The Aging of Lignin Rich Papers upon Exposure to Light: Its Quantification and Prediction

James S. Bond, Rajai H. Atalla, Umesh P. Agarwal, Chris G. Hunt
USDA Forest Service, Forest Products Laboratory
One Gifford Pinchot Drive
Madison, Wisconsin 53705-2398 USA
E-mail: jbond/fpl@fs.fed.us

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. In support of this, indepth studies of photodegredation were undertaken in sufficient detail to establish the validity of the protocol. 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 older to accelerate photoaging. our studies included monitoring the changes in physical and chemical properties that result from the aging process. They also included spectral and chemical characterization of the species that are photosensitive, as well as their chemical transformations. The results and implications of this multiyear effort will be discussed.

INTRODUCTION

The American Society for Testing and Materials (ASTM) through its subsidiary organization, the Institute for Standards Research (ISR), is currently 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 are to develop guidelines for a credible accelerated photoaging protocol, and to simultaneously carry out in-depth studies of photodegradation sufficient to establish the validity of the protocol. The approach adopted was to carry 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 are observed, it is anticipated that guidelines for a suitable accelerated aging protocol can be developed.

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 and included a variety of fiber compositions ranging from stone groundwood to pure cotton. The photobehavior of six of these papers will be discussed here: acid and alkaline - bleached northern softwood kraft (BNSWK), bleached softwood mechanical pulp (SW-BMP) and 80% softwood stone groundwood / 20% bleached northern softwood kraft (80/20 SW-SGW/BNSWK).

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 could accommodate 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 continuonsly 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.

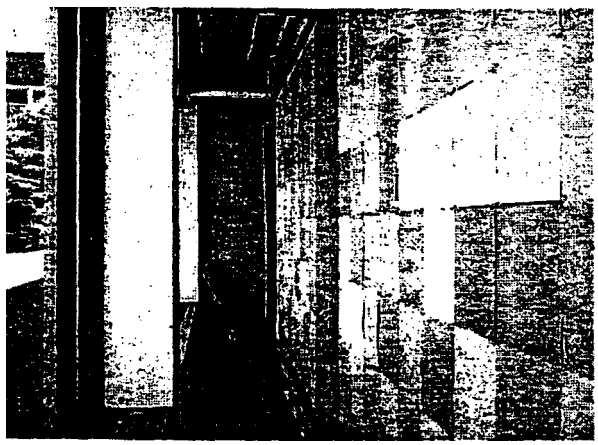

Figure 1. North window chamber. Mounted paper samples can be seen on the right side of the figure.

Accelerated Aging

Initially, a Rayonet photoreactor was used for the accelerated aging studies. This approach proved unsatisfactory because the relative stability of papers was sometimes different than seen in natural (north window) aging. We attributed these effects to the difference in illumination spectra between natural exposure and the Rayonet reactor. In order to minimize these differences, work over a wider range of intensities and have better control of the spectrum, we switched to a xenon arc-based solar simulator (Figure 2).

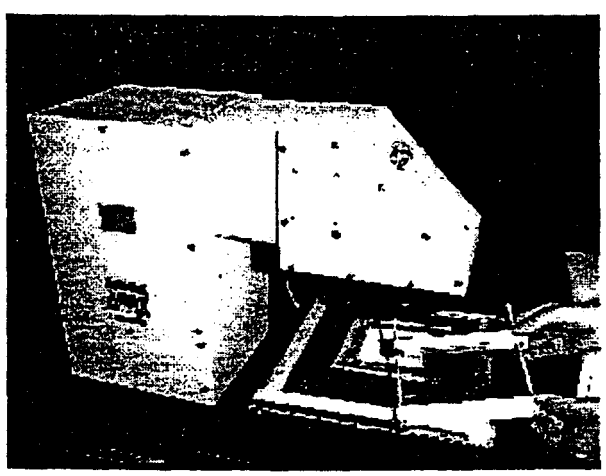

Figure 2. Oriel solar simulator.

This instrument, with appropriate filtration, produces a spectrum that mimics global solar radiation through 1.5 atmospheres (ASTM E892). Neutral density filters were used for intensity control. Window glass was inserted into the light beam to attenuate wavelengths below 340 nm to more faithfully reproduce an indoor illumination spectrum. The instrument was operated in a temperature and humidity controlled room (23°C/50%RH).

