The Deterioration and Preservation of Paper: Some Essential Facts

Paper deterioration is still a problem. But, thanks to decades of scientific research -- much of it supported by libraries and archives -- this deterioration is no longer a mystery. The preservation strategy at the Library of Congress has traditionally benefitted by insights provided by science. Our preservation program has continued to evolve and reshape itself as the underlying science on which it relies has steadily progressed.

From Rags to Ruin: Factors That Promote Paper Deterioration

It is often true that the older a book or manuscript is the better it survives. Paper-based materials that are more than 150 years old are in many cases in better shape than others that are less than 50. Why do some papers deteriorate rapidly while others appear to be little affected by the passage of time?

- Answers are found in the composition of paper, the causes of its deterioration, and the conditions under which it is stored.
- Fibers made of cellulose chains degrade when exposed to an acidic environment in the presence of moisture. In this acid hydrolysis reaction, cellulose chains are repeatedly split into smaller fragments so long as the source of acid remains in paper. This acid hydrolysis reaction produces more acid in the process, and the degradation accelerates in a downward spiral.
- The longer the cellulose chains that comprise paper, the stronger and more supple the paper. This type of paper is also more able to withstand degradation by acids and other abuse without showing visible signs of wear and tear. Conversely, the shortest fibers are the most vulnerable.
- Early papers were made from cotton and linen rags. Most early papers, especially those made up to the middle of the 19th century, are still strong and durable, especially if they were stored properly under conditions that were not overly warm or humid.
- Cotton papers owe their longevity mainly to the length of the fibers used in their manufacture. Even when the length of these fibers is reduced on aging, it is still likely to be longer than that of fibers in relatively young, modern papers.
- The shortest fibers are found in newsprint papers made from groundwood pulps; this pulp is made by the mechanical grinding of wood that is then made into paper without first purifying it chemically. Papers made by this process are substantially weaker than those made of chemically purified wood pulp, which is used to make the fine printing and writing papers that we often see in books.
- Most modern book papers have a relatively short life span, which can be further reduced by improper storage environments. The exception to this general trend is alkaline paper -- that is, paper that contains an alkaline reserve. This alkaline reserve, most frequently chalk, neutralizes acids and also makes the paper look whiter.
- Like cotton papers, alkaline papers can last indefinitely. Acids formed within the papers or those absorbed from the environment are neutralized before they have a chance to degrade the cellulose chains. Such papers often bear a permanence mark (an infinity symbol within a circle).

- The primary source of acid in modern paper is the alum-rosin sizing agent introduced in the manufacturing process. Size is added so that writing and printing inks do not feather. In the presence of moisture, the alum in the sizing agent generates sulfuric acid.
- Acids are also formed in paper by absorption of pollutants -- mainly sulfur and nitrogen oxides. Newsprint paper is particularly vulnerable to pollutants, which it absorbs vigorously from the environment as evidenced by the brown and embrittled edges of bound newsprint volumes and dime novels.
- A new discovery made in the research laboratories of the Library of Congress shows that, as it ages, cellulose itself generates several acids, such as formic, acetic, lactic, and oxalic acids.
- Measurable quantities of these acids were observed to form within weeks of the manufacture of paper while stored under ambient conditions. This research also shows that these acids continue to accumulate within paper as they attach themselves to paper through strong intermolecular bonds. This explains why acid-free (pH neutral) papers also become increasingly acidic as they age.
- Acids are formed even in alkaline paper, although in this case they are probably neutralized by the alkaline reserve before they can do any damage to the cellulose molecule.
- In addition to acid hydrolysis, papers are also vulnerable to photolytic degradation (damage by light), although newsprint papers are much more subject to this form of degradation than most other papers used to print books.
- Oxidation is also believed to play a role in the degradation of paper, although its role is limited as compared with acid hydrolysis, except probably in the presence of nitrogen oxide pollutants.

Development of solutions for preservation of books and paper

To study the effect of different chemical species and storage environments on the life of paper, it is necessary to replicate, in a few short weeks or months, the natural aging of paper, which takes place in real life over several decades. Such "accelerated aging," performed in a laboratory setting, has helped us comprehend the manner in which different papers age. It has also helped us design real life solutions that are rooted in scientific fact. Before such testing, preservation solutions were based essentially on subjective perceptions colored by personal judgements that were as likely to be wrong as right.

- Accelerated life testing is commonly applied to most commercial products in order to improve their quality and to enable the manufacturer to provide a reliable warranty period. If the accelerated testing is properly designed and performed, the product, be it a TV or a toaster, will not be likely to fail before its warranty period.
- Accelerated testing for paper, however, is much more complicated than testing for a single brand of toasters, for example. This is because the same test must work with a wide variety of papers. Also, there can be no misunderstanding about when a toaster has failed. Whereas for paper, every person has his or her own perception of when it is too brittle to be used.
- As with any other science, the science underlying such accelerated testing for paper has evolved gradually -- in this case over several decades.

