Material consequences of the aging of paper

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Abstract

Chemical, physical, and mechanical properties of paper affect decisions regarding its care and treatment. Changes over time in properties including stiffness, strength, and elasticity are examined using both naturally and artificially aged samples. These properties are determined as a function of environmental conditions for new and aged samples. The rate and nature of chemical degradation processes as a function of environment are correlated with changes in physical properties. The results of appropriate accelerated aging conditions correlate with those of natural aging. The results can be used to determine physically safe ranges for the storage of paper artifacts, and to indicate how conditions within this range affect the rate of changes over time.

Keywords

paper, aging, physical properties, degradation, environment, temperature, relative humidity

Introduction

The "aging" of a material such as paper generally refers to the changes that take place slowly over time. This is distinct from changes resulting from catastrophic or short term events such as fire, flood, or abuse, as well as active use of an object. Such changes are more likely to be referred to as wear or damage. In either event, many of these changes affect the care and treatment of objects. The way in which an object is displayed, the conditions in which it is stored, and decisions regarding its treatment are based on perceptions of the condition of the object, such as how strong and flexible it is, as well as on how it is thought to react to changes in its environment. In order to make appropriate decisions regarding the care and treatment of paper objects, one must understand how the relevant properties of paper change over time and how these changes should affect any recommendations that may be made.

For example, an item perceived to be extremely fragile would almost certainly be stored or displayed horizontally. Storage and display conditions are often kept at moderate (45–55%) conditions of relative humidity because it is thought that aged paper is stiffer and more brittle at low humidities and cannot be handled safely. In some facilities, paper is stored at lower relative humidities to increase its chemical stability, but when brought out of storage is equilibrated to a moderate relative humidity before handling . The primary physical and mechanical properties that affect such decisions are stiffness, strength, elasticity, and plasticity. How do such properties change over time, and how are they affected by changes in environmental conditions?

Paper is a fibrous material, with each fiber composed of bundles of cellulose, a polymer of glucose. Its overall physical properties depend on the physical properties of the fibers, the arrangement of the fibers, and the degree of interaction and attachment of the fibers. The primary mechanism of changes in these properties during aging is the chemical degradation of the cellulose molecules. Correlating the physical and chemical changes in cellulose would help to understand the changes that take place during the aging of paper.

Approaches to measuring changes in paper over time

There are two ways to examine the changes in paper that occur over long periods of time ("long" meaning longer than one is willing to wait for results of natural aging experiments). The obvious method is simply to examine samples of naturally aged, old paper. Unfortunately, the conclusions that can be drawn from such experiments are limited because one usually does not know either the original properties of the paper or the conditions of the "experiment" it has been undergoing. The other method of examining the effects of aging is to conduct accelerated aging experiments. Accelerated aging is an attempt to simulate in a short time the effects of long periods of natural aging. Rapid changes in paper can be induced in a number of ways, including the use of elevated temperatures and

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relative humidities, or exposure to bright lights, oxygen, or pollutants. Implicit in most accelerated aging experiments is the assumption that the conditions induce the same types of change that occur during "natural" aging, but at a much faster rate. Such assumptions are not always true, and even if they were it is quite difficult to demonstrate that the process of artificial aging is equivalent to natural aging. Another complicating factor is that "natural" aging can encompass a wide range of quite different conditions and processes. For the rest of this paper, we shall use the term natural aging to refer to dark aging under moderate relative humidities.

Accelerated aging and natural aging

The requirements for two sets of aging conditions to be "equivalent" have been discussed previously (Erhardt and Mecklenburg 1994a). Basically, the same reactions must occur under both aging conditions, and the relative rates of the various reactions should be similar for both conditions. To be equivalent to natural aging, accelerated aging must speed up all reactions by the same factor without introducing new reactions. In the same article, the authors demonstrated that in the range of 50 to 90°C and 30 to 80% RH, the aging process of paper did not vary dramatically, and changed only in the relative rates of individual reactions. (The overall rate of the aging process of course increased with increasing temperature or relative humidity.) It was also shown that in the range of conditions studied the aging process could be speeded up without changing it by increasing the temperature and keeping the relative humidity constant. The conclusion was that the results of tests conducted at elevated temperatures up to at least 90°C would correspond to results for paper naturally aged within a similar range of relative humidity.

