Technical Bulletin

Verso Customer Technical Services Group

Paper Stability and Permanence

In the 1980s, stories appeared in the popular press reporting on deterioration of many holdings in the Library of Congress[1]. Documents only 100-200 years old had become brittle and were disintegrating, while older documents were often in much better condition. The implication was that something in the "modern" papermaking process was the cause.

Interest in the permanency of the handling qualities of paper, the property of most interest to archivists, goes back many years. Scientific study of the deterioration of paper with time and the development of accelerated methods for predicting it started in earnest in the early 1900s, although occasional comments and observations on paper's permanency go back nearly 900 years to the time of its first use in Europe in the eleventh and twelfth centuries.

Figure 1. The Dead Sea Scrolls, written on a non-wood material - parchment, have survived thousands of years but still show the effects of aging. (Picture used by permission of Tyler Williams; http://biblical-studies.ca/dss/dss_pictures/Biberkraut_GenApocryphon.jpg)

Historically, the concern has been that paper will not last for as many generations as will parchment and vellum, which were originally produced from animal skins. Today, we know that some papers clearly will last and remain in usable condition for hundreds of years since there are many thousands of books and documents in an excellent state of preservation that date from before 1600. And, just as surely, we know that there is a great deal of paper, especially paper made since 1800 and continuing still today, that will not last. As will be discussed, it was the use of an acidic chemical, alum, in the papermaking process and later the introduction of groundwood fibers that were at the root of the problem.

What constitutes permanence can vary according to circumstances, but a general definition can be found in the ANSI/NISO Z39.48-1992 (R1997) document, "Permanence of Paper for Publications and Documents in Libraries and Archives."

> *Permanence*—The ability of paper to last at least several hundred years without significant deterioration under normal use and storage conditions in libraries and archives.
>
> The relevant ISO standard, ISO 9706:1994, uses the following:
>
> *Permanence*—Ability to remain chemically and physically stable over long periods of time.
>
> For "archival" paper, we have (ISO 11108:1996):
>
> *Archival paper*—Paper of high permanence and high durability.
>
> *Durability*—The ability to resist the effects of wear and tear when in use.

Permanence clearly depends on the situation. Exposure to light is not a primary concern for books in a library, for example. Archivists and librarians may be more interested in paper's resistance to atmos-

Figure 2. Documents such as the Declaration of Independence, although printed on parchment, have undergone noticeable deterioration. Courtesy of National Archives and Records Administration.

pheric damage. They want to be sure that the pages of the book will have mechanical integrity decades or centuries down the road. Others may be more interested in short-term appearance properties, specifically lightfastness, fade resistance or the tendency not to yellow. Under these circumstances, stability may be a more meaningful descriptor than permanence.

While there are many factors, both in the papermaking process and the conditions of storage that influence the permanency or stability of paper, two of the manu-

Figure 3. Documents such as the Declaration are now stored in special cases that limit their exposure to heat, light and atmospheric pollutants. Courtesy of Earl McDonald, National Archives and Records Administration.

facturing variables that stand out as most important are the purity of the cellulose used and the degree of acidity or alkalinity of the finished paper.

Medieval scholars were concerned with the filthy rags used by papermakers, but those linen and cotton rags were really very pure cellulose and, when made into paper with hard alkaline water or when a mild cook of the rags with lime was undertaken to soften them, they produced an excellent, long-lasting paper. Cotton and linen, however, are totally inadequate for today's paper needs due to supply and cost. Consequently, more than 95% of the world's paper currently comes from wood.

Wood is reduced to papermaking pulp essentially by two different methods. The chemical process cooks the wood with chemicals and steam in a pressure

"Groundwood" can refer to either the particular process for making mechanical pulp — mechanical grinding with what looks like a grinding wheel — or, more loosely, to the product of any mechanical pulping process, regardless of the method used. "Wood-free" or "free-sheet" means the paper contains at least 90% chemical pulp, the remainder being lignin-containing mechanical pulp. "Lignin-free" means that the pulp contains ≤1% lignin. Although the actual amounts vary depending on species, approximately 50% of a tree is water, 24% cellulose, and the rest other components including lignin, the glue that holds everything together. Thus, "wood-free" papers typically contain less than 3% lignin and could be as little as 0%.

cooker and removes the cementing and non-cellulose materials in the original wood structure to produce a chemical pulp. After the pulp is bleached to a white color suitable for printing paper, the yield of usable cellulose fiber is about 45% of the original dry weight of the wood. This bleached chemical wood pulp can be of very high quality, sometimes approaching or even exceeding some grades of rag pulp.

