

**ASSIGNMENT OF THE PHOTOYELLOWING-RELATED 1675  $\text{cm}^{-1}$  RAMAN/IR BAND TO p-QUINONES AND ITS IMPLICATIONS TO THE MECHANISM OF COLOR REVERSION IN MECHANICAL PULPS**

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**ABSTRACT**

Using FT (Fourier-transform) Raman and FT infrared (IR) spectroscopies, a new band was detected at 1675  $\text{cm}^{-1}$ ; this was most likely to have come from the yellow chromophores in photoexposed thermomechanical pulps (TMPs). On the basis of spectroscopic studies that involved both o- and p-quinone models and Fremy's salt-oxidized TMP, the 1675  $\text{cm}^{-1}$  band is assigned to the p-quinone functional group. Moreover, in the presence of known photoyellowing inhibitors, the photoyellowing behavior of methyl hydroquinone was similar to that of TMPs. Another important finding was that the molecular oxygen sensitivity of the laser-induced fluorescence (excited at 514.5 nm) of p-quinone and hydroquinone models was similar to what had been previously observed for yellowed and unyellowed TMPs. Taken together, these results provide strong support for a previously suggested yellowing hypothesis in which a hydroquinone/p-quinone couple was seen as an important leucochromophore/chromophore system in mechanical pulps.

**Keywords:** Photoyellowing, mechanical pulps, lignin, Raman, quinones

**INTRODUCTION**

Finding a practical solution to the problem of photoyellowing of lignin-rich mechanical pulps continues to be a challenging area of research. Of the many proposed approaches to deal with the yellowing problem, no single one is suited to the needs of the

paper industry.<sup>1</sup> However, it is expected that better solutions will be developed when the yellowing mechanism is fully understood. Attaining such a level of understanding is difficult and requires that additional progress be made in a number of areas. For instance, the nature of important yellowness-causing chromophores needs to be determined, the identity of initiating structures that lead to coloration needs to be established beyond a reasonable doubt, and photoyellowing reaction pathways should be established. Although significant progress has been made in these areas, the current knowledge base is not sufficient to allow development of a practical solution.

Research in this area is also important from the viewpoint of sustainability of forests because enhanced use of mechanical pulps would allow more efficient use of the wood resource. In addition, the impact of pulp-producing processes on the environment would be diminished.

Recently published research by the author<sup>2</sup> on spruce thermomechanical pulps (TMPs) indicated that  $\alpha$ -carbonyl and aromatic ring-conjugated ethylenic groups are not the initiators of events that lead to photoyellowing. This result is contrary to the reported observation of some researchers that stilbene derivatives are one of the important contributors to photoyellowing.<sup>3</sup> In author's laboratory, attempts made to detect stilbene derivatives in borohydride-bleached TMP and its acid hydrolysate using Raman spectroscopy (a technique highly sensitive for detecting stilbene structures) were not successful.<sup>4</sup> Failure to detect stilbenes provided further support to the conclusion that aromatic ring-conjugated ethylenic bonds are not important contributors to photoyellowing.

In addition, in the author's reported work<sup>2</sup>, for the first time a Raman and IR band at approximately  $1675\text{ cm}^{-1}$  was detected and linked to photoyellowing. The present report describes research on this topic and shows how the assignment of the  $1675\text{ cm}^{-1}$  band, together with some other evidence, has important implications for the mechanism of photoyellowing.

## EXPERIMENTAL

### Wood

Black spruce (*Picea mariana*) and aspen (*Populus tremuloides*) were obtained and 30-micron-thick cross sections were produced using a microtome. The sections were

treated with toluene/ethanol (2/1) to remove extractives. Extracted tissues were air dried and used in the laser-induced fluorescence (LIF) quenching experiments. Several wood sections were treated with acid chlorite<sup>5</sup> to remove lignin.

### Pulp

Commercial spruce TMP was a gift from Consolidated Papers, Wisconsin Rapids, WI[1]. Some TMP was bleached with sodium borohydride under conditions reported previously.\* To hydrogenate aromatic-ring conjugated ethylenic bonds in lignin, a portion of the bleached pulp was treated with diimide.<sup>2</sup>

Peroxide bleaching was carried out on the acid-pretreated TMP. The pretreatment was done to reduce the metal ion content of the pulp. Peroxide (5%) bleaching was carried out in two stages: Each stage consisted of bleaching the pulp (12% consistency) in the presence of silicate buffer at 70°C for 3 h at initial pH 11.5.

CMP and peroxide-bleached CMP samples were provided by the Finnish Pulp and Paper Research Institute, Helsinki, Finland. CMP was bleached with 4% hydrogen peroxide and 3.4% NaOH at 15% consistency and 65°C for 3 h. DTPA, MgSO<sub>4</sub>, and sodium silicate were used as stabilizers. Additional information on these pulps is available in a previous publication.<sup>6</sup>

Handsheets made from TMPs were photoyellowed using a Rayonet RPR-100 photoreactor. The reactor is equipped with ultraviolet-fluorescent lamps having a Gaussian spectral distribution in the 300-400 nm region (with  $\lambda_{\max}$  at 350 nm). The reactor is also fitted with a cooling fan and a merry-go-round. The intensity of the lamps was such that the temperature of the irradiated sheet did not exceed 40°C.

To methylate phenolic groups in pulps, diazomethane and dimethyl sulfate were used. The conditions were similar to those described previously.<sup>7,8</sup>

TMP was acetylated with a pyridine/acetic anhydride (1/1) mixture. For this, 1 g of pulp was first dispersed in excess ethanol, then filtered. Filtered TMP was air dried at room temperature, and 40 mL of pyridine and 40 mL of acetic anhydride were added to the dried pulp. The pulp suspension was stirred magnetically and purged with nitrogen for 3 days. The pulp was washed sequentially with 1:1 ethanol/water and pure ethanol.

