peroxide bleaching, as seen in Figure 6. Unlike the results of model experiments with coniferaldehyde in which a rapid and complete oxidation with hydrogen peroxide has been observed (30), the results obtained here demonstrate, however, that peroxide bleaching of high yield pulps does not lead to a complete removal of (coloured) coniferaldehyde structures. This implies that current high-yield pulp bleaching technology is not fully optimized.

Diarylpropane and diguaiacyl stilbene structures. Diarylpropane (β -1) structures are among the major lignin building units and this type of linkage amounts to around 7% of the inter-connecting phenylpropane linkages in spruce lignin (31). After hydrolysis of spruce wood, the yield of diarylpropane structures was found to be very high (Figure 2). Analysis with ^1H NMR showed that this type of structure accounted for about 40% of the total amount of lignin hydrolysis products. In contrast, biphenyl (5-5) structures were not detected at all in the hydrolysis mixture and phenylcoumaran (β -5) structures were produced in a very low yield although the latter two types of structures are known to be more abundant than the β -1 structures in spruce lignin (31). This indicates that diarylpropane structures may constitute a preferred type of end group in the native polymer.

In previous work (9) it was shown that the diarylpropane structures are linked to the rest of the lignin macromolecule mainly through the ring B phenolic oxygen (Figure 1) and that this linkage is stable towards mild alkali but sensitive to acid. Hydrolysis of pre-methylated spruce wood shavings showed that most of the diarylpropane end groups bear a free phenolic hydroxyl on ring A (9). In addition, mild acidic sulfite treatment of spruce wood, in contrast to mild neutral or alkaline treatment, was found to liberate a part of the diarylpropane structures from lignin (9).

The natural content of stilbenes is considered to be very low in spruce wood lignin and this was confirmed in the present work (Figure 5). Analysis of the aqueous extracts after mild acidic hydrolysis revealed, however, that from wood to unbleached pulps and further to bleached pulps a stepwise conversion of diarylpropane to diguaiacyl stilbene structures takes place (Figure 5). The content of diarylpropane structures was found to be 25% less in the unbleached pulp samples than in the wood with a simultaneous increase in the content of stilbene structures. After hydrogen peroxide bleaching, the content of diarylpropane structures further decreased and the

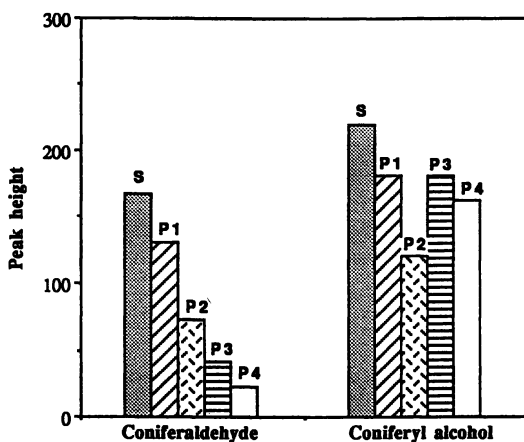


Figure 6. Relative yields of coniferaldehyde and coniferyl alcohol structures from spruce wood (S), unbleached GW (P1), unbleached CTMP (P2), hydrogen peroxide bleached GW (P3) and hydrogen peroxide bleached CTMP (P4) after acid hydrolysis.

stilbene content significantly increased, especially in the bleached CTMP in which most of the diarylpropane structures had been converted into the stilbene.

The conversion of diarylpropane structures into stilbenes during refining as well as during bleaching has previously been observed in model compound studies. In a recent report (26), diarylpropane model compounds were impregnated onto coarse mechanical pulp which was subsequently further refined in a laboratory refiner. Stilbenes were found to be produced in yields ranging from 11 to 19%. The conversion was believed to proceed via a radical reaction mechanism. A stilbene was also formed when a diarylpropane model compound was treated with alkaline hydrogen peroxide at 30°C and at a pH above 12 (27).

Diguaiacyl stilbene shows a strong absorption of UV-radiation at about 350 nm. A comparison of Figure 2 and Figure 7 shows that the absorption of UV-radiation at 350 nm in the hydrolysis extract from spruce wood is attributed mainly to coniferaldehyde structures whereas, after pulping and bleaching, diguaiacyl stilbene constitutes the predominant species absorbing radiation at this wavelength.

Detached side chain structures. It was previously found (15) that detached side chain structures (5-8, 14, Figure 1) can be liberated from spruce wood by mild acidic but not by mild alkaline hydrolysis. All detached side-chain structures were isolated as derivatives of pyruvaldehyde enol ethers in a total amount of approximately 6% (based on ¹H NMR) of the total product mixture from spruce wood.

According to current views on the biosynthesis of lignin, a side-chain displacement reaction in a phenylpropane unit will lead to the formation of a detached glyceraldehyde side-chain structure together with a diarylpropane structure in the lignin polymer (32). It has been shown before (33, 34) that glyceraldehyde structures are unstable and tend to form cyclic dimers of the 1,3-dioxane type at room temperature. That glyceraldehyde structures in lignin condense with each other must, however, be considered unlikely due to the restrictions in mobility in the solid matrix. On the other hand, condensation reactions between glyceraldehyde and carbonyl structures (from lignin or a polysaccharide) to form acetals cannot be ruled out. The presence of such structures in the native lignin could explain the observations made in the present work that linkages between structures containing detached side chains and the rest of the lignin polymer are stable under mild alkaline conditions but sensitive to an acidic treatment (15).

The isolation of pyruvaldehyde enol ethers rather than glyceraldehyde structures during mild acidic hydrolysis may indicate that the latter structures are not stable in their free form but tend to lose water to produce pyruvaldehyde enol ether structures. Such structures may therefore be formed in lignin during technical processes carried out under mild acidic conditions such as the production of TMP. Pyruvaldehyde enol ether structures absorb UV-light above 300 nm and may thus contribute to the photoyellowing process. Under conditions simulating the production of CTMP, on the other hand, it was previously shown that these types of structures are rapidly and completely eliminated presumably by sulfonation reactions (15).

Other lignin structures. Although recent model experiments (25) suggest that phenylcoumaran structures can be converted into phenylcoumarone and stilbene structures during disc refining, the latter types of structures have not been observed in the present work. Phenylcoumaran structures were found to be quite resistant towards all kinds of high yield pulping and bleaching treatments, illustrated by the fact that compound 14 was produced in a similar yield from spruce wood and from unbleached and bleached GW and CTMP during mild acid hydrolysis.

Vanillin structures can be considered to be minor lignin end groups and compounds containing vanillin moieties were isolated from all wood and pulp samples. The yields were, however, much lower than those of either coniferyl alcohol

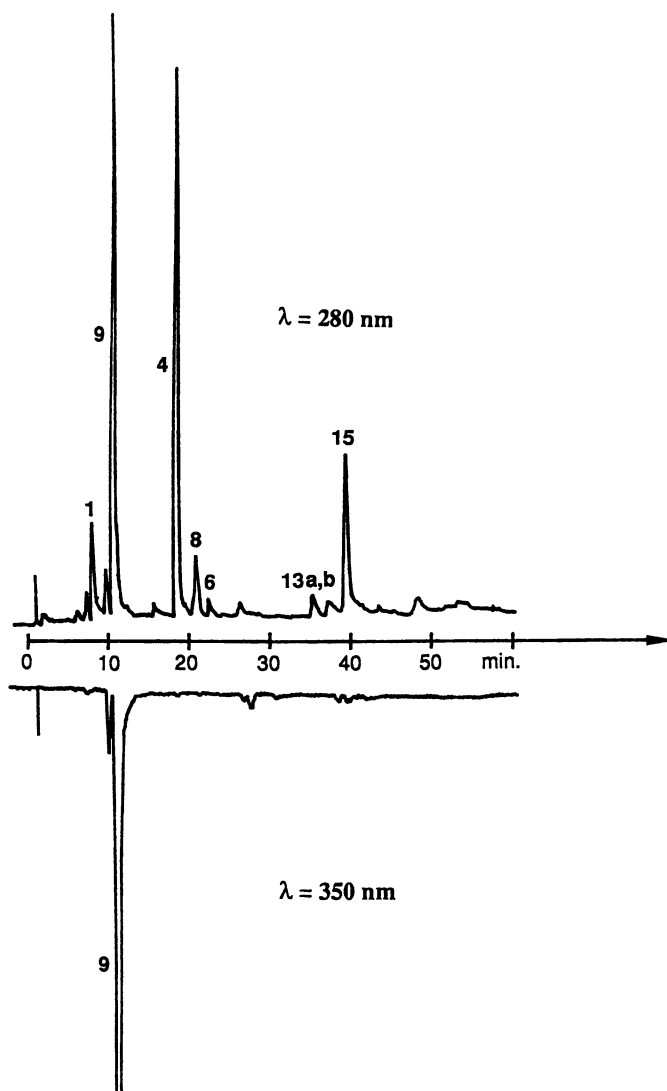


Figure 7. HPLC analysis of the mixture of monomeric and dimeric lignin derived products obtained after acid hydrolysis of bleached CTMP.

or coniferaldehyde. Nevertheless, vanillin structures may contribute to the photoyellowing since they absorb UV-radiation above 300 nm.

Some other compounds (such as **2**, **10** and **11**) were also identified among the hydrolysis products but they can be considered as being stable towards irradiation by sunlight.

Contribution of various lignin structures to photoyellowing

The light-induced yellowing of the four different high yield pulps used in this work is shown in Figure 8. The curves show a fast initial discoloration followed by a slower phase. In the case of bleached CTMP, the first two hours of irradiation cause a brightness loss of 9 ISO-units whereas the second two hours caused a further loss of only 2 units. This phenomenon has also been reported by others (35, 36). The fast initial discoloration (less than 60 min exposure) must be considered the most detrimental since even long periods (days - months) of natural ageing of papers containing high yield pulp are still reflected by a laboratory ageing of less than one hour (37).

Extracts of low molecular weight compounds derived from lignin obtained after acid hydrolysis of spruce wood (SE), unbleached GW (E1), unbleached CTMP (E2), bleached GW (E3) and bleached CTMP (E4) respectively were impregnated onto filter paper sheets. The brightness loss of the paper sheets after 30 min of simulated sun-light irradiation is shown in Figure 9. The strongest discoloration (more than 8 ISO-units) occurred on the filter paper sheet impregnated with E4.

The most sensitive extract, E4, was further fractionated into three sub-fractions by preparative HPLC (Figure 10). Fraction 1 (F 1) contained the stilbene **9** and monomeric products including coniferyl alcohol (**4**) as predominant constituents. Compound **15** and other dimeric products were the major components of fraction 2 (F 2) whereas fraction 3 (F 3) included compounds **19** and **20** together with other trimeric lignols. After irradiation of filter paper sheets containing the various fractions, F 1 was found to cause the greatest yellowing, as shown in Figure 11. The components present in this fraction were further divided into nine subfractions by HPLC, as shown in Figure 10 (fractions a - i). Among these, the subfraction e, consisting mainly of diguaiacyl stilbene (**9**), showed the strongest discoloration after irradiation on filter paper whereas the other monomeric components yielded lower brightness reversion values (Figure 12).

These observations indicate that diguaiacyl stilbene structures are the leucochromophores which are to a large extent responsible for the fast initial discoloration of hydrogen peroxide bleached high yield pulps. As illustrated in Figure 12, other structures present in the various fractions a - i also contribute, however, to the overall yellowing, albeit to different degrees. The identities of some of the minor compounds present in these fractions have not yet been elucidated. On the other hand, the yellowing caused by potentially sensitive structures, such as coniferaldehyde, coniferyl alcohol, pyruvaldehyde enol ethers and vanillin seems to be of a lower magnitude than that of the stilbene.

Conclusions

Coniferaldehyde structures are the major leucochromophore present in spruce lignin. These end groups are also present to a large extent in unbleached mechanical pulps and are responsible for a major portion of the absorption of UV-radiation above 350 nm. Mild sulfite treatment leads to a considerable reduction in the content of coniferaldehyde structures. After bleaching of mechanical and chemimechanical pulps with alkaline hydrogen peroxide, coniferaldehyde structures are to a large extent eliminated and they cannot be considered to be major contributor to the photo-

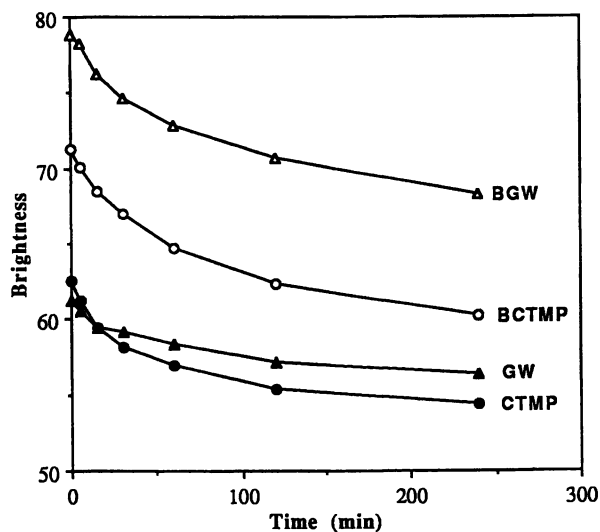


Figure 8. Light-induced yellowing of the various pulps used in this work.

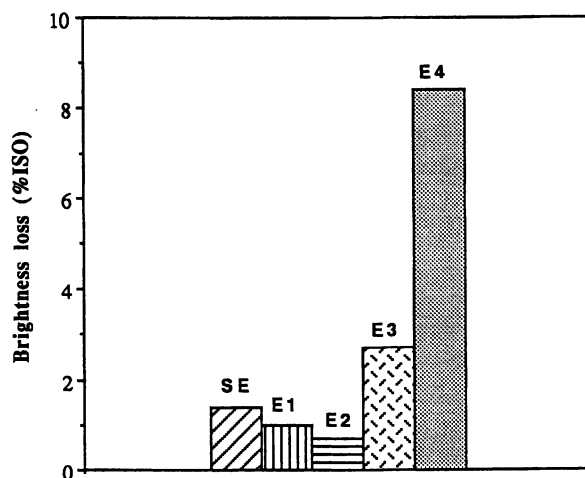


Figure 9. Light-induced yellowing of filter paper sheets impregnated with extracts from spruce wood (SE), GW (E1), CTMP (E2), hydrogen peroxide bleached GW (E3), and hydrogen peroxide bleached CTMP (E4).

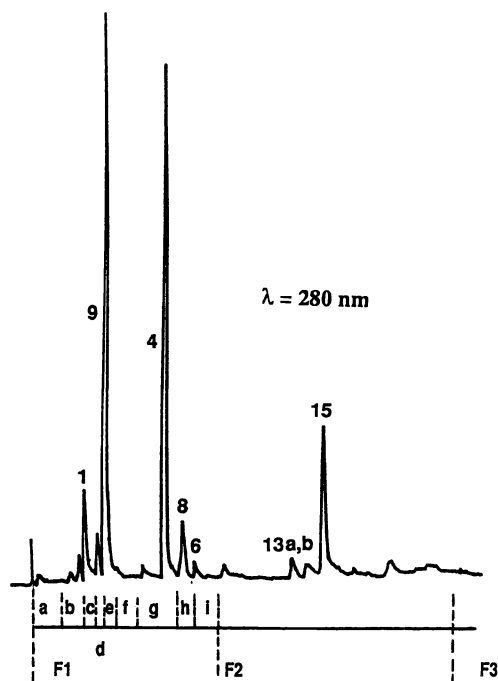


Figure 10. Fractionation of the low molecular weight lignin extract obtained after acid hydrolysis of bleached CTMP.

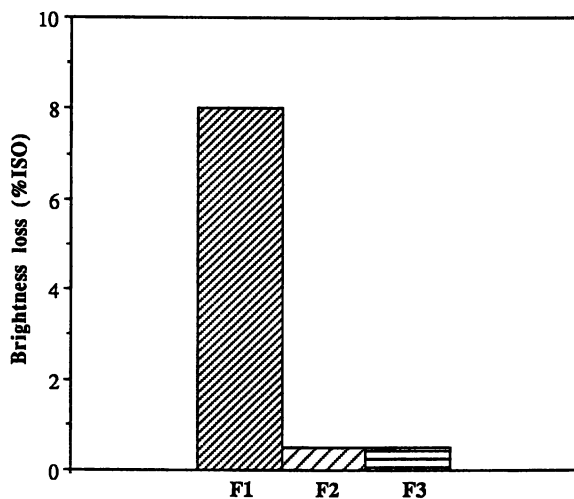


Figure 11. Light-induced yellowing of filter paper sheets impregnated with fractions (F1-F3) of the extract obtained after acid hydrolysis of bleached CTMP (cf. Figure 10).

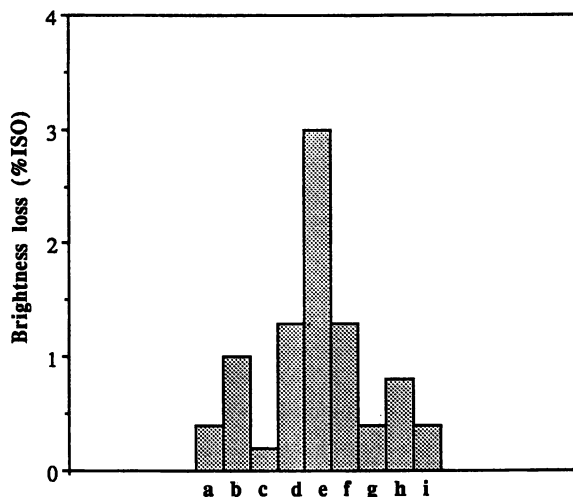


Figure 12. Effects on brightness reversion of individual subfractions from F1 (cf. Figure 10) on irradiation of impregnated filter paper sheets.

yellowing of such pulps. They may, however, still be responsible for a part of the remaining colour in these pulps.

Stilbenes seem to be present in native spruce lignin in trace amounts only. During wood grinding or chip refining, part of the diarylpropane structures present in the lignin are converted into diguaiacyl stilbenes. Alkaline hydrogen peroxide bleaching leads to a further significant formation of stilbenes and these structures seem to be responsible for most of the absorption of UV-light around 350 nm in bleached high yield pulps. Diguaiacyl stilbene, derived from diarylpropane structures, was found to be the most important leucochromophoric structure responsible for the fast initial discoloration of bleached high yield pulps through conversion into coloured products.

Coniferyl alcohol and phenylcoumaran structures are rather stable, and neither phenylcoumarone nor stilbene structures seem to be formed from phenylcoumarans during high yield pulping and bleaching. Pyruvaldehyde enol ether structures may be formed in the pulp lignin from detached glyceraldehyde side chain structures by mild acid treatment at elevated temperatures. Coniferyl alcohol, coniferaldehyde, pyruvaldehyde enol ether and vanillin structures all absorb UV-radiation above 300 nm. These structures may therefore also contribute to part of the yellowing of high yield pulps.

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Chapter 11

Photochromic Behavior of UV-Irradiated Mechanical Pulps

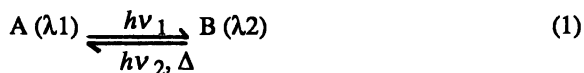
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The degree of light-induced photoyellowing measured on mechanical pulps depends to some extent on the time between the actual irradiation and the brightness measurement. For example, if a sheet is kept for a certain time after accelerated irradiation the brightness increases slowly to reach a new upper limit. If the irradiated and stored sheet is irradiated a second time, the brightness decreases again, i.e. the pulp shows a photochromic effect. The extent of the photochromic effect depends both on the type of mechanical pulp used and on the irradiation time. In this study we have tried to evaluate which factors affect the photochromic effect and to identify the chemical structures responsible.

The use of bleached mechanical pulps is restricted because of their tendency to exhibit photoyellowing on exposure to daylight. We have found that the discoloration occurring during photoyellowing is partly reversible. The degree of daylight-induced yellowing of mechanical pulps depends partly on the time which elapses between the actual irradiation and the brightness measurement. If the sheet is kept in an environment without UV-radiation for a certain time after the irradiation, the brightness slowly increases to reach a new upper limit after about 25 hours. This gain in brightness or reflectance in the visible region (400-700 nm) is completely reversible. If the sheet is exposed for a short second pulse of UV-radiation the reflectance is decreased directly to the brightness value the sample had immediately after irradiation, i.e. the pulp shows a photochromic behaviour. Photochromism is defined as a reversible change of a single chemical species between two states having different absorption spectra, such a change being induced in at least one direction by the action of light, equation 1 (1).



We have evaluated some of the factors affecting the photochromic effect and tried to identify responsible chemical structures.

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Experimental

Pulp Samples. The samples used in the study were; commercial unbleached and peroxide-bleached spruce (*Picea abies*) groundwood (GW), unbleached and peroxide-bleached spruce, and unbleached and peroxide-bleached aspen chemimechanical pulp (CTMP).

Extraction. The pulp was extracted in a Soxhlet apparatus with acetone for 24 hours, after which it was air-dried at room temperature.

Sodium Borohydride Treatment. The pulp (1% consistency) together with EDTA (0.15% consistency) was suspended in water and stirred for one hour at room temperature, after which it was washed and filtered. The pulp was then suspended in water (1% consistency) and sodium borohydride was added (50% on pulp basis). The pulp suspension was stirred at room temperature for two days, followed by filtration, washing with water and air-drying at room temperature.

Ortho-Quinone Enhanced Pulp. The pulp was oxidized with Fremy's salt as described by Lebo (2).

Light-Induced Ageing. The sheets were subjected to accelerated light-induced ageing in an apparatus providing UV and visible radiation (3).

Thermal reversion. The paper sheets were aged at 125°C for 30 minutes.