The other method is known as mechanical pulping. Logs or wood chips are simply torn apart by large grindstones or mechanical refiners that reduce the wood structure down to its fiber elements. Hence, the common name groundwood. Some mechanical pulping processes also utilize chemicals to assist in breaking down the wood, and the resulting mechanical pulp is sometimes bleached. Since all the cementing and non-cellulose components of the original wood remain on the fibers, the yield of pulp is almost 90%, twice that of bleached chemical pulp. Subsequently, only half as many trees are used to produce the same amount of fiber. In addition, groundwood mills require only about 25% of the capital needed to build chemical pulp mills. They have no air pollution problems and much-reduced stream pollution problems. On the negative side, the process is very energy intensive.

Groundwood pulp, compared to chemical pulp, is quite weak and is poorer in color and aging characteristics. Lignin, the cementing material in wood that holds the cellulose fibers together, is quite sensitive to degradation by both impure air and light. Therefore, paper containing lignin tends to age rapidly, most noticeably by yellowing.

Figure 4. A modern paper mill.

Paper can contain combinations of mechanical (groundwood) and chemical pulp. The familiar newspaper is 75% to 85% groundwood, the balance being chemical pulp. Most magazine pages are coated paper, with a base sheet varying from 10% to 70% groundwood, while paper used for high-end advertising, annual reports, etc., often contains little or no lignin-containing groundwood.

The increasing need for more paper on a worldwide basis, and the growing pressure on the forests for fuel and other uses, will force papermakers to use higher-yield processes such as groundwood and related methods, as well as many other varieties of cellulose, including those coming from recycled paper, wheat straw, corn stalks, bagasse and the like. Some of these trends will not help paper permanency; others may not be economically viable. Keep in mind that optical stability does not imply mechanical stability; paper that is mechanically stable might not be optically stable and vice versa.

Most of the focus on permanence and durability has revolved around uncoated paper. The few studies that have been done on coated paper and paperboard suggest that the coating itself may not have as much influence on permanence/durability as does the chemistry and composition of the underlying base stock, particularly the pH of the base stock and its lignin content.

PAPER pH (ACIDITY OR ALKALINITY)

While paper has been produced in a wide range of pHs throughout its history (below 7 is acid, 7 is neutral, above 7 is alkaline), some division into general groups may be made. Before 1800, the papermaker did not deliberately add any material to the pulp to affect its pH. If he used acidic water, the paper would come out slightly acidic; if alkaline water was used, slightly alkaline paper was the result. Any cooking of the rags with lime or wood ashes (sodium carbonate) to soften or degrease them would add alkalinity to the finished paper. Analysis of ancient paper samples, which

