

**ACCELERATED VS NATURAL AGING:
EFFECT OF AGING CONDITIONS ON THE AGING PROCESS OF CELLULOSE**

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ABSTRACT

This paper discusses the kinetics of aging and its implications for the evaluation of changes in the aging process, especially as applied to accelerated aging. The problem of comparing accelerated aging conditions is shown to be separate from that of evaluating changes occurring under one specific set of conditions. Thus tests and measurements that can be used to evaluate the results of a specific accelerated aging experiment are not necessarily valid for use in determining whether two sets of aging conditions are comparable. This distinction is crucial in trying to determine whether a set of aging conditions is comparable to, or accurately simulates, natural aging. The criteria for comparing two sets of aging conditions are defined, and applied to the problem of evaluating accelerated aging conditions. Data from the analysis of individual reaction products of artificially aged paper samples are used to determine the effects of temperature and relative humidity (RH) on the rates of individual reactions. Changes in the distribution of reaction products are used as indicators of changes in the aging process. The aging process of cellulose under the conditions studied (60-90°C, 30-80% RH) is shown to be RH dependent, but relatively temperature independent. Thus raising the temperature at constant RH speeds up the aging process without significantly altering it. If the RH is changed, then the aging process is altered and equivalent states of aging cannot be reached. Accelerated aging should be conducted at the same relative humidity as the conditions to which the results are to be applied. The data also indicate that lowering the relative humidity from 50% to 30% slows the rate of hydrolysis by a factor of three to five times.

INTRODUCTION

Aging is the process of changing over time. Although some things are supposed to improve with age (children, cheese, and wine, for example), the term aging as applied to museum objects generally connotes degradation and deterioration. Aging may be defined as irreversible changes that occur slowly over time. The changes usually are measured relative to a specific state, either the original state or that of a specified time. One of the basic functions of museums is the preservation of the collections. Over the long term, one must attempt to reduce, minimize, or eliminate the effects of aging. In order to do this, it is helpful to understand what the aging process consists of, what factors affect it, and to what extent changing these factors may change the aging process.

MATERIALS TESTING

Industrial testing of materials is concerned primarily with the short term durability of materials and their resistance to degradation during use. The amount of degradation that products undergo during use is so much greater than what occurs when the product is not in use

that "natural aging" often does not have to be taken into account when evaluating materials. Testing procedures that have been adopted by industry tend to be ones that measure physical properties pertinent to the use of the material. For instance, tests used by the paper industry include dry and wet strength, folding endurance, and tear resistance. The study of aging processes in the museum is quite different. By definition, most of the changes during aging occur slowly over a long period of time. This is especially true for museum objects that are kept in conditions intended to retard the aging process. Simple physical tests of unaged materials are not adequate to predict their permanence, defined as resistance to change when not in use. In order to study aging processes as they normally occur, it is necessary either to conduct experiments over very long periods of time, or to measure very minute changes over a shorter period of time and extrapolate from them to predict long-term changes. Both of these approaches are fraught with problems. An alternative is to try to speed up the process of aging so that measurable changes occur within a reasonable time.

ACCELERATED AGING

Accelerated aging is an attempt to simulate in a short time the effects of long periods of natural aging. Its purpose is to evaluate the permanence of materials, or the effects of treatments on the permanence of materials. Accelerated aging can consist of exposure to any combination of potentially damaging environmental factors including heat, humidity, light, oxygen, and pollutants. The underlying assumption of most accelerated aging experiments is that they simply speed up the changes (degradation) that occur during normal aging.

A material that has been subjected to accelerated aging often is assumed to be identical to the same material aged for a longer time under "normal" conditions. Physical, chemical, and/or spectroscopic tests are conducted both before and after aging to determine the suitability or permanence of materials or the effects of treatments. Originally, many of the tests that were used to measure the changes resulting from aging were adopted from industrial testing methods. In essence, the durability of a material was measured before and after aging. This was not totally satisfactory for the evaluation of materials in the museum, since one would hope that durability would not be required of museum objects. The preservation of objects implies not only the retention of functional properties, but also the preservation of the information inherent in the object. Such information may be visual, physical, optical, structural, or chemical in nature. Some tests that measure changes in properties that are more relevant to conservation have been adopted. Thus, varnishes might be evaluated after aging by measuring their solubility and degree of yellowing. Other tests that have been developed measure more fundamental chemical and physical changes in materials and therefore may be better measures of "degradation". Practically, though, there are no real restrictions on the kinds of tests that may be employed. Any test that provides information that is useful in evaluating the effects of aging may be used. It is instead the aging conditions themselves that must meet certain requirements. The basic requirement is that accelerated aging conditions must not produce test results that differ markedly from those that would have been found by aging under normal conditions. If the accelerated aging conditions do not accurately simulate natural aging, then no test conducted on the aged samples can be considered reliable in predicting the effects of natural aging.