Storage conditions. The samples were stored in office light at room temperature (+23°C) or in the dark at different temperatures (-70°, -20°, +6° and +23°C).

Brightness Measurements. The brightness was measured on handsheets according to SCAN C-11:75.

Electron Spin Resonance (ESR) Spectroscopy. ESR spectra were measured with a Bruker ESP 300E spectrometer.

Results and Discussion

Peroxide-bleached groundwood was irradiated for one hour after which it was stored in the dark or in indoor daylight ($\lambda > 400$ nm) at room temperature. The brightness value was monitored after the irradiation and the increase was found to be most pronounced in the sample which had been stored in indoor daylight. Figure 1 shows the effect of storage time at room temperature in indoor daylight, on the brightness increase. The brightness increased by almost one unit during the first hour after which the increase was slower. After about 25 hours, the brightness reached a maximum (+1.7 units) whereafter it apparently started to decrease again. The brightness of the pulp stored in the dark increased in the same way, but the total increase in brightness was slightly less, only about one unit.

If the irradiated and stored samples were UV-irradiated a second time, the brightness again decreased. Irradiation of the sheet in a number of cycles, i.e. one hour irradiation followed by storage for 22 hours in the dark before a repetition of the one hour irradiation, resulted in a total photoyellowing of the same magnitude as if the sheet had been irradiated directly for the same number of hours, as seen in Figure 2. Since the measured brightness is the same regardless of any brightness increase upon storage prior to the irradiation, we have interpreted this increase to be a photochromic effect.

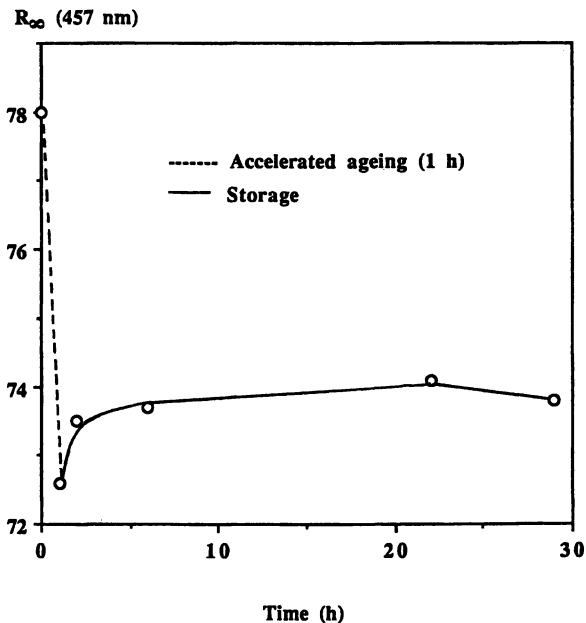


Figure 1. The effect of storage time (+23°C) on the brightness increase after accelerated photoyellowing of peroxide-bleached groundwood for 1 hour.

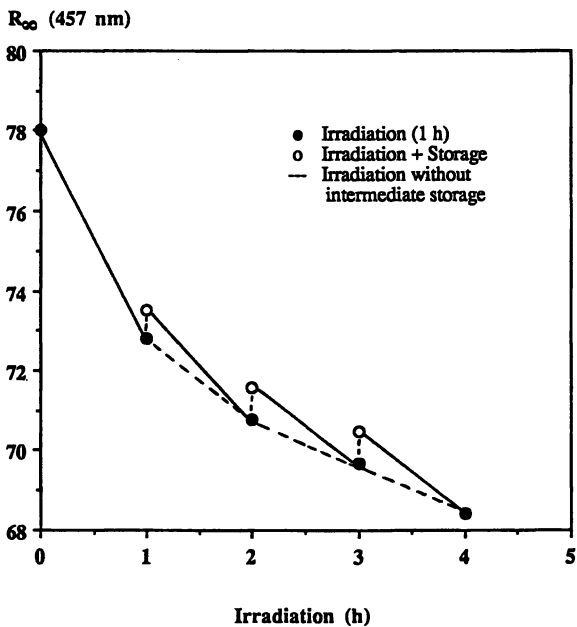


Figure 2. The effect of irradiation in a number of cycles, i.e. 1 hour irradiation + 22 hours storage in dark, on a peroxide-bleached groundwood.

In order to see how soon this photochromism was developed during irradiation, sheets of peroxide-bleached groundwood were photoaged for different periods of time and then stored for 24 hours. As shown in Figure 3, the photochromism is apparent after only a few minutes of irradiation indicating that the chromophoric groups responsible for this photochromic behaviour are rapidly and completely developed in the first half hour of the photoageing.

In a series of experiments with a spruce chemimechanical pulp, it was established that, regardless of the initial irradiation time, a second irradiation period of five minutes with UV-containing radiation after 24 hours storage was sufficient to eliminate the photochromic brightness increase, as shown in Figure 4. If the chromophoric structures are present in the pulp from beginning in their uncoloured or potential chromophore form or whether they are formed by reactions during the initial irradiation is not known and may in fact also depend on the prehistory or the type of pulp.

It is relevant to note that the effect has been observed in all the high-yield pulps that we have studied. The study included commercial unbleached and peroxide-bleached spruce groundwood, unbleached and peroxide-bleached spruce and aspen chemimechanical pulp (Table I).

Table I. Brightness Change (% R_{∞} , 457 nm) during Storage (24 h) after Irradiation (1 h) of High-Yield Pulps

<i>Pulp Sample</i>	<i>Brightness Change</i>
Unbleached GW	0.9
H ₂ O ₂ -Bleached GW	1.2
Extracted Unbleached GW	0.4
Extracted H ₂ O ₂ -Bleached GW	0.7
Unbleached CTMP (aspen)	1.2
H ₂ O ₂ -Bleached CTMP (aspen)	0.4
Unbleached CTMP (spruce)	0.9
H ₂ O ₂ -Bleached CTMP (spruce)	0.8

Storage conditions after irradiation seem to play a minor role with regard to the photochromic behaviour. The brightness of the samples stored in indoor daylight increased slightly more than that of those stored in the dark, but the storage temperature (-70°, -20°C, +6°C and +23°C) had no effect (Table II).

Table II. Brightness Change (% R_{∞} , 457 nm) during Storage (24 h) in Indoor Daylight or in the Dark at Different Temperatures for an Irradiated (1h) Peroxide-Bleached Groundwood Pulp

<i>Temp (°C)</i>	<i>Brightness Change</i>	
+23	1.5	Indoor Daylight
+23	0.7	Dark
+6	0.5	Dark
-20	0.6	Dark
-70	0.6	Dark

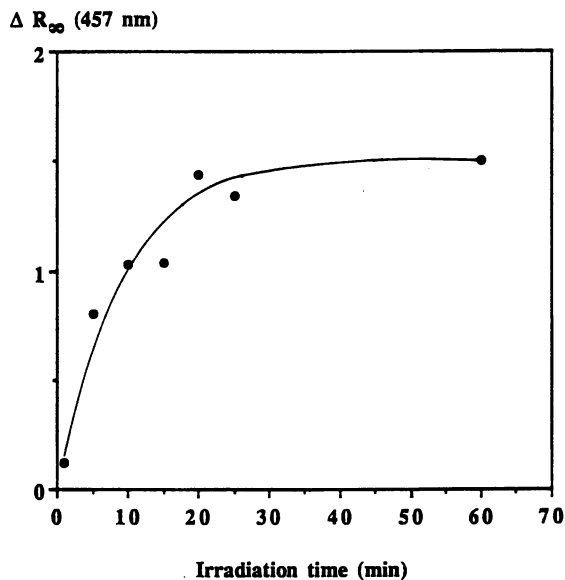


Figure 3. The increase in brightness (%) at 457 nm during storage for 24 h (+23°C) after irradiation for a peroxide-bleached groundwood.

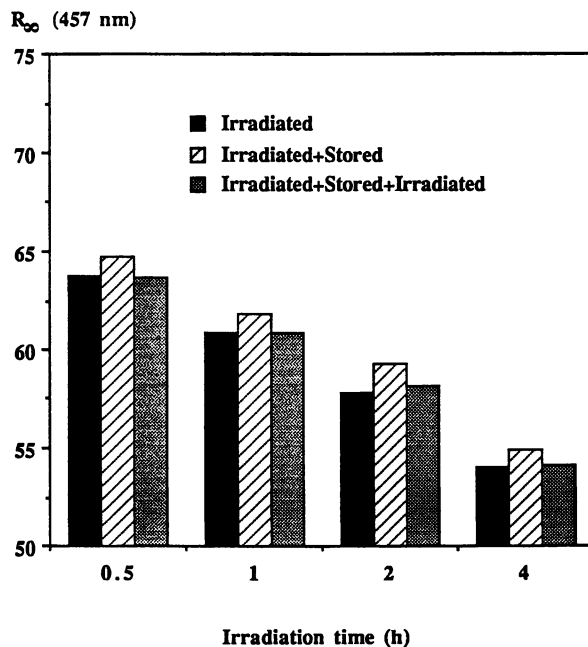


Figure 4. The effect of storage and a second irradiation (5 min) on brightness at 457 nm after irradiation of a peroxide-bleached spruce CTMP.

It was not only exposure to UV-radiation that generated photochromism. Sheets which had been thermally aged (125°C) also showed a slight brightness recovery during storage.

Various tests were carried out in an attempt to obtain further information concerning the nature of the chromophoric groups involved. To study the influence of extractives and other low molecular mass compounds, samples of unbleached and peroxide-bleached groundwood were extracted with acetone and then irradiated. These samples showed a brightness increase upon storage after irradiation but not to the same extent as the reference samples and, thus, part of the reactions responsible may occur in the low molecular compounds removed by extraction.

The peroxide-bleached groundwood pulp was also severely oxidized with Fremy's salt. Although the pulp was almost stabilized against any further brightness decrease during irradiation, the photochromic effect remained (Table III).

Table III. Brightness Change (% R_{∞} , 457 nm) during Storage (24 h) after Irradiation of a Fremy's Salt Oxidized Peroxide-Bleached Groundwood Pulp

<i>Irradiation Time (h)</i>	<i>Brightness Change</i>	
	<i>After Irradiation</i>	<i>After Storage</i>
0.5	0.4	0.8
1	0.0	0.9
2	- 0.2	1.0
4	0.8	1.6

The fact that reduction of the pulps with sodium borohydride did not affect the photochromic behaviour excludes certain functional groups, such as different types of carbonyls, from being the responsible chemical structures. Impregnation of sheets of peroxide-bleached groundwood with ascorbic acid, which can act as a radical scavenger, prior to light exposure did however reduce both the brightness decrease during irradiation (4 h) and the subsequent photochromic behaviour after irradiation and storage (Table IV).

Table IV. Brightness Change (% R_{∞} , 457 nm) during Storage (24 h) after Irradiation (4 h) of a Peroxide-Bleached Groundwood Pulp Impregnated with 2% Ascorbic Acid (AA)

	<i>Before Irradiation I</i>	<i>After irradiation</i>	<i>After Storage</i>	Δ
Reference	76.7	68.1	68.9	0.8
+2% AA	76.7	74.7	75.1	0.3

Based on these results we used electron spin resonance (ESR) spectroscopy to study the formation and stability of free radicals in paper samples after irradiation. Free radicals formed during irradiation but disappeared during storage. Figure 5 shows the

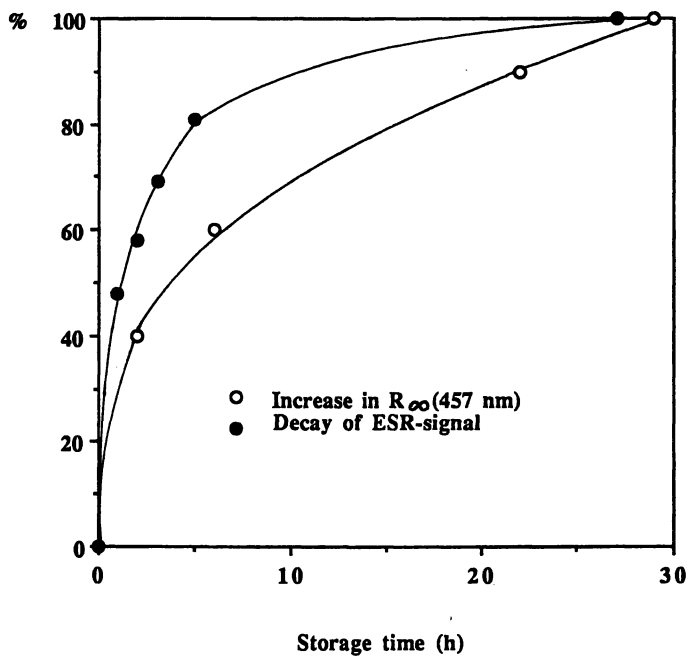


Figure 5. The ESR signal intensity and the brightness increase of a peroxide-bleached groundwood sample after accelerated irradiation (1 h) as a function of storage time at room temperature.

relative decline of the ESR signal intensity and the brightness increase of a peroxide-bleached groundwood sample after accelerated photoageing for one hour as a function of storage time. The decline in radical content and the increase in brightness value seem to follow each other closely. The ESR signal intensity decreased rapidly during the first hour of storage after the irradiation was switched off, and then slowed down. Hon and coworkers (4) also studied the formation and behaviour of free radicals in irradiated wood, and our results are in agreement with those obtained in their ESR study.

Figure 6 shows a difference spectrum between an irradiated pulp sample of peroxide-bleached groundwood and the same sample after storage for 24 hours. The relative reflectance decreases in the UV-region decrease and increases in the visible region.

There are different types of photochromic systems (5), e.g. triplet-triplet absorption, *cis-trans* isomerization or homolytic dissociation reactions. Since lignin has a very heterogenous and complex structure there is probably not a single responsible system, but rather a mixture of systems.

The observed photochromic effect can be due to a triplet-triplet absorption which is the simplest photochromic system in materials containing molecules in the stable ground state and in a metastable photochemically excited state.

Cis-trans isomerization is also a reversible reaction where double bonds can be excited either directly or via spectral sensitizers. The configurational isomers, for example stilbenic structures present in the lignin, usually differ with regard to the positions and intensities of their UV absorption maxima.

Dissociation reactions, i.e. homolytic cleavage of bonds, resulting in the formation of free radicals is an other possible photochromic system. Since the extent of photochromism decreased when a radical scavenger was present during the irradiation and since the brightness increase was accompanied by a decrease in the ESR-signals upon storage, radical-forming reactions can explain the photochromism. When the paper is exposed to UV-irradiation, colour-generating stable radicals may be created which then slowly terminate when the irradiation is turned off, so that the result is a brightness increase. An example of such a radical generating reaction could be the formation of semiquinone radicals from either *ortho*- or *para*-quinones or from the corresponding hydroquinones during irradiation (6-7).

The only very slight photochromic behaviour obtained upon irradiation of bleached aspen CTMP may be due to the presence of syringyl instead of guaiacyl units in hardwood lignin. These structures are less able to form *ortho*-quinones during irradiation than softwood pulps (8).

Conclusions

The observed phenomenon, which we interpret as a photochromic effect, can in principle result in an instant photoyellowing of high-yield pulps upon exposure to ultraviolet irradiation.

The photochromic effect was observed after both UV-irradiation and thermal ageing, but it was not dependent on the storage temperature. Extraction of the pulp had a slight effect. The most pronounced decrease was obtained if the pulp was impregnated with ascorbic acid, which probably works as a radical scavenger. The brightness increase follows the decrease in radicals in the pulp upon storage as monitored by ESR.

Our conclusion is that the photochromic behaviour of high-yield pulps is due mainly to the formation of colour-generating radicals. These radicals can for example be of the phenoxy or semiquinone type, present in the high molecular part of the lignin. However, the contribution of *cis-trans* isomerization reactions can not be excluded.

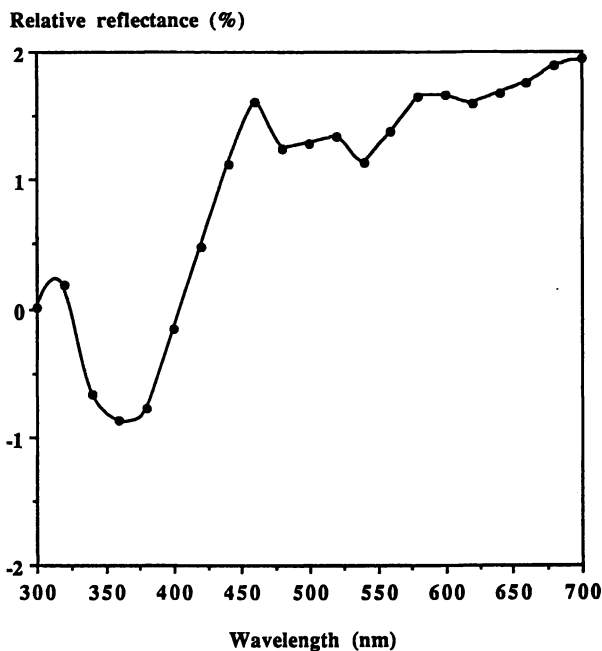


Figure 6. UV-reflectance difference spectrum between an irradiated pulp sample of peroxide-bleached groundwood and the same sample after storage for 24 hours.

Acknowledgments

Stiftelsen Gustaf och Emrich Hellström is gratefully acknowledged for a research grant (to M. Ek).

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Chapter 12

Photocycling of Chromophoric Structures during Irradiation of High-Yield Pulp

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Unbleached and peroxide-bleached thermomechanical spruce pulps were irradiated with monochromatic light at selected wavelengths in the UV and visible region. The formation and destruction of chromophoric structures during irradiation were studied by monitoring the main bands in the difference spectra of the pulps using UV-VIS difference reflectance spectroscopy. Photocycling, performed by irradiation at one of two different wavelengths, one causing photoyellowing and the other photobleaching, was demonstrated for the two pulps during many photocycles. The changes in the band intensities were largely reversible, but a continuous decrease in the reflectance of the pulp in the visible region was observed on increasing the number of photocycles. The amplitude variations during the photocycling, measured e.g. as the change in reflectance during one cycle, were also found to decrease continuously. The number of photocycles required to produce zero brightness difference between two subsequent cycles was determined. Knowledge of the photocycling process brings new insight into the identity and reactions of chromophoric structures in high-yield pulps, which further contributes to a wider understanding of the color reversion process caused by light.

Light-induced yellowing, or color reversion, is a serious drawback in the use of many wood and paper products. Much research, such as studies on the materials themselves and on model compounds, has been done to elucidate the fundamental mechanism of photoyellowing of wood materials, high-yield pulps and lignin-containing papers. The behavior of the active chromophores and intermediates has now been largely characterized by chemical and physical means [1], but the identity of the chromophores and the detailed reaction pathways of the participating species during irradiation and ageing are still unsettled.

In a previous communication [2] it was shown that the irradiation of chemimechanical pulps with monochromatic light at selected wavelengths can be used to obtain new information on the wavelengths that most readily cause photochemical

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changes in high-yield pulps. Photoyellowing and photobleaching of the pulp were observed after exposures to light of different wavelengths. It was also found that consecutive irradiation in the two chromophore bands at 370 and 430 nm observed in the UV-VIS difference reflectance spectra of the sulfonated pulps (unirradiated minus irradiated) caused photocycling of the system. Irradiation in the 370 nm band caused a decrease in the intensity of this band, which was accompanied by yellowing of the pulp, while subsequent irradiation in the 430 nm band caused a decrease in the intensity of this band and a simultaneous increase in the intensity of the band at 370 nm. At the same time the pulp was photobleached. Repeating the irradiation in the 370 nm band again reduced the intensity of this band, while the intensity of the band at 430 nm increased, with discoloration of the pulp as a result. The change in reflectance measured at 457 nm for each single step was 3-5 units. Photocycling of only a few cycles was monitored in that experiment. In the present communication the photocycling of chromophoric structures in unsulfonated pulps, i.e. unbleached and peroxide-bleached thermomechanical pulps, was studied in more detail.

Experimental

Pulps. Thermomechanical pulp (TMP), CSF = 200, was made from fresh industrial spruce chips (*Picea abies*) in a full-scale refiner (at KCL) by pressurized refining. The pulp contained 14.9 mg kg⁻¹ iron, 2.0 mg kg⁻¹ copper and 92.9 mg kg⁻¹ manganese as determined using atomic absorption spectroscopy.

Bleached thermomechanical pulp (TMPB) was prepared by bleaching TMP with 4% hydrogen peroxide and 3.4 % NaOH at 15% consistency and 65°C for 3 h. The stabilizers used were DTPA (0.3%), MgSO₄ (0.05%) and sodium silicate (3.5%). The contents of iron, copper and manganese were 25.9, 1.0 and 2.1 mg kg⁻¹, respectively.

Thick sheets (ca. 400 g m⁻²) were made from the pulps and stored in a freezer before irradiation.

Irradiation. The thick sheets were irradiated with monochromatic light according to ref. [2] using an Applied Photophysics Model 5350 photo-irradiator equipped with a 900 W short arc high pressure xenon lamp, a *f*/3.4 monochromator and an exit lens of quartz providing illumination over an area of 1.3 by 2.4 cm at a distance of 16 cm from the lens. The illumination was uniform over the central area (0.8 by 1.7 cm) which was analyzed. The entrance slit of the monochromator was kept at 5 nm and the exit slit at 10 nm to secure enough output energy. Irradiations were performed at ambient temperatures (ca. 23°C) in air.

Spectroscopy. UV-VIS reflectance spectra of the pulps were recorded directly after irradiation in the wavelength range 250-750 nm on a Perkin-Elmer Lambda 15 spectrophotometer equipped with an integrating sphere. The reflectance values (R_{∞} , strictly speaking the reflectivity of an infinitely thick specimen) at 457 and 557 nm were taken from the reflectance curves. Difference spectra were calculated by subtracting the spectrum of the irradiated pulp from the spectrum of the unirradiated one.