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[<sup>1</sup>]The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Unbleached and bleached kraft pulps were obtained from Consolidated Papers.

### Milled Wood Lignin

Milled wood lignin (MWL) was prepared from black spruce following the procedure described elsewhere.<sup>9</sup> For Raman purposes, a thin pellet of the lignin sample was made using a KBr press.

### Lignin Models

The following lignin models were purchased from Aldrich Chemical Co., Milwaukee, WI: acetoguaiacone (98%), eugenol (99%), coniferyl alcohol (98%), sinapyl alcohol, coniferaldehyde (98%), trans-stilbene (96%), 3-methoxy-catechol (99%), methylhydroquinone (99%) methyl-p-quinone (98%). Purity is indicated by the numbers in the parentheses. Other models,  $\alpha$ -guaicoxy-propio-guaiacone, dehydrodiisoeugenol, pinosylvin monomethyl ether, p-coumaryl alcohol, 4,4'-dipropyl-6,6-biguaiacol, 3-methoxy-o-benzoquinone, and methoxy-p-benzoquinone were synthesized by researchers at the Forest Products Laboratory using published methods. Coniferin was a gift from Professor N. Terashima (formerly at Nagoya University, Nagoya, Japan). The synthesized compounds were evaluated for purity by NMR spectroscopy.

### Fremy's Salt

Borohydride-bleached pulp was treated with Fremy's salt (potassium nitrosodisulfonate,  $\text{ON}(\text{SO}_3\text{K})_2$ ), using conditions described elsewhere.<sup>10</sup> The oxidized pulp had a reddish hue.

### Methylation of Methylhydroquinone

Methylhydroquinone (25 mg) was dissolved in 2 mL methanol and cooled in an ice bath. The solution was stirred magnetically and lightly capped. Freshly prepared diazomethane,<sup>11</sup> in ether (ca. 0.33M), was added in aliquots until a yellow color persisted. The sample was left to react overnight. Some of the sample had sublimed as it was found around the outside of the cap and was discarded. The sample was stripped of the solvent (yield 19 mg). Proton and  $^{13}\text{C}$  NMR indicated mostly starting material with

a small amount of new methoxyl signal. Crude integration of the methyl and methoxyl groups indicated that less than 16% of the material was methylated.

Methyl iodide in acetone over potassium carbonate was also used to methylate the hydroquinone.<sup>12</sup> Acetone (40 mL) was added to a round bottom flask containing a magnetic stirbar. The solvent was bubbled with nitrogen and methylhydroquinone (49 mg) was added, followed by the finely powdered potassium carbonate (55 mg). Lastly, methyl iodide (84 mg) was added. The flask was fitted with a condenser, and the reaction mixture was refluxed for 6 h. A reddish-brown color developed during the reaction. Nitrogen gas bubbling was continued throughout the experiment. After 6 h, the reaction mixture was allowed to cool and was capped and stored in the freezer overnight. Next day, the mixture was brought to room temperature and the acetone was removed under vacuum. Bright yellow clusters of needle-like crystals sublimed into the neck of the flask. These crystals (6.5 mg) were carefully removed. NMR and Raman indicated that it was methyl-p-quinone. The brownish-red residue was dissolved in chloroform and water and was extracted with more chloroform. The combined chloroform extracts were dried over magnesium sulfate. It was a brownish-red solid (14.4 mg). NMR indicated that only about 15% of the material was the expected product (dimethoxy toluene). The aqueous phase along with an emulsion film was acidified with 1M HCl to a pH of about 1. The solution was extracted with chloroform, and the combined extracts were dried over magnesium sulfate. The amount of this fraction was 7.5 mg. The fraction was analyzed by NMR but could not be identified. The aqueous phase and emulsion were left to dry. The residue was stirred with acetone, which was decanted and evaporated to a brown residue (10 mg). This fraction could not be identified using NMR spectroscopy.

After considering reviewers' comment that the methylation reactions should have methylated the methylhydroquinone, these chemical reactions were repeated. However, repeat experiments produced similar results. Therefore, it can be concluded that most of methylhydroquinone could not be methylated using diazomethane and methyl iodide.

#### Photoexposure of 3-Methoxy-catechol and Methylhydroquinone

Methanolic solutions (1%) of 3-methoxy-catechol and methylhydroquinone were separately exposed to light for 24 h in the Rayonet RPR- 100 photoreactor. These models (2% in water/methanol (60/40)) were also photoexposed in the presence of the following

yellowing inhibitors: polyethylene glycol (MW 4000), ascorbic acid, and 1-thioglycerol. Concentration of the inhibitors was approximately 5% (w/w).

### Conventional Raman

A Jobin Yvon Ramanor HG2S (Instruments SA, Metuchen, NJ) spectrometer was used to obtain Raman spectra. This system is based on an argon ion laser as the excitation source. Although several laser wavelengths are available, the 514.5-nm line of the laser was used in our study.

Small-sized (0.5 by 1 cm) wood and pulp samples were used in Raman spectroscopic studies. Pulp samples were studied in the form of handsheets. Lignin models (1% to 5%) were examined by adsorbing them on filter paper. Models were first dissolved in either methanol or 1:1 methanol/dichloromethane, then adsorbed on the paper.

The oxygen flushing technique, described previously,<sup>13</sup> was used to obtain Raman spectra. To study the sensitivity of a sample's LIF to various gases, air, nitrogen, and oxygen were used to flush the sample cell.

