

Aging of Printing and Writing Paper upon Exposure to Light. Part 2. Mechanical and Chemical Properties

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ABSTRACT

Data is presented on chemical and physical changes observed on a series of 15 specially made writing papers as part of the development of the new ASTM standard D6789-02. Papers were exposed to north window, fluorescent, and halogen illumination for several years. Furnish covered the span from stone groundwood to textile cotton, pH 5 to 8.1, with and without alkaline reserve. Degree of polymerization was dramatically reduced, even for the most robust papers under the mildest illumination. All mechanical properties were degraded, lignin aromatic structures were destroyed, and C=O bonds became more prevalent. The data suggests that indicators of long-term serviceability of papers are alkaline buffering capacity, initial strength properties, lignin content, and opacity.

INTRODUCTION

The Forest Products Laboratory conducted aging experiments in conjunction with the development of the new ASTM standard D6789-02, "Standard Test Method for Accelerated Light Aging of Printing and Writing Paper by Xenon-Arc Exposure Apparatus." Physical, chemical, and optical properties of these 15 specially made papers were monitored for over 5 years of exposure to 3 different indoor lighting environments. Optical properties were discussed previously (1). This paper presents physical and chemical changes.

METHODS AND MATERIALS

Paper samples

Table 1 presents the composition of test papers, ordered from high to low lignin content, including alkaline/buffered and acidic/unbuffered versions of the same furnish.

Exposure Conditions

A north-facing room was modified to create three isolated chambers: one each for exposure to halogen and fluorescent illumination, and one for northern exposure to daylight. Each chamber contained 160 8.5x11" sheets of paper. Lights were placed 6-8 ft from the papers and illuminated at the level of a bright office. Halogen and fluorescent chambers were continuously lighted, while the north window followed normal cycles. Typical conditions ranged from 10% relative

humidity and 22°C in winter to 60% and 32°C in summer. Papers stored in a corrugated box in the aging chamber experienced the same conditions without light. Remaining papers were stored in a dark room at 4°C.

Table 1. Paper Composition

| ID | BN SWK | BN HWK | SW BCTMP | HW BCTMP | SW SGW | COT- TON | pH | % CaCO ₃ | Klason Lignin% | Additive |
|----|--------|--------|----------|----------|--------|----------|-----|---------------------|----------------|----------|
| 3 | 100 | | | | | | 5.0 | 0 | 24.9 | A |
| 4 | 100 | | | | | | 8.1 | 5 | 23.6 | |
| 7 | 20 | | 80 | | | | 5.0 | 0 | 23.8 | A |
| 8 | 20 | | 80 | | | | 7.0 | 5 | 22.3 | M |
| 9 | 20 | | 80 | | | | 8.1 | 0 | 11.7 | |
| 10 | 20 | | 80 | | | | 8.1 | 5 | 10.9 | |
| 14 | 50 | | 50 | | | | 5.0 | 0 | 7.1 | AN |
| 13 | 50 | | 50 | | | | 8.1 | 5 | 7.4 | |
| 1 | 100 | | | | | | 5.0 | 0 | 0.7 | AN |
| 2 | 100 | | | | | | 8.1 | 5 | 0.2 | |
| 5 | 100 | | | | | | 5.0 | 0 | 1.7 | AN |
| 6 | 100 | | | | | | 8.1 | 5 | 1.6 | |
| 11 | 100 | | | | | | | 0 | 0.2 | |
| 12 | 50 | 50 | | | | | 8.1 | 5 | 0.2 | |
| 15 | 100 | | | | | | | | 0.4 | SKP |

BN = Bleached Northern SW = Softwood
 BS = Bleached Southern HW = Hardwood
 SGW = Stone Ground Wood
 S(H)WK = Soft(Hard)wood Kraft
 BCTMP = Bleached Chemithermomechanical Pulp
 Additives: A=Alum, N=Hercules Nuphor 635 Rosin
 Size, S=Starch, K=AKD internal size, P=Penford Gum
 external size, M=SMI process low pH CaCO₃

Table 2. Illumination intensity in aging chambers

| Filter Region | | Intensity, W/m ² | | | |
|---------------|---------|-----------------------------|---------|-------------|--------|
| λ, nm | Name | North* | Halogen | Fluorescent | E892** |
| 395-728 | Visible | 3.2 | 6.4 | 5.9 | 445 |
| 347-389 | UV | 0.25 | 0.0 | 0.0 | 25 |
| 374-464 | Blue | 0.79 | 0.3 | 0.7 | 98 |
| 392-602 | Aqua | 2.1 | 1.7 | 4.7 | 286 |

