Chapter 3

Chemical and Physical Changes in Naturally and Accelerated Aged Cellulose

David Erhardt, Charles S. Tumosa, and Marion F. Mecklenburg

Smithsonian Center for Materials Research and Education, Smithsonian Institution, Washington, DC 20560–0534

An understanding of the chemical and physical changes that occur in cellulosic materials is crucial to the preservation of many objects in museums and archives. Decisions regarding care, treatment, and appropriate storage environments are based on their effects on the permanence and condition of the objects. Because many of the changes that occur in cellulose occur too slowly to study easily, accelerated aging conditions such as elevated temperatures are often used to speed up these changes. It is necessary to demonstrate that the changes that occur during such aging are comparable to the changes that occur during "natural" aging in museum collections. Extrapolations based on analyses of the degradation products produced in paper samples aged in a matrix of conditions of temperatures and relative humidities predict that accelerated aging at moderate relative humidities up to at least 90°C should satisfactorily replicate natural aging. Analyses of samples of naturally aged paper and other cellulosic materials bear out these predictions. In addition, important physical properties of naturally aged samples also correspond to those predicted from accelerated aging experiments. The results indicate that it is physically and chemically safe to store cellulosic materials in an environment that varies over a range of moderate relative humidities and temperatures. Within this range, chemical stability is increased at cooler temperatures and lower relative humidities.

The first priority of any museum or archive is the preservation of its collections. The effects of use, wear, and handling can be minimized by fairly obvious measures. The chance of catastrophic damage such as that caused by fire or flood can also be reduced through standard precautions and procedures. Once the risk of immediate damage is minimized, damage caused by slow, long-term degradation processes becomes the primary factor determining the lifetime or permanence of an

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object. Determining how environmental conditions, preservation treatments, and materials and procedures used in conservation or restoration affect the permanence of objects and their materials is not straightforward. It is difficult to study the slow, long-term degradation processes of natural aging on the laboratory time scale. Observed short-term changes may be too small to measure or extrapolate confidently, and often are not representative of the long-term aging process. One alternative is to study naturally aged materials, but these are usually the result of uncontrolled "experiments" where neither the original state of the starting materials nor the experimental conditions are known. The conditions of "natural" aging are rarely well defined or constant. Another alternative is to try to speed up the natural aging process using exaggerated or extreme conditions such as elevated temperatures, humidities, or light levels. "Accelerated aging" is an attempt to simulate in a short time the effects of long periods of natural aging. Implicit in such experiments is the assumption that the accelerated results are equivalent to those of longer periods of natural aging. Such assumptions are not always true, and even if so are difficult to prove. Our research has established methods for evaluating the relevance of accelerated aging conditions and assessing the effects of aging, both accelerated and "natural".

Experimental

The authors have previously reported methods and results for the analysis of the soluble degradation products of artificially aged paper (1,2). Samples of Whatman #1 paper were aged under a matrix of conditions of temperature and relative humidity (RH) ranging from 50 to 90°C and from 30 to 80% RH for times ranging from 34 to 861 days. Approximately one gram portions of the paper samples were finely divided and stirred in 25 mls of water for two hours. Filtered aliquots of the extract were transferred to weighed reaction vials and evaporated in a vacuum dessicator. The weight of the residue was determined, and 0.1 ml of STOX (3) added per 1.5 ml of residue. STOX is a commercial reagent consisting of 25 mg/ml hydroxylamine hydrochloride in pyridine with 0-phenyl-ß-D-glucopyranoside as an internal quantitative standard. The mixture is heated at 70°C for one hour to convert any carbonyl groups in the residue to the oximes. The same volume of a silylating agent such as hexamethyldisilazane is added, any resulting precipitate is allowed to settle, and the supernatant used for analysis. The derivatized extracts were analyzed by gas chromatography on a 50% diphenyl-, 50% dimethylpolysiloxane capillary column on a Carlo Erba 5300 series gas chromatograph with flame ionization detection and on-column injection at 50 KPa pressure. The initial temperature of 50°C was raised immediately by 10°C/min to 250°C and held for ten minutes. Similar procedures were used in the analyses of naturally aged materials for the present study.

The physical property measurements were conducted using custom-built miniature tensile testers as previously described (4). These testers are capable of making measurements on small samples, and can be manually operated. Equilibrium stress-strain curves are generated under constant environmental conditions by allowing stress relaxation to occur between small incremental increases in strain. Dimensional moisture isotherms are generated by making small changes in the

relative humidity and adjusting the gage length to maintain only minimal tension until the specimen equilibrates.

For the present work, naturally aged samples were selected that had no observable damage, such as staining or rot, that would indicate prior exposure to an extreme environment or extraordinary conditions. These included samples of paper from dated books (1804 and 1793), linen thread from the binding of the 1793 book, and samples of wood from a tvihøgdloft (storehouse) in Norway built circa 1650 according to dendrochronological analysis. These samples were analyzed and tested using the same techniques as for the samples in the accelerated aging studies.