### Near-IR FT Raman

FT Raman spectra of samples were obtained using a Bruker RFS 100 instrument (Bruker Instruments, Inc., Billerica, MA). The 1064-nm wavelength of the diode Nd:YAG laser was used for sample excitation.

Pulps and models on paper were sampled in the 180° scattering geometry.<sup>13</sup> A front surface mirror was used behind the samples to enhance the collected amount of Raman signal. Catechol, methylhydroquinone, and their photoexposed counterparts were sampled in a device called "Aluminum Well." The latter is a small-sized hole in a pellet of aluminum from which solids can be sampled. Some models were also sampled on Whatman No. 1 paper.

## RESULTS AND DISCUSSION

### Band Assignment

In previously published work,<sup>2</sup> it was reported that after photoyellowing of TMP a Raman band at approximately at 1675  $\text{cm}^{-1}$  was detected. Preliminary attempts to

determine if this band could be assigned to an *o*- or *p*-quinone group were not successful. It was pointed out that a Raman/IR band was present in the neighborhood of  $1675\text{ cm}^{-1}$  in both the methoxy-*p*-quinone and 3-methoxy-*o*-quinone. Another aspect of the Raman spectral features of these models was that, for the *p*-quinone, the  $1674\text{ cm}^{-1}$  band was somewhat weaker than the  $1640\text{ cm}^{-1}$  band and, for the *o*-quinone model, the  $1660$  and  $1689\text{ cm}^{-1}$  bands had very low intensities compared with the  $1559\text{ cm}^{-1}$  band.<sup>2</sup> In the spectra of photoyellowed TMPs and their extracts, none of these more intense bands ( $1559$  and  $1640\text{ cm}^{-1}$ ) was present. At best, there was a weak broadened contribution at  $1640\text{ cm}^{-1}$  (Fig. 1a). IR spectra of these models were obtained but they failed to clarify the issue of which of the quinones was responsible for the  $1675\text{ cm}^{-1}$  band.<sup>2</sup> To find out if the Raman spectrum of Fremy's salt-treated TMP contained the  $1559\text{ cm}^{-1}$  band (this was the case for the *o*-quinone model) and if indeed other *p*-quinone models showed the  $1640\text{ cm}^{-1}$  band, additional samples were analyzed using FT Raman spectroscopy. Raman spectra of some of them are shown in Fig. 1. For the quinone models, spectra were obtained on Whatman No. 1 filter paper.

As is evident from the spectra (b) and (c) in Fig. 1, a band in  $1640$  to  $1650\text{ cm}^{-1}$  region is only present in one of the two *p*-quinone models. The existence of this band seems to be a function of the structure of a model. In contrast, a band near  $1675\text{ cm}^{-1}$  was detected in both the *p*-quinone models. (Two other models analyzed in our laboratory, 2,5-dihydroxy-*p*-benzoquinone and 2,3-dimethoxy-5-methyl-*p*-quinone, had Raman bands, respectively, at  $1672$  and  $1674\text{ cm}^{-1}$ .) This suggests that for photoyellowed pulps, even though no band is present at  $1640$  to  $1650\text{ cm}^{-1}$ , as long as a band is present in the vicinity of  $1675\text{ cm}^{-1}$ , it is possible that *p*-quinone groups are present. This observation is further supported by the reported carbonyl stretching frequencies of *p*-quinones.<sup>14,15</sup> If *o*-quinone groups were present in the photoyellowed TMPs or their extracts, they should have had a Raman contribution at approximately  $1559\text{ cm}^{-1}$ . This was expected on the basis of the analysis of the spectra of both the *o*-quinone model and Fremy's salt-treated TMP (Fig. 1d, 1e); it is known that Fremy's salt treatment produces *o*-quinone groups in mechanical pulps.<sup>16,17</sup> Indeed, the spectrum of Fremy's salt-treated TMP (Fig. 1e) showed a new feature at  $1558\text{ cm}^{-1}$  indicative of formation of *o*-quinone groups. However, photoyellowed pulps and their extracts did not show a discernible signal at  $1559\text{ cm}^{-1}$ . Therefore, it can be safely

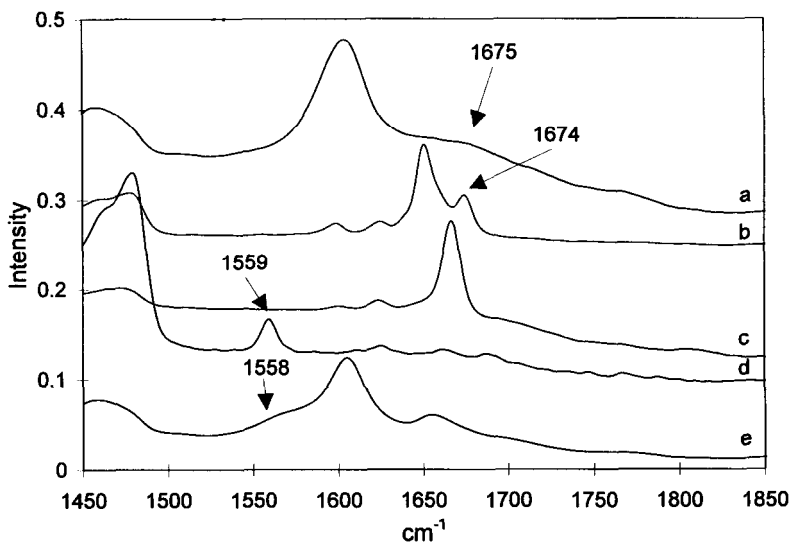


FIGURE 1. FT Raman spectra of (a) 24-h photoyellowed borohydride-bleached TMP, (b) methoxy-p-quinone, (c) methyl-p-quinone, (d) 3-methoxy-o-quinone, and (e) Fremy's salt-treated borohydride-bleached TMP. Important band positions are identified. Spectra of methoxy-p-quinone, methyl-p-quinone, and methoxy-o-quinone were obtained on Whatman No.1 filter paper.