A fan was blown across the sample to maintain a constant temperature of 40 ± 4°C during irradiation. (Thermal aging effects will be minimal at this temperature.) Paper temperatures were recorded with an optical pyrometer.

Physical Testing

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

Chemical Analyses

In order to characterize the similarities and differences between naturally aged and accelerated aged papers, as well as to determine how the distribution of photochemical species changes with different aging conditions in the accelerated protocol chemical analyses of the paper samples were conducted. IR spectroscopy, Raman spectroscopy, gas chromatography/mass spectrometry (GC/MS), high pressure liquid chromatography (HPLC) and Ion Chromatography (IC) were used in the investigation.

RESULTS AND DISCUSSION

Optical Properties

Figure 3 shows the loss of brightness upon north window exposure for the subset of six papers. For the lignin containing papers, the decay was initially very rapid but began to level off after approximately 100 days of exposure. only a small loss in brightness was observed for the kraft papers. 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]

Acid sheets showed a greater brightness loss than their respective alkaline mates. Part of this difference was due to the high brightness precipitated calcium carbonate pigment present in the alkaline papers (5% addition). It can also be seen in Figure 3 that while the initial brightness of the stone groundwood/kraft paper started at a significantly lower brightness level compared to the paper made from bleached mechanical pulp, after approximately 100 days of exposure the brightness relationship was reversed.

This was true for both the acid and alkaline comparisons. This behavior is not well understood

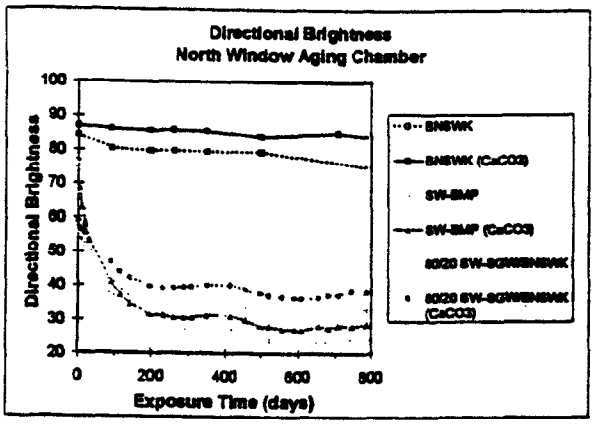

Figure 3. Effect of north window exposure on directional brightness of selected papers.

Although not shown, the yellowness (b*) increased rapidly and then leveled off for the lignin containing papers, and only increased slightly for the lignin-free papers. The yellowing occurs because lignin absorbs shorter wavelength radiation and undergoes photochemical changes to form, in part, yellow colored products.

A feature apparent in the brightness decay curves for the north window chamber is the pronounced hump in the curve centered at approximately 375 days for the lignin containing papers. (It also occurs at 750 days, but is not as pronounced.) Although the feature is shown only for the north window chamber, it occurs for 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 rate of decay appears to slow during these periods and then resumes at the pre-low humidity rate when the humidity level increases. The amplitude of these features is in the order of two to three points of brightness. it has been reported that the rate of photoyellowing is not significantly impacted by changes in relative humidity.* The observed effect is small and might be considered not significant depending on one's frame of reference.

In Figure 4, the decay behavior of the akline SW-BNP paper exposed under the various illumination sources is compared. It can be seen that paper exposed in the north window chamber showed the largest brightness drop. This can, in part, be attributed to the higher proportion of UV in natural light Very little difference in brightness was apparent between the sheets aged in fluorescent and halogen chambers.

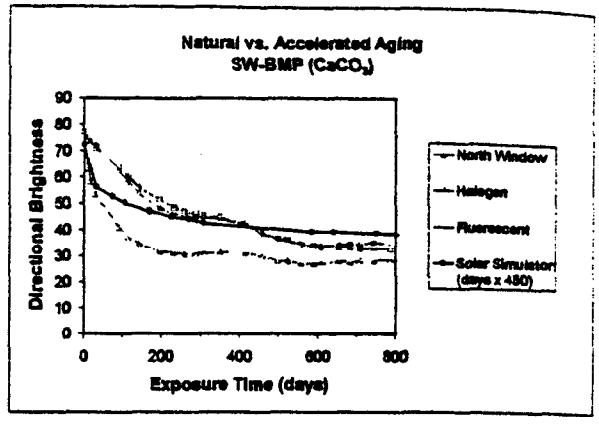

Figure 4. Effect of exposure type on the directional brightness of paper made with softwood bleached mechanical pulp. 5% precipitated. calcium carbonate addition.