Accelerated Aging

It is quite easy to induce changes in materials using exaggerated or extreme conditions, but less easy to prove that the resulting changes are equivalent to natural aging, or more generally, that any two sets of aging conditions are equivalent. The task is further complicated if multiple reactions or processes are taking place, and especially so if the activation energies of the various reactions are similar.

The kinetics of the aging process, and the requirements for different sets of aging conditions to be equivalent, were considered previously by the authors (1,2). Basically, two sets of aging conditions can be considered equivalent if the changes they induce are the same (different amounts of time may be required, of course). This can happen if and only if the same reactions and processes occur under both sets of conditions, and the relative rates of the individual reactions are the same. Accelerated aging, for instance, should speed up all of the reactions of natural aging by the same factor without introducing new reactions. This can be determined most directly by employing methods that can determine the rates of individual reactions rather than just changes in bulk properties. It is difficult to evaluate changes in the aging process using measurements of properties (such as strength or color) that can be affected by more than one reaction. The strength of cellulosic materials, for example, can be reduced either by hydrolysis or oxidation. Once it is established that the chosen accelerated aging conditions are relevant to natural aging, however, any useful property may be used to evaluate the extent or effects of "aging". For example, changes in strength and color are more readily related to the "condition" of paper than is the number of hydrolyzed β-glucosidic bonds, even though such changes may say little if anything about the mechanism or process that produced them.

The authors previously reported the use of analyses of the soluble degradation products of cellulose to compare the effects on paper of aging conditions within a matrix of different temperatures (50-90°C) and relative humidities (30-80%) (1). Figure 1 is a gas chromatogram of the mono- and oligosaccharides and other degradation products extracted from paper aged at 80°C and 77% RH for 278 days. This result is typical of the mixture of degradation products found within the range of environmental conditions of the study, although the distribution of products did vary with the aging conditions and aging time. The predominant products are glucose and its di-, tri-, and tetramers. These are simply short pieces of the cellulose molecule, which is a polymer of glucose, and result from hydrolysis at or near the end of either

the original cellulose chain or larger fragments previously split from the original chain. Some of the other, smaller peaks correspond to products produced by oxidation and scission, but it is clear that hydrolysis of the cellulose chain is the primary degradation mechanism during dark aging within the range of temperatures and relative humidities of the study.

This approach allows the study and comparison of the relative rates of individual reactions (as evidenced by the distribution of the resulting products) as a function of the aging conditions. If the relative rates of all of the reactions relative to each other are the same for different conditions, then the aging process is the same and the aging conditions are equivalent. In other words, changing the aging conditions speeds up or slows down all reactions by the same factor. Different conditions may require different lengths of time to reach the same state of aging, but the aging process does not change. If changing the conditions alters the rates of different reactions by different factors, then the aging process is skewed and equivalent states of aging cannot be reached. For example, if a minor product of one aging condition is the major product of another aging condition, then the two aging conditions are not equivalent.

The overall results showed that the aging process of cellulose did not vary dramatically within the range of conditions studied, and that the differences were primarily a function of relative humidity rather than temperature. Figure 2 (from reference 1) shows a detail of the chromatograms for paper aged under varying conditions to the same relative state of aging as judged by comparable amounts of glucose (the main degradation product). The retention time axes are the same for each chromatogram. The vertical scales of the chromatograms are adjusted so that the glucose peak heights are the same (although offscale), so that amounts of each component can be compared directly. The overall aging rates vary with the aging conditions, so different aging times were required to reach the same "state" of aging (similar amounts of glucose). Chromatograms for different temperatures are most similar when the relative humidity is the same. Thus, the aging process could be speeded up without changing it by increasing the temperature but keeping the relative humidity constant. In the same paper, the authors also demonstrated a correlation between chemical and physical changes, with decreases in strength corresponding to increases in hydrolysis products. Hydrolysis is the primary factor in both the chemical and physical aging of cellulose. The most important conclusion of the study was that results from the accelerated aging of cellulose at a controlled relative humidity and temperatures up to 90°C should be relevant to natural aging at similar relative humidities. It must be emphasized that these conclusions apply only to cellulose aged within the range of conditions of the study, and not to other materials or to significantly different conditions. For example, the aging of cellulose exposed to light is different from the dark aging of cellulose as in the work just discussed.

In this paper, we examine the validity of the conclusions drawn from research conducted with accelerated aged paper by comparing predictions based on the previous accelerated aging work with results for naturally aged materials.

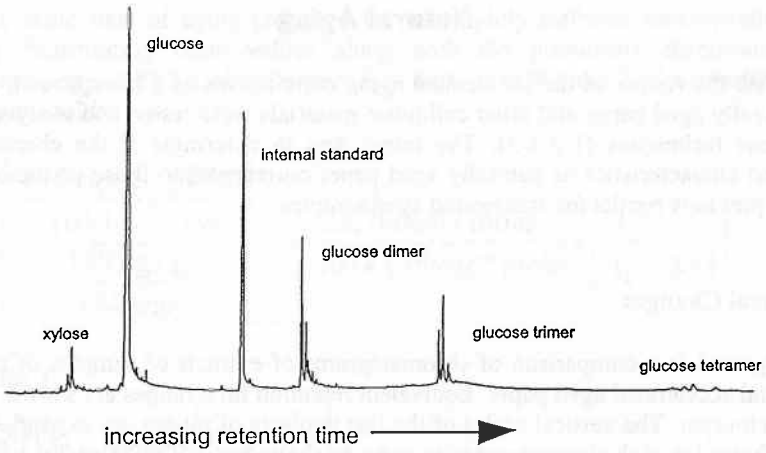


Figure 1. Gas chromatogram of the soluble degradation products in Whatman #1 paper aged at 80°C at 77% relative humidity for 278 days. Saccharides analyzed as the per-trimethylsilylated oximes.