concluded that either o-quinone groups were not present or, if present, their concentration was beyond the detection capability of the FT Raman method. However, note that o-quinones have been detected in photoyellowed mechanical pulps using  $^{31}\text{P}$  NMR spectroscopy.<sup>17,18</sup> Because the most intense Raman band in o-quinones was present at  $1559\text{ cm}^{-1}$  and because this band was not detected in the spectra of photoyellowed TMPs, it is highly unlikely that o-quinones will contribute at  $1675\text{ cm}^{-1}$ . Therefore, if o-quinone structures are not responsible for the contribution at  $1675\text{ cm}^{-1}$ , it is even more likely that the latter band is due to p-quinone groups formed as a consequence of TMP photoyellowing reactions.

Fremy's salt-treated TMP was analyzed using DRIFT, but no clear spectral features attributable to o-quinones could be detected. This was likely because of the low concentration of o-quinones generated in the pulp. As stated previously, IR analysis of quinone models did not provide information that was helpful.



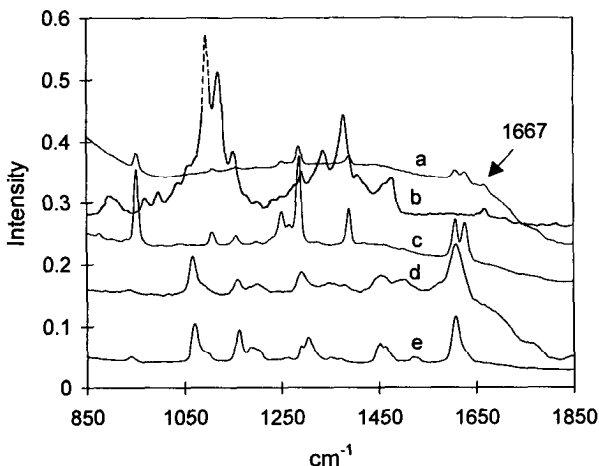


FIGURE 2. FT Raman spectra of (a) photoexposed methyl-hydroquinone, (b) authentic methyl-p-quinone on filter paper, (c) methyl-hydroquinone, (d) photoexposed 3-methoxy-catechol, and (e) 3-methoxy-catechol. Only spectral region 850 to 1850  $\text{cm}^{-1}$  is shown, and spectra have been displaced with respect to each other (intensity axis) for display purposes. Important band positions are identified.

#### Photooxidation of Methylhydroquinone and 3-Methoxy-catechol

To further investigate what happens when hydroquinone and catechol models are exposed to light and to determine if the photoproducts have a Raman contribution near 1675  $\text{cm}^{-1}$ , solutions of methylhydroquinone and 3-methoxy-catechol were exposed to light. Gas chromatographic analysis of the hydroquinone product mixture indicated that methyl-p-quinone was one of the main products—photoexposure generated 4% additional p-quinone. Analysis of hydroquinone showed that it had 0.68% impurity of methyl-p-quinone. Because these experiments were performed under air, it is possible that some percentage of the 4% increase in p-quinone may have been due to the hydroquinone being air oxidized. However, based on the author's experience, such air-oxidation contribution is expected to be quite low. When the photooxidized mixture was subjected to Raman analysis, a band at 1667  $\text{cm}^{-1}$  was detected (Fig. 2; methyl-p-quinone has a Raman band at 1667  $\text{cm}^{-1}$ ). The corresponding hydroquinone (control) did not have a band at 1667  $\text{cm}^{-1}$ . This indicated that it is likely that if hydroquinones are

present in TMPs, upon light exposure they are converted to the corresponding p-quinones. Similarly, when the Raman spectrum of photoexposed 3-methoxy-catechol was recorded and analyzed, no contribution was detected near 1667 or 1675  $\text{cm}^{-1}$ . However, weak contributions at 1561 and 1572  $\text{cm}^{-1}$  were detected.

The photoyellowing behavior of methylhydroquinone was also studied in the presence of polyethylene glycol, ascorbic acid, and thioglycerol (known yellowing inhibitors). In all cases, the resultant yellowness was significantly less compared with the control. This is reminiscent of the photobehavior of mechanical pulps in the presence of these inhibitors.<sup>19</sup> Moreover, for the polyethylene glycol- and thioglycerol-containing samples, the Raman band at 1667  $\text{cm}^{-1}$  attributable to a p-quinone was not detected, indicating that the amount of p-quinone produced was significantly reduced. (Ascorbic acid has a band at 1666  $\text{cm}^{-1}$ ; therefore, in its presence, detection of the p-quinone band was not possible.)

### Laser-Induced Fluorescence

It has been reported that when lignocellulosic and cellulosic materials are excited by 514.5 nm laser light, a strong emission signal is obtained.<sup>20,21</sup> This emission is called laser-induced fluorescence (LIF). Also, it is known that the LIF of wood, mechanical pulps, and milled wood lignin can be quenched by molecular oxygen<sup>13,29</sup> and that the sensitivity of the LIF to oxygen is largely reversible, meaning that if oxygen is replaced by air or nitrogen (whichever was the original sampling environment), the LIF signal intensity is more or less recovered.<sup>20</sup> For example, the oxygen-sensitive nature of the fluorescence of methylhydroquinone (on filter paper) is shown in Fig. 3.