Results and Discussion

Irradiation of the Pulps with Monochromatic Light. Sheets of unbleached and peroxide-bleached thermomechanical pulps (TMP and TMPB) were irradiated with monochromatic light for 2 h at intervals between 250 and 750 nm. The reflectance values obtained from the UV-VIS reflectance spectra of the pulps were plotted against

wavelength; the plots are shown in Figure 1 for TMP and in Figure 2 for TMPB. The curve display minima for radiation wavelengths of 310-320 nm. The minima of the curves for the bleached pulp are considerably deeper than those for the unbleached pulp in agreement with studies on unbleached and bleached chemimechanical pulps [2]. The curves for the unbleached and unsulfonated pulps are very similar to those for unbleached and sulfonated pulps, and the curves for TMPB pulps are similar to those for CMPB pulps. Thus, the sulfonation process does not seem to cause any major changes in the chromophore system. Bleaching, on the other hand, appears to deepen the band minima considerably.

The difference reflectance spectra of TMP and TMPB after irradiation at selected wavelength (Figures 3 and 4) show the formation of both band maxima and minima, depending on the radiation wavelength selected. In general, TMP differed from TMPB in that a minimum around 360 nm was formed for TMP at the most efficient radiation wavelength (320 nm) while for TMPB this band minimum was transformed into a maximum. The present results are in agreement with those obtained previously [3], namely the formation of a minimum (around 370 nm) and a maximum (around 440 nm) for unsulfonated pulps and two maxima (370 and 440 nm) for sulfonated and/or bleached pulps (groundwood and chemimechanical pulps). Strong bleaching (about 4 units) with light of wavelength 370-390 nm caused destruction or modification of the chromophores absorbing at 370 nm leading to yellowing of the pulp (Figures 3 and 4). Photobleaching of both TMP and TMPB was observed with light of region of 450 nm.

Photocycling of TMP. Because the wavelength most readily causing photobleaching of TMP was 470 nm, this wavelength was chosen for irradiation in an experiment where TMP was irradiated consecutively for 16 h with light causing either photobleaching or photoyellowing. The wavelength chosen for photoyellowing was 370 nm. Two sequences were studied, one starting with photobleaching and the other starting with photoyellowing, the total irradiation time was 64 h, corresponding to two complete photocycles. The results in terms of the measured reflectance values at 457 and 557 nm are shown in Table I.

Table I. Consecutive photobleaching and photoyellowing of TMP starting with either a bleaching or a yellowing step

Time, h	Radiation Wavelength nm	R _∞ , % 457 nm	R _∞ , % 557 nm
0		64.13	78.47
Photobleaching first			
16	470	66.67	78.48
32	370	53.60	72.66
48	470	58.05	74.56
64	370	49.51	70.91
Photoyellowing first			
16	370	53.09	72.55
32	470	57.94	74.51
48	370	49.07	70.60
64	470	52.70	72.14

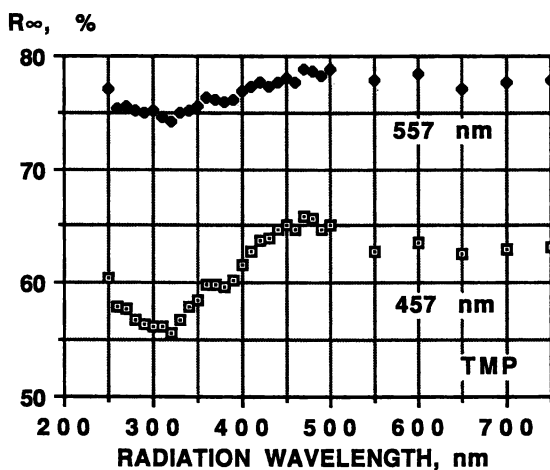


Figure 1. Reflectance (R_{∞}) measured at 457 and 557 nm of unbleached thermomechanical pulp (TMP) irradiated for 2 h with light at selected wavelengths.

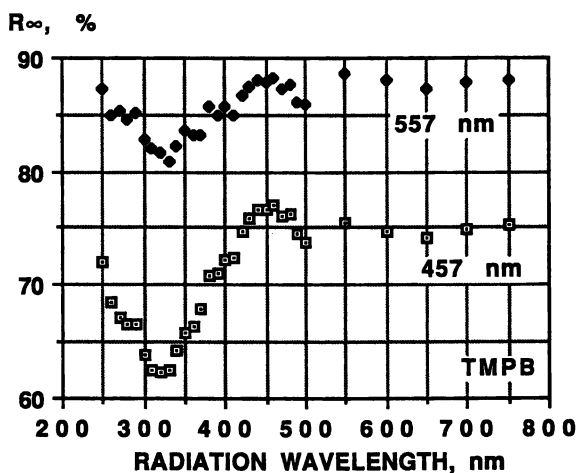


Figure 2. Reflectance (R_{∞}) measured at 457 and 557 nm of peroxide-bleached thermomechanical pulp (TMPB) irradiated for 2 h with light at selected wavelengths.

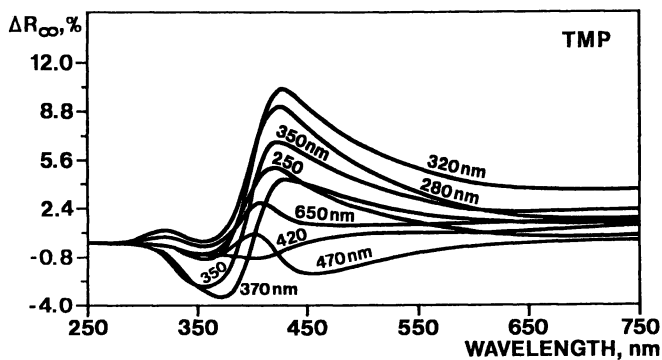


Figure 3. UV-VIS difference reflectance spectra (unirradiated minus irradiated) of unbleached thermomechanical pulp (TMP) after irradiation for 2 h with light at selected wavelengths.

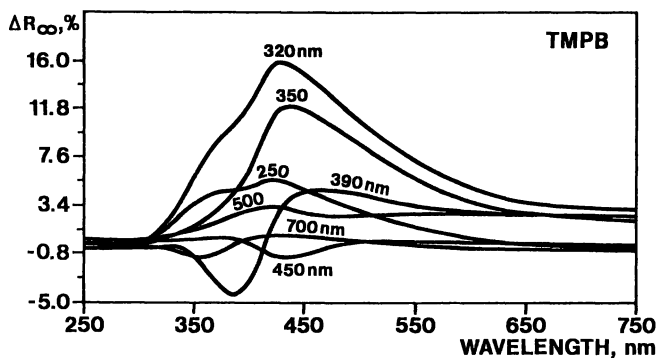


Figure 4. UV-VIS difference reflectance spectra (unirradiated minus irradiated) of peroxide-bleached thermomechanical pulp (TMPB) after irradiation for 2 h with light at selected wavelengths.

When photobleaching was performed first, the reflectance of the final TMP pulp after the whole sequence was markedly lower than that after the sequence starting with photoyellowing. Measured at 457 nm and 557 nm, the differences were slightly more than three units and one unit, respectively. After only one cycle the corresponding values were even larger (four and two units). Photobleaching as an initial event appears to be more harmful than photoyellowing after at least one or a couple of irradiation cycles. The reason for this is not clear.

Photocycling of TMPB. A study of the photocycling of TMPB was performed using irradiation periods of seven hours. Initially, a wavelength of 250 nm was used during irradiation in order to generate the two maxima of similar intensities around 370 and 440 nm observed in the difference spectrum, see Figure 4. After this initial treatment the pulp sheet was alternately irradiated using the wavelengths of the maxima of the two bands obtained after each irradiation step. Because the curve maxima showed a bathochromic shift with irradiation time, the values of the radiation wavelengths were consequently also increased slightly after each cycle. The total sequence was as follows (the difference curves obtained after each step are numbered consecutively): 250 nm (1) → 422 nm (2) → 366 nm (3) → 438 nm (4) → 372 nm (5) → 439 nm (6) → 372 nm (7). The spectral irradiance measured at the sample position of the xenon arc - monochromator assembly at the two radiation wavelengths of interest was found to be of the same magnitude (for 370, 380 and 430 nm → 1.281, 1.342 and 1.342 mW cm⁻², respectively). The result of this sequential treatment is shown in Figure 5, where it is seen from the difference spectra that pumping light energy alternately into the two bands caused one band to increase while the "irradiated band" decreased. Measured at 457 and 557 nm, the result of the total irradiation sequence can be represented as seen in Figure 6. The two photocycling curves show a clear curvature, which is in agreement with previous studies on the kinetics of irradiation of chemimechanical pulps [2], which indicate that the rate is fast during the initial phase but steadily slows down with increasing irradiation time. Nevertheless, using the reflectance values after 16 hours of irradiation, i.e. the last three values for long irradiation times either for photoyellowing or photobleaching, the linear curves in Figure 7 were obtained. The amplitude for the yellowing-brightening cycle decreases markedly with time. Extrapolation of the linear curves gives a total irradiation time of 85-90 h before the two pairs of curves intersect. At the intersection, the reflectance difference between two subsequent photobleaching-photoyellowing cycles is zero and no photocycling should be observed. Accordingly, the photocycling in this experiment stops after about 6 cycles.

The nature of the photocycling was further studied with TMPB by choosing longer irradiation periods (16 h) and starting the actual photocycling after an initial period of irradiation at 290 nm for 16 h followed by two periods of photobleaching at 430 nm. After this sequence (48 h of irradiation) it was assumed that the linear regime of the kinetics of the photoreaction was reached. After this pre-treatment, four periods of cycling were performed, the duration of irradiation totaling 176 h. The reflectance values at 457 and at 557 nm of the pulp after the different treatments are shown in Figure 8. The amount of photoyellowing per cycle at 457 nm was generally 6-7 units and of photobleaching about 4 units per cycle. Measured at 557 nm, the corresponding values were about 3.5 units per cycle for the yellowing and about 2 units per cycle for the bleaching.

The two photocycling curves, shown in Figure 8, seem to progress very smoothly with time, again displaying a continuous decrease in the amplitude of the cycles at longer irradiation times. The number of photocycles observed before zero brightness difference was reached in the same way as in Figure 7, with the difference that regression lines based on the difference reflectance values (ΔR_{∞} , 457 nm) or on

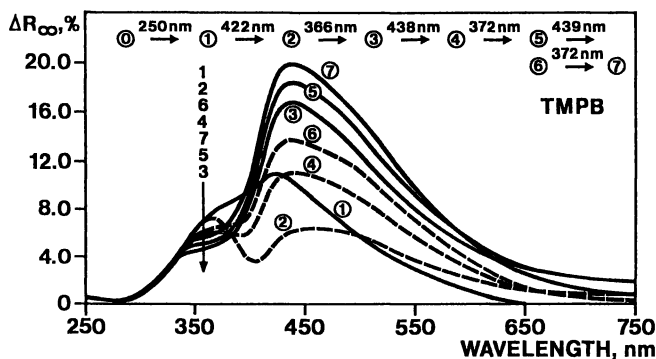


Figure 5. UV-VIS difference reflectance spectra from photocycling of peroxide-bleached thermomechanical pulp (TMPB) performed using consecutively two different radiation wavelengths, one causing photoyellowing and the other photobleaching (irradiation period 7 h).

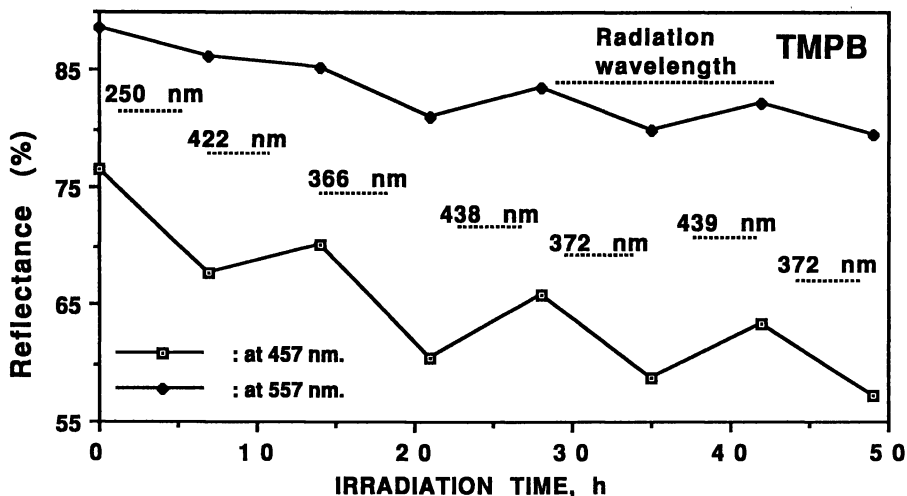


Figure 6. Reflectance values (R_{∞}) after photocycling of peroxide-bleached thermomechanical pulp (TMPB) performed using consecutively two different radiation wavelengths, one causing photoyellowing and the other photobleaching (irradiation period of 7 h).

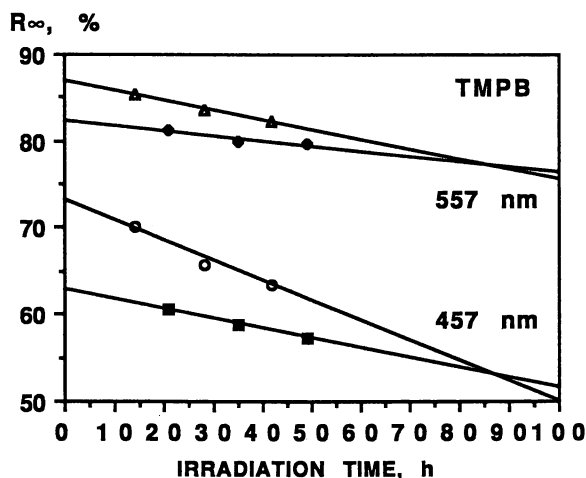


Figure 7. Linear curves obtained from Figure 6 by linking together the reflectance values (R_{∞}) from either the photoyellowing or photobleaching periods as a function of radiation time.

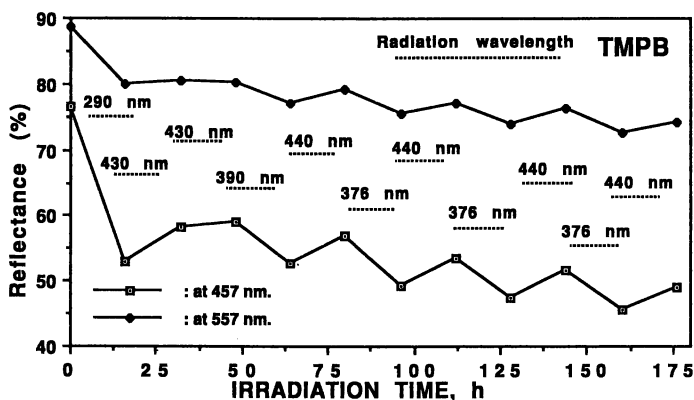


Figure 8. Reflectance values (R_{∞}) after photocycling of peroxide-bleached thermomechanical pulp (TMPB) performed using consecutively two different radiation wavelengths, one causing photoyellowing and the other photobleaching (irradiation period 16 h).

the band maxima intensity values (ΔR_{∞} , 430-440 nm) were used instead. For the photobleaching, the correlation coefficients for the lines were higher (0.99 or more) whereas the correlation coefficients for the photoyellowing were a little lower (0.96-0.99). The irradiation time before the regression lines intersected was calculated to be about 390 h and the number of complete photocycles before zero reflectance difference was thus approximately 12. The reflectance of TMPB measured at 457 nm decreased by about ten units after four photocycles. No value for the number of photocycles could be obtained from the curves measured at 557 nm, since the curves did not converge properly. This result implies that the number of cycles is greater or that the relative error limits are larger because of the smaller changes in the reflectance values. This could be checked by performing a greater number of photocycles and/or increasing the irradiation time per photocycle in order to increase the accuracy.

The results from the two series for TMPB indicate that the number of photocycles tends to increase as the irradiation time per unit operation (yellowing and bleaching) increases.

Suggested Mechanisms of Photocycling

The underlying reactions giving rise to photoyellowing are not yet understood, but at least two mechanisms can be proposed:

1. In the first mechanism it is thought that the two bands are interrelated in some way, either directly or via some intermediates or carrier compounds. The photoyellowing (at ≈ 370 nm) is explained by the reaction of inherent chromophores absorbing at 370 nm and the formation of colored chromophores either directly or with their participation (e.g. photosensitization), which ultimately cause discoloration of the pulp. Photobleaching (at ≈ 430 nm) of the yellow products is caused by the formation of colorless products, or leucochromophores, which absorb light in the UV region. The conversion of chromophores initially absorbing at 370 nm into others absorbing at 430 nm and vice versa need not proceed directly, as interrelated intermediates may participate in the reaction. The experimental results show that the reaction is not totally reversible, and that other products, both colored and colorless not taking part in the photocycling process, are obviously also formed as a consequence of side reactions that gradually reduce the concentration of the initial chromophores. This system, might in the broad sense be regarded as a form of photochromism, which usually demands the reversible induced transformation of one molecular structure either photochemically or thermally, producing a spectral change, typically but not necessarily, of visible color [4]. Redox cycling processes are frequent in the presence of oxygen and suitable candidates for such reactions include the hydroquinone-quinone system [5,6]. Quinone compounds are known to be photoreduced [7] and biologically function as effective electron carriers. These structures may also be incorporated into a larger macromolecular structure, for example they may be part of the oxidized lignin molecule.

2. In the second mechanism, irradiation at ≈ 370 nm excites the chromophores absorbing light in this region, which are transformed or destroyed causing the formation of yellow products and discoloration of the pulp. Alternatively these chromophores can also cause the destruction of other structural elements by functioning as photosensitizers. This initial step is in essence very similar to the initial step in mechanism 1. In the following photobleaching sequence (≈ 440 nm), the yellow products are destroyed (transformed and cleaved) making them more or less transparent to UV light, which during the next photoyellowing phase is able to penetrate into the underlying layer of the pulp and thus to strike fresh structures absorbing at 370 nm. It is well known that light-induced yellowing is only a surface phenomenon. The reaction may be visualized as a process in which modified lignin material is continuously peeled

off from the surface, layer after layer, although the final products remain largely on the surface. These final products are then more or less transparent to the UV light that is so detrimental to the optical properties of pulp. Chromophores in layer after layer are consumed and transformed into material transparent to UV light. From lignin model compound studies [8-10] it is known that light-induced reactions also generate some volatile materials, such as low molecular aldehydes. These compounds may easily escape from the surface of the pulp sheet. The decrease in the amplitude of the photocycles at longer irradiation times can, according to this mechanism, be explained by the formation of final products that are not completely transparent to light. In the final phase of the photocycling they act as photoabsorbers and thus slow down the reaction rates. Changes in surface pH [2] (incorporation of oxygen and the formation of acids [10]), the increase in carbonyl- carboxyl content and the decrease in aromatic content observed using FTIR and NMR spectroscopy [11-13], and decreases in the methoxyl content [11,14] of pulp and paper are further observations which could favor mechanism 2.

It is difficult to distinguish between these two mechanisms, in which the initial step may be very similar. Furthermore, the occurrence of both mechanisms may also be conceivable. On the other hand, finding model systems, e.g. lignin model compounds showing photocycling behavior both in solution and applied to pulps and other carbohydrate matrices, would support mechanism 1. Efforts will be made in that direction in future work.

Chemical cycling of chromophoric structures using alternately photoyellowing (performed by irradiation with the entire spectrum of a xenon arc) and chemical reduction with dithionite solution has recently been reported for spruce groundwood for two cycles [15]. This system is very similar to the photocycling system in the present work, although the photobleaching at 440 nm is replaced with dithionite bleaching. The results from these two studies indicate that the target for both photobleaching and reduction with dithionite is the same. Although the final result is similar for these two treatments, the mechanisms need not be the same. Photoyellowing, as generally accepted, is an oxidative process, as manifested by an increase in oxygen content. It is also known that quinones such as methoxy-p-benzoquinones are photoreduced both with light of the whole spectrum [16] and by selective irradiation at ≈ 350 nm [7]. If such quinones are coupled or attached to the matrix, a photochemically feasible reaction [5,16,17], the quinone formed are absorbing at longer wavelengths than the corresponding monomers. Nevertheless, more experimental results are required in order to establish whether the photobleaching is also a reductive process.

Conclusions

The mechanism of light-induced yellowing or color reversion of unbleached and peroxide-bleached thermomechanical pulps was studied by investigating the phenomenon of photocycling performed alternately using two different radiation wavelengths (370 and 440 or 470 nm). Photoyellowing and photobleaching were demonstrated for both pulps during many cycles. The amplitude, expressed as the change in the reflectance, of the cycles was found to decrease continuously with longer irradiation times. For the unbleached pulp, reversing the sequence showed that photobleaching was more detrimental than photoyellowing when carried out first. The number of photocycles observed for the bleached pulp was calculated to be from 6 to 12, depending on the length of time used for the cycle period. Two possible mechanisms were proposed for photocycling, but further experimental studies are required before any conclusions can be made on which, if either of these applies.

