

Predicting photoyellowing behaviour of mechanical pulp containing papers

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ABSTRACT

It is well known that paper produced from mechanical-pulp-containing fiber furnish yellows upon exposure to light. Although the accelerated light-aging test method has been used to compare papers and predict long term performance, the reliability of the light-aging method has been questioned. Therefore, a method that can correctly predict a paper's light stability is desirable. In this work, a new technique is proposed that is capable of ranking papers for their photoyellowing characteristic and is based upon the amount of the pulp-hydroquinone present. The technique entails quenching, by oxygen, of the laser-induced-fluorescence (LIF) of paper. The LIF of both mechanical pulp containing papers and hydroquinone model was found to be sensitive to molecular oxygen indicating that the latter structures were almost certainly the cause of the oxygen sensitivity of the paper's LIF. The hydroquinone structures have already been shown to be involved in the mechanism of photoyellowing. Using the LIF method, photoyellowing behavior of 15 printing and writing papers - both mechanical pulp-containing and mechanical pulp-free - was predicted and compared to the papers' ranking based on the accelerated light aging test. For these papers, photostability rank from accelerated aging and fluorescence quenching were found to be somewhat different. The reasons for such differences are not yet clear. Irrespective of the disparity, the conclusion was that the oxygen sensitivity of the LIF is a method that is potentially suitable to predict the photostability of the mechanical pulp containing papers.

INTRODUCTION

Because of high lignin content mechanical pulp fiber containing papers lose their brightness (turn yellow) when exposed to light. Considering that brightness stability is an important optical property that paper manufacturers would like to measure, accurate test methods are needed to predict this characteristic of papers. Although accelerated light aging test methods have been used [1], these methods have limitations due to high light intensity and the amount of UV component in the spectral output of

the light sources. Therefore, they do not reproduce the end-use conditions very well and the reliability of these methods has come under questioning [2]. Recently, an ASTM method (D-6789-02) was published which provided a scientifically credible and improved protocol for the light aging test method for both lignin-containing and lignin-free papers [3].

Here we provide a new method, for lignin-containing papers, that is founded on the fact that the visible laser (514.5 nm) excited LIF of the mechanical pulp containing papers is quenchable by molecular oxygen. The correlation between the photoyellowing and fluorescence quenching seems to arise from the observation that the same sub-group of lignin structure, namely, hydroquinone is responsible for both of these phenomena. Previously, using the method of oxygen sensitivity of LIF, hydroquinone units were found to exist in milled-wood lignin (MWL), mechanical pulp, and wood [4]. This finding was based on the work carried out in the author's laboratory and arose from the fact that the LIF of hydroquinone is quenchable by molecular oxygen. In MWL and lignin-rich mechanical pulps, hydroquinone units are likely to be responsible for a significant part of the 514.5 nm-excited LIF signals [4].

In light of these results, it should be possible to quantify hydroquinones in a mechanical pulp. Additionally, assuming that most photoyellowing is caused by the oxidation products of hydroquinones in lignin, it should also be possible to predict the photostability of papers that contain mechanical pulps. The method is based on the hypothesis that any variation in the hydroquinone concentration (among papers) will be reflected in the intensity of the O₂-sensitive LIF signal. For the present study, all 15 ASTM papers were selected although only the mechanical pulp-containing papers are expected to show oxygen-sensitive LIF. These papers were made from a variety of fiber compositions ranging from stone groundwood to cotton.

EXPERIMENTAL

Papers

Papers used in this study are listed in Table 1 and were composed of a variety of fiber types. Some of the papers contained pulp-lignin whereas others were free of lignin. Although not identified here, the selection included both acid (pH 5) and alkaline (pH 8) papers. The same papers were previously used in the American Society for Testing Materials (ASTM) conducted research program [3] that created a scientifically sound accelerated light aging test method for the prediction of the life

expectancy of printing and writing papers. In addition to the chemical composition, Table 1 lists Klason lignin content which was measured at the FPL.

