The Aging of Printing and Writing Papers upon Exposure to Light: Part 1 - Optical and Chemical Changes due to Long-Term Light Exposure

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ABSTRACT

A program was undertaken at the Forest Products Laboratory in conjunction with the American Society for Testing and Materials (ASTM) to develop guidelines for a credible accelerated photoaging protocol for printing and writing papers. Photoaging was carried out in two different environments. The first was intended to simulate natural aging conditions with exposure to artificial and daylight illumination. The second environment provided higher photon flux levels in order to accelerate photoaging. This report will present the results of long-term natural aging of fifteen types of paper ranging from stone groundwood to bleached kraft. Emphasis is on the optical and chemical changes brought about by this exposure. The implications of this work will be addressed.

INTRODUCTION

The American Society for Testing and Materials (ASTM) through its subsidiary organization, the Institute for Standards Research (ISR), is concluding a multi-year effort research program to create scientifically sound test methods for the prediction of the life expectancy of printing and writing papers. The objectives of this program are to further the understanding of the fundamental mechanisms of paper aging and to develop accelerated test methods that correlate well with natural aging results.

Five research laboratories are engaged in this work and include:

*The U.S. Library of Congress in Washington, DC and the Canadian Conservation Institute in Ottawa, Canada - Thermal Aging,

*The Image Permanence Institute at Rochester Institute of Technology in Rochester, New York - Atmospheric Pollutant Aging,

*The USDA Forest Products Laboratory in Madison, Wisconsin and the Finnish Pulp and Paper Research Institute in Helsinki, Finland - Light Aging.

This paper will discuss the Light Aging Research Program at the USDA Forest Products Laboratory. The goals of the program were to develop guidelines for a credible accelerated photoaging protocol, and to simultaneously cany out in-depth studies of photodegradation sufficient to establish the validity of the protocol. The approach adopted was to cany out photoaging studies in two different environments. The first was intended to simulate natural aging conditions, with exposure to both artificial and daylight illumination. The second environment provided higher photon flux levels in order to accelerate the photoaging process. These studies included monitoring the changes in physical and mechanical properties that result from the aging process. They also included spectral and chemical characterization of the species that are sensitive to light, as well as their chemical transformations. Through comparison of the results of aging in the different environments, and characterization of the changes that were observed, guidelines for a suitable accelerated aging protocol were developed. This report will discuss the optical and chemical changes brought about by long-term natural photoaging, specifically due to natural light exposure.

EXPERIMENTAL

Paper Samples

An array of fifteen papers was specially manufactured for the ASTM Institute for Standards Research program The array included both acid (pH 5) and alkaline (pH 8) papers with a variety of fiber compositions ranging from stone groundwood to pure cotton. The make-up of these papers is shown in Table 1.

Table 1. Paper Composition

Paper No.	Composition	pH	$CaCO_3$ %
1	100% BN-SWK	5.0	0
2	100% BN-SWK	8.1	5
3	100% SW-BCTMP	5.0	0
4	100% SW-BCTMP	8.1	5
5	Textile cotton	5.0	0
6	Textile cotton	8.1	5
7	20% BN-SWK+80% SW-SGW	5.0	0
8	20% BN-SWK+80% SW-SGW	8.1	5
9	20% BN-SWK+80% HW-BCTMP	5.0	0
10	20% BN-SWK+80%HW-BCTMP	7.0	5
11	50% BN-SWK+50% BN-HWK	8.1	0
12	50% BN-SWK+50% BN-HWK	8.1	5
13	50% BN-SWK+50% HW-BCTMP	8.1	5
14	50% BN-SWK+50% HW-BCTMP	5.0	0
15	50% BN-SWK+50% BN-HWK	8.1	5

Code:
BN = Bleached Northern SW = Softwood,
SGW = Stone Groundwood HW = Hardwood,
S(H)WK = Soft(Hard)wood Kraft,
BCTMP = Bleached Chemithermomechanical Pulp

Natural Light Aging Chambers

A north facing room with large windows was modified to create three isolated chambers: one each for exposure to halogen and fluorescent illumination, and one for northern exposure to daylight. Figure 1 shows the north window chamber. Each chamber accommodated 160 - 8.5"x11" sheets of paper. Lights were placed 6 to 8 feet from the papers in the two artificially illuminated chambers. The light intensity was approximately 100 foot-candles (1000 lux). This is equivalent to the level of illumination in a bright office according to established office design guidelines. The halogen and fluorescent chambers were continuously lighted, while the intensity in the north window chamber followed the normal diurnal cycle. Temperature, relative humidity, and light intensity were monitored continuously. Optical properties (brightness and CIELAB) were measured monthly.