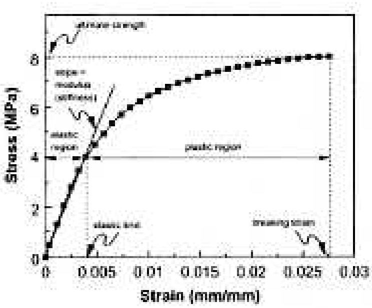

Figure 1. Stress-strain curve at 47% RH in the crossmachine direction for new Whatman #1 paper. The force per cross-sectional area (nominal stress) is plotted as a function of dimensional change (strain). The initial linear portion defines the elastic (reversible) region, the slope of this area is the modulus, or stiffness. The later portion of the curve represents the plastic region in which permanent deformation occurs. The end of the curve is the breaking point.

The properties of new paper

A typical stress-strain curve for paper (See Fig. 1) provides a number of types of information. The curve plots the amount of strain (dimensional change) and the corresponding nominal stress (force per unit cross-sectional area). The initial linear section of the curve is the elastic region. In this region, the paper recovers and returns to its original size when the force is removed. The slope of this linear section of the curve is the modulus, or stiffness. The subsequent curved and less steep region of the plot is the plastic region, in which the paper has been irreversibly stretched and will only partially recover if the force is released. Materials with little or no plastic region are referred to as "brittle". This concept is often confused with stiffness. A stress-strain curve for a material more brittle than that in Fig. 1 would have a similar curve that simply ended earlier. A stiffer material would have a steeper slope at the beginning of the curve. The end of the curve is where the sample breaks, and represents the maximum possible stress (force) and stretch the paper can take (ultimate strength and breaking strain, respectively). The area under the curve represents the total amount of energy per cross-sectional area required to break the paper. New paper has an elastic limit, or yield point, similar to that of many other materials, and typically can be reversibly stretched by about a 0.4% change in dimension. Paper also has a significant plastic region, and can be deformed quite a bit before breaking. For instance, an analysis by us of stress-strain and fold endurance measurements for naturally aged acidic paper published by Brandis and Lyall (1997) showed that old paper samples that had a breaking strain greater than 1% could survive at least one fold. Folding probably induces a strain of about 1%. This does not break new paper, but does produce a permanent crease (deformation) because it exceeds the elastic or reversible limit. With proper care and under reasonable environmental circumstances, paper should never leave the elastic region, since either improper handling or quite wide environmental changes are required to produce irreversible strains in paper (See Erhardt et al. 1997 and references therein for discussions of calculating allowable relative humidity ranges).

The properties of paper depend on the conditions under which they are measured. Typically, though, changes in the critical properties of stiffness, strength, breaking strain, and elastic limit are not significant over a fairly wide

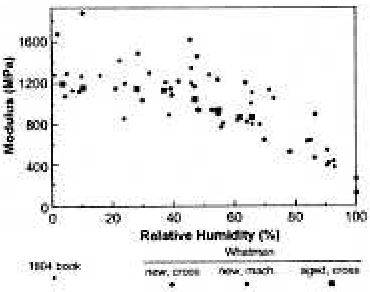

Figure 2. Modulus (stiffness) of new and accelerated aged (80°C, 77% RH, 105 days) Whatman #1 paper and paper from a book printed in 1804 plotted as a function of relative humidity. There is little change in the modulus of each paper from 5% to above 50% RH.

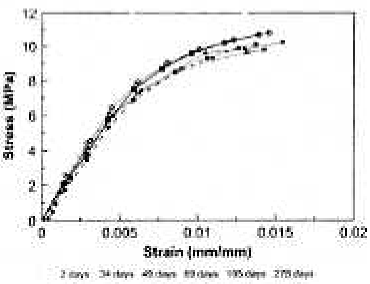

Figure 3. Stress-strain curves at 47% RH in the machine direction for Whatman #1 paper aged at 80°C and 77% RH for various lengths of time. The modulus (initial slope) and elastic region remain essentially constant, the strength and plastic region are reduced during aging.