Pulps

In addition to the papers, 2 thermomechanical pulp (TMP) samples were included in the study for comparative purposes. TMP was first irradiated, for 21 h in 0.04% NaOH solution, by the 350 nm lights (Rayonet photoreactor), and then the pulp was bleached separately with sodium borohydride and alkaline hydrogen peroxide. This was done to determine if the photoexposure-before-bleaching samples contained hydroquinones and if there were differences in the amount between the 2 TMPs. Details of bleaching were same as previously reported [4, 5]

Raman

A Raman microprobe system (Spex Triplemate 1877 based on 514.5 nm laser excitation) with a macro attachment was used to obtain LIF spectra of various samples. Pulps were converted to

thin handsheets. For sampling, a small strip, ½ x 1 cm, was cut from each of the papers and handsheets and was sampled in the high pressure sample cell as previously mentioned [6]. The reflected light from the sample was collected in the 180 degree geometry and detected using a liquid N₂ cooled CCD detector. Time-dependent and steady-state fluorescence spectra in N₂ and O₂ environments were obtained. The 540-nm region (~ 2600 cm⁻¹ Raman shift) of the spectrum was studied because that's the region where the maximum LIF signal was detected. The system was equipped with Spectramax program which was used to run the instrument and process the collected data. For the present work, steady-state was defined as less than 10% signal change in spectra that were obtained ½ h apart.

RESULTS AND DISCUSSION

The paper samples listed in Table 1 and the TMPs were analyzed. The papers were part of the ASTM study and their photostability rank has been previously obtained using the accelerated light aging method [3].

Table 1: Composition of papers ^{a,b}

Paper ID	Pulp 1:Pulp 2	Klason lignin, %	Additives
3	100:0 (SW-BCTMP)	24.9	yes
7	80:20 (SW-SGW:BN-SWK)	23.8	yes
4	100:0 (SW-BCTMP)	23.6	no, had CaCO ₃
8	80:20 (SW-SGW:BN-SWK)	22.3	SMI process, had CaCO ₃
9	80:20 (HW-BCTMP:BN-SWK)	11.7	no
10	80:20 (HW-BCTMP:BN-SWK)	10.9	No, had CaCO ₃
13	50:50 (HW-BCTMP:BN-SWK)	7.4	no
14	50:50 (HW-BCTMP:BN-SWK)	7.1	Yes
5	0:100 (cotton)	1.7	yes
6	0:100 (cotton)	1.6	no, had CaCO ₃
1	0:100 (BN-SWK)	0.7	yes
15	50:50 (BN-SWK:BN-HWK)	0.4	Yes, also CaCO ₃
2	0:100 (BN-SWK)	0.2	no, had CaCO ₃
11	50:50 (BN-SWK:BN-HWK)	0.2	no, had CaCO ₃
12	50:50 (BN-SWK:BN-HWK)	0.2	no, had CaCO ₃

^aBN is bleached northern; BS is bleached southern; S(H)WK is soft(hard)wood kraft; SW is softwood; HW is hardwood; BCTMP is bleached chemithermomechanical pulp; SGW is stone groundwood

^bPapers in bold were produced with mechanical pulp fibers in the furnish

There are 2 different ways to carry out the LIF experiments. One option is to start by sampling under N₂ - an inert gas. The second alternative was to sample under O₂ which provides an oxidizing

environment, especially under laser irradiation. Nevertheless, in both options, subsequently, the gaseous atmosphere was changed to discover the result of a specific atmosphere on the LIF intensity.

For paper 4, which is made from 100% SW-BCTMP (Table 1), experiments were performed both ways. However, after the initial drench-quenching and reaching a steady-state (after about 200 min in O₂-first option, Fig.1 and 300 min in N₂-first option, Fig 3) no matter which gas one started with, the LIF signal was always higher under N₂ (Figs. 1 and 2). It was also noted that in the case of O₂ exposure, compared to N₂ the LIF signal always declined more rapidly (Figs. 1 and 2) no matter at what stage the gases were switched. This raises the possibility that

the effects on the sample of the two gaseous atmospheres are different and under oxygen, oxidation of the components or certain structures in a component (particularly lignin) can not be ruled out. To minimize the latter possibility, it was decided that samples would first be exposed to nitrogen and only when the LIF had declined significantly and a steady-state has been reached, the gaseous environment would be switched to O₂. All paper and pulp samples were analyzed in this way.