Figure 1. North window chamber. Mounted paper samples can be seen on the right side of the figure.

Optical Testing

All optical testing was done in accordance with the procedures set forth by the Technical Association of the Pulp and Paper Industry (TAPPI).

Chemical Analyses

IR spectroscopy, Raman spectroscopy, gas chromatography/mass spectrometry (GC/MS), high-pressure liquid chromatography (HPLC) and Ion Chromatography (IC) were used in the investigation to characterize the changes that occurred to the papers during, photoaging.

RESULTS AND DISCUSSION

Optical Properties

Figures 2a and 2b show the loss of brightness upon north window exposure for the lignin-containing and lignin-free papers, respectively. For the lignin containing papers, the decay was initially very rapid but began to level off after approximately 100 days of exposure. For lignin-free papers, the decay was very slow. Even after four years north window exposure, the brightness loss of these papers was minimal. This behavior is consistent with the literature. Upon photoexposure, chemical changes take place mainly in lignin; cellulose and hemicellulose are not modified to any significant degree.[1]

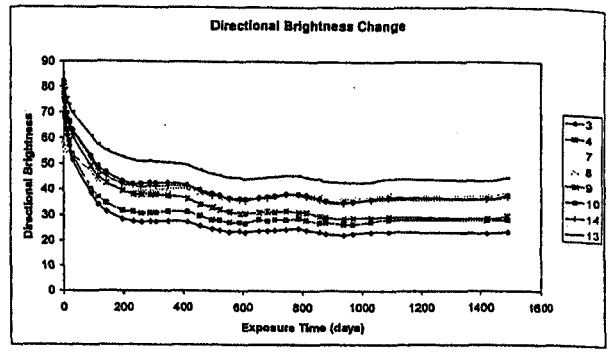

Figure 2a. Effect of north window exposure on directional brightness of lignin-containing papers.

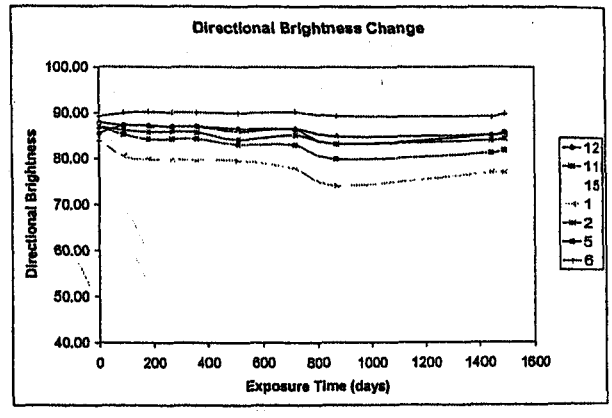

Figure 2b. Effect of north window exposure on directional brightness of lignin-free papers.

The effect of calcium carbonate addition on the brightness stability of alkaline paper is shown in Figure 2b. Papers 11 and 12 were alkaline papers and had the same fiber composition, the only difference was that paper 12 contained 5% $CaCO_3$, while paper 11 did not. After four years north window exposure, paper 11 had a brightness loss of more than 6 points, while for paper 12 the brightness was less than 2 points. The reason for this is not entirely clear but may be do to the buffering of organic acids produced during photoaging.

Acid papers showed a greater brightness loss than their respective alkaline counterparts for both lignin-containing papers (compare 3 to 4, 7 to 8, 9 to 10, and

14 to 13 in Figure 2a) and lignin-free papers (compare 1 to 2,5 to 6 in Figure 2b). The following three factors may play a role in this difference: 1. Acid contributed to paper yellowing; 2. Alkaline papers contained 5% $CaCO_3$, which may act as a buffer to acid produced during the aging process; 3. The high brightness of $CaCO_3$ itself. The extent each factor contributed to the brightness loss is not clear and will be explored further.

A feature apparent in the brightness decay curves for the north window chamber was a pronounced hump in the curve at approximately 375 and 750 days. Although the feature is shown only for the north window chamber, it occurred in the decay curves from all three chambers. The feature corresponds to very low levels of relative humidity in the chambers during the winter months. The chambers are not humidity controlled. As a result, relative humidity commonly drops below 10% during the winter, and can rise to a maximum of 65% in the summer. The amplitude of these features is in the order of two to three points of brightness. The reason for this phenomenon is not well understood. A possible explanation involves the competing' nature of photoyellowing and photobleaching reactions. At the initial stage, photoyellowing was dominant because of high concentration of the reactive species, At the leveling off stage, photoyellowing and photobleaching reactions were in equilibrium During the dry conditions in winter, photobleaching reactions were favored which caused an increase of paper brightness.