To date, the oxygen-sensitive aspect of the LIF has remained unexplained.<sup>29</sup> In addition, because only the LIF of lignin-containing samples were oxygen-sensitive, it was decided that studying lignin models would be a good approach to understanding this phenomenon.

When excited at 514.5 nm, behavior of lignin models (with respect to the issue of oxygen sensitivity), varied quite significantly. Results of these experiments are summarized in Table 1. Some of the models did not produce any LIF. Others produced LIF that was not quenched by molecular oxygen (sometimes trace amount of impurities

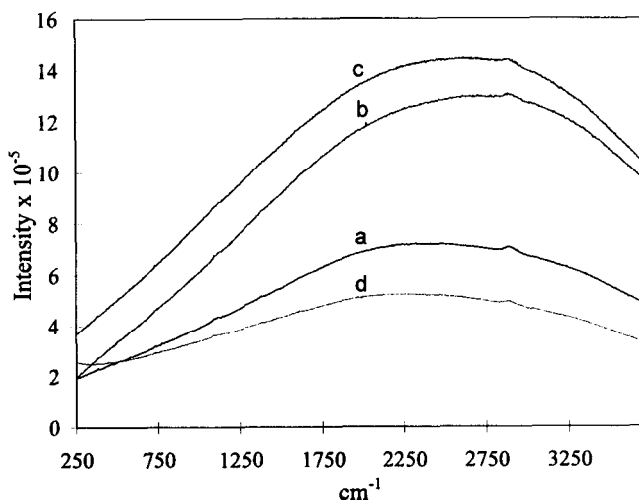


FIGURE 3. Laser-induced fluorescence (514.5 nm excited) of methyl-hydroquinone and its sensitivity to molecular oxygen: (a) spectrum of sample in air, (b) spectrum when nitrogen is flushed through the sample cell, (c) after 1 h nitrogen flushing, and (d) spectrum when nitrogen is being replaced by molecular oxygen. Molecular oxygen clearly quenches the fluorescence of the hydroquinone.

can give rise to LIF). However, there were still other lignin models, representing quinones, hydroquinone, and catechol, that produced oxygen-sensitive LIF. Together with the lignin models, different types of pulps and woods were examined for the occurrence of this phenomenon. The sensitivity of LIF to molecular oxygen is included in Table 1, column 3. For lignin models where LIF was found to be oxygen-sensitive, the extent of quenching depended upon the concentration of the model. Therefore, the sensitivity is reported only as "yes" instead of "+++" or "++" (wood, pulp, and lignin section). Table 1 also indicates how the sample area appeared after extended (48 h or more) irradiation in the presence of oxygen.

The yellowing reported in Table 1 was due to laser light, no thermal effects were encountered. For a pulp-area that is being sampled, a temperature increase can be measured by calculating the ratio of anti-Stokes to Stokes Raman lines. Using this approach, the irradiated area was found to have remained at constant temperature.

**TABLE 1. LIF (514.5 nm excited) and its Sensitivity to Molecular Oxygen When Wood, Pulp, Lignin, and Lignin Models are Irradiated**

Sample	LIF	O <sub>2</sub> sensitivity <sup>a</sup>	Appearance of irradiated area
<b>Wood, Pulp, and Lignin</b>			
Spruce	Yes	+++	Yellow
Aspen	Yes	+++	Yellow
Delignified spruce	Yes	None	Same
Unbleached TMP	Yes	+++	Yellow
BH <sub>4</sub> -bleached TMP	Yes	+++	Yellow
Peroxide-bleached TMP	Yes	+++	Yellow
Chemimechanical Pulp, CMP	Yes	+++	Yellow
Peroxide-bleached CMP	Yes	+++	Yellow
Hydrogenated TMP	Yes	+++	Yellow
Photoyellowed TMPs	Yes	+++	Bleached
Methylated TMP	Yes	++	Less yellow
Acetylated TMP	Yes	None	Same
Unbleached kraft	Yes	None	Same
Bleached kraft	Yes	None	Brighter
Spruce MWL	Yes	++	Yellow
<b>Lignin Models</b>			
α-Guaicoxy-propioquiaceone	No	None	Same
Acetoguaicene	Yes	None	Same
Dehydrodiisoeugenol	No	None	Same
Pinosylvin monomethyl ether	No	None	Same
Eugenol	No	None	Same
Coniferin	No	None	Same
Coniferyl alcohol	No	None	Same
p-Coumaryl alcohol	Yes	None	Same
Sinapyl alcohol	Yes	None	Same
Coniferaldehyde	No	None	Same
4,4'-Dipropyl-6,6'-biguaiacol	No	None	Same
trans-Stilbene	No	None	Same
3-Methoxy-catechol	Yes	Yes	Same
Methylhydroquinone	Yes	Yes	Yellow
3-Methoxy-o-benzoquinone	Yes	Yes	Bleached
Methoxy-p-benzoquinone	Yes	Yes	Bleached
Methyl-p-quinone	Yes	Yes	Bleached

<sup>a</sup>+++ means highly sensitive, ++ means less sensitive.

Note in Table 1 that hydroquinone, catechol, and quinone models have fluorescence that is sensitive to molecular oxygen. In addition, for methylhydroquinone, the oxygen sensitivity of the fluorescence and the appearance of the irradiated area were characteristics similar to those of unyellowed, underivatized TMPs (Table 1). In both cases, the LIF was sensitive to oxygen and the laser-focused area yellowed upon prolonged irradiation. This yellowing of TMP, caused by the 514.5-nm line of argon ion laser, was similar to the yellowing induced by near-ultraviolet (UV) light. The sample containing 3-methoxycatechol did not change color upon irradiation under oxygen atmosphere (Table 1); therefore, catechol structures are not likely to be the precursors of yellowness in photoexposed TMPs. Furthermore, the behavioral characteristics of methyl-p-quinone and yellowed TMPs were similar (Table 1). Both showed LIF that was oxygen sensitive and both underwent bleaching upon laser excitation.