*year-long average **ASTM standard noon direct solar illumination

Testing

Testing was done according to the following TAPPI standards: Viscosity, T230; surface pH, T529; fold, T511, using each strip for multiple tests; tear, T414; zerospan tensile, T231; tensile, T494, with half the standard sample length. Infrared analysis was performed with a Mattson Galaxy 5000, Raman with a Bruker RFS 100 using 1064-nm excitation.

Lignin was removed from BCTMP and SGW containing paper before viscosity measurement by the following method. To 2g paper add 80ml solution in sealed bottle, react at 75° for 30 min, add 40ml additional solution, react 30 more minutes. Filter, wash

with water then acetone, dry. Solution contains 400ml water, 1.25ml glacial acetic acid, 3.75g sodium chlorite.

Water soluble sugars were extracted by soaking paper in water/.02% sodium azide for 3 days at room temperature and filtering to 0.45 μm . Extracts were hydrolyzed for 1 h at 120°C with 4% H₂SO₄. Analysis was done with ion chromatography (Dionex Carbo-Pac PA1 column) and pulsed amperometric detection as described by Davis (2).

RESULTS AND DISCUSSION

Chemical Changes

Viscosity/DP

Long-term light exposure resulted in dramatic viscosity decreases in the most stable papers even under halogen and fluorescent illumination (Table 3). The north window exposure did produce a higher chain scission rate (Table 4), though the difference was quite small considering there was no measurable UV component in the halogen and fluorescent chambers. In these chambers, the degradation was primarily due to photosensitized reactions with visible light. Similar observations had been made previously (3). The absence of degradation in the corrugated box storage proves that the damage was due to light, not pollution or heat. Most of this change in viscosity was evident after only 29 months of aging.

Table 3. Viscosity (Cps) of lignin-free papers after 5 years.

| pH/ Buffer | Papers | North | Halogen | Fluorescent |
|------------|--------|-------|---------|-------------|
| 5/No | 1,5 | 3.8 | 3.4 | 3.3 |
| 8/No | 11 | 4.6 | 2.2 | 2.7 |
| 8/Yes | 2,12,6 | 2.6 | 2.4 | 1.7 |

To gain information about the rate of cellulose depolymerization, the following equation can be used to estimate cellulose degree of polymerization (DP) (4):

$$DP \cong -673 + 711.3 * (\ln(\text{TAPPI viscosity}))^{0.96559}$$

From DP, we can calculate the number of chain scissions, n, per 1000 glucose units.

$$n = \{(DP^0/DP^t) - 1\} * 1000 / DP^0$$

Table 4. Estimated number of cellulose chain cleavages per 1000 glucose units

| Pulp | pH/ Buffer | ID | North | Halogen | Fluorescent |
|--------|------------|----|-------|---------|-------------|
| Kraft | 5/No | 1 | 5.2 | 3.7 | 3.7 |
| | 8/No | 11 | 4.6 | 2.2 | 2.7 |
| | 8/Yes | 12 | 1.7 | 1.7 | 1.2 |
| | | 2 | 3.1 | 2.6 | 2.1 |
| Cotton | 5/No | 5 | 2.4 | 3.1 | 2.9 |
| | 8/Yes | 6 | 2.9 | 2.7 | 1.9 |

The relative rate of cellulose chain scission can be inferred from Table 4. Though the data is somewhat noisy, it is clear that fluorescent and halogen exposure produced similar depolymerization rates and north

window exposure was only somewhat more damaging. Also, alkaline buffered papers were much more resistant to chain scission than acidic, unbuffered sheets. Note that Table 4 does not represent acid hydrolysis in the classic sense. Papers stored in a box in the same room had no measurable viscosity change. Therefore, depolymerization is produced by an interaction of acid, light, and photo-sensitizer, probably through a radical mechanism.

The viscosity of lignin-containing papers is presented in Table 5. Since these papers had to be delignified before dissolving in CED, these viscosity values cannot be compared to the lignin-free values. They are presented to show that the same trends in buffering and pH in lignin-free papers are also true for lignin-containing papers.