Chemical Analysis

Chemical changes that occurred to the papers after four years north window exposure were investigated with DRIFT and FT-Raman spectroscopies. Figures 3a and 3b show DRIFT spectra of a representative lignin-containing paper (paper 3, SW-BCTMP) and a lignin-free paper (paper 1, BN-SWK), respectively. For the lignin-containing papers, the most striking change occurred to the 1508 cm^{-1} band. In the DRIFT spectra of the control papers, there is a sharp peak of medium intensity at 1508 cm^{-1}, while in the DRIFT spectra of aged papers, this band is reduced to a barely recognizable shoulder. The band at 1508 cm^{-1} is characteristic of the aromatic structure[2] and has been assigned to the ring-breathing vibration in lignin[3]. Assuming this assignment is correct, it appears that after four years of photoaging, the aromatic structure of lignin in lignin-containing papers is mostly destroyed. Another dramatic change that occurred in the DRIFT spectra of lignin-containing papers is the appearance of a strong band at 1720 cm^{-1} after photoaging. This band has been assigned to the carbonyl (C=O) stretching vibration. (Carbonyls are known to be formed by the oxidation of lignin and Polysaccharides.) A subtle, but significant change that also occurred in the DRIFT spectra is the disappearance of the band at 1208 cm^{-1} following photoexposure. In the spectra of the control paper, the 1208 cm^{-1} band shows as a weak shoulder, but it is not apparent in the spectra of photoaged paper. The band at 1208, cm^{-1} has been assigned to a phenolic–OH mode. The disappearance of this band after photoaging suggests that the phenolic structure has been destroyed.

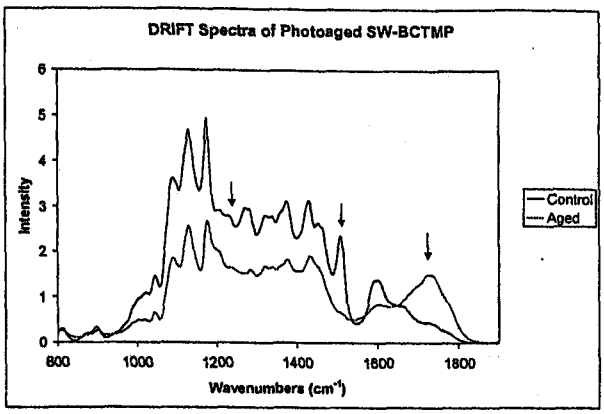

Figure 3a. DRIFT spectra of SW-BCTMP (paper 3)

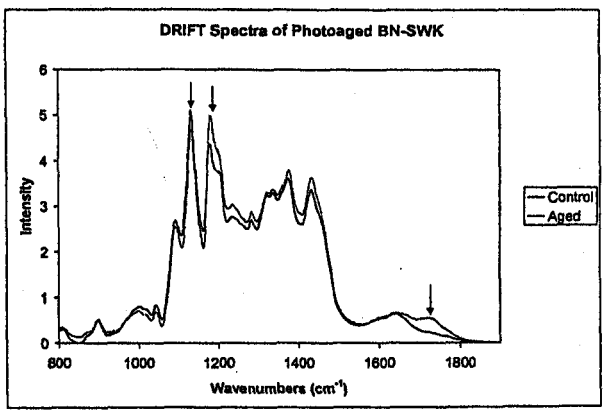

Figure 3b. DRIFT spectra of BN-SWK (paper 1)

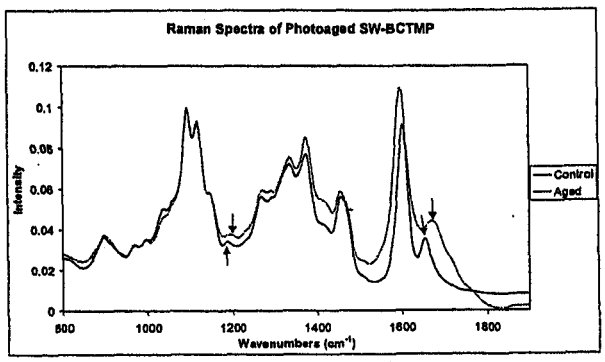

Figure 4. Raman spectra of SW-BCTMP (paper 3)

For the lignin-free papers (representative spectra shown in Figure 3b), one significant change in their DRIFT spectra after photoaging was the appearance of a band at 1720 cm^{-1}, which has been assigned to the C=O stretching vibration. The appearance of this band suggests that after four years photoaging, polysaccharides undergo some degree of oxidation. Another significant change in DRIFT spectra of lignin-free papers after photoaging was the change in the relative intensity of the bands at 1181 cm^{-1} and 1132 cm^{-1}. The reason for this difference is not well understood. Since these two bands mainly are due to the C-O stretching vibration, their relative intensity change may reflect selective oxidation of the hydroxyl groups and the breakage of C-O-C linkage.