Acknowledgments

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Chapter 13

Gamma-Ray Induced Chromophore Modification of Softwood Thermomechanical Pulp

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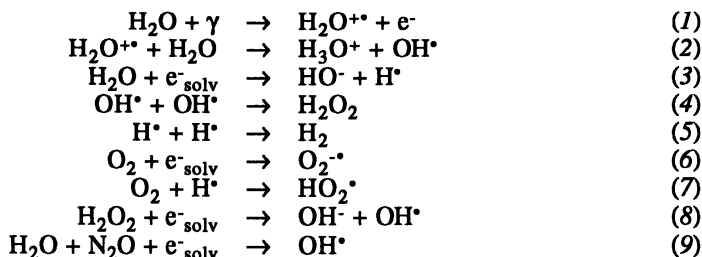
This study focuses on the bleaching of a softwood (black spruce, balsam fir) thermomechanical pulp with gamma irradiation. The effects of sodium borohydride, oxygen, hydrogen peroxide, nitrous oxide and water along with gamma ray irradiation of the pulps were studied. The optimal dose and dose rate, the influence of radical scavengers such as oxygen on the bleaching effect of gamma ray irradiation of pulps as well as the various degrees of bleaching of these pulps were measured. Evidence is presented to relate this bleaching to the generation of reactive species upon gamma ray irradiation of water. These species possess a behavior similar to hydrogen peroxide toward lignin, but are detrimental to cellulose, particularly to the micro fibrils. The main change is to the physical properties and scattering coefficient of the fibers. It is possible to relate the influence of the dose rate to the disappearance of chromophores on lignin, but the effect is very small.

Over the last few years, studies were conducted to determine the mechanisms involved in the bleaching and yellowing of thermomechanical pulps (TMP). Bleaching studies of Holah and Heitner (1) on stone groundwood and TMP have shown that under the attack of hydrogen peroxide, a decrease in the absorption spectrum of TMP at $\lambda_{\max} \approx 358$ nm can be attributed to the reaction of the coniferaldehyde moiety of lignin with the OOH^{\bullet} radical. Also, an observed decrease in the 420-500 nm region is interpreted as a transformation of quinones to carboxylic acids upon reaction with the OO^{\bullet} radical-ion. All these various experiments pinpoint the culprit of the photoyellowing process to the phenolic hydroxyl and phenacyl aryl ether groups. The exact mechanism of the photoyellowing process is not totally understood, but it is now accepted that one of the major processes involves the reaction of radicals such as OH^{\bullet} and OOH^{\bullet} with the phenolic hydroxyl or the phenacyl aryl ether group (2-3-4). The attack of these radicals leads to the β -O-aryl ketyl radical cleavage that eventually leads to the formation of quinolic structures (2-5-6).

There are several alternative ways of generating these radicals. One can use chemistry or irradiation with high energy particles. High Energy photons such as gamma (γ) rays are known to generate these high energy particles. The gamma ray photon passing through water generates high energy electrons from the water

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molecules, which further generate reactive species (like radicals) and ultimately become solvated electrons (e^-_{solv}), according to Draganic and Draganic (7):



Usually, when the high energy electrons travel through the aqueous media, they leave behind these reactive species in spheres centered on the point of impact where the electrons strike the molecules suspended in the media. As the irradiation dose rate increases, the concentration of these spheres of reactive species increases, we observe a concentrated ionization path, as those observed with protons and neutrons.

When talking about radiation, it is important to differentiate between dose (expressed in rad) and dose rate (expressed in rad/h). At high dose rates, radicals and other reactive species are created in high concentration. Thus, their recombination rate is favored as compared to their reactivity as opposed to what is observed at low dose rate, where the radicals and other reactive species are allowed to move farther away from each other, increasing their chance to interact with the surrounding matrix.

This ionization property of γ rays was used by many scientists to study the effects of radicals on mechanical pulps and lignin model structures. Meshitsuka and Nakano (8) have already demonstrated that dissolved oxygen is indispensable to the radiolytic degradation of 11 different lignin model compounds, when using gamma (γ) irradiation at a 350 krad/h dose rate and a dose of 2 to 5 Mrad. This leads to the condensation of phenols. They have also shown that the carbons next to the α carbonyl group and conjugated double bonds are extremely sensitive to γ irradiation. On the other hand, Gierer *et al* has recently shown (9) that, when using a milder 144 krad/h dose rate and a 432 krad dose, oxygen has no effect on the coupling and demethoxylation of different lignin model compounds. Instead, mild γ irradiation of phenols leads to the formation of coupling products, and produces demethoxylation and hydroxylation of non-phenolic models. Their experiments also indicated that under the conditions studied it was impossible to open the aromatic ring of the model compounds used.

Chauaqui *et al* (10) show that γ irradiation of two types of kraft lignin with about 2.4 Mrad of dose leads to polymerization materials. High dose of 10 Mrad are required to induce degradation reactions with loss of methoxyl groups. Their results indicate that the most important free radicals formed involved phenolic hydroxyl groups, α carbonyl groups and α ethylenic double bonds. Unfortunately the dose rate used was not reported.

Finally, Sjögren *et al* (11) have shown that hydroxy radicals formed with γ irradiation during hydrogen peroxide bleaching of chemithermomechanical pulps (CTMP) leads to an increase in brightness of the pulp. The hydrogen peroxide concentrations used were between 2 and 14% (w/w). Concentration of OH^\bullet and $\text{O}_2^{\bullet-}$ increased with an increase in the concentration of peroxide, thus increasing pulp brightness. However, no dose or dose rate of γ irradiation used was reported in the paper.

The work described in this paper uses gamma rays to generate free radicals *in situ* in a pulp suspension. It is hoped that this proximity of radicals and chromophoric moieties in lignin will lead to enhanced bleaching and a better understanding of the bleaching and yellowing processes of TMP.

The technology of electron beams is well known and widely used in the industry. Since the primary source of highly reactive species in both electron beams and gamma rays is the high energy electron (Equation 1), the results obtained in this study can be extrapolated to a possible use of an existing technology.

Materials and Methods

The thermomechanical pulp contained 25% balsam fir (*Abies balsamea*) and 75% black spruce (*Picea mariana*). The chips were provided by Kruger Inc. (Trois-Rivières, Québec) and sorted with a Rader model M-2215 classifier. TMP pulp was prepared according to the following procedure. Chips were washed with fresh water and steamed for 6 minutes at 151 kPa. They were refined in a one-stage process with a CD300 Sunds Defibrator refiner at the Université du Québec à Trois-Rivières. The specific energy was 2398 kWh/ADMT (air dried metric ton). The pulp was then washed with fresh water and thickened to about 20% consistency. It had a freeness of 110 mL and a brightness of 57.6% ISO. The pulp used for control experiments was used as prepared, and stored at 4°C in light-sealed polypropylene bags.

The pulp (20 g, air-dried) was pretreated with 0.4% Na₅DTPA (sodium diethylenetriaminepentaacetate) to complex the undesirable heavy metal ions. This treatment was undertaken at 60°C for 15 minutes at 0.3% pulp consistency. The initial pH was about 6.1±0.2.

The pulp was then divided into samples of 7 grams (dry weight) each. The consistency was brought to 6% to allow enough free water to generate radicals as well as enough fluidity to obtain a homogeneous suspension when gases (Nitrogen, Oxygen or nitrous oxide) were bubbled through the suspension. Each sample was degassed in an ultra-sonic bath for 6 hours, and then bubbled with the desired gas (N₂, O₂ or N₂O) in an Erlenmeyer. The gas was released into the pulp suspension through an annular perforated tube that ensure an even distribution of gas and agitated the pulp.

Irradiation of the samples was performed at the Institut Armand-Frappier (IAF). Four irradiators with different dose rates were used. In all instances, Cobalt-60 (⁶⁰Co, half-life 5.26 years, 1.25 MeV γ ray photon) was used as the gamma ray source. The GammaCell I, II, III and the Calibrator emit γ rays at 107, 350, 700 and 3000 krad/h respectively. At the end of the experimental runs, the 107 and 350 krad/h dose rates of the GammaCell I and II were down to 85 and 265 krad/h respectively, due to the ⁶⁰Co half-life. The calibrator was kept constant at 3000 krad/h. The exact value of the various dose rates was constantly monitored during the experiments.

The effects of these dose rates were studied on an unbleached TMP and on a hydrogen peroxide bleached TMP (P-TMP). The effects of dose from 500 to 3000 krad in increments of 500 krad on these TMP and P-TMP were also studied. This was done so as to compare with the 2.5 Mrad dose reported in the literature (8-10) and used in the industry to irradiate medical papers (12).

To obtain a one stage hydrogen peroxide bleached pulp (P-TMP) we used the following procedure. We used 0.05% magnesium sulfate (MgSO₄ • 7H₂O) and 3% of sodium silicate (Na₂SiO₃, 41° Be) to help stabilize hydrogen peroxide through the formation of peroxy-silicates. Then 2% hydrogen peroxide solution was added. The pH was set at 11.0 with NaOH, and the consistency adjusted to 15% with deionized water. The temperature was raised to 70°C, and held for 2 hours. Consumption of peroxide was 1.97% (0.03% residual hydrogen peroxide) as determined by iodometric titration. After bleaching, we neutralized the mixture with sodium pyrosulfite (Na₂S₂O₅) at 3% consistency to obtain a pH of 5.5. Deionized water was used for washing and, following the treatment, the pulp was filtered and thickened.

Co-irradiation experiments with chemicals were carried out according to the following procedure. To the unbleached TMP pulp suspension (DTPA pre-treated, saturated with Nitrogen by bubbling) a small amount of hydrogen peroxide (H₂O₂ 1%) or

sodium borohydride (NaBH_4 0.3%) was added. These chemicals were added immediately before the unbleached pulp suspension was put inside the irradiator (350 or 3000 krad/h for a 2500 krad dose). The sodium borohydride used came from the commercial Borol solution in NaOH. This Borol solution and the hydrogen peroxide solution used were both at pH 12. This set of experiments was conducted to measure the influence of an oxidizing and a reducing chemical co-irradiated with the pulp suspension. A TMP pulp suspension saturated with nitrous oxide (N_2O) by bubbling the gas through the suspension was also used. The e_{solv}^- generated by γ rays is known to react with N_2O to produce OH^\bullet according to Eq (9). This experiment was performed to measure the influence of OH^\bullet on the optical properties of the pulp. All the experiments were carried out in triplicate.

All the handsheets were prepared from pulps according to the CPPA Standard Method C.5. Optical properties (ISO brightness, CIE $L^*a^*b^*$) were measured using a photoelectric reflectance photometer (Technibrite Micro TB-1C) according to the CPPA Standard Method E.1 and E.2. Absorption coefficient measurements were made using thin sheets according to the method described by Schmidt and Heitner, (13-14). The UV-Visible diffuse reflectance spectra were recorded with a Cary 3 spectrophotometer (Varian) equipped with a 73 mm integrating sphere (BaSO_4 coated, side-on R928 PMT detector).

Results and Discussion

In all the experiments, the measurements using the CIE $L^*a^*b^*$ coordinates did not give any conclusive results. The CIE L^* varies in the same way as the ISO brightness, the CIE a^* does not vary significantly from a null value and the CIE b^* shows very small variations, not much bigger than the variations of the experimental errors. Therefore, most analyses of the optical properties used ISO brightness measurements that showed measurable variations.

The effect of dissolved Oxygen in the unbleached TMP pulp suspension on ISO brightness was studied, and compared to the suspension saturated with Nitrogen. The 3 Mrad/h Calibrator was used to irradiate the samples to various doses from 500 to 3000 krad. The results show no significant effect of dissolved O_2 over saturated dissolved N_2 on the ISO brightness of the pulp. According to Eq. (6) O_2 reacts with solvated electrons (e_{solv}^-) to generate $\text{O}_2^{\bullet-}$. At low dose (432 krad) and low dose rate (144 krad/h), Gierer *et al* (9) have shown that oxygen has no effect on aromatic lignin model compounds during γ irradiation. However, a marked decrease in the UV-visible absorption band of different model compounds has been reported by Meshitsuka and Nakano (8) who used much higher dose (5 Mrad) and higher dose rate (350 krad/h). In our experiments, at the doses used which are lower than those of Meshitsuka and Nakano, no reaction of $\text{O}_2^{\bullet-}$ was observed. Since it is very probable that this species is created during irradiation of pulp suspension saturated with O_2 , it implies that $\text{O}_2^{\bullet-}$ does not react with the surrounding pulp matrix. A radiation dose of at least 5 Mrad is needed to generate enough $\text{O}_2^{\bullet-}$ to obtain a significant modification of the ISO brightness. Our results confirm those found by Gierer *et al* (9). However, to eliminate potential problems from dissolved O_2 on the bleaching or yellowing of the pulp, it was decided to work with nitrogen saturated suspensions.

The optimum dose and dose rate were then studied. The three γ ray sources were used for this comparison. Figure 1 presents the dependence of unbleached TMP ISO brightness on radiation dose for the three different dose rates available. The variations in ISO brightness are small, but significant. At the higher dose rate available (3000 krad/h), no variation in the ISO brightness of the pulp was observed. The use of lower dose rates increased, however, the ISO brightness of the pulp.

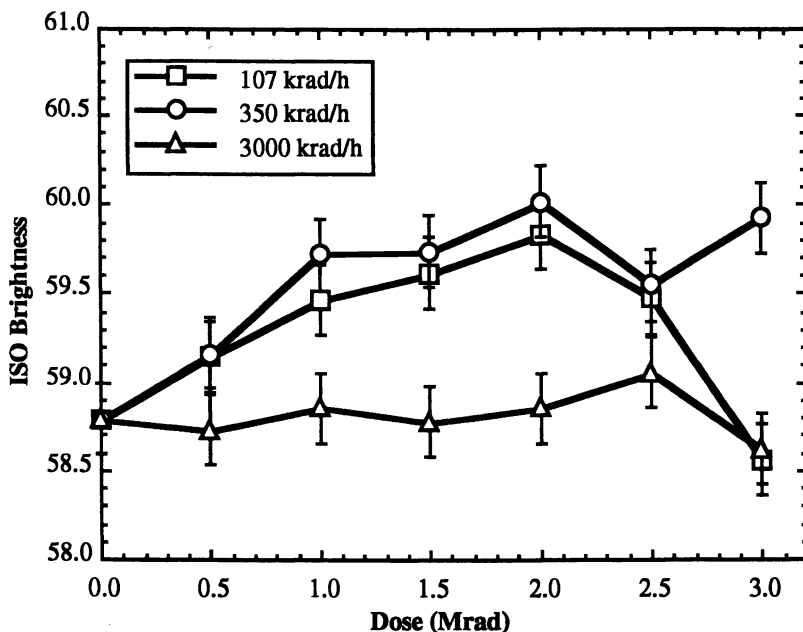


Figure 1. ISO brightness versus γ ray dose for all dose rates.

A conclusion must be drawn from these experiments, The concentration of reactive species generated at dose rates as high as 3000 krad/h is sufficiently high so that they recombine with one another and do not have the time to diffuse and react with the surrounding lignin matrix. This is not the case when the dose rate is lower, the concentration of these reactive species is such that they have the time to diffuse and react with the lignin matrix. The result is an increase in the pulp ISO brightness. To compare our results with those used in literature (8-10-12), a 2.5 Mrad dose was chosen.

The effects of dose rate (0, 107, 350, 700 and 3000 krad/h) on the pulp ISO brightness, for a constant 2.5 Mrad dose for the unbleached TMP and a peroxide bleached TMP (P-TMP) are presented in Figure 2. The ISO brightness of both pulps as shown increases. However, at the highest dose rate available (3000 krad/h) the increase in ISO brightness is much smaller.

To identify the chromophoric groups responsible for the monitored change in brightness, absorption coefficient measurements (Δk) using thin sheets were made according to the method described by Schmidt and Heitner, (13-14). The results for the unbleached TMP and P-TMP under a 265 dose rate γ irradiation are presented in Figure 3. The curve indicated by a SQUARE represents the effect of γ rays on the unbleached TMP. The strong decrease in the Δk below 375 nm, and the shoulder around 330 nm indicate that some types of aromatic ketone or coniferaldehyde groups are destroyed in the process (1-2-6). A decrease in the Δk around 440 nm is associated with the destruction of quinone groups (1-2-6). The difference in the Δk at 457 nm is about $-0.4 \text{ m}^2/\text{kg}$ and is associated with an increase of 2.3 in ISO brightness. At the same time, the scattering coefficient (not shown for clarity) remains constant.

When bleaching a TMP with alkaline hydrogen peroxide, the coniferaldehyde units around 335 nm are destroyed (6) as well as quinone groups around 440 nm. Francis (15-16) has also reported that peroxide bleaching decreases the concentration

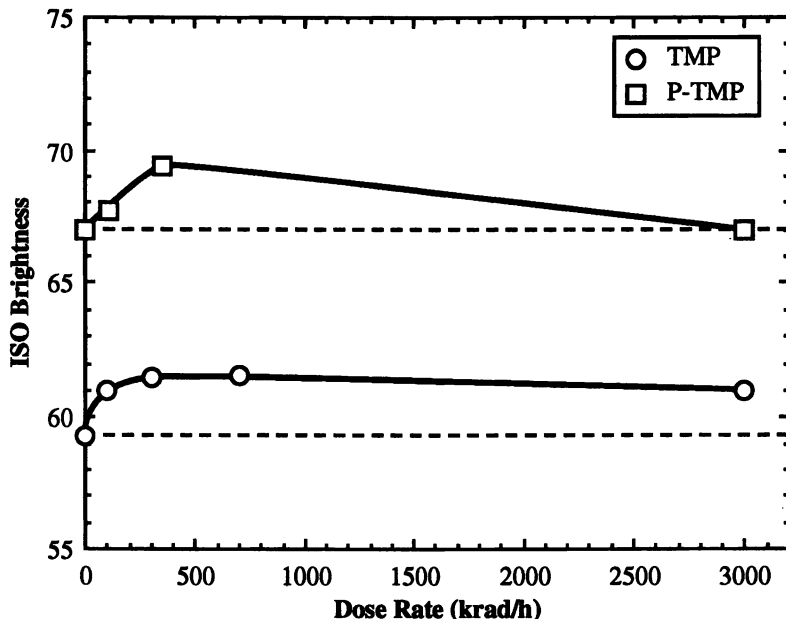


Figure 2. ISO brightness versus dose rate for a 2.5 Mrad dose (error bars are hidden by the size of the symbols).

of hydroxy phenolic groups in a TMP from 185 to 166 $\text{mmol}\cdot\text{kg}^{-1}$. However, it should be noted that Gellerstedt (17) has observed the opposite while bleaching kraft pulps with oxygen. Thus, the bleaching of a TMP with peroxide (P-TMP), would deplete the pulp in phenolic hydroxyl groups as a result of the process.

The curve marked by a DOT represents the bleaching effect of alkaline hydrogen peroxide. The difference in the absorption coefficient at 457 nm is about $-2.0 \text{ m}^2/\text{kg}$ and associated with an increase of 4.1 in the ISO brightness as the result of peroxide bleaching. Upon γ irradiation of an alkaline hydrogen peroxide bleached pulp (P-TMP), one still attacks the phenolic hydroxyl groups or coniferaldehyde groups around 350 nm as indicated by the curved marked with a DIAMOND.

The difference in the absorption coefficient at 457 nm is about $-0.1 \text{ m}^2/\text{kg}$ and too small to account for the 2.2 increase in the ISO brightness as the result of γ irradiation. However, the scattering coefficient (not shown for clarity) of the P-TMP increases significantly, thereby increasing the ISO brightness.

But why does the scattering coefficient increase? To find an answer, one must look at the physical properties of the paper handsheets made from the pulp after γ irradiation. These results are presented in Figure 4 for an unbleached TMP. The results are similar for the P-TMP.

Without presenting too much of the detail, the decrease observed in all three physical properties (breaking length, tear index, burst index) indicate a very strong decrease in the paper strength. The loss observed is equivalent to a refining pushed too far. As the dose rate increases, the detrimental effect of γ rays on the paper becomes stronger in magnitude.

Measurements of the fiber length using a Kajaani instrument indicate that γ irradiation does not affect the length of the fibers. The average fiber length is

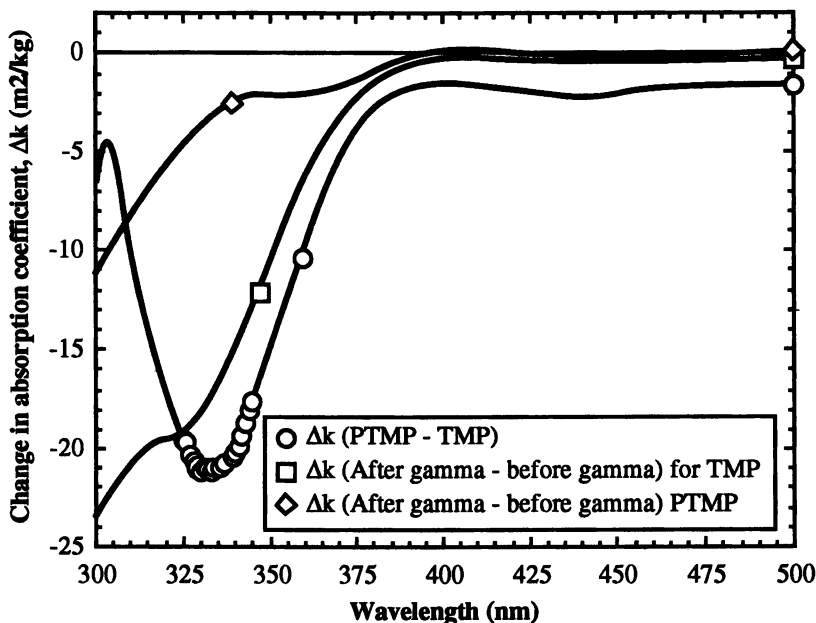


Figure 3. Change in the absorption coefficients for TMP and P-TMP with wavelength for a 2.5 Mrad dose at 265 krad/h dose rate (the initial 350 krad/h at the end of the experiments). Some of the data points are shown on one curve to indicate the precision of the spectrum recorded.