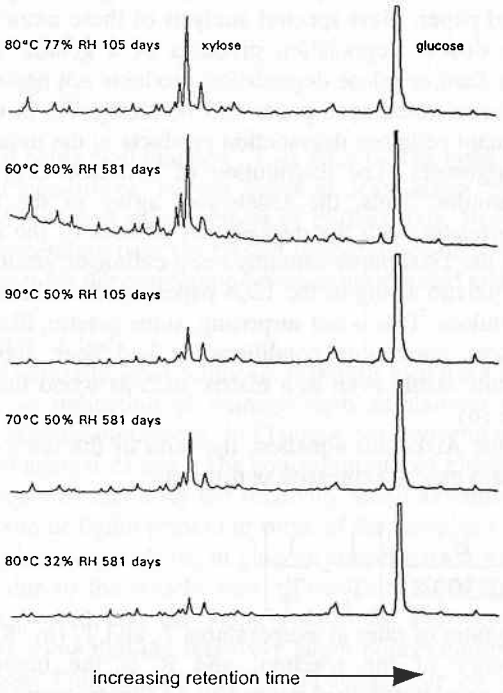


Figure 2. Details of gas chromatograms of the soluble degradation products in samples of Whatman # 1 paper aged under a matrix of conditions. Saccharides analyzed as the per-trimethylsilylated oximes.

Natural Aging

With the results of the accelerated aging experiments as a background, samples of naturally aged paper and other cellulosic materials were tested and analyzed using the same techniques (1-2,4-5). The intent was to determine if the chemical and physical characteristics of naturally aged paper correspond to those predicted based on the previous results for accelerated aged samples.

Chemical Changes

Figure 3 is a comparison of chromatograms of extracts of samples of naturally aged and accelerated aged paper. Equivalent retention time ranges are shown for each chromatogram. The vertical scales of the last two sets of ranges are expanded by the same factor for each chromatogram in order to show detail. The naturally aged paper is from the interior of a book printed in 1804, and thus has undergone about 200 years of dark aging. The samples have similar quantities of glucose present, and thus can be considered to be of roughly equivalent "chemical" ages. The types and distribution of reaction products are similar. The chromatogram for the naturally aged paper does have a number of extra peaks corresponding to compounds not present in the accelerated aged paper. Mass spectral analysis of these extra peaks indicated that they are primarily due to degradation products of a gelatin sizing added during manufacture, rather than cellulose degradation products not present in the artificially aged sample. The accelerated aged paper had no sizing. As in the accelerated aged paper, the predominant cellulose degradation products in the naturally aged paper are glucose and its oligomers. The distribution of cellulose degradation products is similar in both samples. Thus, the accelerated aging of the cellulose in a pure cellulosic paper correlates with the degradation process of the naturally aged 1804 paper, even though the 1804 paper contains a non-cellulosic additive. The presence of a small amount of gelatin sizing in the 1804 paper seems to have had little effect on the aging of the cellulose. This is not surprising, since gelatin, like cellulose, is a quite stable material under reasonable conditions. It had been shown previously that cellulose can be quite stable even in a matrix such as wood that contains materials other than cellulose (6).

According to the Arrhenius equation, the ratio of the rates of a reaction at two different temperatures can be expressed as follows:

$$\log\left[\frac{k_2}{k_1}\right] = \frac{E_a}{2.303R} \bullet \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where (k_2/k_1) is the ratio of rates at temperatures T_1 and T_2 (in °K, or °C + 273), E_a is the activation energy of the reaction, and R is the universal gas constant, 1.99cal/°mole. The accelerated aged paper had 147 micrograms of glucose per gram of sample after aging at 80°C (353°K) for 105 days. The 1804 paper had 139 micrograms of glucose per gram of sample after 194 years of natural aging. The ratio of the rates of the two reactions is the inverse of the ratio of the times they take to

reach the same state of aging (adjusted for the slightly different concentrations of glucose). Substituting these values along with the previously determined (1) activation energy of 22.7 kcal/mole with $T_2 = 80°C$ (353°K) and T_1 the natural aging temperature yields:

$$\log\left[\frac{\frac{147\mu g/g}{105d}\bullet\frac{365d}{1yr}}{\frac{139\mu g/g}{194year}}\right] = \frac{22{,}700cal/mole}{2.303\bullet 1.99cal/°\,mole}\bullet\left[\frac{1}{T_1}-\frac{1}{353}\right]$$

Solving for T_1,

$$\log(713) = 4960°\bullet\left[\frac{1}{T_1}-\frac{1}{353}\right]$$

$$2.85 = \frac{4960°}{T_1} - 14.05$$

$$16.90 = \frac{4960°}{T_1}$$

$$T_1 = 293°\,K = 20°\,C$$

The calculated natural aging "temperature" T_1 is 20.5°C. The book obviously was not aged under constant conditions, having spent at least some time in an attic, a basement, and a used bookstall on the streets of Philadelphia. Nevertheless, deriving an effective aging temperature near the typical temperatures of interior environments provides further support for the correlation between accelerated and natural aging.