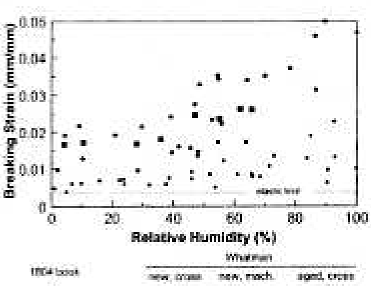

Figure 4. Breaking strains of new and accelerated aged (80°C, 77% RH, 105 days) Whatman #1 paper and paper from a book printed in 1804 plotted as a function of relative humidity. If the breaking strain is greater than the elastic limit, the paper can safely tolerate proper handling and moderate environmental fluctuations.

range of relative humidity that includes the range that might be considered for display or storage. For example, the modulus of paper is relatively constant from 5% to about 50–60% RH (See Fig. 2). This dependence of measured properties on RH is a separate issue from whether or how these properties change during aging at specific relative humidities, however. That question is answered by determining how these properties and their dependence on environmental conditions change during aging.

Results from accelerated aging

Accelerated aging of paper at moderate relative humidities produces a loss of strength, but little change in stiffness (See Fig. 3). Aged paper yields a similar curve, but simply breaks sooner. The paper is not stiffer, but simply weaker, i.e. more brittle. This is often perceived as stiffness because it is so easy to force weakened paper beyond its breaking strain simply by folding it (i.e., the corner fold test used by librarians). Even quite degraded paper, though, usually has most if not all of its elastic limit intact and can safely tolerate careful handling.

The dependence of paper's properties on the environmental conditions under which they are measured does not change significantly with aging. For example, it can be seen that the modulus of paper that has undergone accelerated aging is not only similar to that of the new paper, but has the same dependence on RH (See Fig. 2). The breaking strain of paper does decrease slightly with decreasing RH, but stays above the elastic limit unless the paper is severely degraded (See Fig. 4). Aged paper will break slightly more easily at low RH, but only as the result of improper handling that would likely cause damage even at moderate RH. As long as the elastic limit is intact, the paper will also safely tolerate the same environmental fluctuations as new paper. Paper, old or new, does not become significantly stiffer or weaker at low RH, and can be stored and handled at the reasonably low relative humidities used to improve chemical stability. It does not have to be equilibrated to moderate RH before it can safely tolerate proper handling. (Values below about 25% RH should be avoided not because the paper is brittle or stiff, but because crosslinking of the paper fibers can occur over time at very low RH. Extremely dry conditions can result in irreversible shrinkage and collapse of the cellulose fibers.)

These physical changes in paper result from chemical changes in the cellulose molecules of the paper. An analysis of the soluble degradation products found in accelerated aged paper confirms that the reactions taking place in cellulose are primarily hydrolytic (See Fig. 5). Hydrolysis breaks the cellulose chain and

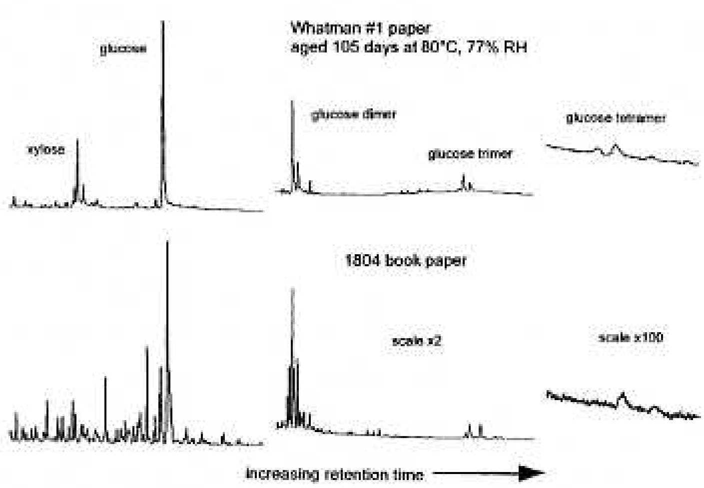

Figure 5. Gas chromatographic analyses of the soluble degradation products of Whatman #1 paper aged at 80°C and 77% RH for 105 days and paper from a book printed in 1804. Accelerated aging produces a product mixture that matches that of the naturally aged paper quite well in both the type and amount of degradation products. The extra peaks in the chromatogram of the 1804 paper are due primarily to non-cellulosic additives, i.e. sizing.

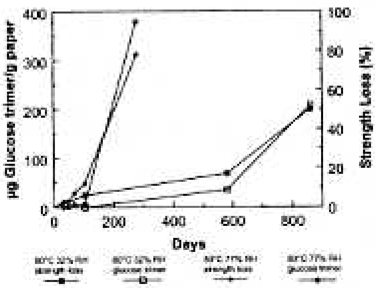

Figure 6. The amount of glucose trimer, a product of the hydrolysis of cellulose, plotted against the loss of strength of Whatman #1 paper for various times and aging conditions. The quantity and strength loss axes are adjusted to show the correlation between the extent of hydrolysis and the loss of strength.