In fact, different aging conditions can produce quite different results. Aging in the dark at high temperature and high relative humidity (RH) can be quite different from aging under

ultraviolet lights at room temperature and moderate RH. "Natural" aging itself can cover a wide range of conditions and yield a wide range of results. This was demonstrated by a comparison of the environments for two collections in different climates and of the state of preservation of books that were present in both collections.¹ The aging process can consist of any of a number of different reactions, each of which may independently speed up or slow down depending on the aging conditions. A specific set of accelerated aging conditions may produce degradation, but that does not mean that the changes that occur are the same as those that would have occurred during natural aging. How does one know whether a set of accelerated aging conditions will produce valid results? In order to answer this, one must consider both the aims of accelerated aging and the kinetics of the aging process.

There are two basic approaches to accelerated aging. One is to attempt to simulate natural aging as closely as possible, in order to determine the overall long-term behavior of a material or effects of a treatment. In other cases, a specific behavior or reaction is under consideration, and the purpose of accelerated aging is to exaggerate or speed up a particular reaction without regard to whether other changes occur as they would under normal aging. One may want to determine, for instance, if a material proposed for use in a display case emits volatile acids. If so, other aging characteristics can be ignored, and the aging conditions can be designed to emphasize the outgassing process without regard to whether other reactions that occur during natural aging are similarly speeded up. The main consideration in this type of experiment is that the reaction under consideration, such as outgassing, should occur under the accelerated aging conditions if and only if it would occur under normal conditions.

More extreme accelerated aging conditions yield results more quickly (and often more obviously), but there are limits to how far accelerated aging conditions can be pushed. Beyond these limits, the aging process becomes so different from what occurs under normal conditions that the results become irrelevant to natural aging. There is rarely a sharp distinction between valid and invalid conditions, because generally there is a continuous change in the aging process as conditions change. Exceptions would include changes that occur at obvious critical temperatures. The aging process of a material certainly changes above its glass transition temperature, melting point, or ignition temperature. One of the fundamental objectives of research in accelerated aging is to determine the range of conditions that reasonably simulate the natural aging of the types of materials under consideration.

In the case of cellulose, the main component of paper, the limits within which accelerated aging is equivalent to natural aging have not been well defined, nor is there a universally accepted set of standard aging conditions. Even the paper industry has at least three standard aging conditions that are quite different from each other.² Two of these conditions are intended as generalized aging conditions. The third set of conditions is used to test for a specific undesirable property, that of color reversion after bleaching. The conditions for this test were chosen specifically because they tend to exaggerate the color reversion reaction.

Outside of the paper industry, and especially within the conservation field, many very different aging conditions for paper and other cellulosic materials have been used. Often, this is because it is recognized that natural aging itself is not a single or consistent process. For instance, aging while on display can differ radically from aging in storage, with photochemical processes predominating in the former and thermal processes in the latter. Thus, exposure to intense light may be used to simulate aging while on display, while aging in the dark at elevated

temperatures is more appropriate for evaluating the behavior of materials while in storage. The aging processes of paper are in general extremely slow (even "bad" paper can last easily fifty years), and slight changes in storage conditions can result in large effects on the relative rates of the individual aging reactions. Because cellulose is such a stable material, it invites (necessitates?) the use of extreme aging conditions in order to produce results within a reasonable time frame. Researchers have used aging conditions that range from relatively mild to nearly as extreme as conditions known to produce degradation processes very different from those of normal aging. It is therefore difficult to determine whether a specific set of accelerated aging conditions is relevant to a given set of "normal" aging conditions, much less to compare the results of the various research papers.

The main question to be answered before a set (or range) of accelerated aging conditions for paper or any other material will be widely accepted is: How extreme can accelerated aging conditions be before they are no longer related to natural aging? The answer to this question depends on an adequate comparison of the effects of aging conditions. The ability to determine whether two aging conditions are comparable also implies knowing at what rate each condition produces the equivalent state of aging, in other words, how fast aging occurs during a specified set of conditions. This allows one to predict the effects of altering the storage conditions on the rate of degradation, and to determine what set of conditions within a realistic range best preserves a collection. This leads to the fundamental question: How can two sets of aging conditions be compared?