Glucose as an Indicator of Age

Other samples of naturally aged cellulosic materials also have been analyzed. We chose samples with no indication of damage such as staining or rot that would indicate exposure to extreme conditions. In Figure 4, the concentration of glucose for each sample is plotted against its age. (The concentrations of glucose are for the bulk material. No correction was made for the relatively small amounts of non-cellulosic materials such as gelatin or lignin present in some of the samples.) As expected, there is a general increase, due to hydrolysis, in glucose concentration with age. The plot is not linear, probably due to the widely varying nature of both the cellulose sample matrix (paper, linen, wood) and the aging conditions. For example, calculations similar to those above show that the relatively larger concentration of glucose in the 1804 book paper from Philadelphia can be accounted for by assuming that the average temperatures it experienced in Philadelphia were about 4-10°C warmer than the temperatures for the samples from London and Norway.

One interesting implication of this graph is that the degradation process of cellulose, at least as indicated by the amount of glucose, is relatively independent of

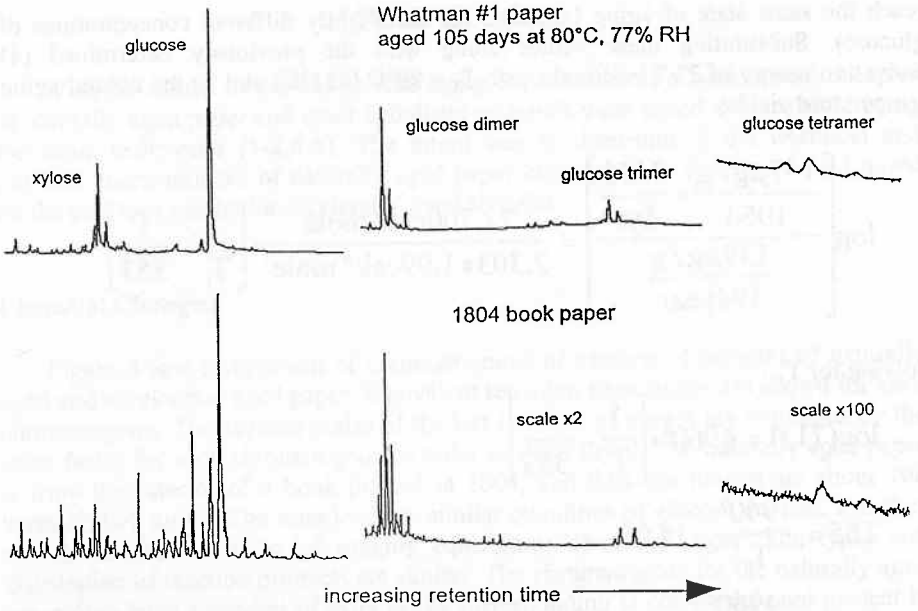


Figure 3. Comparison of gas chromatograms of the soluble degradation products in Whatman #1 paper aged at 80°C, 77% relative humidity for 105 days and paper from a book printed in 1804. Saccharides analyzed as the per-trimethylsilylated oximes.