- The first accelerated tests were undertaken in the late 1920s at the former U. S. National Bureau of Standards, which has since been renamed the National Institute of Science and Technology.
- Ever since, there have been two schools of thought on accelerated aging of paper -- those who thought that it provided a reliable tool, and others who believed that it did not and could never duplicate natural aging.
- For several decades these tests involved aging of paper samples at elevated temperatures. William Barrow used similar testing in the 1940s to project lifetimes of paper samples, which have since proven to be erroneous. To this day, Barrow's data is used by detractors of accelerated aging as proof of the fallibility of such testing.
- However, such critics overlook the changes that this test has undergone since then. The problem with the earlier tests was that they ignored the essential role that moisture plays in the acid hydrolysis of paper, the major reaction by which paper ages. For the past few decades, accelerated aging tests have been routinely performed in a humid environment.
- A five-year research effort completed in 2000 at the Library of Congress undertook an unprecedented comparison of natural and accelerated aging of paper. It analyzed the chemical products that form in the aging of paper under the two sets of conditions and found extensive similarities.
- As an ultimate test, several naturally-aged papers were subjected to additional aging in the laboratory. In each case, the complicated mixture of degradation products formed originally during natural aging just increased in concentration but retained its original identity. All of the degradation products already formed during natural aging increased proportionately. No new reaction products besides the ones already formed in nature were formed in the accelerated aging process. These experiments left no doubt about the similarity between natural and artificial aging. It can be confidently stated now that accelerated aging is a very good approximation of natural aging and that it is a valid and reliable test for predicting paper longevity.[1]

These experiments also clearly demonstrate that the rate of degradation and embrittlement of paper increases with time because of the increasing accumulation of acids in paper as it ages. This observation is contrary to the subjective experiences of some observers who have suggested that the aging of paper slows down with time and almost comes to a stop. No scientific evidence exists to support such claims.

- Other findings from this research and earlier work published from the Library of Congress show that paper bound in books ages faster than loose sheets of paper in ventilated boxes. Paper inside a book structure has a greater tendency to retain acids that develop as it ages.
- This last observation was confirmed in an as-yet-unpublished survey of cotton rag papers at the National Archives, and also in recent investigations from Australia, the Netherlands, and elsewhere, cited in a recent research review by Henk Porck. These reports suggest that paper at the center of a book often tends to be weaker than the paper at the edges.[2]
- At first blush, this may seem to be contrary to the experience of many people who have observed deteriorated edges of popular paperbacks or bound newsprint volumes. The paper in these types of volumes contains lignin, which absorbs pollutants such as sulfur

and nitrogen oxides more readily than fine papers on which most hardcover books are printed. The deterioration at the edges of pages of such bound-format materials is caused by acid hydrolysis that results from the accumulation of acids formed from the absorbed sulfur and nitrogen oxides.
- The assumption that a bound book structure squeezes out air and thus stabilizes the paper flies in the face of research cited above, which has repeatedly shown that paper bound in books or aged inside airtight enclosures ages faster than single sheets open to the environment. The fact is that the book structure and other enclosures cannot protect paper from the air, because the paper itself contains the moisture that contributes to acid hydrolysis and, thus, destruction of the paper. Even worse, the restricted environment within a bound book efficiently retains the acidic degradation products, which accelerate its aging even more.

Is There Any Hope?

Printing on and creating documents on alkaline or permanent papers is obviously improving the situation, at least for modern materials that are created on papers of higher quality. But what of the sizable backlogs of retrospective materials on acidic papers that challenge the preservation budgets of libraries and archives worldwide?

- Deterioration of paper due to its chemical composition and other factors can be dramatically minimized by treating the paper with a process that neutralizes the acids in the paper. Many of those materials that are acidic but not already highly embrittled can be saved today through use of a new technology known as mass deacidification.
- The deterioration due to accumulation of acids -- whether they are acids absorbed from pollutants, introduced in the manufacture of paper, or formed as paper ages -- can be arrested by deacidification. Any paper can be made to last several times its anticipated life, however indefinite that life may be calculated to be.
- Deacidification treatment enables libraries and archives today to treat books and manuscripts so they will remain in usable condition for several centuries rather than becoming brittle and unusable in only fifty to a hundred years. If the information on a paper substrate is to be saved by employing this technology, it is advisable to treat it while the paper still has significant measurable strength.

The Synergy of Deacidification and Improved Storage

Institutions can extend the life of paper-based materials hundreds of years by storing them in improved environmental conditions afforded by new facilities like the Library of Congress modules at Fort Meade, Maryland, and the Harvard depository. Why, then, should we bother with mass deacidification, which also guarantees a life extension of several hundred years?

- Some materials will be deacidified and retained in existing facilities under normal environmental storage conditions, while others may be transferred to state-of-the-art cold storage facilities without ever being deacidified. In either case, the rate of degradation will be slowed appreciably and the life-extension factors will be impressive.

- While it may seem that the two efforts are duplicative, in practice they are complementary preservation measures - i.e. both mass deacidification and improved storage conditions contribute synergistically to the long-term useful life of books and other paper-based materials.

For many of our more valuable and/or endangered collections and records, these modern, cost-beneficial preservation options are not mutually exclusive. Particularly for books and manuscript materials that are already in weak or brittle condition, the best option is to use both approaches -- deacidify them and store them under cooler, improved storage conditions.

[1] American Society for Testing and Materials Institute for Standards Research (ASTM/ISR). *ASTM Research Program into the Effect of Aging on Printing and Writing Papers: Final Reports on Accelerated Aging Test Method Development.* West Conshohocken, Pennsylvania: ASTM/ISR, 2001 [in process].

[2] Henk J. Porck and René Teygeler. *Preservation Science Survey.* Washington, DC: Council on Library and Information Resources, 2000. Pp. 5-6.