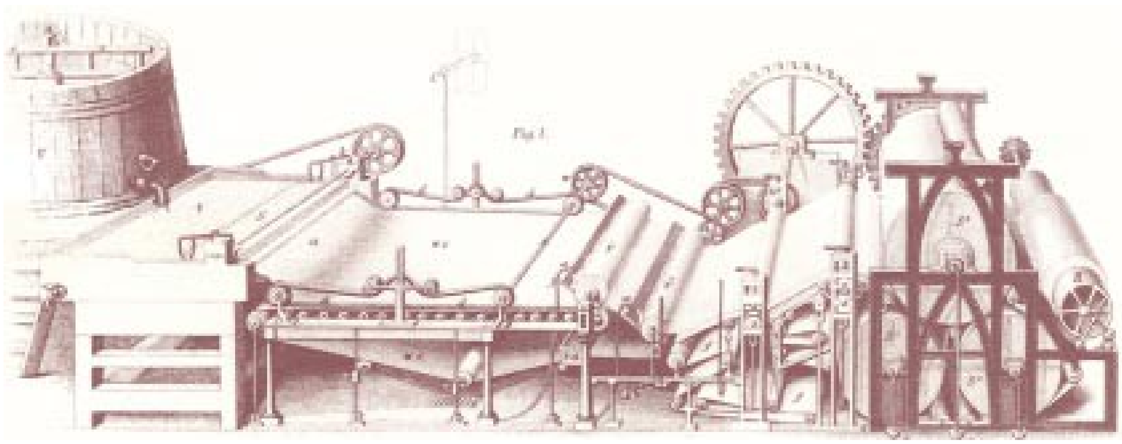


Figure 5. An old engraving, circa 1850, depicting machine-made papermaking. Helena E. Wright, "300 Years of American Papermaking," Smithsonian Institution exhibition booklet, December 1990-November 1991.

contain little if any lignin, does show that those that had higher pH values fared much better over time.

After 1800, when aluminum sulfate, or alum, and rosin were introduced to the papermaking process as sizing agents (materials that control the ink and water repellency of paper), the great majority of the paper produced was somewhat acidic. The precipitated rosin is a debonding agent; it interferes with cellulose fibers bonding to one another, making paper somewhat weaker. And since it is an acid salt, it also makes the paper acidic, sometimes very much so. Acidic paper was found to lack mechanical stability/permanence, but acidity alone may not be the entire explanation; some authorities feel that the aluminum in alum is a part of the problem as well.

In the last 20-25 years, with the availability of sizing materials and procedures that permit sized paper to be made neutral or alkaline, there has been a trend back to higher pH levels (neutral or alkaline). In the United States, the majority of fine paper now produced is made using alkaline sizing materials. This has greatly enhanced paper's stability/permanence with respect to mechanical properties.

LIGNIN

Historically, paper was produced from cotton, linen (flax) and other plant-derived fibers. These fiber sources contain little or no appreciable lignin, the chemical adhesive found in wood. The introduction of wood-based cellulose fiber in the 1850s added a new concern. The lignin found in groundwood fibers also deteriorated over time upon exposure to the elements, aggravating the permanency problems caused by the use of alum. In the case of lignin, the deterioration most often noticed in paper is yellowing.

Why weren't these problems noticed earlier? In fact, they were; what was unknown was what a serious problem it was, at least for archival documents. It took decades or centuries for the problems to manifest themselves, and accelerated testing methods were not available or were not reliable.

Cellulose purity and pH are, thus, the two key factors affecting stability and permanence. Whenever well-preserved, mechanically stable papers are examined, they are neutral or alkaline in pH. On the other hand, papers that have become appreciably discolored with time are likely to contain groundwood pulp.

For the vast majority of paper users, long-term permanency or the lack of it is of little consequence. Paper permanency is of most critical importance in libraries. These institutions, charged with storing and preserving all sorts of information, mostly on paper, are finding that a very high percentage of their collections are literally falling to dust on the shelves. For them, the permanency of paper is critical to their basic function: the storage of literature, periodicals, history and records of all kinds. In addition, the preservation, protection and recopying of impermanent documents and books is a major financial burden.

As mentioned earlier, the permanency of paper is made up of two broad general characteristics: permanency and durability. The permanent paper in a book 300 years old or more will still have good color and brightness and the pages will be able to be turned. The paper will have retained enough of its original strength that it will still be usable, able to be handled by different people with no more than normal care.

Thus, assessment of permanence is usually based on mechanical properties. Historically, it has been found that fold strength is the most sensitive criterion, followed by others such as tear resistance. Optical properties generally have not been a concern, because regardless of the mechanical condition of the paper, images are still legible and readable. In some market segments, however, visibility alone may not be sufficient; retention of color qualities may be as important.

RECENT DEVELOPMENTS

The aging of paper is due to the breakdown (degradation) of the cellulose and related materials that make up the fibers, as well as degradation of any other materials that may be present in the base paper or coating. Mechanical and optical degradation result from chemical reactions, and it has been known for many years that increasing the temperature enormously speeds up just about all chemical reactions.