2.28 ± 0.07 mm for an unirradiated pulp and 2.37 ± 0.07 mm for a γ irradiated pulp. Since the fibers are not broken, the only remaining explanation is that the only structures affected are the micro fibrils at the surface of the fiber. These micro fibrils created during the refining process are responsible, for a large part, for the interfiber links and therefore for the physical strength of the paper. These micro fibrils are almost exclusively made from cellulose. As one destroys the link between these micro fibrils and the fibers, one would obtain a more uniform surface of the pulp. This new surface will scatter more light, and thus an increase in the measured ISO brightness will be observed. Thus, reactive species, created during γ ray irradiation; attack cellulose in the micro fibrils located on the surface of the fibers.

We have shown by our ISO brightness and Δk measurements that the lignin was attacked by the reactive species created by the γ irradiation. The results indicate that the reactive species created attack indiscriminately the phenolic hydroxyl or coniferaldehyde groups and the quinone groups. The decrease in physical properties is associated with the attack on the micro fibrils cellulose. However, at 3000 krad/h, the increase in the ISO brightness is smaller than the one observed around 300 krad/h for the TMP, while the physical properties of the pulp are affected more profoundly at 3000 krad/h than at 300 krad/h. The physical properties of the P-TMP behave similarly, while the increase in brightness is negligible at 3000 krad/h for P-TMP.

The results imply a competition for the reaction sites between the lignin and the cellulose, and therefore a low specificity of the reaction between the reactive species and the surrounding pulp suspension has been observed. The intensity of the variation in the measured properties (the increase in ISO brightness or the decrease in physical properties) is proportional to the dose rate used, and therefore to the concentration of

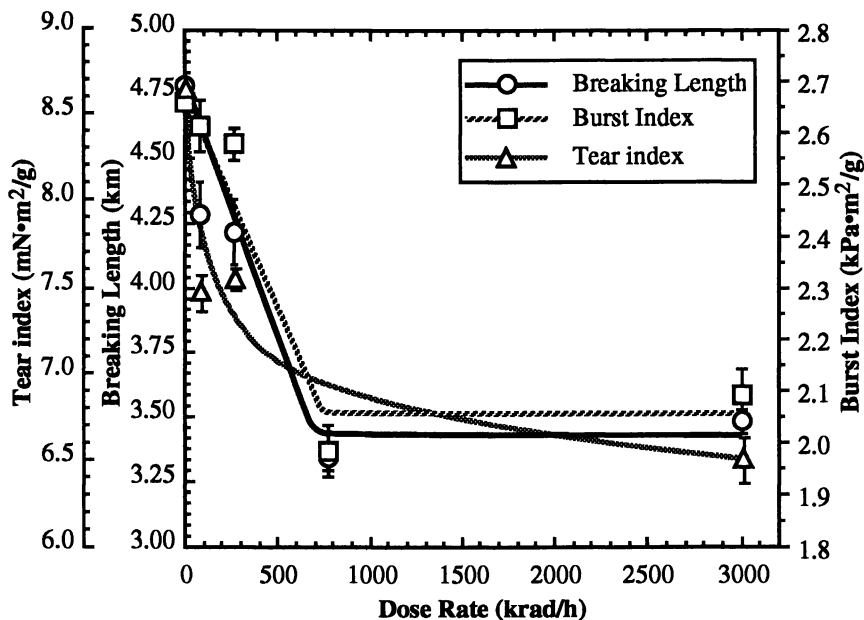


Figure 4. Physical properties of the handshheets made from γ irradiated TMP for a 2.5 Mrad dose.

the reactive species generated by the γ rays irradiation. Since the effect of a 3000 krad/h dose rate on the ISO brightness is smaller than what has been observed around 300 krad/h, while it is the opposite for the physical properties, it must be concluded that the reactivity of the species formed at high dose rate (like 3000 krad/h) in the aqueous media is more pronounced toward the cellulose than toward the lignin.

The optimal dose rate to obtain the highest increase in ISO brightness and to induce the least physical damage to the fibers is thus around 300 krad/h. This is similar to the changes in UV-visible spectra obtained on model lignin compounds by Meshitsuka and Nakano (8) at 5 Mrad dose with a 350 krad/h dose rate. Lower dose rates do not significantly increase the brightness, while higher dose rates strongly damage the fibers. These results are similar to the degradation observed by Chauqui *et al* (10) using 10 krad dose on kraft lignins, even if the dose rate used was not reported.

The next experiments consisted of irradiating the unbleached TMP pulp suspension in the presence of 1% hydrogen peroxide or 0.3% sodium borohydride. This was done to measure the influence of an oxidizing and a reducing chemical co-irradiated with the pulp suspension. Also, H_2O_2 is known to react with e^-_{soln} to produce OH^\bullet (equation 8). The effect of saturated nitrous oxide in pulp suspension was also studied. In presence of γ rays, N_2O is known to react with e^-_{soln} to generate OH^\bullet . The experimental results are shown in Figure 5.

Influence of co-irradiating with NaBH_4 – From the results presented, only a small decrease in the ISO brightness was observed between 500 and 1500 krad. For the 3000 krad/h dose rate, the measured brightness level is nearly constant. Above 2000 krad at 350 krad/h dose rate, one obtained the original brightness level. However, since the experimental errors are of the same order as the deviations observed, any

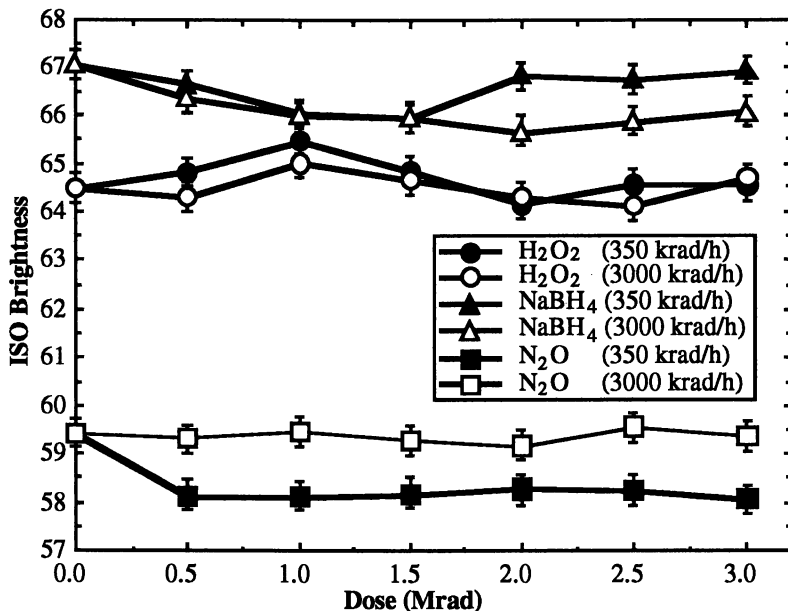


Figure 5. ISO brightness versus dose for concurrent chemical treatment of an unbleached TMP with 1% H₂O₂, 3% NaBH₄ or saturated N₂O in pulp suspension for a 2.5 Mrad dose

conclusion drawn from these results will be hazardous. The observed bleaching thus comes only from the addition of NaBH₄ and is independent of γ rays irradiation.

Influence of N₂O saturated solution – At 3000 krad, one observed no modification of brightness. This is an indication that no net reaction with the lignin occurs at this particular dose rate. However, one can see that at 350 krad/h dose rate, the ISO brightness is lower at every dose observed. Since N₂O is known to generate quantities of OH[•] in presence of e⁻_{solv}, one can conclude that the OH[•] generated reacts with the lignin to decrease the brightness. To understand the OH[•] with lignin, one must look at the third set of curves obtained with the peroxide.

Influence of co-irradiating with H₂O₂ – From the results shown in Figure 5, one can see that, within the experimental errors, γ irradiation in the presence of H₂O₂ does not have any effect on the ISO brightness of the unbleached TMP either at 350 or 3000 krad/h dose rate. The observed bleaching (compared with the 59.6 ISO brightness of the initial unbleached TMP) comes only from the addition of H₂O₂. During the γ rays irradiation, H₂O₂ reacts with the e⁻_{solv} created to generate OH[•]. Since these OH[•] do not decrease the ISO brightness, as opposed to what was observed with N₂O, it implies that OH[•] is in direct competition with H₂O₂. Since H₂O₂ reacts with conifer-aldehyde units around 335 nm (6) and quinone groups around 440 nm (see also Figure 3), it implies that OH[•] reacts with the same chromophores. Since the γ rays co-irradiation with H₂O₂ gives no net effect on the brightness at both dose rates, it implies that the reaction with OOH⁻ is faster than the one with OH[•]. The extrapolation of the results of Sjögren *et al* (11) from their Figure 9 indicates clearly that, as the concentration of H₂O₂ present during co-irradiation is lowered toward 1%, no net effect on the ISO brightness of the CTMP in the presence of γ rays is observed.

Conclusions

A high dose rate such as 3 Mrad/h is not suitable for use as a source of radicals and reactive species in a suspension of pulp. At this dose rate, a small increase in the ISO brightness is observed, while at the same time a large loss of paper physical properties is seen. With the dose rate around 300 krad/h one can increase the ISO brightness, and not adversely affect the physical properties of the pulp.

Some of the reactive species formed during the γ rays irradiation are relatively non selective in their attack of the surrounding pulp suspension: they attack both cellulose (in the micro fibrils) and lignin. However, when OH^{\bullet} are generated, they attack the same chromophores as H_2O_2 during alkaline bleaching (phenolic hydroxyl groups, coniferaldehydes, quinones) and H_2O_2 and OH^{\bullet} radicals are thus in direct competition with one another.

Acknowledgments

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Chapter 14

Weathering and Photodegradation of Cellulose

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Research on the weathering and mechanism of photo-degradation of cellulose is reviewed. It is pointed out that many factors such as dyes and delustrants, in the case of regenerated cellulose fibers, as well as the ambient atmosphere and the wavelength of the irradiation may affect the rate of degradation. Recent work on the photodegradation of oxidized cellulose is described.

As the name implies lignocellulosics are composed of several compounds. Thus when attempting to elucidate the mechanism of photodegradation of a lignocellulosic it is important that the photochemistry of the components be known. In this paper we first review the photodegradation and weathering of cellulose fibers, specifically cotton and regenerated celluloses, and then describe some of our recent work in this area. After it has been scoured and bleached, cotton is about 99% cellulose (1). Regenerated cellulose fibers are slightly less pure. Depending on the fiber type R_{18} values for the pulps from which they are manufactured range between 94 and 97% and the R_{10} values from 90 to 95%. R_{10} and R_{18} , as defined by ASTM, are the portions of cellulose pulps that are insoluble in 10% and 18% sodium hydroxide, respectively (2).

Weathering

The resistance to degradation of cellulosic materials subjected to outdoor exposure, or weathering, is of significant importance for the quality and end-use of the products. The mechanism of weather-related degradation is complex and not yet fully understood. The intensity and wavelength of the incident sunlight is by far the most important factor for causing environmental damage. Other generally less important factors, include the amount and pH of any moisture which is present, fluctuations in

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temperature (day/night), and any atmospheric contaminants such as dust, smog particles, sulphur dioxide, oxides of nitrogen, and ozone. The effectiveness of these secondary factors depends largely on the geographical area and season. For outdoor weathering tests prolonged exposure periods and precise recording of climatic conditions and of the immediate environmental ambience are essential. However, similar trends have been found for results of weathering tests accomplished under severe and under mild climatic conditions (3). Detailed experimental descriptions of natural, accelerated and artificial weathering are given by Davis and Sims (4) and by Rabek (5).

The degradative effect of sunlight on cellulosic fibers has been known for many years. Pioneering studies were carried out by Egerton (6,7). He described two possible mechanisms for photochemical degradation of cellulosic materials. The first is initiated by short wavelength uv light (2537 Å) which is absorbed and causes direct C-C and C-O bond rupture (photolysis). The second mechanism requires a photosensitizer such as a dye or pigment. Such products absorb light energy and transfer it to ambient oxygen to form activated oxygen which in turn reacts with moisture to form hydrogen peroxide. The activated oxygen and/or hydrogen peroxide subsequently can oxidize the cellulose (photooxidation).

Numerous studies by different research groups on the weather resistance of textile materials under defined outdoor conditions have been performed at various testing sites (8-13). Their observations were usually documented in terms of strength retention and fluidity or degree of polymerization (DP). The results of selected studies which focused on the effect of exposure of cotton and rayon materials on their tensile properties are summarized in Tables I-IV. From studies which included simultaneous exposure of both rayon and cotton, it generally appears that cotton degrades less rapidly than viscose rayon. As expected, all samples degraded more slowly when exposed under glass (Tables I and IV) since glass filters out the far uv (5). However, there seems to be an exception in the work of Little (12) when rayon degraded faster under glass than under direct exposure (Table IV). The reason for this is unknown. The presence of titanium dioxide significantly affects the photodegradation of rayon. Bright rayon, which does not contain titanium dioxide, degrades more slowly than semidull or dull rayon which does. In these cases, titanium dioxide is acting as a photosensitizer (24). As mentioned later, there is evidence that in some instances titanium dioxide can prevent degradation rather than induce it.

The incident light on a sample not only has to be absorbed by the textile material but it has to be of sufficiently high energy to effectively cause chemical changes in the molecular structure (7,14). The deterioration of the samples is more when exposed to sunlight of late spring and summer when compared with the light of fall or winter (Tables I and IV) (9,13). It has been shown that within the U.S. the fraction of uv light in sunlight is less during the winter than in the summer. This has been attributed to the ozone layer being thicker in winter (15).

Although nominally of similar chemical composition, it is difficult to draw specific conclusions of the cause of the differences in behavior of the

Table I. Weathering of samples in Florida

Sample description and citation ^a	Exposure conditions	Exposure time [months]	Loss in strength [%]
Combed cotton yarn, 30/2 Viscose yarn, semi-dull, 3 denier 2 1/2 inch staple, 30/2 (8)	Outdoor	3.5	50
		2.5	50
Deltapine cotton yarn 30/1, 5 plies, 765 denier (9)	Direct		
	Spring	2	50
	Fall	3	48
	Under glass		
	Spring	4	45
	Fall	6	52
Viscose rayon yarn, bright, 50 fil., 1 ply, 925 denier (9)	Direct		
	Spring	2	60
	Fall	3	59
	Under glass		
	Spring	2	57
	Fall	3	39
Saponified cell. acetate yarn, natural, 180 fil., 6 plies, 935 denier (9)	Direct		
	Spring	1	62
	Fall	1	61
	Under glass		
	Spring	1	49
	Fall	1	42

^aCitation in parentheses

Table II. Weathering of samples in Kano, Nigeria and Didcot, United Kingdom

Sample description	Exposure conditions	Exposure time [months]	Loss in strength [%]
Kano		Winter to Summer	
Cotton yarn, 4/54s, 382 denier		5	50
High tenacity viscose yarn, 160 fil., 421 denier		3.75	50
Viscose yarn bright, 160 fil., 407 denier		3.5	50
Viscose yarn dull, 126 fil., 423 denier		3	50
Didcot		Summer to Fall	
Cotton yarn, 4/54s, 382 denier		3	50
High tenacity viscose yarn, 160 fil., 421 denier		1.75	50
Viscose yarn bright, 160 fil., 407 denier		3.75	44
Viscose yarn dull, 126 fil., 423 denier		less than 1	50

SOURCE: Data are from reference 10.

Table III. Effect of location in the United Kingdom on weathering of cotton

Sample description	Exposure conditions	Exposure time [months]	Loss in strength [%]
Cotton fabric, 11 oz./yd ²	Rural sites	3	4-9
		12	27-39
	Semi-rural sites	3	5-10
		12	48-70
	Urban sites	3	12-22
		12	71-88
Cotton fabric, 16 oz./yd ²	Rural sites	3	0-12
		12	20-40
	Semi-rural sites	3	0-13
		12	35-57
	Urban sites	3	1-13
		12	60-82

SOURCE: Data are from reference 11.

Table IV. Results of miscellaneous weathering studies

Sample description and citation ^a	Exposure conditions	Exposure time ^b	Loss in strength [%]
<u>United Kingdom study (12)</u>			
Cotton yarn, no details available	Direct	200 s-h	50
	Under glass	280 s-h	50
Viscose rayon yarn, no details available	Direct	240 s-h	50
	Under glass	200 s-h	50
<u>New Orleans study (13)</u>			
Cotton print-cloth, bleached	Direct		
	Oct.-April	6 mo	29
	Feb.-August	6 mo	50
	July-Jan.	6 mo	33
	Under glass		
	Oct.-April	6 mo	26
	Feb.-August	6 mo	—
	July-Jan.	6 mo	21
	Cotton print-cloth, mercerized under tension	Direct	
Oct.-April		6 mo	14
Feb.-August		6 mo	26
July-Jan.		6 mo	21
Under glass			
Oct.-April		6 mo	11
Feb.-August		6 mo	—
July-Jan.		6 mo	11

^aCitation in parentheses^bs-h = sun-hours; mo = months

rayon and cotton samples on exposure to radiation. The degree of polymerization of cotton is much higher than that of rayon. Cotton also tends to be the purer cellulose. Furthermore in the samples presented in Tables I-IV the cotton samples did not contain titanium dioxide which can act as a photosensitizer. Degree of crystallinity and crystal form may also be factors. Cotton has a much higher crystallinity than rayon and it has the cellulose I crystal form while rayon has the cellulose II form (2). In this context it is interesting to note that nonmercerized cotton fabric lost strength faster than its mercerized counterpart (Table IV). Mercerization decreases crystallinity and converts the crystal form of cotton to cellulose II. Mercerization also causes the cross-sectional shape of cotton fibers to become rounder. As will be mentioned below this may also influence degradation.

Photodegradation is a topochemical reaction and thus is affected by fabric and yarn structure (16) and by the fineness and cross-sectional shape of the fibers. The faster deteriorating outer layers are believed to have a protecting effect by allowing less radiation to penetrate the interior of the construction (11,16,17). Because of the irregularity of the attack there may be some variability in the fluidity data of the bulk material (11,17). Desai (17) took the thickness of the material into account and measured the DP of the exposed and the unexposed side separately and found considerable differences in the data.

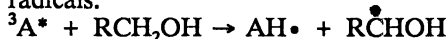
The contribution of atmospheric and climatic conditions to photochemical processes are complex and difficult to control on a reproducible basis. Studies (Table II) (10) have been carried out distinguishing between a desert climate with high sun intensity and virtually no humidity (Kano, Nigeria) versus moderate conditions with frequent changes between wet and dry (Didcot, U.K.). Cotton as well as viscose rayon degraded considerably faster under the influence of high humidity with pigmented regenerated yarns losing strength more rapidly than the bright ones. Generally, cotton performed better under humid conditions than any of the other cellulosic fibers.

Little and Parson (Table III) (11) performed a study which was carried out at 8 different sites in the United Kingdom with rural, semi-rural or industrial environments. It was found that the more acidic air and higher concentrations of pollutants at the urban sites accelerated photochemical degradation, especially in the case of a lightweight fabric (11,18). The differences were more distinct after 12 months of exposure. Sulfur dioxide and traces of acid-forming substances were assumed to have accelerated the rate of deterioration. However, since the amount of acid produced is small (12), acid hydrolysis of cellulose as proposed earlier by Howard and McCord (16) is rather unlikely. In this regard, in a study using a Weather-Ometer, Zeronian (19) exposed cotton and regenerated cellulose fibers to radiation from a xenon arc lamp with borosilicate filters. Exposures were made with and without the atmosphere contaminated with 0.1 ppm SO₂. The presence of SO₂ caused additional loss in strength over that caused by light exposure alone. Using copper number and carboxyl content as measure of degradation it appeared that the properties of samples exposed to light and SO₂ differed from that of acid hydrolyzed counterparts which had suffered similar losses in strength.

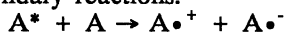
Influence of Dyes, Pigments and Additives

It has been found that greige cotton goods degrade less rapidly than bleached material when exposed to sunlight (13). This was explained as a shielding effect due to the impurities, such as waxes, in the greige goods. It was assumed the bleaching process did not chemically damage the cellulose structure.

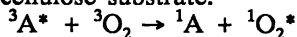
A large number of studies (20-24) has been carried out in order to examine the effect of dyes and pigments, metal ions and lignin which are capable of absorbing the uv region of sunlight and thus can accelerate or retard photodegradation of cellulosic materials. Vat dyes and related compounds are by far the most investigated dye class. While the yellows, oranges and reds in general have a photosensitizing effect, other vat dyes improve the resistance to light or have no effect (13,24). Although extensive work was done on this subject the assertions of the different research groups were often contradictory. It is widely accepted today that the major primary process consists of the interaction of the dye with the substrate (26). Based on model compound investigations Phillips and Arthur Jr. (25,26) proposed the following mechanisms to explain phototendering in the presence of vat dyes. The photoexcited anthraquinone system which is usually in the triplet state ($^3A^*$), will abstract a hydrogen atom from an alcoholic compound and produce two free radicals:



At low concentrations of photoexcited dye and in competition with radiationless deactivation processes the radicals can react with oxygen to form additional radicals and/or hydrogen peroxide. At higher concentrations electron transfer reactions to semi-reduced ($A\cdot^-$) and semi-oxidized ($A\cdot^+$) anthraquinone compounds can occur which in turn undergo secondary reactions.



In addition, singlet oxygen which is formed by reaction of the photoexcited anthraquinone with atmospheric oxygen is believed to react chemically with the cellulose substrate.



Correlations between the color of the dye and the photosensitizing effect were also found for sulfur dyes (16) but for all other dye classes no general mechanistic pattern has been suggested so far (22).