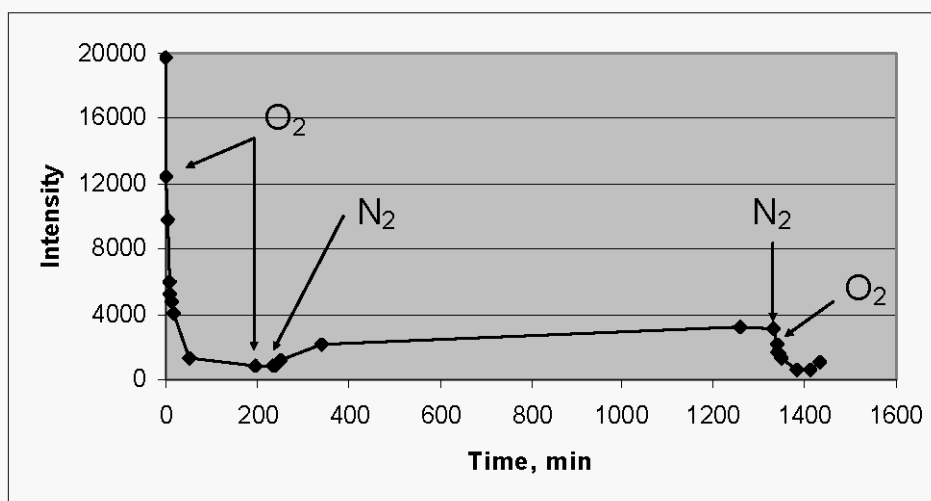


Fig. 1: LIF signal intensity at 540 nm (or 2600 cm⁻¹ Raman shift) as a function of time and gaseous atmosphere. For paper 4, under O₂ sampling, the intensity declined rapidly from about 20,000 to 800 counts. The signal increased under N₂ and declined again under O₂ showing the reversible nature of part of the LIF.

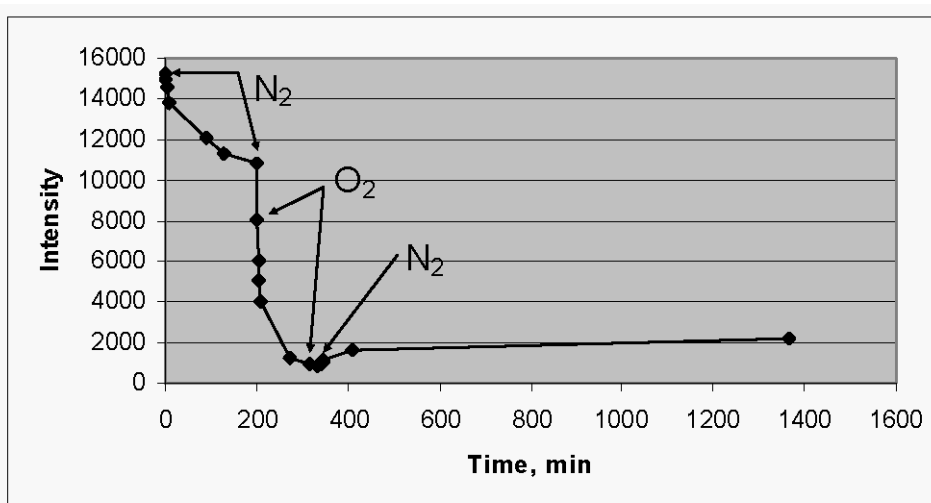


Fig. 2: LIF signal intensity at 540 nm (or 2600 cm⁻¹ Raman shift) as a function of time and gaseous atmosphere. For paper 4, initially under N₂ sampling, the intensity declined slowly from about 15,000 to 11,000 counts. The signal showed a further rapid decline under O₂ (from 8000 to 900), before going up in intensity as O₂ was replaced with N₂.

There seems to be at least two components present in the fluorescence of the mechanical pulp-containing papers. One component has the attribute that its intensity is higher under nitrogen compared to oxygen and this component is present in both oxygen-first and nitrogen-first plots of paper 4 (Figs. 1 and 2). In contrast, the second LIF component distinguishes itself by having the feature of its intensity declining continually with time under both nitrogen and oxygen atmospheres. Nevertheless, it declines at a faster rate under oxygen sampling (Fig. 2). Perhaps the fluorescing species is being photomodified or photobleached. In cellulose, such

components were shown to be trace amounts of transition metal ions [7].

While trying to determine which models of lignin structure were capable of imitating the behavior of the first component in the paper's LIF, where the intensity went up under N_2 compared to O_2 , a number of models were studied [4]. One of the models methyl-hydroquinone was one of the few models whose behavior was equivalent to that of paper 4. LIF spectra obtained from a paper that contained methyl-hydroquinone are shown in Fig. 3.