Although having a low lignin, alkaline-sized sheet was recognized as being critical for permanence, not a lot was known about how alkaline the sheet needed to be, the acceptable value for lignin level, and how the values were going to be determined. This interest was prompted by the fact that there was an increasing demand for groundwood-containing—hence, lignin-containing—paper.

The most important part of any presentation on permanency concerns the testing procedures to be used in determining whether the paper in question will, indeed, be permanent. Any discussion of this must be tempered by two facts:

1. The people who make, specify or use such paper today will not be around to see how it all comes out 100, 300 or 500 years hence.

2. The paper to be tested must be subjected to some accelerated aging procedures as an essential part of the test. We must telescope time; we must artificially age the paper in a few days or weeks to the condition it would have reached after many years.

To address these issues, a committee of interested parties met to discuss how to modify the existing ANSI (American National Standards Institute) standard on permanence[2] and, in 1992, summarized their recommendations for coated paper as follows in **Table 1**.

Table 1. Permanence properties of coated paper, according to ANSI.*

Property	Value
pH**	7-10
Tear Index	3.50 mNm²/g
Alkaline Reserve	2%
Fiber	1% lignin

* ANSI/NISO Z39.48-1992
** of core (basesheet)

These recommendations were based not only on the decades of experience showing the need to have an alkaline paper with little or no lignin, but also on the latest findings. Keep these three important points in mind:

1. The pH referred to is that of the base sheet of paper, not the coating.

2. Only a mechanical property, tear, is addressed. (Although fold strength is the most sensitive property, tear is more easily assessed in mill quality testing).

3. No reference is made to an accelerated testing procedure.

The search for accelerated testing protocols resulted in an extensive industry-wide study beginning in 1994. The results of this multi-year study, using uncoated paper, were reported in 2002[3] and confirmed that paper, including paper that is alkaline-sized and/or lignin-free, can deteriorate both mechanically and optically upon exposure to heat, light or environmental pollutants. The effects of paper composition on the rate and extent of deterioration generally fall into four broad categories depending on compostion (lignin content, pH) and properties (optical or mechanical).

Optical properties—There is a major delineation between lignin-containing and lignin-free papers. The optical properties of lignin-containing papers, notably brightness and color, deteriorate significantly faster and to a greater extent than do those of lignin-free papers. Alkaline papers are slightly more stable than acid papers, but the differences are not as pronounced as they are between lignin and lignin-free papers. Lignin-free alkaline papers are considered to be optically stable, in the face of light, heat and atmospheric pollutants.

Mechanical properties—Based on fold-endurance and tear-resistance data, alkaline papers retain their strength properties significantly better than do acid papers. When the fundamental strength properties of papers differ, as in free-sheets and groundwood papers, stability can best be assessed using the retention percentage of fold and tear properties. By these criteria, paper acidity is the key variable; the retention percentage in strength is primarily dependent on pH, not on lignin content.

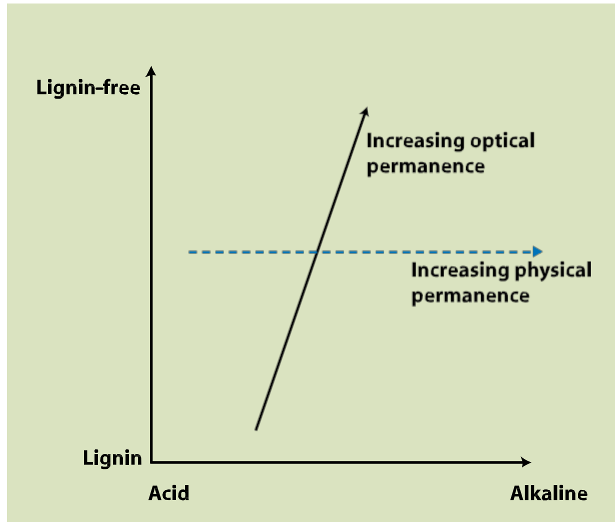
These general relationships are depicted in **Figure 6.**

Additional general findings included:

1. Papers stacked together, such as in books, aged faster than single sheets.

2. Brightness losses in uncoated alkaline papers with no groundwood typically ranged from 5-10 units. When groundwood was present, the losses were much larger; deterioration appears to be proportional to groundwood (lignin) content.