Titanium dioxide which is often used as a delustrant is usually thought to have a photosensitizing effect. In the study of Fels (10) (Table II), bright viscose was by far superior in light resistance to its dull counterpart. However, humidity seemed to play an additional role (cf. Kano and Didcot exposures). Angster (27) suggested that low concentrations of TiO_2 have an accelerating effect on photodegradation while at higher concentrations TiO_2 could act as uv absorber and thus protect the fiber. In the opinion of Rozmarin (24) TiO_2 acts as an oxidizing agent on hydrated cellulose or cellulose derivatives, however without splitting any bonds.

Urea formaldehyde and thiourea resins were reported to have a protective effect on viscose rayon and cotton fabrics upon exposure to

mercury vapor lamp radiation (28). Later (29) it was demonstrated that the amount of protection that is afforded cotton varies depending on the type of resin applied. During exposure it was noted that the wrinkle recovery of the samples decreased indicating the crosslinking of the fabric induced by the resins had been reduced. Exposure in this instance was to light from a xenon arc lamp with borosilicate filters.

Like pigments, the effect of other contaminants such as dust and smog particles varies depending on their chemical nature (30,31). In some cases photooxidation can be induced and the rate of degradation accelerated, in other cases the products act as uv absorbers.

Mechanism of Photochemical Degradation

The mechanism of the reactions occurring in cellulose during photodegradation has been investigated for many years (6,7,17,25). In order to correlate specific regions of the uv/visible spectrum of the sunlight with chromophoric groups in cellulose, various light sources with different spectral distributions have been used (32); namely, mercury vapor lamps, emitting almost monochromatic light at 2540 Å (33,34), xenon arc lamps (19) and carbon arc lamps (21,35) in conjunction with suitable filters. The uv absorption spectra of various cellulosic materials have been documented in numerous publications (36-38). A film of purified cellulose absorbs near 2600-2700 Å with a shoulder at about 3000 Å (26,37). It has been shown that wavelengths greater than 3100 Å are ineffective in terms of the direct photolysis of pure cellulose but a mercury vapor lamp emitting 2537 Å is capable of inducing photodegradation processes (26,37,39).

To investigate the mechanism of the photodegradation Desai (17) and Desai and Shields (40) analyzed the main volatile products obtained after irradiation of cellulose. The products were found to be low molecular weight compounds such as hydrogen, methanol, ethanol, methane, carbon dioxide, and acetone. The same compounds were also generated when oligosaccharides, as model substrates, were exposed to a uv light source (39). It was concluded that the primary photolytic process consists of a chain scission between the anhydroglucose units and the formation of gaseous products is a secondary process. However, contradictory opinions existed whether water vapor and/or oxygen necessarily participate in the photolytic reaction.

Launer and Wilson (33) carried out experiments in dry and wet atmospheres in air or nitrogen. They stated that the water vapor has an inhibiting effect on the rate of photodegradation and the influence of oxygen can be neglected. Phillips and Arthur Jr. (25) hold that for the decomposition of cellulose, oxygen is necessary. Photooxidative reactions proceed at a faster rate in atmospheres of higher humidity. Hydrogen peroxide can be formed and thus, participate also. Daruwalla et al. (35) differentiated between low and high moisture contents. At low humidities water can inhibit degradation. In contrast, at high humidities in the presence of oxygen the formation of additional H and OH radicals is likely and decomposition accelerates. They pointed out that the observed effects depend also on the light source used.

At present, it is generally recognized that the rate of degradation at 2537 Å is independent of oxygen and the reason for former disagreements is found in the use of different light sources with different spectral outputs (26). Moisture has a great influence on the formation of radicals, especially when photosensitizing agents are present.

Although many attempts have been made the reaction mechanism for photodegradation is still not clarified nor are the primary light absorption events fully understood (25,26,35). After irradiation of cellulose at wavelengths between 2500 Å and 3100 Å a large number of radicals such as hydrogen atoms and formyl radicals were identified by Hon (41-43) and Ogiwara et al. (44) with the help of ESR spectra while above 3400 Å no radicals were found in pure cellulose. Conceivable radicals and their transformations according to current information (46) are presented by Phillips and Arthur Jr. (26) and Hon (45).

With respect to the primary light absorption process several alternative groups in the cellulose structure have been suggested as the chromophores but not yet proved. Flynn et al. (47) proposed that the hydroxyl groups on the surface were responsible, forming carbonyl groups and liberating hydrogen. Carbonyl and carboxyl groups formed during sample preparation, impurities or products of secondary photooxidative processes have also been suggested (26,31,36).

At present, it is accepted (26) that the acetal group at the C1 position of the anhydroglucose unit acts as a chromophore which in high molecular weight polysaccharides produces a band absorption and thus induces direct photolysis reactions.

Photodegradation of Oxidized Cotton Cellulose

In a recent study (48) we demonstrated how different functional groups affected the photodegradation of cellulose. For this purpose the cellulose in the form of scoured cotton yarn was selectively oxidized with sodium metaperiodate resulting in the formation of aldehyde groups at the C2 and C3 positions of the glucose unit with simultaneous cleavage of the C2-C3 bond (2). The oxidation was extended only up to an oxygen consumption of 2.45 atom per 100 anhydroglucose units (agu) since during the initial stages of the oxidation side reactions are not significant and the strength loss of the oxidized products is not lowered by more than 34%. The oxidation is known to be permutoid in nature and thus not limited to the accessible regions. However, the aldehyde groups cannot be expected to be uniformly distributed along the cellulose molecules due to the inhomogeneity of the reaction.

Following the periodate oxidation, the 2,3-dialdehyde celluloses were either reduced with potassium borohydride to form the dialcohol or oxidized with sodium chlorite to give dicarboxyl celluloses. The strength loss of the former products was kept lower than 27% and that of the latter 37%.

All three modified celluloses, as well as the nonoxidized starting sample, were exposed to uv light for various periods of time using a Weather-Ometer. The light source in the Weather-Ometer was a xenon

arc lamp with borosilicate inner and outer filters. The effect of the different functional groups was studied in terms of changes in yarn tensile strength, sample intrinsic viscosity and fiber morphology and compared to the respective nonexposed counterpart and to the nonoxidized control.

The starting cotton yarn lost 2-3% of its strength after the first and the second week of exposure, and it had fallen by further 14% after the fourth week. The intrinsic viscosity of the sample that was exposed for four weeks dropped by 67% compared to the nonexposed cotton.

Subjected to the same irradiation as the control samples, the breaking strength of the dialdehyde celluloses decreased almost linearly by 10-15% each week within the same oxidation level and no distinct accelerating effect of the introduced groups could be observed. After four weeks exposure, the intrinsic viscosity decreased by about 50-60% with respect to the nonexposed counterpart and by 70 to 80% with respect to the nonexposed unoxidized control.

Upon irradiation the breaking strengths of the dialcohol celluloses were initially higher than or equal to their counterpart dialdehydes and then became lower as the degree of oxidation was increased further. The turning point shifted towards lower oxidation levels as the exposure duration was progressively increased (Figure 1). Thus it appears that the introduced primary alcohol groups acted as chromophores and accelerated the photodegradation process. However, a certain number of these groups in the cellulose structure seems to be necessary before acceleration of the degradation begins.

A comparison of the intrinsic viscosity of the dialdehyde and the dialcohol celluloses showed that the exposed dialcohol samples had distinctly lower values than the comparable dialdehydes. For example at an oxygen consumption of 2.45 atom per 100 agu the intrinsic viscosities of the exposed dialdehyde and dialcohol were 3.23 and 2.21 dl/g, respectively.

When dicarboxyl celluloses were exposed in the Weather-Ometer, the highest decreases in breaking strength relative to the other treatments were found at degrees of oxidation higher than about 0.65 atom per 100 agu (Figure 2). Lower intrinsic viscosities were found also. For example at an oxygen consumption of 2.45 atom per 100 agu the intrinsic viscosities of the dialdehyde, dialcohol and dicarboxyl cellulose were 3.23, 2.21 and 1.78 dl/g, respectively. The standard error for intrinsic viscosities was 0.02. In this case the turning point in breaking strength when compared to the periodate oxycellulose did not shift as the exposure duration increased. The deterioration of the dicarboxyl celluloses may be partly due to autohydrolysis induced by the carboxyl groups. Thus, the structural breakdown of these samples may have proceeded by chemical as well as photo-induced processes.

When examined with a scanning electron microscope, none of the exposed chemically modified celluloses exhibited any significant changes in morphology beyond the appearance of fractured fiber ends and fibrillar cracks. Such damage was also detected in the exposed nonoxidized control.

In summary it appears from this study that the introduction of primary alcohol groups induced more photodegradation than the presence of aldehyde groups in the cellulose. The potential effect of the aldehyde groups might have been modified by the aldehyde groups forming hemiacetals or hemialdals in the cellulose. The severer changes observed

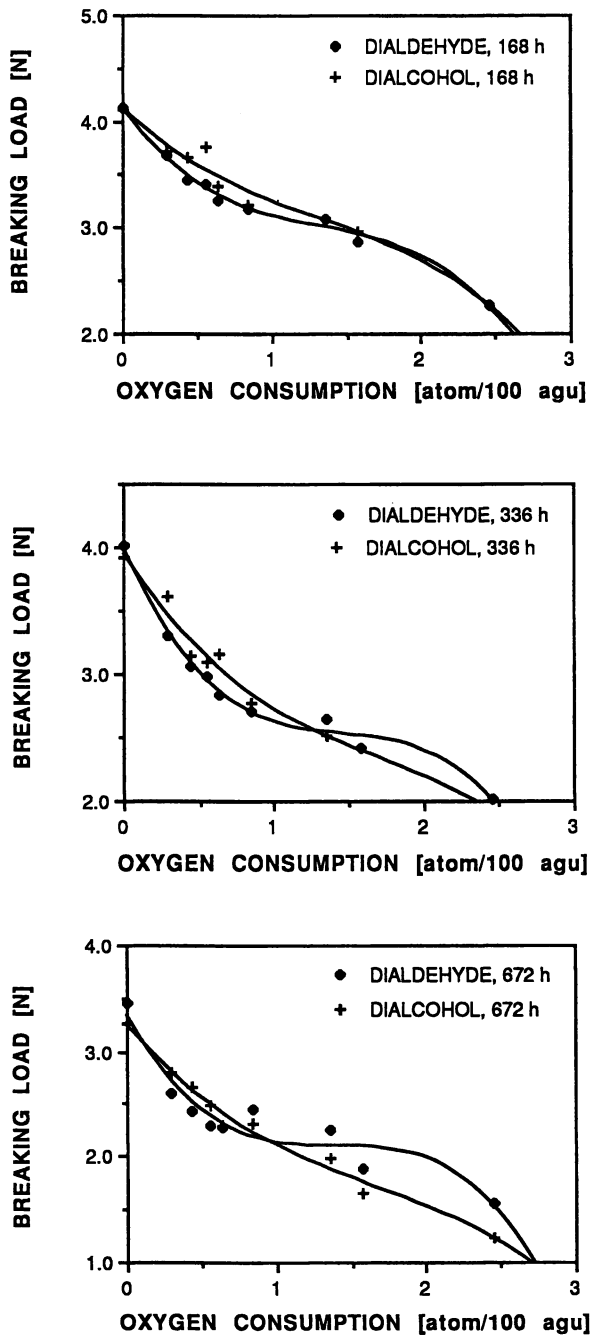


Figure 1. Breaking strengths of dialdehyde and dialcohol celluloses with increasing levels of oxidation and exposure duration.

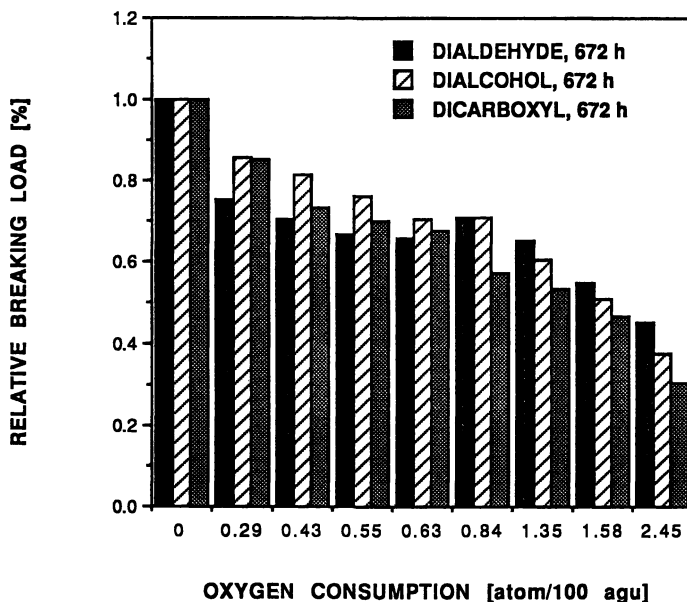


Figure 2. Relative breaking strengths of dialdehyde, dialcohol and dicarboxyl celluloses after irradiation for four weeks.

with the dicarboxyl cellulose might have been caused by autohydrolysis as well as photodegradation. Consequently the photodegradation of dicarboxyl cellulose needs to be studied further.

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Chapter 15

Inhibition of Light-Induced Yellowing of Lignin-Containing Paper

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Three methods of inhibiting the light-induced yellowing of lignin-containing paper have been proposed over the last 25 years. The first suggestion was the modification of lignin by alkylation or acylation of the phenolic hydroxyl group, alone or together with reduction of the aromatic carbonyl groups. This approach only stops about 30% of the total yellowing, because 70% of the yellowing proceeds through cleavage of the β -O-4-aryl ether group by the interaction of light-induced peroxy and alkoxy free-radicals. The second method of inhibiting the formation of yellow chromophores is impregnating the paper with uv absorbing compounds that can dissipate the light energy through energy-wasting keto-enol tautomerization. If all of the incident near-uv light is absorbed, all photochemical reactions are stopped. There is no formation of phenoxy free-radicals either by direct excitation of phenolic groups or by cleavage of the β -O-4-aryl ether group. The third method is quenching phenoxy free-radicals by impregnating the paper sheet with compounds that readily donate hydrogen. The types of free-radical scavengers used have been ascorbates, thiols, thioethers and formates. Although free-radical scavengers stop the oxidation of phenoxy radicals, they do not prevent cleavage of the β -O-4-aryl ether group.

Research on the inhibition of light-induced yellowing was initiated nearly 47 years ago (1), by determining the ability of a large variety of organic compounds to inhibit light-induced yellowing of lignin-containing paper including phenols, carboxylic acids and their esters and salts, amines, aldehydes, ketones, alcohols, carbohydrates and halogenated and nitrated hydrocarbons. No significant inhibition of yellowing was observed when any of these compounds were applied to paper made from groundwood. The progress of such research was hampered by a lack of knowledge of any of the reactions forming coloured chromophores.

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Modification of Functional Groups in Lignin

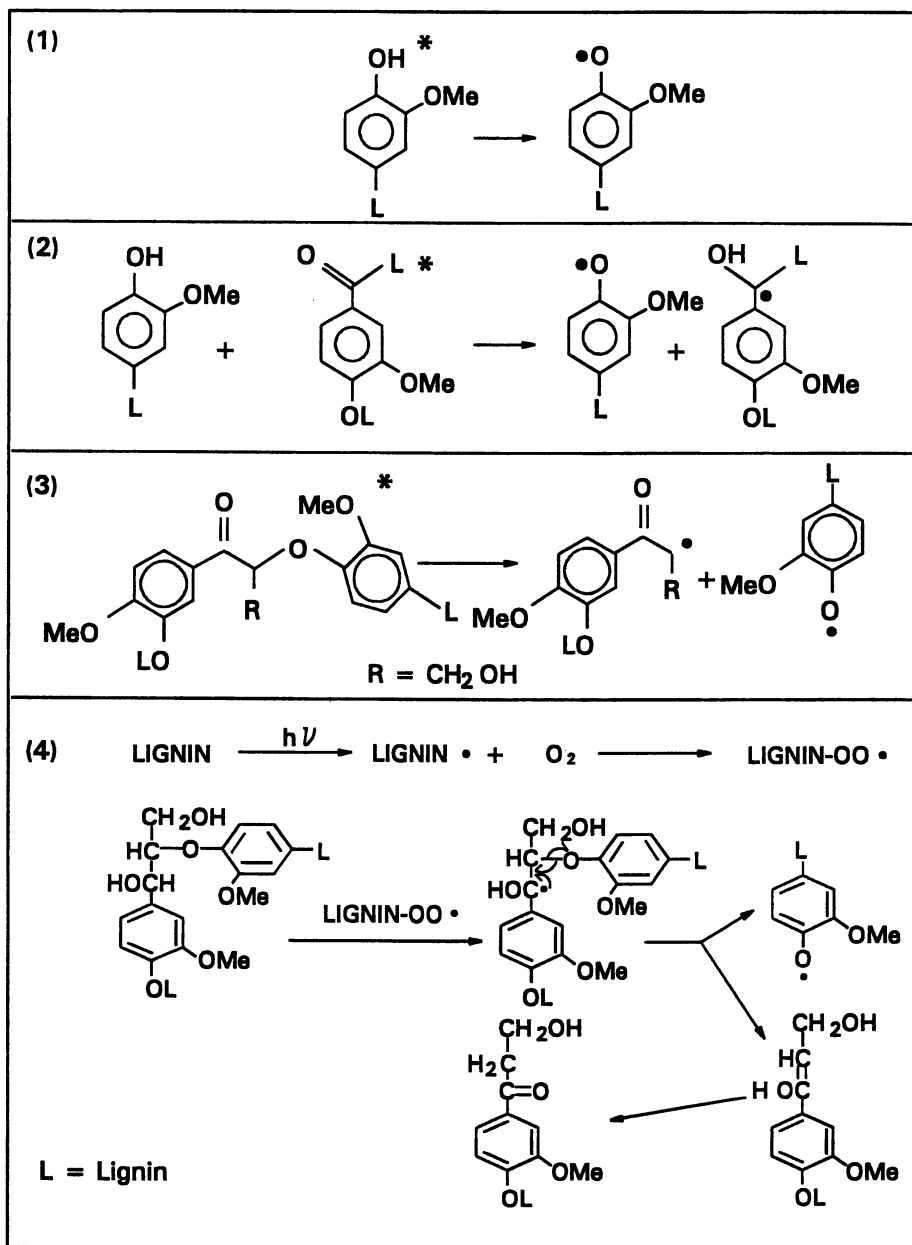
Subsequent efforts to inhibit photochemical yellowing of lignin-containing paper were based on what was believed to be the dominant reaction pathways to yellow chromophores: the formation of phenoxy free-radicals by direct excitation of phenolic groups and the abstraction of phenolic hydrogen by the aromatic carbonyl triplet excited state, as shown by reactions 1 and 2 in Scheme 1. The approaches used by researchers were modification of lignin by;

- etherifying or esterifying the phenolic hydroxyl groups,
- reduction of the aromatic carbonyl groups,
- combination of etherification of phenolic hydroxyl and reduction of carbonyl groups.
- hydrogenation of vinyl groups.

Etherifying and Esterifying the Phenolic Hydroxyl Groups. The objective of early research was to stabilize newsprint to uv irradiation by replacing phenolic hydroxyl hydrogen with alkyl or acyl groups. Singh (2,3) and Leary (4) were the first to observe the effects of etherification and esterification of phenolic hydroxyl groups on the rate and extent of light-induced yellowing of newsprint. Methylation and acetylation decreased the extent of yellowing, but did not appreciably affect the rate. Singh and Andrews (3) claimed that unbleached and bleached stone groundwood pulps that were methylated with dimethyl sulphate or benzoylated with benzoyl chloride had a lower degree of light-induced yellowing after 1 hour near-uv irradiation. Similar results were obtained by Francis *et al.* (5) and Schmidt and Heitner (6) for alkylation and benzoylation. Etherification of phenolic hydroxyl decreases the amount of light-induced yellowing, but there are other functional groups in lignin, such as phenacyl- α -O-4-aryl and the guaiacylglycerol- β -arylether groups, that give rise to phenoxy free-radicals that are oxidized to yellow chromophores.

Castellan *et al.* (7) found that etherification or esterification of bleached chemithermomechanical pulp in the presence of cationic phase transfer catalysts significantly decreased the degree of light-induced yellowing, compared to the same treatments without the phase transfer catalyst. However, the improved photostability of these pulps was accompanied by a catastrophic decrease in interfibre bonding. Apparently the addition of phase transfer catalysts increases the reactivity of the alkylating and esterifying agents so that they also react with cellulosic hydroxyl groups that contribute to interfibre bonding. If the etherification and esterification of cellulosic hydroxyl groups are being catalyzed by these phase transfer agents, then it is reasonable to propose that other non-phenolic hydroxyl groups, such as benzylic hydroxyl are also being replaced. This may slow down cleavage of the β -O-4-aryl bond of the guaiacylglycerol- β -arylether group, which could explain why phase transfer catalysis of methylation or acetylation is more efficient in inhibiting light-induced yellowing than the non-catalyzed treatment.

If both phenolic and benzylic hydroxyl hydrogens could be replaced without adversely affecting interfibre bonding, then it may be plausible to develop



Scheme 1

Four reaction pathways forming phenoxy radicals.

economical methods of etherification or esterification to inhibit the light-induced yellowing of bleached mechanical and ultra-high yield pulps.

Reduction of the Aromatic Carbonyl Groups. Carbonyl groups were recognized at the early stages of research on light-induced yellowing as a possible participant in the reactions leading to the formation of yellow chromophores. Two of the four reaction pathways proposed involve carbonyl excited states. The first is abstraction of phenolic hydrogen by the triplet state of a neighbouring carbonyl group and the second is cleavage of a phenacyl- α -O-4-aryl ether bond. Therefore, reduction of carbonyl groups with NaBH_4 should affect light-induced yellowing. The reduction of carbonyl groups in unbleached mechanical pulps appears to slow the rate of yellowing (4). Treatment of newsprint with NaBH_4 increased the time for complete yellowing from 500 to 1200 hours. The rate of light-induced yellowing of hydrogen peroxide bleached TMP reduced with NaBH_4 was the same as that of untreated bleached TMP (5,6,8). Apparently, light-induced of bleached TMP can occur without the participation of carbonyl groups.