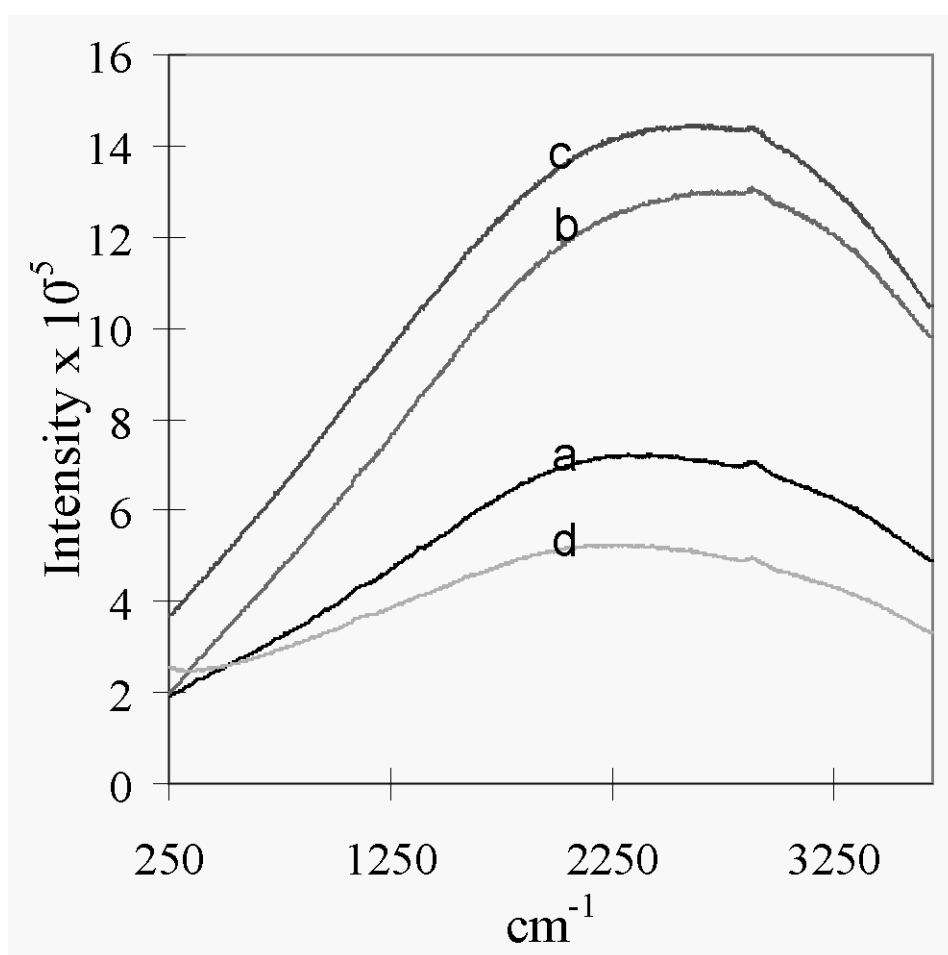


Figure 3: Laser-induced fluorescence (514.5 nm excited) of methyl-hydroquinone (MHQ) and its sensitivity to O_2 ; (a) spectrum of MHQ-containing filter paper in air, (b) spectrum when N_2 is flushed through the sample cell, (c) after 1 h of N_2 flushing, and (d) when N_2 flushing is stopped and O_2 flushing is started. Molecular oxygen clearly quenches the fluorescence of the hydroquinone. Taken from reference [4].

Fig. 3 suggests that the O_2 -sensitive LIF signal can be correlated to the concentration of

hydroquinones in the sample. If the peak signal intensity of the normalized spectrum "d" in Fig. 3 is

subtracted from that of spectrum “c” it would produce the portion of the LIF signal that is sensitive to O₂. The oxygen sensitive signal is expected to be directly proportional to the concentration of the hydroquinones. Using various concentrations of hydroquinone model a calibration curve can be generated and used to estimate the concentration of hydroquinones in the mechanical pulp containing papers.

Ratio of LIFs

To estimate the level of signal quenching by oxygen, the ratio of under- N₂ (Φ_F) and under- O₂ (Φ_F^Q) LIF signals was calculated. In such a calculation, the Φ_F signal was after the O₂ steady-state has been attained and the LIF signal had reached a maximum value under N₂. For example, for paper 4 in Fig. 2, the data for Φ_F^Q and Φ_F was taken respectively, at 331 and 2213 minutes after starting the laser irradiation of the samples. The bar plots of

Φ_F / Φ_F^Q for various papers and the 2 TMPs are shown in Fig. 4.

Mechanical pulp-containing papers

Of the mechanical pulp-containing papers (bold in Table 1), the highest value for the ratio Φ_F / Φ_F^Q was found for paper 3. Although both papers 4 and 3 were produced from 100% SW-BCTMP fibers, the reason for their different response is not clear. It is possible that additives and pH (4 is alkaline and 3 is acid and had additives) may play a role. Other pairs of similar fiber furnish also showed small differences in the Φ_F / Φ_F^Q ratio data. Based on the values in Fig. 4 the order of stability was $14 \approx 13 > 10 > 9 > 7 > 8 > 4 > 3$. This differs somewhat from the ASTM method based stability ranking - most to least stable, $8 > 7 > 13 > 10 > 14 > 4 > 9 > 3$. Nevertheless, in both, the order $13 > 10 > 4 > 3$ was correctly predicted but differences are evident for the remaining papers. It is hoped that future studies will explain this disparity.