Table 5. Viscosity of lignin-containing paper after 5 years photexposure and delignification.

| Klason Lignin | pH/ Buffer | ID | North | Halogen | Fluorescent |
|---------------|------------|----|-------|---------|-------------|
| 20+ | 5/No | 3 | 4.1 | 4.3 | 3.7 |
| | | 7 | 3.7 | 4.4 | 3.9 |
| | 7/Yes | 8 | 4.5 | 4.8 | 4.3 |
| | 8/Yes | 4 | 4.8 | 5.0 | 4.7 |
| ~10 | 5/No | 14 | 5.4 | 6.7 | 5.7 |
| | 8/No | 9 | 5.4 | 8.2 | 7.1 |
| | 8/Yes | 10 | 6.3 | 9.5 | 8.5 |
| | | 13 | 5.7 | 7.2 | 7.1 |

The viscosity losses suggest that MD wet zero span tensile index might be a useful way to quickly evaluate the condition of lignin-free papers. This test minimizes the contribution of fiber bonding and may be a good way to get information on fiber damage without resorting to viscosity measurements. It also uses very little sample. This method may not be useful for lignin-containing papers, however. We have observed that because photoexposed high lignin sheets are brittle and do not disperse in water, their wet properties are not the same as those of unexposed papers.

Surface pH

Cellulose depolymerization leaves carboxyl groups on the chain end, which would tend to accelerate further paper decay by promoting acid hydrolysis. The creation of acidic end groups in lignin-free papers is suggested by the drop in surface pH, as shown in Table 6. The link to cellulose depolymerization is not as clear in lignin-containing papers because they have many possible acid generating photochemical mechanisms.

Surface pH measurements also demonstrate important variables in stopping acid degradation of paper. Comparing papers 14 with 9 and papers 1 and 5 with 11 shows that the pH during paper formation is much less important than the presence of buffer in

determining final surface pH and viscosity. The buffer was the most important factor in maintaining pH during photoexposure. Buffered lignin-containing papers did not drop below pH 5.7 and lignin-free papers stayed above pH 6.7. Their unbuffered counterparts dropped as low as pH 3.0 and 3.7, respectively. We should note that it was difficult to obtain reliable values for surface pH of carbonate papers because the pH kept increasing during measurement.

Table 6. Surface pH after 5 years exposure. Papers with very similar results were averaged together.

| Klason Lignin | pH/Buffer | ID | Cold Room | Box | North | Halo gen | Fluore scent |
|---------------|-----------|---------|-----------|-----|-------|----------|--------------|
| 20+ | 5/No | 3,7 | 4.7 | 4.4 | 3.2 | 3.2 | 3.2 |
| | 7/Yes | 8 | 7.4 | 7.0 | 5.9 | 5.9 | 5.8 |
| | 8/Yes | 4 | 7.8 | 7.0 | 5.8 | 5.7 | 5.8 |
| ~10 | 5/No | 14 | 5.0 | 4.6 | 3.3 | 3.4 | 3.2 |
| | 8/No | 9 | 7.1 | 6.2 | 3.4 | 3.4 | 3.4 |
| | 8/Yes | 10,13 | 8.1 | 7.3 | 6.3 | 6.3 | 6.3 |
| <2 | 5/No | 1 | 4.5 | 4.4 | 3.7 | 4.0 | 3.8 |
| | | 5 | 6.0 | 5.8 | 4.1 | 4.4 | 4.3 |
| | 8/No | 11 | 5.7 | 5.4 | 3.8 | 3.9 | 3.8 |
| | 8/Yes | 2,12,15 | 8.0 | 7.8 | 7.0 | 7.0 | 7.2 |
| | | 6 | 8.5 | 8 | 7 | 6.8 | 7.1 |

Moisture Content

High lignin papers exposed to significant irradiation cracked rather than folded and did not disperse in water. We also observed changes in mechanical properties that would be consistent with reduced moisture content. The average equilibrium moisture content of lignin-free sheets declined from 6.0% to 5.7% and that of lignin-containing sheets from 7.4% to 6.7% after 29 months in the north window.

Soluble Sugars

Analysis of constituent sugars in water-soluble extracts revealed that significant quantities of hemicellulose and a small amount of cellulose were liberated after 35 months exposure.