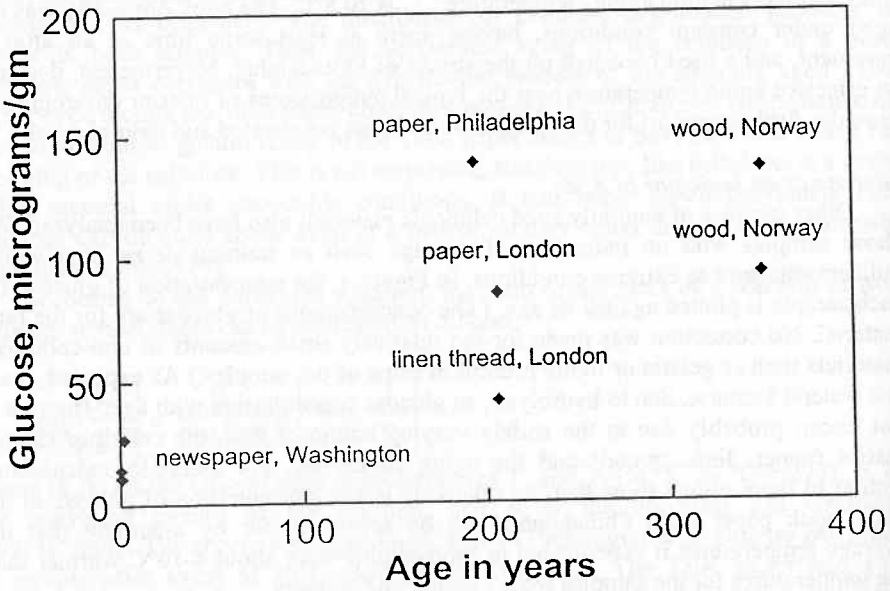


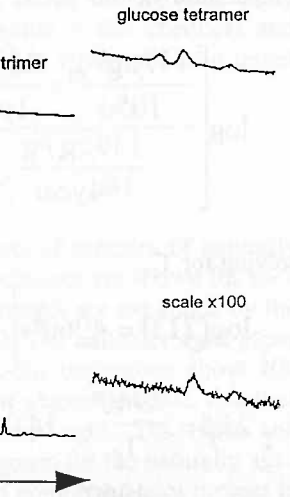
Figure 4. Glucose concentration vs age for naturally aged cellulosic materials.

its source or the matrix it is in (as long as the cellulose is not destabilized by treatment processes or other materials). Further work will refine this model and determine if better correlations between age and glucose content may be obtained by adjusting for known aging conditions, or restricting the plot to samples of similar materials or aging conditions. Such a prospect is illustrated in Figure 5, where glucose concentrations of samples of paper from different dates of The Washington Post are plotted against their age at the time of analysis. From an archivist's point of view, these samples were stored under identical constant conditions, notably the commonly accepted museum "ideal" of 22 C and 50% RH with minimal variation. Evidently, measurable chemical degradation of the cellulose polymer was already occurring even under favorable storage conditions. For these similar samples stored under similar conditions, the plot is linear. This plot, though, predicts much larger amounts of glucose than is found in the older samples. Presumably, the typically acidic nature of newsprint (due to the acid processing of the wood pulp from which it is derived) causes it to degrade at a faster rate than cotton or linen based papers or native cellulose as found in wood (though yielding the same types of products). In this case, the processing does destabilize the cellulose. Thus it will be necessary to take the nature of the sample into account when using the amount of free glucose as an indicator of age. Continuing work will determine the calibration curves that are required. The measurement of glucose concentration provides a sensitive indicator for the process of cellulose decay.

Though yellowed, the newspaper samples were still structurally sound. The yellowing of newsprint is due primarily to the lignin component, but the yellowing of the lignin is a separate process from the hydrolysis of the glucose and is not directly related to changes in strength. The breaking strains of the samples were greater than 2%, indicating that they could tolerate normal handling quite readily.

Physical Changes

The physical properties of naturally aged paper samples also were examined to determine if they were as predicted based on the results from accelerated aging. The evaluation of chemical changes was the primary tool in evaluating the relevance of aging conditions. Once that relevance has been established, appropriate physical tests are required both to validate the interpretation and effects of the chemical mechanisms and to describe the behavior of the cellulosic materials as structural entities. Unfortunately, many of the physical (as well as chemical) tests historically used for paper either do not provide the data required to evaluate the effects of aging or are only minimally useful in assessing the condition of the paper. Many tests are dependent on surface phenomena and not the bulk properties of the paper. Analyzing the types and amounts of degradation products has clarified the effects of environmental conditions on the aging process as well as the relationship between natural and accelerated aging. Measuring the stress-strain behavior of the cellulosic materials has clarified the structural interpretation of the effects of aging. Measurements of the response of cellulosic materials to changes in relative humidity and temperature, and their stiffness, strength, and elastic and plastic behavior are



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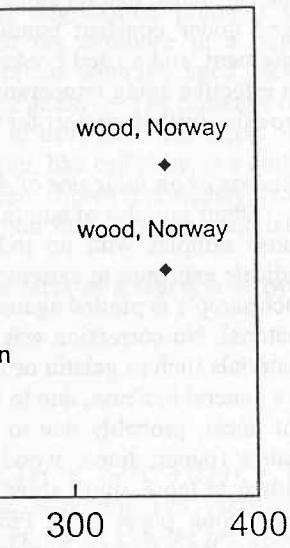

d cellulosic materials.

required to calculate the physical response of these materials to handling and preservation treatments as well as environmental influences. This in turn allows the determination of protocols for treatment and handling, and allowable environmental ranges in which no damage or permanent deformations are produced (7,8). Once a physically safe environmental region has been defined, other factors can be considered in deciding whether one area of this region is more suitable or if further restrictions are necessary. Such factors include environmental effects on the rate of chemical degradation processes, the presence of other materials in the collection, phase transitions, the deliquescence of salt contaminants, and the cost, effort, and reliability of controlling the environment within a specified range (8,9).