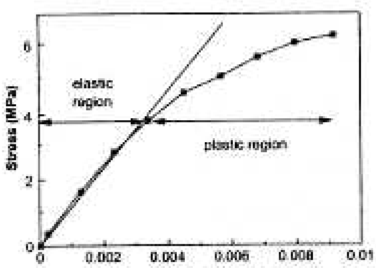

Figure 7. A stress-strain curve at 47% RH for naturally aged paper from a book published in 1804. The stress-strain curve is as predicted from accelerated aging experiments. The modulus and elastic region are typical of those for new paper, but the strength and plasticity are reduced.

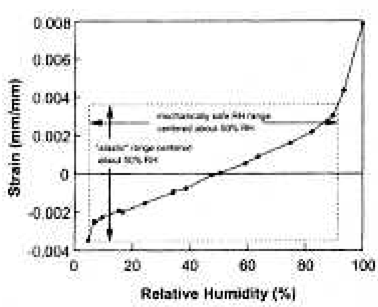

Figure 8. A dimensional moisture isotherm for paper from a book printed in 1804. The change in dimension of the unrestrained paper is plotted as a function of relative humidity. The dimensional changes that occur over nearly the entire RH range are less than those that would be required to produce irreversible deformation if the paper were restrained during changes in RH.

produces smaller units, including glucose itself. Glucose and its dimer, trimer and tetramer (small chains comprised of two, three, and four glucose molecules) appear in the analysis. A number of smaller peaks correspond to products resulting from other reactions such as oxidation and thermal scission. These account for only a small proportion of the degradation product mixture. It is primarily the breaking of cellulose chains by hydrolysis that weakens the fibers. The amounts of hydrolytic products can in fact be correlated with the loss in strength (See Fig. 6). Activation energies for these chain-breaking reactions have been calculated by following individual reactions at various temperatures, and are approximately 23 Kcal per mole (Erhardt and Mecklenburg 1994a). The same paper determined the relative humidity dependence of the hydrolytic reactions. This information can be used to determine the relative rates of these reactions (and the resulting loss in strength) as a function of temperature and relative humidity. Extrapolations can be made to room temperature where such experiments are not feasible because of the long times that would be required. It is then possible to examine naturally aged samples to determine if their properties match those predicted by accelerated aging experiments.

The correlation of accelerated and natural aging

Stress-strain measurements of samples of old paper, and properties derived from them, are as predicted by accelerated aging experiments. The modulus (stiffness) is comparable to new paper (See Fig. 2) but the strength and strain to break are reduced (See Fig. 7). Additionally, these properties are relatively constant within the low to moderate RH range (See Figs. 2,4), as is true of new paper and paper subjected to accelerated aging. The physical properties of naturally aged paper are as predicted by appropriate accelerated aging conditions. The remaining task is to show that the changes during natural aging occur by the same mechanism as during accelerated aging.

Analysis of the soluble degradation products of a sample of naturally aged paper yields a product mixture similar to that for paper aged under accelerated conditions to a "comparable" age (similar levels of glucose) (See Fig. 5). Not only are the same compounds present, but the amounts of the important products (glucose and its oligomers) are comparable. The old sample does have some extra peaks due mostly to the non-cellulosic sizing. The relative ages of these comparably aged papers can be used with the experimentally derived activation energy and the aging temperature of the experimental paper to derive a quite reasonable aging temperature for the naturally aged older sample of approximately 20 C! Obviously, the old paper was not aged at constant temperature, but such calculations further support the equivalence of natural aging and accelerated aging conducted under appropriate conditions.

Paper properties as a function of environmental conditions

Environmental conditions affect the properties of paper in two ways. The first is the immediate effect, the dependence of properties on the specific condition under which they are measured. For example, paper is much less stiff at high (>60%) relative humidities than at low to moderate relative humidities (See Fig. 2). The second is the long term effect of storage under a specific condition. Storage at high relative humidity increases the rate of hydrolysis, so paper loses strength faster than at lower relative humidity. The relevant properties of paper are fairly constant when measured within the range of low to moderate relative humidities (approximately 25–55% RH), but there are differences in the rate at which properties change over time within this range. The degradation rate increases by a factor of approximately two to four in going from the lower to higher relative humidity.