THE KINETICS OF DEGRADATION

Degradation is rarely, if ever, a simple process consisting of a single chemical reaction. Most materials can undergo a number of reactions and physical changes. This is especially true if the material is not a pure compound, but consists of a number of chemical components. Even reasonably pure cellulose contains impurities, cellulose chains of different length, hemicellulosic side branches, and regions with differing degrees of crystallization. The degradation of cellulose occurs through a number of reactions and processes such as hydrolysis, oxidation, crosslinking, ring opening, chain scission, and changes in the degree of crystallization. Each of these reactions is affected by a number of external factors.

It is possible for two sets of aging conditions to produce very different distributions of the possible degradation reactions: a reaction that predominates under one set of conditions may be only a minor factor in the aging process under different conditions. If so, then the two aging conditions may produce different results for the same material. For the total degradation processes of a material under two sets of aging conditions to be comparable, the following requirements must be met:

- 1) The same reactions must take place under both sets of conditions.
- 2) The relative rates of the various reactions should be similar under both sets of conditions.

In other words, to simulate natural aging accurately, accelerated aging should speed up all reactions by the same factor without introducing new reactions.

This is easy to state, but not to test experimentally. One problem is that many of the tests that are used to evaluate degradation are not reaction-specific, but involve the measurement of secondary or tertiary properties. Tests of cellulose degradation, for instance, include the measurement of properties such as tear strength, fold endurance, and brightness, that depend on many aspects of the chemistry and physical state of cellulose. For example, oxidation, hydrolysis, crosslinking, and thermally induced changes in the degree of crystallization all can affect the fold endurance of cellulose. It is possible to use combinations of tests and conditions to follow specific types of reactions, but it is rare that individual reactions are monitored. A consideration of the kinetics of some simple reaction systems can demonstrate some of the problems involved in the study of degradation processes.

The Rate Equation

The rate constant, k , for a reaction is given by the Arrhenius equation

$$k = A \cdot \exp(-E/RT) \quad (1)$$

where A is the Arrhenius factor (a reaction-specific constant), \exp is the exponential function, E is the activation energy for the reaction, R is a universal constant, and T is the temperature in degrees Kelvin. The rate for a simple one-step reaction between two compounds X and Y is the product of the rate constant for that reaction and the activities $[X]$ and $[Y]$ of the reactants (activity is related to and sometimes equal to the concentration). For the reaction of reagents X and Y , the equation is

$$\text{Rate} = [X] \cdot [Y] \cdot k \quad (2)$$

Substituting for k using the Arrhenius equation,

$$\text{Rate} = [X] \cdot [Y] \cdot A \cdot \exp(-E/RT) \quad (3)$$

For constant conditions during the initial stages of degradation before much of X and Y have reacted, the concentrations of the reactants can be considered constants. They can then be combined with the constant A to give a pseudo-constant A' ,

$$A' = [X] \cdot [Y] \cdot A \quad (4)$$

Substituting A' in Equation 3 yields

$$\text{Rate} = A' \cdot \exp(-E/RT) \quad (5)$$

$$= k' \quad (6)$$

This is equivalent to Equation 1 for the rate constant k , except that it now depends on the reactant concentrations that were combined with A to give A' . This k' is the type of "k" often determined in experiments involving the degradation of chemically complex materials, where the nature and roles of the various reactants are not clear. It is not feasible to factor out reactant concentrations in this case. A' and k' can be mathematically manipulated similarly to A and

k, but one must remember that A' and k' depend on reactant concentrations that in turn can be affected by the aging conditions. For instance, changing the RH can change A' and k' if water is a reactant in the degradation process. In addition, k' usually is valid only in the initial stages of degradation, before the amounts of the starting materials X and Y are significantly reduced.