Stress-strain Behavior of Paper

Figure 6 is a stress-strain curve for the 1804 book paper, in which the stress resulting from an applied strain (dimensional change) is plotted. This curve is similar in shape and magnitude to those for modern and accelerated aged papers, although it ends (the paper breaks) earlier than with unaged paper. An important part of the curve is the initial linear section, which represents reversible (elastic) deformation. If this deformation is not exceeded, there is no damage, either breakage or permanent deformation, to the paper. Aged paper tends to lose its ability to plastically deform (the stress-strain curve ends sooner) but retains its elastic range unless it is so degraded that it has almost no physical integrity. The loss of the plastic region means the paper is more brittle, i.e. it breaks at a shorter extension with less stretching. The ability to plastically deform is less relevant than the retention of the elastic region, however, in determining allowable environmental fluctuations based on reversible behavior. The plastic region becomes more important in considering handling, since a larger plastic region provides a greater range where inappropriate handling or treatment will produce (permanent) deformation rather than breakage. For example, an analysis of the results of classic folding endurance tests indicates that "failure" occurs when the paper is unable to sustain a strain of about 1% (10), which is well beyond the elastic limit. In new paper which has a plastic region extending beyond 1% strain, folding results only in a permanent crease. Old or degraded paper with a breaking strain reduced to below 1% simply fails when folded even if its elastic limit is still intact. Under appropriate environmental conditions and with careful handling, the elastic (reversible) limit should not be exceeded. Information obtained from the stress-strain curves and moisture absorption isotherms (see below) enables one to determine these conditions.

A number of other materials properties can be derived from the stress-strain curve, including the ultimate (breaking) strength, breaking strain, and the modulus (stiffness), which is the slope of the initial section of the curve. Such curves are run under constant environmental conditions. If individual curves are generated for a matrix of environmental conditions, the derived properties can then be determined as a function of the environment. In Figure 7, the moduli (stiffness) of naturally aged, new, and accelerated aged papers are plotted as a function of relative humidity. The older paper is isotropic. The direction of measurement in the anisotropic Whatman paper is indicated. Two important pieces of information derive from this plot; first, the modulus of paper does not change significantly with age; and second, the modulus of paper, new or aged, does not change significantly within the range of

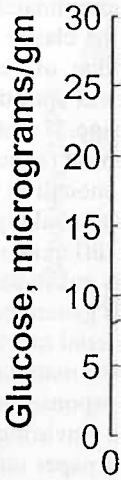

Figure 5. Glu
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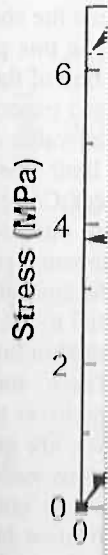

Figure 6. Equ

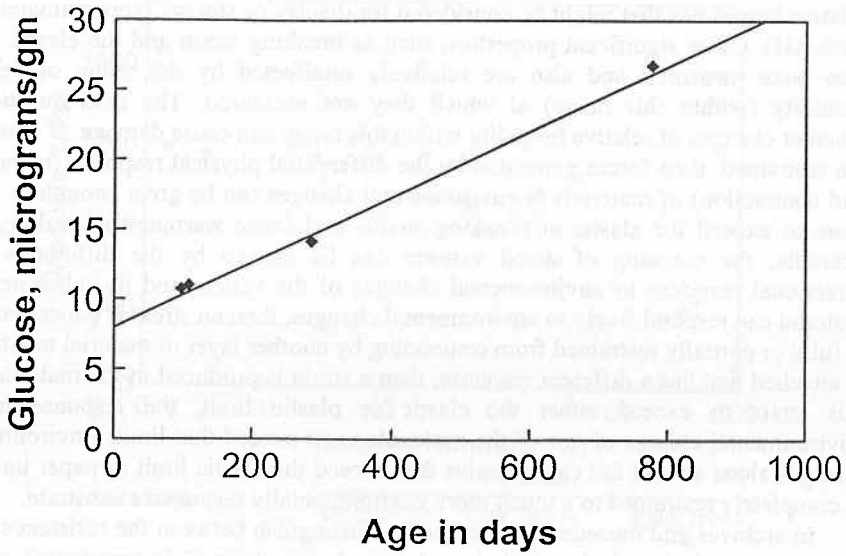

Figure 5. Glucose concentration vs age for newsprint samples from The Washington Post stored at 22°C and 50% relative humidity.

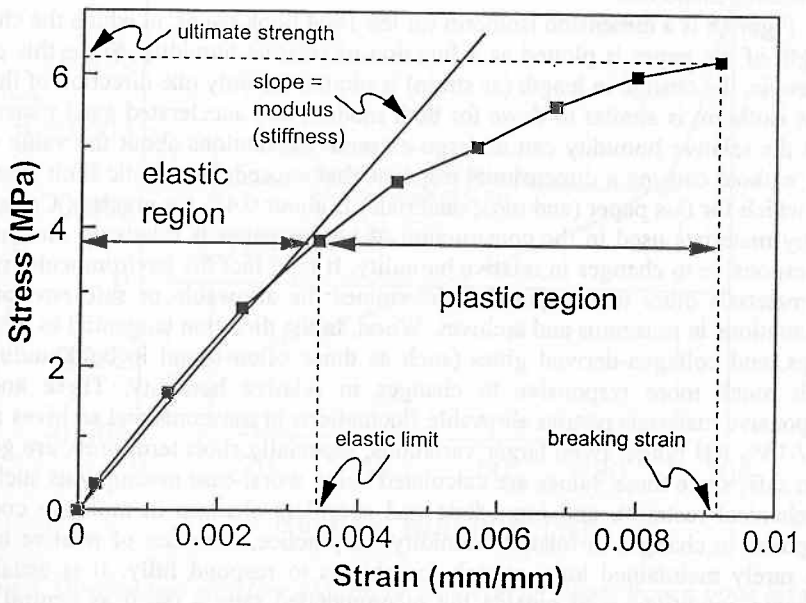

Figure 6. Equilibrium stress-strain curve for paper from a book printed in 1804.