Raman spectra of lignin-free papers do not show any significant change after four years of north window exposure, but there is a significant change for the lignin-containing papers. One noticeable change is the disappearance of the band at 1188 cm^{-1}. In the Raman spectra of the control papers, there is weak band at 1188 cm^{-1} while in the spectra of aged papers this band is not apparent. The band at 1188 cm^{-1} has been assigned to a phenolic vibration mode[4]. The disappearance of this band is consistent with DRIFT evidence (1208 cm^{-1} band) that the phenolic structure in lignin has been destroyed during photoaging. Also noticeable is the appearance of a band at 1225 cm^{-1} in the Raman spectra of the lignin-containing aged papers. This band is also seen in the spectra of lignin-free papers (control and aged, spectra not shown). Although unassigned, we believe that it is one of the cellulose bands. It is likely that in the Raman spectra of lignin-containing control papers, this band is hidden by the band at 1188 cm^{-1}. When the 1188 cm^{-1} band disappeared, the 1225 cm^{-1} became apparent. The most pronounced change occurring to the Raman spectra after photoaging is in the region of 1500 - 1800 cm^{-1}. Specifically the band at 1654 cm^{-1} disappeared, while a new band at 1675 cm^{-1} appeared. The band at 1654 cm^{-1} has been identified with ringconjugated C=C stretching vibration[4], and the disappearance of this band suggests that this structure has been destroyed. The emergence of the band at 1675 cm^{-1} indicated the formation of quinone structures[5], which may have been formed through the oxidation of phenol structure.

Interestingly, both Raman spectra of control paper and photoaged paper have a band at approximately 1600 cm^{-1}. This band has been assigned to the aromatic ring-breathing mode of lignin[3]. We believe that this assignment is correct for the control paper, but for the photoaged paper, since most of the aromatic structure in lignin has been destroyed as discussed above, the 1600 cm^{-1} band may belong to C=C stretching vibration of quinone structures that are formed by photoaging.

Chemical changes have also been investigated by analyzing the materials extracted from photoaged papers. Methanol extracted materials from papers photoaged for 29 months were analyzed by GC-MS and HPLC. The following compounds have been identified 4-hydroxy benzoic acid, vanillic acid, syringic acid, vanillin and syringaldehyde. These compounds are all aromatic in structure. FTIR spectra of methanol-extracted materials from papers photoaged for 4 years (the same papers as those used for DRIFT spectra) indicated that those extracted materials were also aromatic in structure (1508 cm^{-1} and 1600 cm^{-1} bands). When these results are compared to the results obtained from DRIFT spectra of photoaged papers, we seemingly have a contraction: on one hand, DRIFT spectra of photoaged papers suggest that photoaging destroyed most of the aromatic structure in lignin, on the other hand, the methanol extracted materials analysis indicated that photoaging generated materials with aromatic structure. The reason for this phenomenon is still to be clarified, one explanation is that photoaging broke a small portion of lignin aromatic structure at a-carbon, and led to the formation of aromatic compounds discussed above, the –COOH or –CHO groups in these compounds made them more stable than the aromatic structure in lignin, so some of these structure were preserved in the aged paper. Because of their relative small amount in the aged paper, DRIFT spectra were not able to pick up their signal, but methanol extraction concentrated them and made it possible for GC/MS, HPLC and FTIR to detect them. The destruction of the majority of the aromatic structure in lignin may be through a different pathway, such as through oxidation to quinone structure.