Hydrogenation of Vinyl Groups. Lin and Kringstad (9) demonstrated that NaBH_4 reduction followed by heterogeneous catalytic hydrogenation stopped light-induced yellowing of methylcellulose solutions of milled wood lignin. However, Castellan *et al.* (10) found that NaBH_4 reduced MWL that was hydrogenated over a Pd/C catalyst yellowed significantly after near-uv irradiation in a hydroxypropylcellulose, film, in contrast to the results obtained by Lin and Kringstad (9). This difference may be due to one or a combination of factors that include the differences in media, methylcellulose solution *versus* hydroxypropylcellulose, differences in uv lamp and differences in species, spruce *versus* pine. Castellan *et al.* did find that catalytic hydrogenation of milled wood lignin that was bleached with H_2O_2 and reduced with NaBH_4 did decrease the amount of yellowing. Successful hydrogenation of lignin vinylic groups in thermomechanical pulp would require a homogeneous catalyst. Hydrogenation of vinyl groups with either a soluble, $\text{RhCl}(\text{PPh}_3)_3$, or a heterogeneous, Pd/C, catalyst did not decrease light-induced yellowing (11). Also, hydroboration and reaction with dimide were equally ineffective. However, the question arises regarding whether catalytic hydrogenation, hydroboration with diborane or reduction with dimide can efficiently reduce vinylic double bonds in the pulp fibre.

Etherification of Phenolic Hydroxyl and Reduction of Carbonyl Groups. The belief that carbonyl and phenolic hydroxyl groups play a direct role in light-induced yellowing has led to the strategy to stop light-induced yellowing by reducing carbonyl groups and etherifying phenols in lignin. Tchirner and Dence (5) found that NaBH_4 reduction followed by complete alkylation with dimethyl sulphate, propylene oxide or diazomethane completely stopped light-induced yellowing for 2 hours. This series of treatments has been proposed as 2 parts of a 3 stage process to inhibit light-induced yellowing (12). The 3 stage treatment is composed of reduction with NaBH_4 , followed by hydroxypropylation with propylene oxide. The

treated sheet is then coated with a fluorescent material. Paper thus treated showed a decrease in the extent of light-induced yellowing. Unfortunately, the time of exposure to near-uv light was not mentioned in this patent.

Although a combination of etherification of phenolic hydroxyl and reduction of carbonyl groups delays yellowing for up to 2 hours, there was no information on the effect of long term exposure of treated paper to uv light. Figure 1 shows the effect of reduction and methylation of bleached thermomechanical pulp on the change in specific absorption at 420 nm (13). Reduction and methylation delays the yellowing for 1.5 hours; results that are similar to those of Tchirner and Dence (5). However, after 1.5 hours of near-uv irradiation yellowing, as measured by Δk_{420} , increases at about the same rate as that for untreated paper. Cleavage of the β -O-4-aryl ether bond of the guaiacylglycerol- β -aryl ether group produces phenoxy free-radicals which in turn are oxidized to coloured chromophores. This means that reduction of carbonyl groups and the etherification of phenolic hydroxyl groups in lignin only delays yellowing for a short time. Successful inhibition of light-induced yellowing requires a method that will prevent cleavage of the β -O-4-aryl ether bond and oxidation of the phenoxy free-radical.

Addition of Inhibitors

Some of the earliest research on the inhibition of light-induced yellowing screened a large amount of inorganic and organic compounds that have been used to stabilize a wide variety of materials to light (1). This first research initiative was not successful in finding inhibitors of light-induced yellowing. The following section will describe various type of compounds added to paper that affect the degree and rate of yellowing caused by exposure to near-uv light.

UV Absorbers. Ultraviolet absorbers, compounds that absorb uv light and dissipate the light energy by a non-yellowing mechanism, have been used extensively to prevent light-induced degradation of a wide variety of polymers. It has been recognized during the early stages of research that these compounds, when added to the surface of paper, would decrease light-induced yellowing. The effect of uv absorbing additives on the light-induced yellowing of groundwood based paper was first reported by Nolan (14). Sheets treated with Eastman Ultraviolet Sensitizer required twice the amount of uv exposure as untreated sheets for a given decrease in brightness. Kringstad (15) found that the addition of 2-2'-dihydroxy-4-methoxy benzophenone or 2,2',4,4'-tetrahydroxybenzophenone to bleached groundwood-based paper decreased the light-induced yellowing. Similar results were obtained by Gellerstedt *et al.* (16) using 2,4-dihydroxybenzophenone and by Fournier de Violet *et al* (17) with a series of 2-hydroxybenzophenones. However, 93% stability required more than a 4% charge of uv absorber, an amount which was too expensive. These compounds absorb uv light and form the *o*-quinonemethide, which then dissipates the light energy as heat by tautomerizing to the starting material, as shown in Scheme 2.

Polymeric Inhibitors. Polyethylene glycol has been used to prevent light-induced yellowing of wood surfaces and of paper (18,19). The effectiveness of polyethylene glycol in inhibiting light-induced yellowing increased as its degree of polymerization was increased from 2 to 90 (20). Although the mechanism of polyethylene glycol inhibition of light-induced yellowing is not well understood, it has been suggested that this material inhibits yellowing by excluding air from the paper fibres (20).

Free-Radical Scavengers

All four reaction pathways of light induced yellowing, shown in Scheme 1, involve a series of free-radical reactions leading to a phenoxy free-radical (4,9,13,21-23). Also, it is seen in Scheme 3 that the phenoxy free-radical reacts with oxygen based alkyl radicals to form the coloured chromophore (25). The most successful methods to inhibit light-induced yellowing of lignin-containing papers were those that scavenged free-radicals. Ascorbates, thiols and thioethers all stabilize lignin in paper by quenching the phenoxy free-radical, the species that is oxidized by peroxy and alkoxy free-radicals.

Ascorbates. The fact that ascorbic acid and sodium ascorbate inhibit light-induced yellowing of lignin-containing papers was first reported 25 years ago (15). For a limited time ascorbic acid stops yellowing, but eventually yellowing proceeds at the same rate as the untreated paper (6,17), as seen in Figure 2.

The ability of ascorbates to inhibit light-induced yellowing may be understood if the relationship of this biological antioxidant to α -tocopherol is considered. Niki *et al.* (25) observed that α -tocopherol radical, generated by alkoxy radical, rapidly disappeared when mixed with ascorbic acid. The ESR spectrum of α -tocopherol radicals, generated in oxidized chicken fat, was replaced by the ESR spectrum of the ascorbyl palmitate radical after the addition of ascorbic acid palmitate (26). Thus, ascorbic acid reduces the phenoxy radical of α -tocopherol. Similarly, ascorbic acid reduces the phenoxy radicals in lignin-containing paper produced by exposure to near uv light. Bleached thermomechanical pulp irradiated with near-uv light exhibited a large ESR signal due to phenoxy radical. The addition of ascorbic acid caused a rapid decrease in the phenoxy radical ESR signal accompanied by the observation of a persistent ESR signal attributed to the ascorbyl radical (Wan, J.K.S., *et al.*, *J. Wood Chem. Technol.*, in press).

Ascorbic acid inhibits light-induced yellowing for a finite time, 1 to 2 hours when irradiated with near-uv light with an intensity of 9.2 mW/cm² (6). This limitation has been attributed in part to photooxidation of ascorbic acid. In addition to air oxidation, ascorbic acid is oxidized by photochemically produced peroxy radicals, superoxide radical anion and singlet oxygen (27,28). If ascorbic acid is to be an effective inhibitor of light-induced yellowing its oxidation must be slowed.

Agnemo (29) in his patent application describes the effect of treatment of bleached aspen chemithermomechanical pulp with ascorbic acid and sodium sulphite. Figure 3 is a plot of the specific absorption at 457 nm against the time of irradiation. It appears that relative to the initial specific absorption, adding Na₂SO₃ and ascorbic

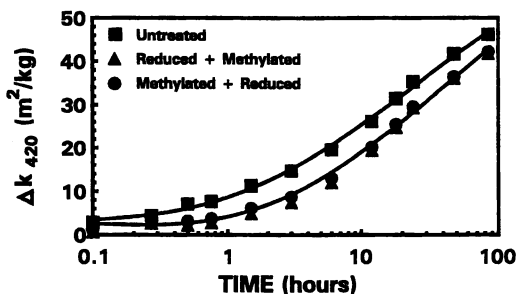
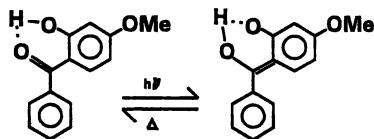
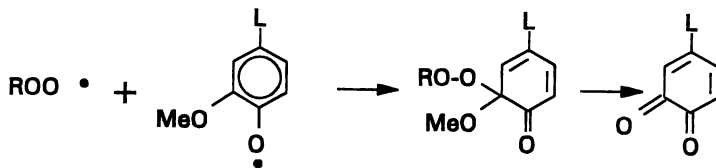


Figure 1. The combination of NaBH_4 reduction of aromatic carbonyl groups and methylation of phenolic hydroxyl groups delays light-induced yellowing for 1.5 hours (data obtained from reference 13).



Scheme 2

Light-induced tautomerization of the 2-hydroxybenzophenone chromophore.



Scheme 3

Oxidative demethoxylation of the phenoxy free-radical

acid to paper did not decrease light-induced yellowing anymore than did ascorbic acid alone. Addition of ascorbic acid to bleached aspen chemithermomechanical pulp increases the specific absorption from 0.85 to 1.41 m²/kg, while the addition of Na₂SO₃ and ascorbic acid does not increase initial light absorption. That is, Na₂SO₃ prevents yellowing caused by the addition of ascorbic acid. This patent application addresses rather short times of near-uv exposure, 9 hours.

Thiols. Aromatic thiols such mercaptobenzothiazoles, mercaptobenzimidazole, β -naphthylthiol, and alkyl thiols such as dodecylmercaptan have been used as effective stabilizers for a wide variety of polymers (30). The first example of the use of thiols to inhibit light-induced yellowing of lignin-containing papers was sodium thiopropionate (15). In a preliminary study, Janson and Forsskåhl (20) have shown that thiols are one of the more effective inhibitors of light-induced yellowing. An intensive study on the effect of impregnating groundwood paper with thiols, thioethers and their derivatives was recently completed (31). Cole, Sarkanen and Hooper found that there were 2 types of behaviour thiols exhibited when added to lignin-containing paper (31,32). When thiols were added to paper brightness increased. Similar results were obtained by Fournier de Violet (17). Adding glycol dimercaptoacetate CH₂CH₂(OOCCH₂SH)₂ to peroxide bleached cottonwood chemimechanical pulp and thioglycerol (HOCH₂CH(OH)CH₂SH) to peroxide bleached loblolly pine thermomechanical pulp increased the brightness by 3.5 (31) and 5 (32) percentage points respectively. Kutney (33) found that certain dithiols and mercaptoacids were effective bleaching agents of mechanical pulps. This effect has been attributed to Michael type addition of thiol to α - β unsaturated ketones and quinones, as seen in Scheme 4. Lee and Sumimoto have isolated Michael-addition products from 3,4-dimethoxy stilbene-*p*-quinone irradiated in the presence of thioglycerol (34).

In addition to the bleaching, both glycol dimercaptoacetate and thioglycerol inhibit light-induced yellowing of lignin-containing papers (17,31). It appears that the ability of thiols to inhibit light-induced yellowing is associated with the propensity to bleach ultra-high yield pulps. It was found that the effectiveness of the inhibitor depends on the molecular structure and size. For example, the esters of thiocarboxylic acids were better inhibitors of light-induced yellowing than the acid analogues (17,31,32). Bleached cottonwood chemimechanical pulp treated with glycol dimercaptoacetate lost 2.6 percentage points of brightness after 15 days irradiation *versus* 12.4 percentage points for pulp treated with thioglycolic acid. The effectiveness of thiocarboxylate esters depends on the location of the thiol group in the molecule relative to that of the carboxylate group. Thiol groups in the α position to the carboxylate group are far more effective in inhibiting yellowing than the same thiol group located β to the carboxylate group. That is, bleached cottonwood chemimechanical pulp treated with glycol dimercaptoacetate did not lose brightness after 5 days irradiation whereas glycol dimercaptopropionate CH₂CH₂(OOCCH₂CH₂SH)₂ lost 5.8 percentage points. Also, the molecular dimensions are an important factor in the inhibition of yellowing. Polyethylene glycol dimercaptoacetate does not inhibit light-induced yellowing of bleached cottonwood chemimechanical pulp;

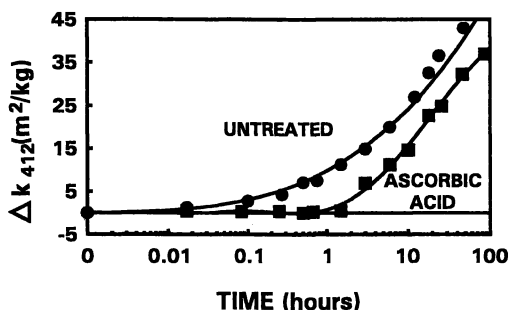


Figure 2. The addition of a 5% charge of ascorbic acid delays light-induced yellowing for 2 hours (data obtained from reference 6).

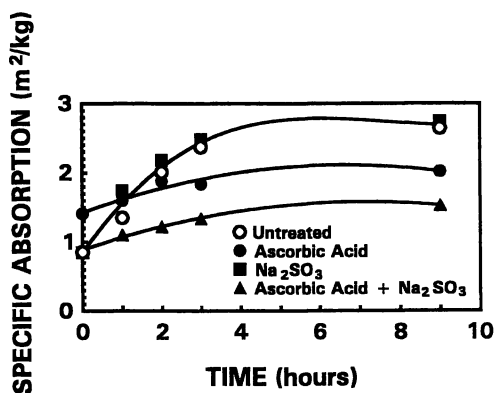
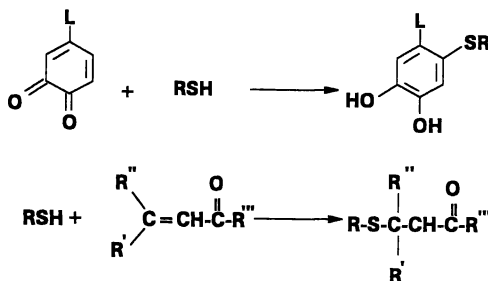


Figure 3. The rate and extent of light-induced yellowing is the same for paper impregnated with ascorbic acid or sodium sulphite plus ascorbic acid. The sodium sulphite prevents darkening caused by the application of ascorbic acid alone (data from reference 29).



Scheme 4

Michael-type addition of thiols to *o*-quinone and α,β -unsaturated ketones

whereas the monomeric analogue, glycol dimercaptoacetate, is a very efficient inhibitor of yellowing (32).

Until recently, the mechanism of the inhibition of light-induced yellowing was subject to speculation. However, solid state ESR and CIDEP have provided insight into the mode of inhibition by thiols (Wan, J.K.S., *et al.*, *J. Wood Chem. Technol.*, in press). Near-uv irradiation of unbleached and peroxide bleached thermomechanical pulp impregnated with thiols caused a rapid increase of the thiol radicals. The time resolved CIDEP spectrum, however, shows a symmetric broad band characteristic of the polarized phenoxy radical. This result suggests that thiols quench triplet generated phenoxy radicals in a secondary thermal process.

Thioethers. S-methyl-1-thioglycerol ($\text{CH}_3\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$), unlike its parent thioglycerol, does not bleach mechanical pulp, but retains the ability to inhibit light-induced yellowing (33). It is believed that the methylene hydrogens α to the electron donating sulphide group in S-methyl-1-thioglycerol are readily abstracted by the phenoxy radicals. Thioethers of thiocarboxylic acids such as methylthioacetic acid in which the sulphide group is α to the carboxylic acid group are effective inhibitors of light-induced yellowing (17). If the sulphide group is β to the carboxylic acid group, as in dilauryl thiopropionate, the thioether does not inhibit yellowing (32). These results can be explained by invoking activated methylene hydrogen atoms. The electron donating sulphide group and the electron withdrawing carboxylic acid group combine to improve on the hydrogen donor character of thioethers of thiocarboxylic acids.

Formates. Another type of hydrogen donating group, formate has been proposed as an inhibitor of light-induced yellowing (35). Sodium formate together with a trace amount (80 ppm) of Cu^{++} or 0.1% ascorbic acid decreased light-induced yellowing by 67% and 50% respectively. The stated purpose of adding ascorbic acid and Cu^{++} was to quench the superoxide radical anion.

Summary

There are four modes of inhibiting light-induced yellowing of lignin-containing paper, chemical modification of lignin by alkylation of the phenolic hydroxyl group, reduction of aromatic carbonyl group and hydrogenation of the vinylic $\text{C}=\text{C}$, blocking near-uv light with uv absorbing compounds that dissipate the energy of light by the energy wasting keto-enol tautomerization or quenching the phenoxy free-radical with a hydrogen donating compound. Chemical modification only partially stops the yellowing, because about 70% of the light-induced yellowing proceeds through cleavage of the guaiacylglycerol- β -O-4-guaiacyl ether. Blocking the uv light stops the photochemical process at the first stage; cleavage of the β -O-4-aryl ether bond does not take place. However, as stated earlier these uv blocking agents are too costly. The use of ascorbic acid, thiols, thioethers and formates to quench the phenoxy free-radical does not prevent photodegradation of the lignin macromolecule via cleavage of the β -O-4-aryl ether bond.

Stability of lignin-containing paper to near-uv light could be improved if phenoxy-radical quenchers are combined with compounds that will prevent cleavage of the β -O-4-aryl ether bond. Detailed knowledge of the mechanism governing the inhibition of light-induced yellowing by various reagents is essential if an economical method to maintain pulp brightness and whiteness is to be developed. As mentioned in this review, some progress has been made in the understanding of the molecular processes that prevent the formation of yellow chromophores

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Chapter 16

Effect of Chemical Modification with Polyethylene Glycol on the Brightness Stability of Lignin Model Compounds and High-Yield Pulp

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Phenolic hydroxyl groups in lignin model compounds, organosolv lignin, and bleached chemithermomechanical pulp (BCTMP) were blocked by etherification with polyethylene glycol (PEG). Blockage of free phenolic hydroxyl groups in hardwood BCTMP and the lignin dimer model compound, dehydrodiisoeugenol, significantly inhibited light-induced yellowing.

Currently, high-yield pulps are used for newsprint and magazine papers, but they cannot be used in higher quality papers for two major reasons: (1) high-yield pulps undergo photo-induced discoloration (yellowing), and (2) papers produced from high-yield pulps are not as strong as those made from chemical pulps. Unfortunately, today's market demands pulps and papers of increasingly high strength and long-lasting brightness, which severely limits the use of high-yield pulps.

For over fifty years, researchers have attempted to elucidate the mechanisms responsible for photo-induced color reversion of papers. Although complete and indisputable mechanisms remain elusive, it is generally accepted that photooxidation of lignin, resulting in the formation of phenoxyl free radicals, is primarily responsible for yellowing. The role of free phenolic hydroxyl groups has been demonstrated in numerous studies (1-11). When free phenolic hydroxyl groups are eliminated by methylation with dimethyl sulfate and alkali (10-13), acetylation (10, 12, 14) or benzylation (10), intermediate phenoxy radicals cannot be formed and the rate of photo-induced yellowing is inhibited significantly. The problem is that these treatments do not selectively modify the lignin phenolic positions. Thus, large amounts of chemicals are required and the pulps produced have reduced strength properties because hydrogen-bonding hydroxyl groups in cellulose are derivatized also. Selective reaction of phenolic hydroxyl groups is possible, however, since careful control of pH allows ionization of the relatively acidic phenolic hydroxyl groups ($pK_a \sim 10-11$) to form phenoxide ions, while aliphatic hydroxyls ($pK_a \sim 12-13$) are not ionized (15). Selective modification of lignin phenolic hydroxyl groups has been demonstrated in several studies (15-18).

The strength of a particular pulp, or the paper produced from it, depends largely on the chemical and physical characteristics of the fibers making up that pulp. High-yield fibers are stiff, rod-like structures that do not collapse to give large bonding areas

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(19). In addition, the fibers produced in high-yield processes tend to be coated with lignin, and contain large amounts of lignin internally (20). Because lignin is comparatively hydrophobic, interfiber hydrogen bonding is greatly diminished. Therefore, the tensile strength of high-yield pulps is much lower than that of chemical pulps. Based on these known characteristics, it can be postulated that selective derivatization of phenolic hydroxyl groups in lignin with hydrophilic materials will increase brightness stabilization as well as improve strength properties in high-yield pulps.

Modified polyethylene glycols (PEG) or oligoethylene glycols (OEG) are compounds potentially capable of providing both effects. Polyethylene glycol (I) is an inexpensive material produced commercially in a wide range of molecular weights. PEG is remarkably hydrophilic and even at relatively high molecular weights is water-soluble. PEG is easily derivatized since the alcohol end groups are much more reactive than the polyoxyethylene chain (21). These characteristics make PEG an ideal material to react with lignin in high-yield pulps. In a brief investigation, Fredholm and coworkers (16, 17) treated the mesyl and epoxide derivatives of oligoethylene glycols with lignin model compounds, ball-milled lignin, and TMP. With the latter, moderate increases in pulp strength were observed.