Comparing the optical properties of papers exposed for a short time at high intensity to those receiving a similar number of photons in natural chambers, the papers exposed in natural chambers were always darker than those exposed in the accelerated chamber. This is shown in Figure 4 for the alkaline SW-BMP paper. In this figure, the time scale of the accelerated decay was expanded (450x) and overlaid on a north window decay curve.

It appears that there are two classes of processes occurring during natural photoexposure. Initially there is a period where only direct photochemistry drives the changes in optical properties of paper. It seems that there are photo-initiated chemical pathways that then proceed regardless of whether light continues to impinge on the sheet. Since these photo-initiated pathways need time to proceed to completion, we suspect that they are under represented in accelerated aging.

Although not shown, the ranking of the fifteen papers in terms of their final brightness and color when exposed in the natural and artificial illumination chambers was generally preserved when the sheets were accelerated aged using the solar simulator. (There are some changes in order among papers of similar brightness.)

Mechanical Properties

The effect of photoexposure on MIT fold is shown in Figure 5. All papers studied showed a loss in logfold following photoexposure regardless of composition or illumination spectrum. North window exposure was

found to be more severe in terms of strength loss than either the halogen or fluorescent illumination.

The acid papers consistently showed a larger fold loss than their respective alkaline mates. The reason for this behavior may be due to the presence of the calcium carbonate buffer serving to neutralize any lignin-based organic acids formed during the aging process.

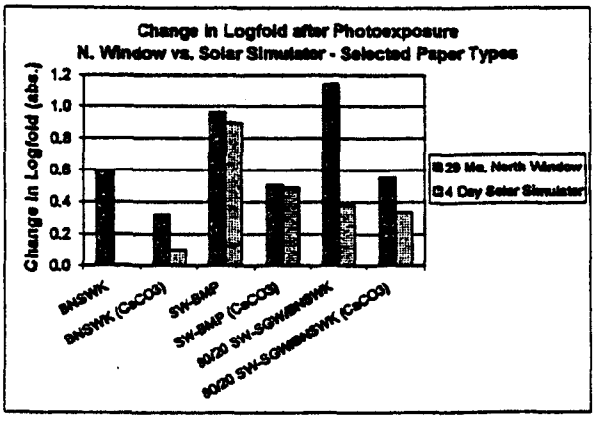

Figure 5. Change in logfold after photoexposure for selected papers.

The loss of fold of the alkaline kraft paper may, in part, be caused by cellulose degradation. Degradation of the mechanical properties of cellulose with light above 340 nm is documented.[3-6] Although cellulose itself cannot absorb at these wavelengths, photosensitizers such as transition metals are almost always present The result is that cellulose chain scission is possible with wavelengths of light that are present in normal indoor illumination conditions.

Even though the kraft papers fold loss was pronounced, these paper still retained significant fold strength after photoexposure.

When illuminated at high intensity for short times (accelerated conditions), mechanical properties degraded in a manner similar to natural aging.

Chemical Analyses

To investigate whether light-induced changes depended upon the illumination spectrum, the acid SW-BMP paper was exposed to north window indirect sunlight (ISL) end 350 nm radiation (Rayonet photoreactor - RPR). Raman spectra were run on the papers and their (methanol) extracts. The results showed that the spectra obtained from the two types of exposure were very similar.

The changes in the 1600 cm^{-1} region are shown in Figure 6. Cellulose's 1098 cm^{-1} band was used to normalize the spectra. The most pronounced change occurred in lignin's 1654 cm^{-1} bend. This band has been identified with ring-conjugated C=C and C=O stretching vibrations.[7-9] After photoexposure this band declined in intensity and a new feature at a slightly longer wavenumber developed. We believe that this new feature is due to the paraquinone formation.