Another critical property is the dimensional response of paper to changes in relative humidity. If paper is restrained during changes in relative humidity, or attached to materials that respond differently to RH changes, the resulting forces can deform or buckle the paper. However, even aged paper has a relatively low dimensional response to changes throughout most of the RH range (See Fig. 8). If the dimensional changes do not exceed those defined by the elastic region of the paper, no damaging forces are produced in the paper even if it is totally restrained and not allowed to shrink or swell.

Discussion

Some common perceptions about paper that affect storage, display, and treatment policies are either incorrect or imprecise and have often resulted in more effort and expense than required for proper preservation (and have sometimes resulted in worse conditions!). For example, one common perception is that paper is so much stiffer and brittle at low RH that it must be equilibrated to moderate RH before it can be handled safely. In some cases, the "need" for such equilibration is avoided by not reducing the relative humidity in storage areas, and maintaining the same higher than necessary RH values throughout the collection. This in turn results in a reduced lifetime for the collection, and in extreme cases may even cause damage to the building because of condensation during cold weather. In fact, the mechanical properties of paper, old as well as new, are fairly independent of relative humidity in the low to moderate range. Paper can be stored at low (25–40%) relative humidities without having to equilibrate it to moderate RH before handling.

The terms brittle and stiff sometimes seem to be used interchangeably when referring to old paper. The stiffness of paper in fact changes little over time. The brittleness of old paper is a result of its lowered strength, and a reduced ability to be deformed beyond its elastic limit. Even quite degraded paper retains most of its elasticity, and it is only "abuse", such as folding over a corner, that results in damage. Careful handling is still safe. It is reasonable to restrict the use or lending of a book in degraded condition to situations in which it is handled only under strict supervision or by those aware of appropriate methods of care. The book's life as a utile object may be over, but with proper care it will last much longer. The book as "museum object" has a much longer lifespan than the book in general circulation. The information it contains is still available, but must be extracted more carefully.

Changes in relative humidity within the low to moderate RH range do not produce damaging forces in paper unless it has degraded so much that even its elastic region has been severely reduced. Such paper is so obviously degraded that it may receive exceptional treatment, such as storage or display in a microenvironment buffered from RH changes in the general environment. Such an approach is more efficient than maintaining extremely tight RH control throughout the collections area just for a few exceptional items.

Recommendations

Cellulose is inherently an exceptionally stable material. Except for types of paper with known problems of stability such as acid processing or acid sizing, most damage to cellulosic objects results from catastrophic or short term events such as wear, abuse, mold, flood, fire, or environmental extremes. Proper care of paper materials includes the avoidance of such events. The avoidance of environmental extremes prevents physical damage during storage. Drier and cooler environments within the allowable range provide increased chemical stability. It is not necessary to maintain absolutely constant environmental conditions, or to equilibrate paper to moderate RH for handling. In fact, appropriate seasonally adjusted conditions (cooler and drier in winter, slightly warmer and moderate RH conditions during summer) not only save money but can result in an increase in expected lifetime for most collections.

Most of these recommendations also apply to other materials that might be found in collections (Erhardt and Mecklenburg 1994b; Erhardt et al. 1997). There are exceptions. For less stable materials and objects such as acidic paper and some photographs, other options must be considered. Deacidification is one obvious alternative for acidic paper, as is cold storage. For objects such as photographic materials, especially color prints and negatives, that cannot be made suitably stable at room temperature, cold storage must be considered and is the only appropriate approach if the objects can safely tolerate lower temperatures (McCormick-Goodhart 1996).

Conclusions

An understanding of the properties of paper and the way in which they change with time and environmental conditions is critical to determining appropriate and safe collections policies. This understanding must be based on the careful and thorough measurement and testing of relevant properties and the changes that occur with aging or environmental fluctuation. Some current approaches to the preservation of collections are based on common misconceptions and misunderstandings. Unnecessary procedures and protocols may be implemented, and incorrect or unnecessarily rigid environmental standards may be maintained. At best, such approaches waste only time and resources. At worst, they result in both waste and increased damage to the collections and building and divert attention from other more significant problems. Time and resources are best expended in efforts that have the greatest effect in safely extending the lifespan of the collections.

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