Results and Discussion

Proposed Reactions. Under alkaline conditions, etherification of phenolic hydroxyl groups proceeds via an $\text{S}_{\text{N}}2$ mechanism. The phenoxide ion is a strong nucleophile that reacts with compounds possessing good leaving groups. This reaction sequence, written specifically for the substrates used in this study, is shown in Figure 1.

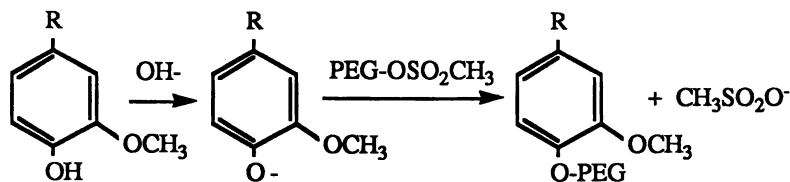


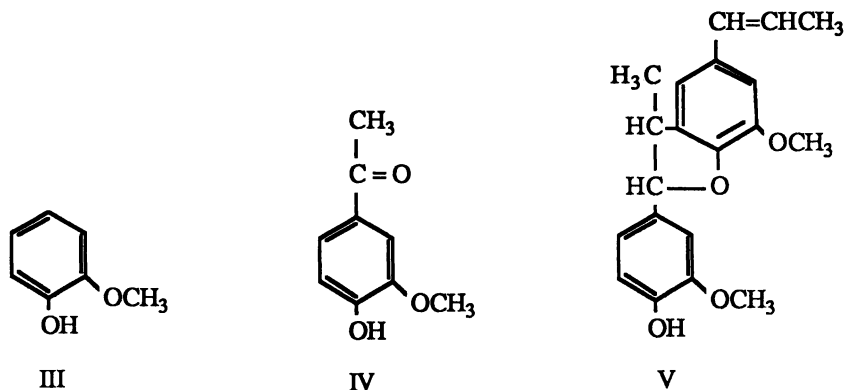
Figure 1. The reaction of PEG-mesylate with lignin and lignin model compounds.

Polyethylene Glycol Derivatives. To react with phenolic groups in models or in lignin, polyethylene glycol must be derivatized to provide reactive functional sites. In this study, the mesyl derivative of PEG methyl ether (II) was used. PEG methyl ether, in which one hydroxyl group is blocked by a methyl group, was chosen as the starting material to facilitate product separation and analysis and to avoid crosslinking reactions. PEG-mesylate is known to be exceptionally stable and the mesylate group has high reactivity in $\text{S}_{\text{N}}2$ reactions (22). In addition, low molecular weight PEG-mesylates are soluble in water and in various organic solvents. In this study, yields of

approximately 90% were obtained when PEG methyl ether (MW 350) was reacted with methanesulfonyl chloride using triethylamine as a catalyst.



Model Compound Studies. To optimize reaction conditions and gain information to aid in the interpretation of modified lignin and pulp results, it is essential to conduct model compound studies. PEG-mesylate (II) was reacted with guaiacol (III), acetoguaiacone (IV), and dehydrodiisoeugenol (V). Dehydrodiisoeugenol, which contains a phenylcoumaran structure, was selected as the dimer model because it is easily prepared in large quantities and the NMR spectra are well resolved and easily interpreted. Phenylcoumaran units are important structural segments of lignin that are believed to play a major role in yellowing of high-yield pulps (13, 23).



Initial studies with guaiacol indicated that a minimum pH of 12.6 was required to form an acceptable yield of PEG-modified product at ambient pressure and 80°C. At lower pH and temperatures, little product was obtained. Etherification of guaiacol, acetoguaiacone, and dehydrodiisoeugenol with II at pH=12.6 gave yields of 80%, 64%, and 82%, respectively. The etherification products were identified using ^1H -nmr and ^{13}C -nmr. Characteristic peaks at 3.1 and 4.4 ppm in the ^1H -nmr spectrum of PEG-mesylate disappeared in the modified models, while a new signal appeared at 4.2 ppm, verifying the formation of the ether. In addition to the appearance and disappearance of signals, shifts of the ring carbon signals were clearly evident in the ^{13}C -nmr spectra following modification of the models. Details of the NMR spectra are provided in the Experimental section of this paper.

We also verified PEG etherification of all three model compounds using simple solubility tests. Guaiacol, acetoguaiacone, and dehydrodiisoeugenol have limited solubilities in water while the PEG-modified products were completely water-soluble. This observation not only confirms the existence of a chemical bond between PEG and the models, but it also gives support to the concept that attachment of PEG to lignin in pulp will increase its hydrophilicity.

Lignin Studies. The chloroform-soluble fraction of an organosolv lignin obtained by methanol water pulping of black cottonwood was utilized in this study. Lignin was reacted with PEG-mesylate under conditions similar to those used in the model compound studies. After purification, the PEG-modified lignin was characterized using ^1H -nmr, ^{13}C -nmr, solubility properties, and phenolic hydroxyl content measurement. In the ^1H -nmr spectrum of the product, signals at 3.36 ppm ($-\text{OCH}_3$ endcap in PEG), 3.5 ppm (ethylene hydrogens in PEG) and 3.73 ppm ($-\text{OCH}_3$ in lignin), and the lack of a signal at 3.08 ppm ($-\text{OSO}_2\text{CH}_3$), provided evidence for the presence of a PEG-modified lignin. Similarly, in the ^{13}C -nmr spectrum, signals derived from PEG (57.9 ppm, OCH_3 endcap; 69.7, ethylene carbons) and lignin (55.8 ppm, OCH_3) were observed and the peak at 36.7 ppm for the mesylate methyl carbon was not present. Further indication of etherification of lignin with PEG was provided by the observed differences in solubilities between lignin and lignin-PEG. While the chloroform-soluble fraction of the organosolv lignin was completely insoluble in water, the PEG-modified lignin was fully water-soluble.

The Effect of PEG on Brightness Stabilization. Using BCTMP and the dimer model compound, dehydrodiisoeugenol, we investigated the effects of PEG modification on brightness and brightness stabilization. Solutions of known concentration (0.03 M) of dehydrodiisoeugenol (dimer) and dehydrodiisoeugenol-PEG (dimer-PEG) were adsorbed onto lignin-free filter papers. ISO brightness was measured for the treated sheets which were subjected subsequently to ultraviolet irradiation in a Rayonet photoreactor for 8 hours. Brightness was measured several times during the irradiation period. The results of these experiments are shown in Figure 2. The initial brightness of the dimer-PEG treated sheet was lower than that of the dimer treated sheet probably due to absorbing impurities in the dimer-PEG. Ultraviolet-visible spectroscopy of 2.5×10^{-3} M solutions of dimer and dimer-PEG supported this explanation. The dimer solution did not absorb appreciably between 380-450 nm while the solution containing dimer-PEG had a significant absorbance in this region. It can be seen, however, that PEG-modification inhibited brightness reversion of the dimer significantly. The brightness of the sheet treated with dimer alone dropped very quickly from 77.6% to 53.6% in the first two hours of irradiation and then continued to drop more slowly until a final brightness of 50.9% was obtained after 8 hours. The brightness of the dimer-PEG treated sheet lost only 4 units of brightness, 72.8% to 66.8%, in the first two hours and then stabilized at a brightness of 65.7% for the remainder of the 8 hour irradiation period. Thus, while the unmodified dimer lost 26.7 units of brightness overall, dimer that had been modified with PEG lost only 7.1 units.

Small handsheets prepared from chelated, sodium borohydride reduced, and PEG-modified aspen BCTMP, were irradiated with ultraviolet light for 8 hours in a Rayonet photoreactor. The ISO brightness of these samples was measured before irradiation and after 1, 2, 4, and 8 hours. The results of this study are shown in Figure 3. As expected, the brightness of the pulp chelated with a dilute solution of diethylenetriaminepentaacetic acid (DTPA) dropped significantly, from 80.1% to 53.8%, during the irradiation period. Pulp that was chelated and subsequently reduced with sodium borohydride demonstrated brightness stability greater than that of chelated pulp, although the original brightness (76.7) of this pulp was somewhat lower. It is possible that the high alkalinity during reduction caused a decrease in the specific scattering coefficient of the reduced pulp resulting in a lower initial brightness. The overall brightness loss in the reduced sample was 16.6%. This observation is consistent with results obtained by Castellan and coworkers (24).

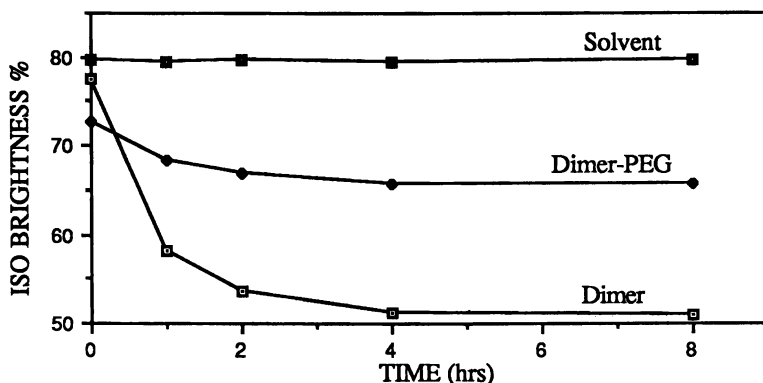


Figure 2. The effect of PEG-modification on the lignin model compound, dehydrodiisoeugenol (dimer). Solvent = acetonitrile, $t = 0$ is the brightness recorded immediately after adsorption of compound on filter paper. The brightness of untreated filter paper is 80.1%. (Cole, B.J.W.; Huth, S.P.; Runnels, P.S., *J. Wood Chem. Technol.*, in press.)

Brightness stability was enhanced further by reaction of the previously chelated and reduced pulp with PEG-mesylate. While the PEG treatment lowered the initial pulp brightness (74.3%) to a greater degree than the borohydride treatment, the final brightness (64.1%) of the PEG-treated pulp was higher after 8 hours of irradiation. The overall brightness loss of the PEG-modified sample was 10.2%. Thus, brightness reversion of BCTMP was retarded significantly by modification with PEG. We believe, however, that more extensive blockage of free phenolic hydroxyl groups will be required to completely inhibit the photo-induced yellowing of this pulp.

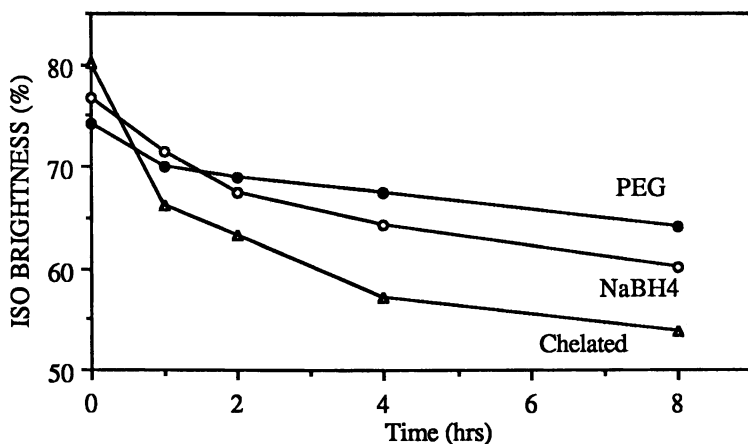


Figure 3. The effect of PEG modification on the brightness and brightness stability of aspen bleached CTMP. (Δ) - chelated BCTMP; (o) - BCTMP + DTPA + NaBH₄; (\bullet) - BCTMP + DTPA + NaBH₄ + PEG.

Experimental

General Experimental Procedures. ^1H -nmr and ^{13}C -nmr spectra were recorded on a Varian XL-200 spectrometer. ^1H -nmr spectra were obtained in CDCl_3 , and ^{13}C -nmr spectra in $\text{DMSO}-d_6$.

Model Compounds, Lignin, and Pulp. Compound III (guaiacol) was purchased from Aldrich Chemical Company, Inc. ^1H -nmr: 3.89 ($-\text{OCH}_3$), 5.59 ($-\text{OH}$); ^{13}C -nmr: 145.85 ($\underline{\text{C}}-\text{OH}$), 146.94 ($\underline{\text{C}}-\text{OCH}_3$).

Compound IV (acetoguaiacone) was purchased from Aldrich. ^1H -nmr: 3.96 ($-\text{OCH}_3$), 6.08 ($-\text{OH}$); ^{13}C -nmr: 146.72 ($\underline{\text{C}}-\text{OH}$), 150.94 ($\underline{\text{C}}-\text{OCH}_3$).

Compound V (dehydrodiisoeugenol) was synthesized according to the method of Leopold (25). Isoeugenol (5.0 g, purchased from Aldrich) was dissolved in 45 mL of ethanol (95%) and 20 mL of water. To this solution was added 7.0 g of ferric chloride in 20 mL of water. The solution, which turned dark green and cloudy, was refrigerated for at least 24 hours. The reddish white crystalline solid which formed was collected by vacuum filtration and washed with 45% ethanol. The resulting product (yield = 30%) had a melting point of 132-133 °C which is in agreement with that reported in the literature (25). The ^1H -nmr spectrum was identical to that reported in The Handbook of Proton-NMR Spectra and Data (26). The phenolic hydroxyl proton was observed at 5.62 ppm. ^{13}C -nmr spectral data coincided with that in the literature (27). The carbon adjacent to the phenolic hydroxyl was observed at 145.5 ppm.

Organosolv lignin was isolated from black cottonwood (*P. trichocarpa*) which had been pulped using a methanol/water (70/30) solvent system with NaHSO_4 as a catalyst (28). The chloroform-soluble fraction of this lignin was utilized in this study. ^1H -nmr: broad peaks were observed at 3.7 and 6.7 ppm; ^{13}C -nmr: 55.9 ($-\text{OCH}_3$), and other typical lignin peaks were observed from 103 ppm to 152 ppm.

Peroxide-bleached, chemithermomechanical aspen pulp (BCTMP), prepared by Tembec of Quebec, was used in this study. Prior to chemical modification, the pulp was diluted to 1.5% consistency and stirred for approximately 15 minutes at room temperature with diethylenetriaminepentaacetic acid (0.5% of o.d. pulp) to complex undesirable heavy metal ions. The chelated pulp was washed thoroughly with distilled water and reduced subsequently with sodium borohydride. The method used for reduction was similar to that of Castellan and coworkers (24). The pulp was diluted to 3% consistency and homogenized for 5 minutes with sodium borohydride (40% based on o.d. pulp). The mixture was transferred to glass containers and was shaken frequently over a 6 hour period at room temperature. The reduced pulp was washed with distilled water until a neutral pH was reached.

PEG Compounds. Compound I (PEG methyl ether, MW 350) was purchased from Aldrich Chemical Company. ^1H -nmr: 3.38 ($-\text{OCH}_3$), 3.65 ($-\text{OCH}_2\text{CH}_2\text{O}-$); ^{13}C -nmr: 59.47 ($-\text{OCH}_3$), 69.04 ($-\text{OCH}_2\text{CH}_2\text{O}-$).

Compound II (PEG-mesylate) was synthesized according to the method of Harris and coworkers (22). Methanesulfonyl chloride (0.39 mL, 5 mmol), in 60 mL of

methylene chloride was mixed at 0°C with 0.35 g (1 mmol) of PEG methyl ether (MW 350) and 0.28 mL (2 mmol) of triethylamine dissolved in 60 mL of methylene chloride. The reaction mixture was stirred for 2 hrs at 0°C. Excess ammonium salt was precipitated by the addition of ether (twice) and ethyl acetate (once), and removed by filtration. The viscous liquid which remained was purified by passage through a cation exchange column (Dowex 50W-X8, 20-50 mesh, hydrogen form). The sample was dissolved in a small amount of water or methanol and passed through the column using water as the solvent. The PEG-mesylate was extracted from the water phase with methylene chloride at least twice, and evaporated. An anion exchange column (Dowex 2-X8, 20-50 mesh, chloride form), converted to the hydroxide form with NaOH, was used for further purification. The sample was again dissolved in water and passed through the anion column using water as the solvent. The purified PEG-mesylate was extracted from the water phase with methylene chloride and evaporated. $^1\text{H-nmr}$: 3.08 (-OSO₂CH₃), 3.38 (-OCH₃), 3.65 (-OCH₂CH₂O-), 4.38 (-CH₂CH₂OSO₂CH₃); $^{13}\text{C-nmr}$: 36.7 (-OSO₂CH₃), 57.93 (-OCH₃), 69.63 (-OCH₂CH₂O-).

Guaiacol-PEG was synthesized using a method similar to that of Fredholm and coworkers (16). A 20% aqueous dioxane solution of 0.4 M NaOH was prepared. To 4 mL of this solution, guaiacol (0.154 mL) and PEG-mesylate (0.3424 g) were added. NaOH (0.4 M) was added dropwise until a pH = 12.6 was obtained. The solution was stirred at 80°C for 24 hrs. The product was extracted from the aqueous phase with methylene chloride and the organic phase evaporated. The NMR spectrum of the viscous liquid showed a mixture of guaiacol and guaiacol-PEG. Column chromatography with silica gel (230-400 mesh) and an ethyl acetate/methanol gradient, was used for the separation. Pure guaiacol-PEG was obtained in 80% yield. $^1\text{H-nmr}$: 3.35 (-OCH₃ from PEG), 3.63 (-OCH₂CH₂O- from PEG), 3.83 (-OCH₃ from guaiacol), 4.2 (-CH₂CH₂-O-Ø); $^{13}\text{C-nmr}$: 59.46 (-OCH₃ from PEG), 69.17 (-OCH₂CH₂O- from PEG), 147.26 (C-OPEG), 148.34 (C-OCH₃ from guaiacol).

Acetoguaiacone-PEG was prepared according to the procedure described for guaiacol-PEG except that 0.231 g of acetoguaiacone was treated in a 20% dioxane solution of 0.25 M NaOH with a pH of 10.4. A silica gel column, as described above, was used for isolation of acetoguaiacone-PEG. Pure acetoguaiacone-PEG was obtained in 64% yield. $^1\text{H-nmr}$: 3.38 (-OCH₃ from PEG), 3.65 (-OCH₂CH₂O- from PEG), 3.91 (-OCH₃ from acetoguaiacone), 4.25 (-CH₂CH₂-O-Ø); $^{13}\text{C-nmr}$: 59.47 (-OCH₃ from PEG), 69.04 (-OCH₂CH₂O- from PEG), 147.88 (C-OPEG), 151.55 (C-OCH₃ from acetoguaiacone).

Dehydrodiisoeugenol-PEG was prepared as described above for guaiacol-PEG. Dehydrodiisoeugenol (0.457 g) was used in the reaction. Column chromatography with silica gel (230-400 mesh) and a methylene chloride/ethyl acetate/methanol gradient was used for the isolation of the product. Pure dehydrodiisoeugenol-PEG was obtained in 82% yield. $^1\text{H-nmr}$: 3.37 (-OCH₃ from PEG), 3.65 (-OCH₂CH₂O- from PEG), 4.2 (-CH₂CH₂-O-Ø); $^{13}\text{C-nmr}$: 68.8 (-OCH₂CH₂O- from PEG), 145.32 (C-OPEG).

Organosolv lignin-PEG was synthesized using a procedure similar to that used for the lignin model compounds. A 20% dioxane solution of 0.4 M NaOH was prepared. To 6 mL of this solution, 0.6 g of the chloroform soluble fraction of organosolv lignin

and 0.488 g of PEG-mesylate were added. NaOH (0.4 M) was added dropwise until pH=12.6 was reached. The solution was stirred at 80°C for 24 hrs. Extraction with methylene chloride gave a viscous black material. The product was washed with several portions of ether to remove excess PEG-mesylate, and was filtered through a sintered glass funnel. The remaining light brown powder weighed 0.370 g. $^1\text{H-nmr}$: 3.36 (-OCH₃ from PEG), 3.5 (-OCH₂CH₂O- from PEG), 3.73 (-OCH₃ from lignin); $^{13}\text{C-nmr}$: in addition to the typical peaks observed for lignin, such as -OCH₃ at 55.8 ppm, PEG peaks were seen at 57.9 (-OCH₃) and 69.72 (-OCH₂CH₂O-).

BCTMP-PEG was prepared by diluting 1.6 g (o.d.) of pulp, that had been chelated and reduced with borohydride previously, to 1.5% consistency. NaOH (2M) was added until a pH=12.6 was reached. Dioxane (20% based on total weight) and 0.38 g of PEG-mesylate were added and the mixture was stirred at 80°C for 24 hours. The alkaline solution was removed by filtration. The remaining pulp was homogenized with 0.01 M HCl and washed thoroughly with distilled water.

Brightness Reversion Study. Solutions of dehydrodiisoeugenol (0.033 M) and dehydrodiisoeugenol-PEG (0.036 M) were prepared using acetonitrile as the solvent. A 100- μL aliquot of each solution was carefully adsorbed onto a 4.25 cm Whatman filter paper. The sheets were air dried and brightness values were measured using a Technibrite brightness meter. The sheets were irradiated in a Rayonet RPR-100 merry-go-round photochemical reactor (Southern New England Ultraviolet Co., Branford, CT). Sunlight phosphor lamps providing 21 W of energy and a maximum output of 300 nm were used. The brightness of each handsheet was determined after 1, 2, 4, and 8 hours of irradiation.

BCTMP handsheets were prepared by passing an aqueous slurry containing 0.13 g o.d. pulp through a 4.25 cm Buchner funnel fitted with a piece of filter paper. The handsheets were pressed and air dried. The sheets were irradiated in a Rayonet RPR-100 merry-go-round photochemical reactor. Blacklight phosphor lamps providing 24 W of energy and a maximum output of 350 nm were used. The brightness of each handsheet was measured with a Technibrite brightness meter before irradiation and after 1, 2, 4, and 8 hours of irradiation.

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