From the information in Table 1, another interesting observation can be made for methylated and acetylated TMPs. Following methylation of the pulp, its sensitivity to oxygen was only partially diminished, implying that the groups responsible for the sensitivity were not completely removed. This is further supported by the reduced yellowing of this sample (Table 1). This observation is similar to the photoyellowing behavior of methylated mechanical pulps<sup>7</sup> where it was found that methylation resulted in reduced yellowing.

In contrast, the LIF of acetylated pulp did not show any sensitivity to oxygen and the laser-exposed area did not develop color. This suggests that the groups/structures that were responsible for the oxygen-sensitive nature of the LIF are also responsible for the development of the yellow color. The nonyellowing behavior of the laser-irradiated acetylated TMP is similar to its nonyellowing behavior under near-UV light.<sup>22,23</sup>

Taken together, these results strongly support the likelihood that hydroquinones exist in TMPs and are responsible for the photoyellowing. Such a hypothesis involving a hydroquinone/p-quinone redox system has already been proposed.<sup>24</sup> Our studies provide good supporting evidence for this hypothesis.

To reveal the Raman spectral nature of the chemical changes that occurred in the laser-irradiated pulp area upon yellowing, the 514.5-nm laser-excited Raman spectrum of the irradiated area obtained before yellowing was subtracted from the spectrum

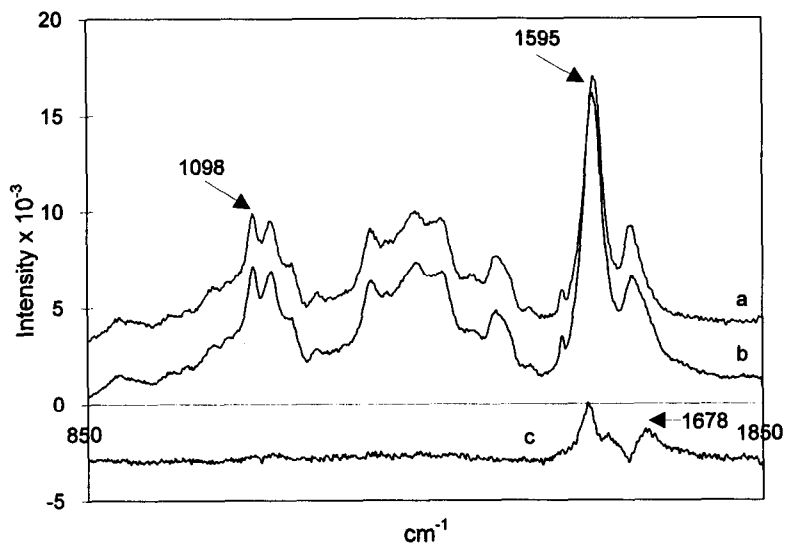


FIGURE 4. 514.5 nm excited Raman spectra of borohydride-bleached TMP (a) before and (b) after photoyellowing of the irradiated area. (c) is (b) - (a). A yellowing related band appears at  $1678\text{ cm}^{-1}$ .

obtained after the yellowing. (This was done for the borohydride-bleached TMP.) Fig. 4 shows the spectra before and after laser-light yellowing and the result of spectral subtraction. Upon yellowing, a new band appeared at  $1678\text{ cm}^{-1}$ . This band position is similar to the one detected at  $1675\text{ cm}^{-1}$  in the spectra of near-UV photoyellowed pulps.<sup>2</sup> This indicates that p-quinones are also generated by green laser light and that the yellowing, caused by near-UV and 514.5-nm laser light, is similar.

### Implications

Results of the present study provide strong evidence in support of the previously proposed hypothesis<sup>24</sup> in which a hydroquinone/p-quinone redox couple was suggested as being responsible for most of the yellowing in mechanical pulps. This scheme is outlined in Fig. 5. In this figure,  $R_1$  represents a lignin fragment and  $R_2$  is most probably a methoxyl group. The reverse reaction is driven in presence of reducing agents such as alcohols and aldehydes.

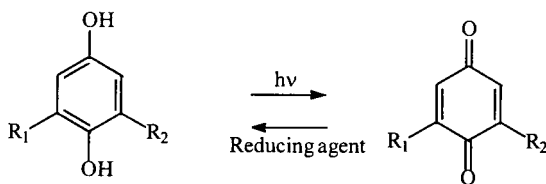


FIGURE 5. HQ /p-Q Oxidation/reduction couple.<sup>24</sup>

When hydroquinones are present in a mechanical pulp, the above redox couple is likely to prevail. That hydroquinone structures are capable of significant light absorption beyond 300 nm is supported by published studies<sup>25,26</sup> as well as by this author's work.<sup>23</sup> However, it is important to know if hydroquinone species exist in mechanical pulps. As described previously, the oxygen sensitivity of LIF in the 514.5-nm irradiation of lignin-rich samples supports the presence of hydroquinones/p-quinones. Additional evidence comes from the lignin studies,<sup>27</sup> suggesting that very small quantities of hydroquinones were present in Bjorkman lignin. However, it is anticipated that trace amounts of hydroquinones are not likely to be enough to account for the LIF quenching results reported here or to account for the photoyellowing behavior of mechanical pulps. It was expected that the concentration of hydroquinones would be significantly greater than what has been reported. The difference between the reported hydroquinone amount<sup>27</sup> and what is expected can be reconciled when the reaction conditions under which the hydroquinone groups in lignin were methylated<sup>27</sup> are examined. In particular, it is likely that methylation of lignin by dimethyl sulfate/diazomethane did not succeed in methylating most hydroquinone groups. This is supported by this author's results of methyl hydroquinone methylation experiments (see Experimental). Consequently, it is likely that a significant portion of hydroquinone units survived the methylation step and could not be detected upon permanganate oxidation. Therefore, it is important that suitable methods be developed for detecting hydroquinones in pulps and lignin.