relative humidities that might be considered for display or storage (approximately 20-60% RH). Other significant properties, such as breaking strain and the elastic limit, also were measured and also are relatively unaffected by the value of relative humidity (within this range) at which they are measured. The next question is whether changes of relative humidity within this range can cause damage. If materials are restrained, then forces generated by the differential physical response (expansion and contraction) of materials to environmental changes can be great enough to cause them to exceed the elastic or breaking strains and cause warping or breaking. For example, the cracking of wood veneers can be caused by the differential and directional response to environmental changes of the veneer and its substrate. If a material can respond freely to environmental changes, then no stress is generated. If it is fully or partially restrained from responding by another layer or material to which it is attached that has a different response, then a strain is produced in the material. For this strain to exceed either the elastic or plastic limit, the response to the environmental change of one of the materials must exceed that limit. Environmental changes alone should not cause strains that exceed the elastic limit of paper unless it is completely restrained to a much more environmentally responsive substrate.

In archives and museums, it is crucial to distinguish between the resistance of an object to physical and chemical degradation during "aging" (permanence) and to mechanical damage caused by use (durability). For example, a book may no longer be durable enough to be lent out indiscriminately, but still be quite permanent and retain its value as an object or research tool. In this case, the book has undergone the transition from utile object to icon.

Dimension Isotherms

Figure 8 is a dimension isotherm for the 1804 book paper, in which the change in length of the paper is plotted as a function of relative humidity. Since this paper is isotropic, the change in length (as strain) is plotted for only one direction of the sheet. This isotherm is similar to those for both modern and accelerated aged papers. Note that the relative humidity can undergo extreme fluctuations about the value of 50% RH without causing a dimensional response that exceeds the elastic limit (see Figure 6), which for this paper (and most materials) is about 0.4% (or greater). Compared to many materials used in the construction of books, paper is relatively dimensionally unresponsive to changes in relative humidity. It is in fact the environmental response of materials other than paper that determines the allowable or safe environmental fluctuations in museums and archives. Wood, in the direction tangential to the growth rings, and collagen-derived glues (such as those often found in bookbindings) are both much more responsive to changes in relative humidity. These and other responsive materials restrict allowable fluctuations in museums and archives to about a +/-15% RH range. Even larger variations, especially short term ones, are generally also safe, since these values are calculated using worst-case assumptions such as full mechanical restraint, and immediate and complete changes in moisture content in response to changes in relative humidity. In practice, extremes of relative humidity are rarely maintained long enough for objects to respond fully. It is usually only extreme conditions well outside the recommended ranges (such as central heating without humidification in cold climates) that cause mechanical damage to cellulosic materials. The +/-15% value is appropriate because it is safe and attainable without

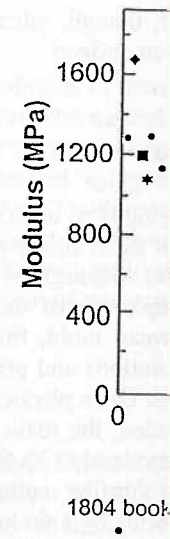

Figure 7. Modulus (s and 77% relative hu measured in both the

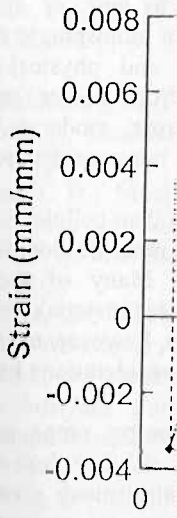

Figure 8. Dimensione 1804. The allowable irreversible strains co

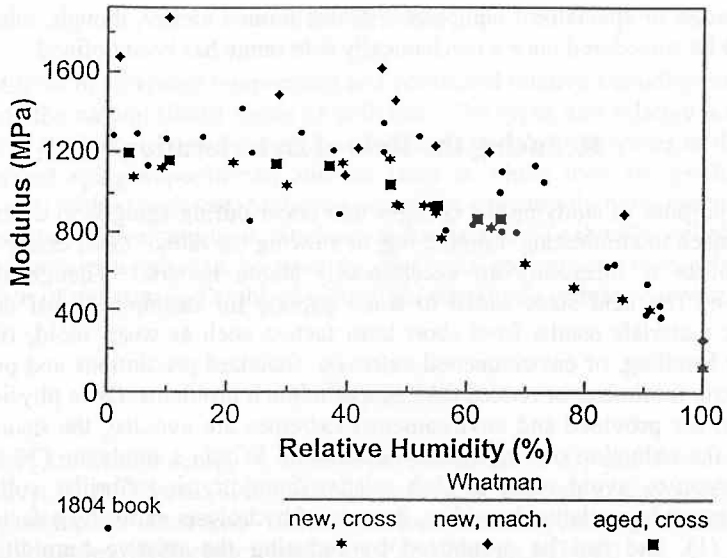

Figure 7. Modulus (stiffness) vs relative humidity for new, accelerated aged (80°C and 77% relative humidity for 105 days), and naturally aged paper. New paper measured in both the machine and cross-machine directions.