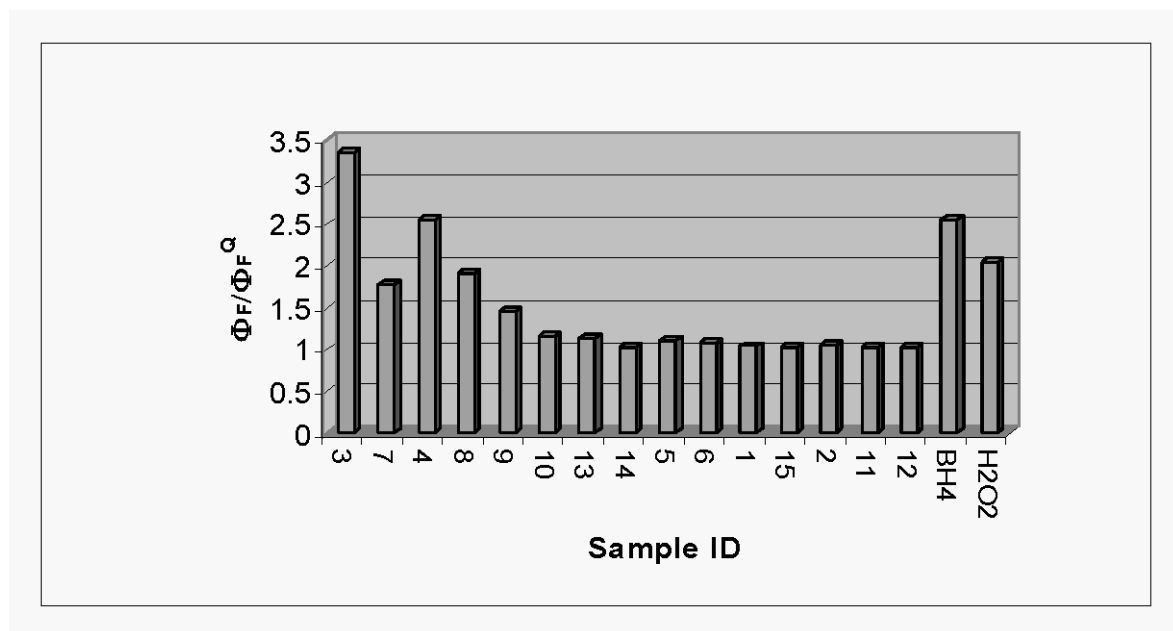


Figure 4: Ratio of Φ_F / Φ_F^Q for the 15 papers and 2 TMP pulps. Higher ratio indicated more photoyellowing potential. Papers 1, 2, 5, 6, 11, 12, and 15 show a value of 1 because for them the N₂-LIF intensity is about same as the O₂-LIF intensity. These papers are classified as mechanical pulp-free papers and can not be evaluated using the present method.

Mechanical pulp-free papers

As expected papers whose fiber furnish was free of mechanical pulp content (Table 1, papers 1, 2, 5, 6, 11, 12 and 15) shows LIF that was not quenched by O₂. The Φ_F / Φ_F^Q ratio was very close to 1 (Fig. 4) due to the fact that no significant enhancement of the

LIF intensity occurred under N₂ after a steady state was achieved under O₂. This implied that the O₂-sensitivity of the LIF method can not be used to predict the photostability of mechanical pulp-free papers

TMPs

For both alkaline peroxide and sodium borohydride bleached TMPs the Φ_F/Φ_F^Q ratio was ≥ 2 indicating that the photostability of the pulps was very poor. Compared to the peroxide bleached TMP the borohydride treated pulp was more unstable. Although the reasoning behind this observation is not clear, it may have something to do with either the differences between the bleaching agents themselves or the fact that the TMP was exposed to light prior to bleaching.

CONCLUSIONS

A new method, O_2 -sensitivity of laser-induced-fluorescence (LIF), was developed for predicting photostability of mechanical pulp-containing papers. It was applied to study the set of 15 papers that were used in a prior ASTM research program. Of these 8 papers contained mechanical pulp and 7 did not. In addition, 2 TMPs were analyzed using the new approach. A photostability rank based on the new method was obtained but was found to be somewhat different from that obtained

using the ASTM accelerated light aging protocol. The finding was that the LIF method can be used for classifying papers for predicting photostability.

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