Table 7. Extracts from papers aged 35 months (% of total paper mass)

| ID | 3 | 4 | 7 | 8 | 9 | 10 | 14 | 13 | 1 | 2 | 5 | 6 | 11 | 12 |
|----------|-------|-----|-------|---------|-------|--------|-------|-----|-----|-----|-----|-----|-----|-----|
| Furnish | BCTMP | SGW | BCTMP | -50/50- | Kraft | Cotton | Kraft | | | | | | | |
| pH/buffe | 5/N | 8/Y | 5/N | 7/Y | 8/N | 8/Y | 5/N | 8/Y | 5/N | 8/Y | 5/N | 8/Y | 5/N | 8/Y |
| Control | 0.5 | 0.2 | 0.2 | 0.02 | 0.7 | 0.4 | 0.3 | 0.2 | 0.1 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 |
| North | 7.8 | 7.1 | 6.4 | 6.4 | 6.0 | 4.5 | 4.2 | 3.5 | 0.9 | 0.5 | 0.3 | 0.2 | 1.1 | 0.8 |

Fiber type significantly influenced water-soluble sugars. Since hemicellulose is so much more soluble than cellulose, only high yield pulps had significant soluble sugars. Buffering had some effect, as seen in papers 9 and 10, and the effect of pH was smaller yet.

There are many paths by which the carbohydrates could be released upon photoexposure. Carbohydrates that were physically trapped in the lignin matrix could be released as the lignin matrix changed. Reactive lignin fragments produced upon photoexposure could attack carbohydrates. Also, metal ions (and possibly lignin chromophores) adsorbed onto the carbohydrates could act as photosensitizers, allowing photo-oxidation of carbohydrates either directly or through formation of free radicals.

Diffuse Reflectance Infrared (DRIFT)

We observed three significant changes after 4 years exposure. First, a strong peak appeared at 1720 cm^{-1} , characteristic of C=O vibration and indicative of carbonyl/carboxyl formation. This was true of both lignin-free and lignin-containing papers. In lignin-containing papers, the peak at 1508 cm^{-1} assigned to lignin aromatic structure and the 1270 cm^{-1} peak assigned to guaiacyl ring breathing with C=O stretch disappeared from the front side of the papers. These indicate that aromatic structures were completely destroyed. Both peaks were still present on the back side of the paper, however.

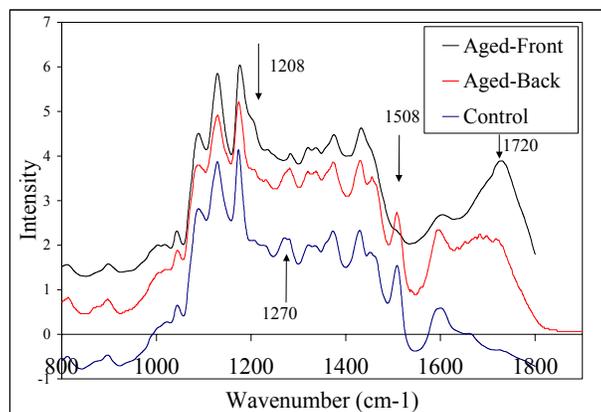


Fig. 1. DRIFT spectra of paper 3 after 4 years in north window. Front & Control offset for clarity.

Raman and Micro-Raman

A micro-Raman analysis was performed to determine the extent of aromatic lignin destruction. Ten spots through the thickness of the paper were analyzed for the ratio of aromatic to cellulosic vibration intensity (I_{1600}/I_{1095}). Table 8 shows the destruction of aromatic structures on the photoexposed surface, as well as an increase in aromatic intensity deeper in the sheet. We attribute this increased intensity to C=O bonds formed on the aromatic structures during initial stages of oxidation.

Macro-Raman analysis revealed a shift of the 1654 cm^{-1} band to 1675 cm^{-1} . These have been assigned to ring conjugated C=C stretching and quinone structure, respectively, indicating the production of

quinones. Also, a very small peak at 1188 cm⁻¹ (phenolic vibration) shifted to 1205 cm⁻¹ (unassigned).