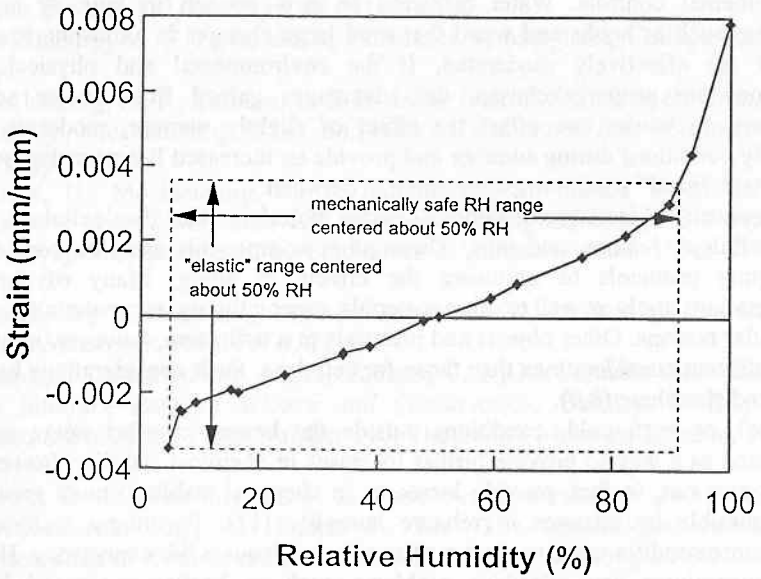

Figure 8. Dimensional moisture absorption isotherm for paper from a book printed in 1804. The allowable range centered about 50% relative humidity in which no irreversible strains can occur even if the paper is fully restrained is indicated.

great expense or specialized equipment. As mentioned earlier, though, other factors must also be considered once a mechanically safe range has been defined.

Reducing the Rate of Deterioration

The purpose of studying the changes that occur during aging is to determine the best approach to eliminating, minimizing, or slowing the rate of these changes.

Cellulose is inherently an exceptionally stable material. Though it can be destabilized (by acid sizes added to some papers, for example), most damage to cellulosic materials results from short term factors such as wear, mold, fire, flood, improper handling, or environmental extremes. Standard precautions and procedures can prevent, minimize, or reduce the chances of such problems. Once physically safe conditions are provided and environmental extremes are avoided, the main concern becomes the reduction of long term deterioration. Within a moderate (30-60% RH) range chosen to avoid mold at high relative humidity and fibrillar collapse and crosslinking at low relative humidity, the rate of hydrolysis varies by a factor of two or three (1), and can be minimized by reducing the relative humidity. Lower temperatures also provide increased chemical stability, and, at least within the human comfort range, introduce no new problems (But see below). Moderate fluctuations of temperature and relative humidity are safely tolerated and have no significant effect on the materials properties of cellulosics (6), so environmental conditions can be modified seasonally to save energy and to avoid the need for specialized or overbuilt environmental controls. Water diffusion is slow enough in bulk or composite structures such as books and wood that even large changes in atmospheric moisture content are effectively moderated. If the environmental and physical storage conditions are properly chosen, the advantages gained from cooler and drier conditions in winter can offset the effect of slightly warmer, moderate relative humidity conditions during summer and provide an increased life expectancy relative to constant "ideal" conditions somewhere in between.

Composite objects such as books contain materials other than cellulose, such as glue, celluloid, leather, and inks. These other components must be considered in developing protocols to minimize the effects of aging. Many of the above considerations apply as well to other materials, especially organic materials, and often for similar reasons. Other objects and materials in a collection, however, may require quite different considerations than those for cellulose. Such considerations have been addressed elsewhere (8,9).

Cool, or even cold, conditions outside the human comfort range are often considered as a way to provide further increases in chemical stability. Lowering the temperature can, in fact, provide increases in chemical stability much greater than those possible by changes in relative humidity (11). For many materials, low temperature conditions are necessary to ensure an adequate life expectancy. However, low temperatures can introduce problems such as brittleness caused by glass transitions and unacceptable changes in moisture content due to temperature dependent moisture absorption isotherms. A complete discussion of such problems is beyond the scope of this article. See reference 10 for a discussion of the considerations related to the cold storage of photographic materials, for example.

Conclusions

Conditions of increased temperature and controlled relative humidity can be used to replicate the natural (dark) aging of cellulose. The types and relative amounts of degradation products in naturally aged cellulosic materials correspond to those seen in accelerated aging experiments, and the rates at which they are produced also correlate well with experiment. Materials properties of naturally aged specimens also are as predicted from experiment. Analyses and tests of both naturally and accelerated aged cellulosic materials can be used to determine appropriate approaches to the preservation of museum and archival collections containing cellulosic materials.

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