The Raman/IR evidence that p-quinones are yellowing chromophores in mechanical pulps reported here provides much needed support for previously published photoyellowing-related research<sup>24,26,28,29</sup> In one study,<sup>26</sup> the photochemistry of

methoxy-p-benzoquinone and methoxy-hydroquinone in solid 2-hydroxy-propyl-cellulose films and filter paper was studied. It was concluded that the quinone and hydroquinone chromophores play a key role in the discoloration process of high-yield pulps.

Results of yet another study<sup>28</sup> indicated that the redox equilibrium between hydroquinones and their corresponding p-quinones exist in pulps and, depending upon the history of pulps (e.g., bleaching and acetylation), both hydroquinones and p-quinones are capable of reactions that lead to yellowing. However, in this work,<sup>28</sup> the hypothesis of the authors that catechols and o-quinones are also responsible for such reactions is not supported by our investigation. In this context, note that most o-quinones are red but photoexposed pulps are yellow.

The photobehavior of methylated and acetylated mechanical pulps can be explained on the basis of the present findings. It is known that methylation with dimethyl sulfate and diazomethane does not render pulps completely photostable.<sup>7,8,30</sup> Methylated pulps yellow but at a lower rate. Although, to the best of our knowledge, no reports have been published showing that hydroquinones are present in methylated pulps, based on the finding that the LIF of a methylated pulp is oxygen-sensitive (Table 1), it is likely that not all hydroquinone groups were methylated and that the remaining hydroquinone groups were responsible for the yellowing of methylated pulp. The level of oxygen sensitivity seems to be an indicator of the extent to which such groups remain unmethylated. The difficulty with which hydroquinones undergo methylation was further demonstrated when methyl hydroquinone was methylated using diazomethane and methyl iodide (see Experimental). In both cases, only a very small amount of starting material could be methylated. This being so in the case of a homogeneous reaction mixture, it is expected that the reaction would be even less successful when the hydroquinone groups are methylated in a heterogeneous lignocellulosic matrix. In contrast, acetylation of TMP with pyridine/acetic anhydride easily acetylated hydroquinone groups. This was evident both from the photostability of the pulp<sup>23</sup> and by the lack of oxygen sensitivity of the LIF signal of the acetylated TMP (Table 1).

For methylated TMP, it has been estimated that the concentration of free phenolic groups is about 0.76/100 C<sub>9</sub> units.<sup>8</sup> Although it is possible that these residual phenoxy groups are of the hydroquinone type, it is not clear if the aminolysis and periodate



methods (used to detect phenoxy groups) can detect hydroquinone phenoxy groups. If not, then the concentration of hydroquinones could be even greater. In this context, it is noteworthy that the periodate method fails to detect methoxyl-free phenolic and hydroquinone units.<sup>31</sup> Suitability of these methods for accurately detecting hydroquinones needs to be established before phenoxy concentration data of methylated pulps can be properly interpreted. Additional information in support of the possibility of incomplete methylation of the hydroquinone groups comes from the analysis of acetylated pulps. No free phenolic groups could be found in fully acetylated pulps.<sup>32</sup> This suggests that acetylation is a better derivatizing agent for the hydroquinone functionality.

The effect of yellowing inhibitors like polyethylene glycol, ascorbic acid, and thioglycerol on the photoyellowing behavior of pulps can be explained by previously suggested mechanisms,<sup>33-36</sup> some of which are based on the chemistry of p-quinones/hydroquinones.<sup>34</sup> The present findings provide much needed evidence in support of these reaction mechanisms, because the assumptions for the existence of p-quinones and hydroquinones are no longer necessary.

It is a well recognized fact that after pulps are photoexposed, a band at about  $1727\text{ cm}^{-1}$  is detected in their IR spectra.<sup>2,37</sup> In the author's work on spruce TMPs,<sup>2</sup> the intensity of this band was found to be linearly correlated with the post color number. It was reported that this suggests that the sequence of chemical events leading to formation of carbonyl groups (non-quinonoid) is related to the photoyellowing reactions. In this author's opinion, photoreduction of p-quinones in the presence of primary or secondary alcohols, which act as hydrogen donors, can account for the formation of carbonyl groups. In pulp, either carbohydrates or lignin can play the role of a hydrogen atom donor. Such photochemical reactions are known to occur in p-quinones.<sup>38</sup> In the proposed hypothesis, shown in Fig. 6, a lignin fragment is indicated by the letter L, and an  $\text{OCH}_3$  group is represented by  $\text{R}_1$ . A primary or a secondary alcohol structure is denoted by  $\text{R}_2\text{R}_3\text{CHOH}$  and is expected to be present in TMP.