Figure 6. Overview of key factors affecting paper permanence.



Some specific findings included:

FOR HEAT-INDUCED DETERIORATION

1. Accelerated temperature aging was found to affect paper in a manner comparable to natural aging; hence, a new accelerated aging test method for heat-induced deterioration was proposed and subsequently adopted (ASTM D 6819-02). The method involves heating samples in sealed glass tubes, which prevents the samples from drying out, for 120 hours at 100˚C.

2. Thermal yellowing was generally worse than light-induced yellowing.

FOR LIGHT-INDUCED DETERIORATION

1. Natural light-induced aging results were highly dependent on locations (latitude and inclusion of direct sunlight). In some cases, where brightness losses were found at one location (northern light exposure), brightness increases were noted at the other location (direct southern light exposure).

2. Even lignin-free papers deteriorated slowly under natural (northern) and artificial (incandescent or halogen) light, particularly with regard to folding strength.

3. Based on the test results, it was recommended that accelerated light aging of paper involves exposing samples to the light in high-intensity xenon arc light cabinets for 48 hours. The recommendation was adopted (ASTM D 6789-02).

WITH RESPECT TO ATMOSPHERIC POLLUTANTS

The main culprits are NOx gasses, particularly when it comes to the yellowing of lignin-containing papers and the loss of fold strength in acidic papers. This could have implications for warehouse storage of papers exposed to tow-motor fumes.

COATED PAPER

To date, the bulk of the work on permanence and stability has dealt with uncoated paper. Reports about coated paper often focused on the mechanical properties: fold strength, tear resistance and tensile strength. The role of the coating and whether, for example, an alkaline coating is beneficial independent of the pH of the base stock is not entirely clear.[4]

But what about the optical properties? Surely the coating, typically based on mineral pigments, must be resistant to changes in color. Any changes would surely be limited to "burnout" or degradation of the fluorescent whitening additives (FWAs) used in many papers. These chemicals have the ability to absorb invisible ultraviolet radiation and transform it into visible light, primarily in the blue end of the visible spectrum, in the case of paper or, for that matter, laundry detergents. Under the proper lighting conditions, the paper will have a bluish-white appearance and typically, we prefer blue-shade whites, whether in clothing or paper.

Figure 7. Temperature-induced changes in paper brightness.

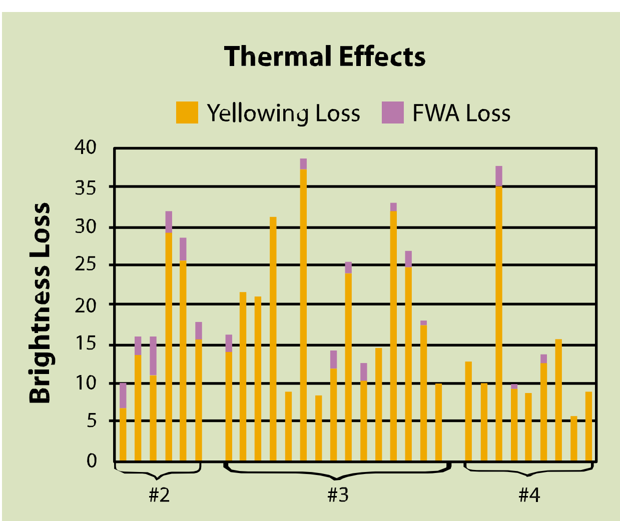
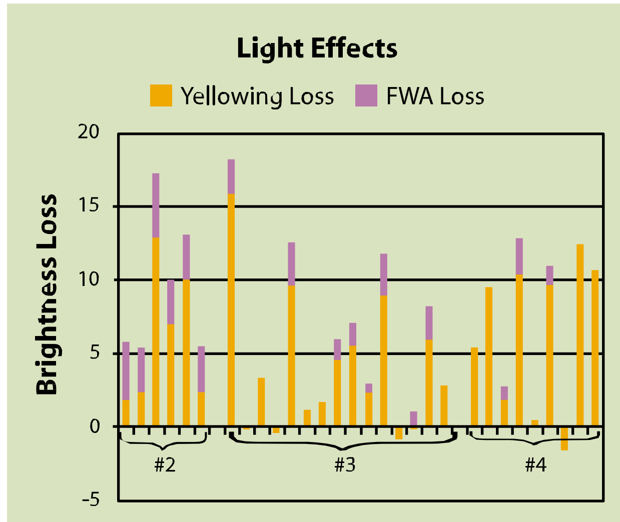