Table 8. Raman aromatic lignin/cellulose intensity with depth in BCTMP paper 3 after 4 years north exposure

| | Approximate Depth Below Front Surface, um | | | | | | | | | | |
|--------------------------------------|---|-----|-----|----|-----|-----|-----|-----|-----|-----|-----|
| | 0 | 16 | 32 | 48 | 64 | 80 | 96 | 112 | 128 | 144 | 160 |
| I ₁₆₀₀ /I ₁₀₉₅ | 0.4 | 0.8 | 0.9 | 1 | 1.1 | 1.2 | 1.4 | 1.6 | 1.7 | 1.5 | 1.4 |

I₁₆₀₀/I₁₀₉₅ of unaged paper is 1.1: Average paper thickness 163um.

Physical Changes

Early stages of the program hoped to establish which mechanical properties were best indicators of the early stages of aging. Log of MIT fold was found to have the highest statistical significance per area of paper tested.

After 5 years exposure, all 15 papers were tested in all 3 aging chambers. Table 9 indicates the range of property degradation observed. Even the best papers experienced notable property degradation, though buffered sheets, such as paper 6, fared better than expected considering the loss in viscosity. The variability of the fold test is also evident.

Table 9. Retention (%) of CD properties after 5 years exposure. Average of all lighting conditions.

| | ID | Log | | Zeros | Ten | | Brit | Stretch | |
|--------|--------|------|------|-------|------|-----|------|---------|----|
| | | Fold | Tear | pan | sile | TEA | tle | | |
| Cotton | Buffer | 6 | 81 | 76 | 88 | 98 | 84 | 120 | 87 |
| BCTMP | | 4 | 21 | 66 | 61 | 69 | 30 | 167 | 47 |
| Kraft | Acid | 1 | 49 | 45 | 58 | 73 | 44 | 128 | 60 |
| BCTMP | | 3 | 44 | 63 | 73 | 74 | 35 | 178 | 49 |

Table 10 gives a more precise picture of how each composition variable impacted aging performance. The strongest factor in preserving properties was the use of alkaline pH during papermaking. In contrast to DP and surface pH data, the mechanical properties of alkaline buffered sheets were very similar to those of unbuffered sheets. However, these papers were not exposed to airborne (generally acidic) pollutants or long exposures. Both of these conditions would accelerate acid hydrolysis. Therefore buffering capacity is still an extremely important component of permanent paper.

Lignin content was also a significant factor in contributing to the degradation of physical properties. Anecdotal evidence supports the theory that high lignin papers are more prone to become brittle, which is supported by the logfold, TEA, and brittleness data.

Properties of papers exposed in the north window were consistently 5-7% lower than those of papers exposed to halogen and fluorescent light, except for elongation (15%) and TEA (20%).

Table 10. % retention of CD properties after 5 years exposure. Average of all lighting conditions.

| | Papers | Log Fold | Tear | Zero span | Ten sile | TEA | Brit tle | Elong |
|-------------------|-------------------|----------|------|-----------|----------|-----|----------|-------|
| lignin | 3,4,9,10 13,14 | 55 | 61 | 74 | 81 | 52 | 142 | 63 |
| lignin free | 1,2,5,6,1 1,12 | 64 | 60 | 75 | 87 | 59 | 128 | 67 |
| Acid | 1,3,5,7,1 3 | 44 | 56 | 67 | 79 | 44 | 145 | 57 |
| Alkaline Buffered | 2,4,6,8,1 4 | 62 | 65 | 76 | 84 | 53 | 136 | 62 |
| No Buffer | 9,11 | 66 | 66 | 82 | 88 | 60 | 131 | 68 |
| Buffered | 10,12 | 65 | 59 | 81 | 89 | 66 | 122 | 74 |

SUMMARY

Visible light can cause substantial damage to even the most stable of papers. Factors that result in papers with good mechanical properties after long-term exposure are alkaline reserve and alkaline papermaking process, low lignin content, high initial strength, and high opacity. Acid and lignin are discussed at length in the text. High initial strength is beneficial because strong papers can lose a larger percentage of their initial properties and still be serviceable. Finally, the damage found in this study was caused by light hitting the paper fiber. Highly opaque papers will effectively prevent a significant fraction of the light from reaching the inner layers of the sheet, effectively preventing photodegradation. High opacity can be seen as self-protective. Finally, keeping light levels (as well as temperature and pollution levels) low will contribute to the longevity of paper records.

This collection of papers was custom made for this ASTM project. Unused sheets of all 15 papers, as well as extensive baseline data, are available from the authors.

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