The scheme in Fig. 6 suggests that light drives both the hydroquinone-to-quinone (forward) and the quinone-to-hydroquinone (reverse) reactions. Upon light exposure, the former (**1**) is converted first to a semiquinone radical (**2**), then to **3**, a quinone. The quinone (**3**) absorbs light to produce a triplet state (**4**) or a diradical which, in presence of

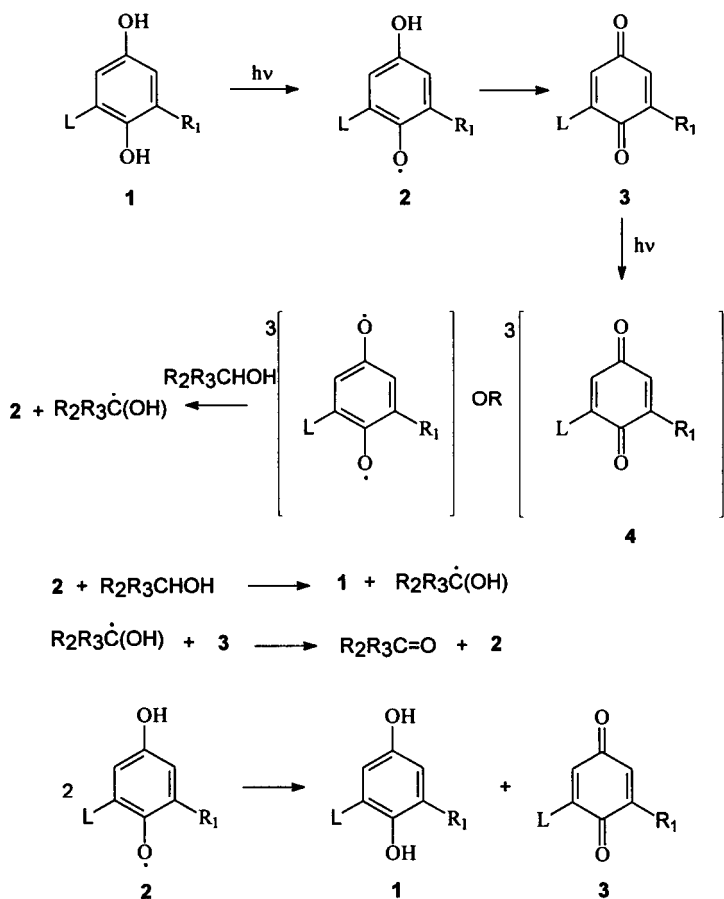


FIGURE 6. A mechanistic representation of hydroquinone and p-quinone reactions. The quinone triplet state reacts with a primary or secondary alcohol group and leads to the formation of a carbonyl group. Additional reactions of radicals, not depicted here, are also possible.

an alcohol, produces **2** and a hydroxy $\text{R}_2\text{R}_3$  radical (H abstraction). In a subsequent step (Fig. 6), the hydroxy radical reacts with a quinone to generate a keto group. The formation of the latter functionality can account for IR absorption at  $1727\text{ cm}^{-1}$  in yellowed TMPs.<sup>2</sup> The semiquinone radical (**2**), generated by the excited state quinone (**4**) reacts with another molecule of alcohol and regenerates hydroquinone (**1**). Lastly, it

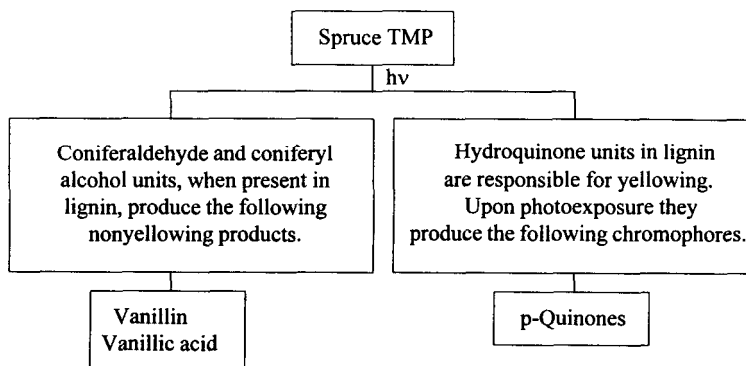


FIGURE 7. A summary of light-induced changes in spruce TMP.

is possible that two semiquinone radicals (2) interact and disproportionate, by simultaneous reduction and oxidation, into a hydroquinone and a quinone. However, in a matrix that is solid and where hydroquinone concentration is low, the latter reaction is not likely to be encountered. Additional reactions of semiquinone and hydroxy radicals, not shown here, are also possible, for example, grafting reactions.

It is possible that the forward and reverse reactions have different rates and different dependencies on the wavelength of light. These possibilities are intriguing, because if true, they can explain why a pulp that has been yellowed by near-UV light undergoes bleaching upon exposure to visible light;<sup>39-42</sup> the p-quinone chromophores are reduced to hydroquinones. The observation that pulp brightness measured immediately after photoyellowing is lower compared with its equilibrium value<sup>43</sup> can be explained if it is assumed that the rate of the quinone-to-hydroquinone reaction is lower than the rate of the hydroquinone-to-quinone reaction. In the immediate measurement, the first reaction is not complete and the brightness continues to increase as additional quinone fragments are converted to hydroquinones.

In summary, when a lignin-containing mechanical pulp is exposed to light, both yellowing and nonyellowing reactions occur. A brief outline of these changes, based on our investigations, is represented in Fig. 7. Also note that the scheme in Fig. 7 by no means represents everything that happens when mechanical pulps are exposed to light.

### CONCLUSIONS

The Raman/IR band at  $1675\text{ cm}^{-1}$  that was detected in photoyellowed TMP pulps was assigned to p-quinone groups. It is suggested that such groups are formed from corresponding hydroquinones present in pulps. Raman data did not provide support for the possibility that o-quinone groups are generated upon photoyellowing. For lignin-rich samples, using the molecular oxygen sensitivity of 514.5 nm excited laser-induced fluorescence, information can be obtained to determine if quinone/hydroquinone groups are present in the samples. A hydroquinoneip-quinone redox system successfully accounted for a large number of photoyellowing results.

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