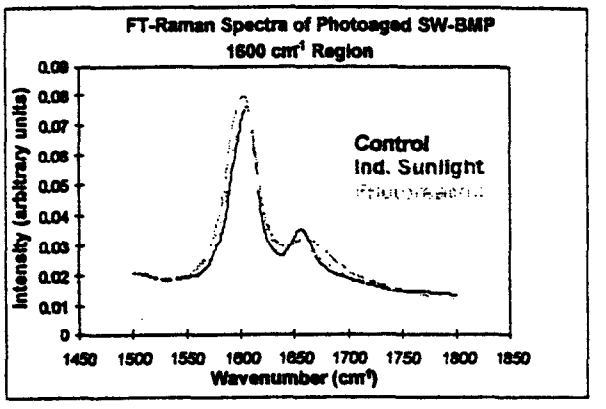

Figure 6. Raman spectra of photoaged SW-BMP paper with precipitated calcium carbonate filler.

Methanol extracts of photoyellowed (ISL and RPR) SW-BMP paper was analyzed using GC/MS to further investigate the impact of the illumination spectrum on light-induced chemical changes. Most GC peaks were present in all four extracts. This implied that the same types of chemical changes were occurring under both types of exposure. In the extracts, vanillin, vanillic acid, and syringaldehyde were identified. Extracts of hardwood and softwood papers were different in some respects, which was probably due to hardwood/softwood component differences.

HPLC was also used to investigate the dependency of chemical changes on the light source spectrum. The same paper extracts that were studied in the GC analysis mentioned above were used in this analysis. From the studies so far, it does not appear that there are components that are generated under only one kind of illumination, i.e. quantities of the degradation products differ but not the actual products themselves.

An IR analysis of the ISL and RPR exposed papers (alkaline SW-BMP paper) indicated that at the same brightness level, the carbonyl content of the ISL yellowed paper was approximately 37% higher as

compared to an RPR paper. This finding supported a recently proposed hypothesis[10] on the mechanism of photoyellowing. This hypothesis states that the chemical structure causing most yellowing in photoexposed paper is paraquinone.

The effect of photoexposure on carbohydrates was investigated using ion chromatography. Prior to analysis, water extracts 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 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.[11] Only small amounts of glucose were extracted.) The total amount of soluble carbohydrates on a dry weight percent basis for the six papers is shown in Figure 8.

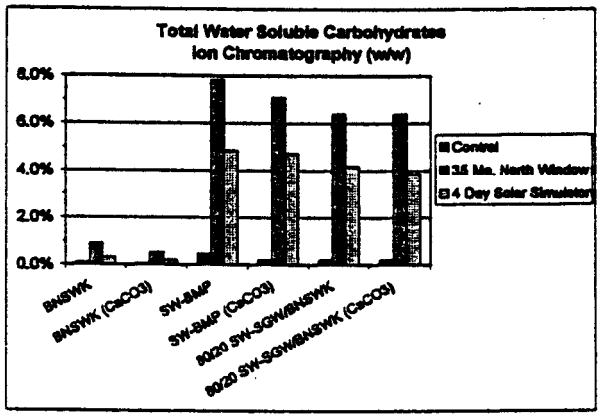

Figure 8. Total water soluble carbohydrates as determined by ion chromatography.

Following photoexposure, the lignin containing papers had significantly larger amounts of water extractable carbohydrates than did the lignin-free papers. Only slightly more soluble carbohydrates were found for the acid papers relative to their alkaline mates after photoexposure. A possible explanation for these observations is that the hemicelluloses, being in close proximately to lignin, are very vulnerable to lignin-based organic acid attack. This close association may partly override the protective action of the calcium carbonate filler.

carbohydrate analysis showed similar degradation products between natural and accelerated aging (data not included here). The relative amounts of total carbohydrates extracted from north window and solar simulator exposed sheets were very similar.

CONCLUSION

Accelerated aging causes many physical, optical and chemical changes similar to those seen in natural aging Our data indicates that:

- we get an accurate rank order of optical photo-stability of papers,
- In general, the trends in mechanical property loss are similar between natural and accelerated aging,
- There is a fairly good correlation between natural and accelerated aging chemical analyses.

The Finnish Pulp and Paper Research Institute will conclude their investigation into the effects of light aging in June 2000. Following completion of their research program, the two groups will jointly develop a light aging protocol based on our research findings.

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