Figure 8. Accelerated light-induced changes in paper brightness.



Unfortunately, the coating on paper may not afford complete protection for all properties. Heat-induced changes have been seen with coated board, the changes due to non-fluorescent causes being significantly larger than could be attributed to the degradation of FWAs.[5]

In our own laboratories, we have tested a number of coated papers using the ASTM procedures for accelerated light and temperature aging. Because of the interest in the effect of FWAs on optical stability, we have reported our results, seen in **Figures 7 and 8**, based on the decrease in brightness (yellowing) after accounting for losses in fluorescence. This is different than the definition used in the ASTM procedures.

The samples have been grouped into their current AF&PA brightness categories. Samples labeled #2 are all wood-free; samples labeled #4 all contain greater than 10% groundwood. #3 sheets can either be wood-free or groundwood-containing, so the lignin content can range from 0% on up. Typically, it is more likely that high-brightness papers, such as the #2s, will contain FWAs, and less likely that the lower-brightness #4 grades will.

As seen in **Figure 7**, brightness losses are not entirely due to loss of FWAs. Typically, 80%-100% of the fluorescent activity is lost upon exposure, but the severity of the change goes far beyond that contribution, similar to what was seen in the coated board study[5]. While the optical properties of the minerals in coating may be insensitive to thermal effects, other components in coating may not be. Additionally, coating is not 100% opaque; optical changes occurring in the base sheet also contribute to overall yellowing. This is not to say that FWAs don't degrade faster than other materials in the paper, only that continued exposure to the test conditions cause other changes to occur as well.

Similar changes are seen for light-induced fading in **Figure 8,** although not nearly on the scale seen for thermal effects. In fact, we cannot entirely discount the possibility that some thermal degradation occurs here as well. The ASTM study concluded that the sample temperature during paper's exposure to light (ASTM D 6789-02) should be kept below 40˚C; the method itself specifies keeping the temperature ≤30˚C. In our tests, we could not keep the sample temperature from rising to a maximum of 46˚C. Based on the ASTM study, this heating might account for an additional loss of a few brightness units due to changes in the base sheet during heating. However, without measuring the brightness losses reported here as a function of temperature, this is just an estimate.

Table 2. Descriptors for describing brightness changes in paper due to light or heat exposure.

Stable	≤5% reflectance loss
Moderately Stable	>5% and <20% reflectance loss
Unstable	≥20% reflectance loss

Nonetheless, light-induced changes, although noticeable—a difference of 1-2 brightness units constitutes a just-noticeable difference—may still be acceptable. According to the ASTM D 6789-02 method, the descriptors shown in **Table 2** can be used when talking about the accelerated effects of aging on optical changes.

All the samples would be considered at least moderately stable under prolonged direct-light exposure. The stability of all the samples may, however, be entirely adequate under practical conditions of use.

Several observations are noteworthy:

1. Total brightness losses due to accelerated thermal aging are more severe than those due to accelerated light aging. This was also noted in the ASTM program. A significant portion of the changes in brightness are due to non-FWA changes.

2. Interestingly, there is no clear distinction between the groundwood papers and the free-sheets. This may reflect the ability of the coating to screen/protect the underlying base sheet.

3. Some brightness increases are seen in the light-aging study, a phenomenon also seen in the ASTM study.

SUMMARY

Are the changes suggested in **Figures 7** and **8** meaningful for most printing and writing paper users? Keep in mind that the accelerated-light exposure results are equivalent to about three years of direct exposure to natural light. This is not a normal condition of use for most printed material. Books are normally closed and sitting on shelves or tables, out of direct sunlight. Does the ambient temperature reach 100+˚F and stay there for prolonged periods of time? What about the printed image itself? Many of the common printing ink colorants are not lightfast.