The effect ,of photoexposure on carbohydrates was investigated using ion chromatography. Prior to analysis, water extracted materials from control and photoexposed paper were treated with acid to hydrolyze the soluble carbohydrates to their component sugars. (The principal extracted sugars were mannose and xylose, The types and amounts of these sugars reflected the composition of the fiber furnish. That is, the principal hemicelluloses in softwoods are galactoglucomannans and arabinoglucuronoxylan while in hardwoods the principal hemicellulose is glucuronoxylan.[6]. Only small amounts of glucose were extracted.) The sugar composition and total amount of soluble carbohydrates on a dry weight percent basis for the 15 papers are shown in Table 2,

Following photoexposure, only very small amount of carbohydrates were extracted from the cotton papers. For the other lignin-free papers, the extractable carbohydrates were also limited (about 1% or less, except for paper 15, which contained starch as additive; the exceptionally high percentage of glucose apparently came from starch). The lignin containing papers had significantly larger amounts of water extractable carbohydrates. Only slightly more soluble carbohydrates were found for the acid papers relative to their alkaline counterparts after photoexposure. Two reasons may have contributed to the significantly larger amount of extractable carbohydrates from lignin-containing papers. First, the hemicelluloses, being in close proximately to lignin, were very vulnerable to lignin-based organic acid attack; and second, photoaging damaged the lignin network and freed carbohydrates that were either physically or chemically trapped in the lignin network. Because acid papers released only slightly more carbohydrates than alkaline papers, the second reason may be the dominant factor.

Table 2. Carbohydrates in water extracts

Paper No.	Total Carb%	Ara. %	Gal. %	Glu. %	Xyl. %	Man. %
1	0.91	0.09	0.03	0.10	0.53	0.15
2	0.54	0.04	0.02	0.08	0.31	0.10
3	7.84	0.65	0.75	0.86	3.32	2.15
4	7.10	0.57	0.69	0.75	3.08	1.93
5	0.30	0.03	0.01	0.19	0.07	0.00
6	0.15	0.01	0.01	0.09	0.04	0.00
7	6.41	0.42	0.63	0.96	1.61	2.74
8	6.41	0.37	0.59	0.97	1.72	2.71
9	5.97	0.23	0.20	0.21	4.99	0.16
10	4.52	0.20	0.17	0.15	3.75	0.11
11	1.14	0.06	0.02	0.12	0.83	0.11
12	0.83	0.04	0.02	0.11	0.55	0.10
13	3.53	0.16	0.13	0.14	2.87	0.12
14	4.18	0.19	0.14	0.18	3.99	0.16
15	3.73	0.05	0.02	3.07	0.50	0.09

Note: Paper 15 has starch as additive, the high percentage of glucose and total carbohydrates in the water-extracted materials apparently come from starch.

CONCLUSION

1. Long-term natural photoaging resulted in the destruction of most of the aromatic structure in the lignin-containing papers, and polysaccharides began to show some degree of oxidation in lignin-free papers.
2. Vanillin, vanillic acid, 4-hydroxybenzoic acid, syringic acid and syringaldehyde were identified as the main photoaging products.
3. Brightness of lignin-containing papers decreased rapidly upon exposure to natural light at the initial stage, and then began to level off. Lignin-free papers showed only limited brightness even after four years exposure to natural light. Alkaline papers had less brightness loss than their acid counterparts, and paper with $CaCO_3$ had less brightness loss than paper without the addition of $CaCO_3$.

REFERENCES

1. Heitner, C., "Light-induced Yellowing of Wood Containing Papers", in The Photochemistry of Lignocellulosic Materials, C. Heitner and J. Scaiano (eds.), ACS Symp. Series 531, Chapter 1, Washington, DC, Amer. Chem. Soc. (1993).
2. Lin-Vien, D., Colthup, N. B., Fateley, W. G., Grasselli, F. G., in The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, page 279-282, Academic Press (1991).
3. Hergert, H. L., in Lignins: Occurrences, Formation, Structure and Reactions, page 272-273, ed. Sarkanen, K. V., Ludwig, C. H., Wiley-Interscience (1971).
4. Agarwal, U. P., "An Overview of Raman Spectroscopy as Applied to Lignocellulosic Materials", in Advances in Lignocellulosics Characterization, page 208, Ed. Argyropoulos, D. S., TAPPI Press (1999).
5. Agarwal, U. P., "Assignment of Photoyellowing Related 1675 cm-1 Raman/IR Band to p-Quinones and its Implication to the Mechanism of Color Reversion in Mechanical Pulps", J. Wood Chem. Technol., 18(4):381 (1998).
6. Sjöström, E., in Wood Chemistry – Fundamentals and Applications, page 60, Academic Press, NY (1981).on, D.N.S., "Formation of Free Radicals in Photosensitized Cellulose III – Effect Of Photosensitizers", J. Polym. Sci., Polym. Sci. Ed. 13:1933(1975).

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