In practice, the optical stability of paper is dependent on many variables, most of which are beyond our control. The best practice is to compare, under identical conditions, the performance of one paper to another. If the test conditions are those described in the ASTM protocols, you will be able to form some conclusion about long-term exposures. What you have to judge is whether those conditions are realistic. The appearance of a book made from alkaline pulp and sitting on a shelf will likely be unchanged after decades or even hundreds of years under normal conditions. It's also important to keep in mind that any small color or brightness changes that might occur would become noticeable only when the sample is compared to another that has been well preserved.

Frequently Asked Questions

Q

1. I've heard some in the paper industry talk about the life expectancy of paper. What are they referring to?

A

ASTM defines (ASTM D 1968) the life expectancy of paper as the "length of time a product can be expected to maintain its functional characteristics (that is, physical, chemical, appearance, and so forth) when stored under prescribed conditions." This is often expressed in terms of the number of years it is expected to be usable: LE 50, LE 100, LE 1000, meaning the usable life expectancy is 50 years, 100 years, or 1000 years, respectively. Clarification of this, relative to offset and book papers, can be found in ASTM D 5634, where suggested brightness retention percentage for the various life expectancies is shown on the top **(Table A1)** and the results from our samples on the bottom **(Table A2)**:

Thus, by this definition and the method we used for aging the samples, the samples would have medium life expectancy, on average. Inspection of **Figure 8** shows that the variability among the samples is great, however.

Table A1. Definitions of paper life expectancy as used in ASTM D 5634.

Percent Brightness Retention

Medium Life Expectancy	High Life Expectancy	Maximum Life Expectancy
LE-50	LE-100	LE-1000
90%	92%	95%

Table A2. Average brightness loss of the sample shown in Figure 8.

Relative brightness loss – accelerated light fading

Grade	Relative Brightness Drop	# of Samples
2	11%	4
3	7%	17
4	9%	9

Frequently Asked Questions (continued)

Q

2. My ink supplier talked about permanency testing and made reference to a "blue wool" standard. What is this?

A

The textile industry has, as might be expected, a major interest in permanency of dyed textiles. They have developed a testing protocol for fading due to light exposure that utilizes the fading properties of a piece of dyed blue wool as a control. The degree of fading has often been associated with the number of years of exposure (AATCC Test Method 16-2004). Thus, someone may run a light exposure test on an ink or a print and include the blue wool standard as a control. But the degree of fading of the wool, which may loosely translate into years of permanency for textiles, has not been shown to reflect changes in paper.

[1] McCrady, E.; "Book Preservation Pressures Speed Up Conversion of Acid Paper to Alkaline." Pulp and Paper, pp 122-124 (January 1990). The author gives a good overview of activities in the 1980s.

[2] Humphreys, B., Kalina, C.; "Revising the American National Standard for Permanence of Paper (ANSI Z39-48-1984): Changing Market Factors, Changing Paper Technology, and New Research Questions." TAPPI – 1991 Papermakers Conference, pp 243-249. This is an excellent review of what the issues were and how the parties came to a consensus for the new standard.

[3] Arnold, R; "ASTM Paper Aging Research Program." ASTM International, West Conshohocken, PA (2002). The results are presented in a CD obtainable from ASTM. R. Bruce Arnold served as chairman of the committee and has prepared a most helpful summary of the results.

[4] Shanani, C., McComb, R.; "A Clarification on Specifications for Archival Paper." TAPPI J., p 128 (September, 1987). In a short study, the authors confirm earlier reports that coating a paper (alkaline paper with alkaline coating) reduces fold strength, but not tear and tensile strength.

[5] Vancina, V. and Letnar, M. "Durability of Coated and Uncoated Boards," Adv. Print. Sci. Tech. Vol. 27 pp 41-55. (2001). The authors look at the effects of accelerated temperature aging on both coated and uncoated board samples.