The pseudo-rate constant k' can be determined for a specific set of conditions by monitoring the progress of the degradation process over a period of time. Concentrations of reactants or products, or other measurements of change, can be plotted versus time. The result may be simple linear or exponential plots, or more complex depending on the specific conditions and reaction mechanism.³ A plot of the logarithm of a concentration versus time often yields a linear plot. Again, remember that the pseudo-constant A' depends on reactant concentrations, and eventually will change as degradation reduces the amount of the material under study. The plot will then no longer appear linear after a certain time. The value of k' generally is determined from the initial linear portion of the plot. If k' is determined for more than one temperature, then A' and E can be determined. Taking the natural log of both sides of the equation

$$k' = A' \cdot \exp(-E/RT) \quad (7)$$

yields

$$\ln(k') = \ln(A') - E/RT \quad (8)$$

A plot of $\ln(k')$ versus $1/RT$ (the "Arrhenius plot") is a straight line of slope $-E$ that intercepts the y axis at $\ln(A')$. Once E and A' have been determined, then k' can be calculated for any T. In other words, the reaction rate can be calculated for any given temperature (assuming nothing else changes).

Temperature Dependence

A consideration of the form of the rate equation reveals, not surprisingly, that reaction rates increase with temperature. A widely used rule of thumb is that reaction rates double with every 10°C rise in temperature. This statement is a part of conservation and chemical folklore⁴, but like most myths does have a grounding in fact. As seen above, reaction rates are exponential functions not just of the temperature, but of the activation energy as well. Thus the activation energy (which is constant for a specific reaction) determines how sensitive the rate of a reaction is to temperature. The activation energy is a measure of the energy barrier that must be cleared for the reaction to occur. The higher this barrier, the slower the reaction (all other factors being equal). Interestingly, though, a higher activation energy makes a reaction more sensitive to temperature, and increasing the temperature increases the rate relatively more than that for a reaction with a lower activation energy. This phenomenon can be demonstrated by calculating relative reaction rates at different temperatures for reactions with various activation energies.

The ratio of the rates of a reaction at two temperatures T_1 and T_2 is

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k_2}{k_1} = \frac{A \cdot \exp(-E/RT_2)}{A \cdot \exp(-E/RT_1)} \quad (9)$$

The factor A cancels out. The exponential function of one number divided by the exponential function of another number is the exponential function of the first minus the second number. Thus

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \exp((-E/RT_2) - (-E/RT_1)) \quad (10)$$

or, combining and manipulating,

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \exp(E(T_2 - T_1)/RT_1T_2) \quad (11)$$

If one sets $T_1 = 293^\circ\text{K}$ (20°C), then Equation 11 can be used to calculate the rate of a reaction with activation energy E at a temperature T_2 relative to the rate of the reaction at 20°C . By doing this at a number of temperatures for reactions with various activation energies, one can determine the sensitivity to temperature of each reaction. Table I presents the results of such calculations.⁵ For a specific activation energy, the numbers in the corresponding column give the rate of a reaction with that E relative to the rate at 20°C . For instance, for a reaction with an activation energy of 15 kcal, the rate at 30°C is 2.34 times that at 20°C , while at 10°C it is 0.40 times as fast. The rate relative to temperatures other than 20°C also can be calculated. At 30°C , the reaction is $2.34/0.40 = 5.85$ times as fast as at 10°C . Note that this chart can only be used to compare relative rates of a single reaction at different temperatures (within a column), and cannot be used to compare rates of different reactions (within a row).

Table I. Relative rates vs temperatures for reactions of various activation energies.

Temperature °C	Activation energy, kcal						
	5	10	15	20	25	30	35
	Rate relative to 20°C						
0	0.53	0.28	0.15	0.08	0.04	0.02	0.01
5	0.63	0.40	0.25	0.16	0.10	0.06	0.04
10	0.74	0.55	0.40	0.30	0.22	0.16	0.12
15	0.86	0.74	0.64	0.55	0.47	0.41	0.35
20	1.00	1.00	1.00	1.00	1.00	1.00	1.00
25	1.15	1.33	1.54	1.78	2.06	2.37	2.74
30	1.33	1.76	2.34	3.11	4.13	5.48	7.27
35	1.52	2.31	3.51	5.33	8.10	12.3	18.6
40	1.73	3.00	5.19	8.98	15.6	26.9	46.6

Most reactions that occur at a reasonable rate at or just above room temperature (and that are the ones likely to be studied in the lab by aspiring young chemists) have activation energies in the range of 10-15 kcal. It can be seen from Table I that the sensitivity to temperature of these reactions is such that they do indeed approximately double in speed with a 10°C rise in temperature, making such a guideline useful in undergraduate laboratories. The use of this principle in the museum field is inappropriate, though. Most of the reactions that the materials of museum objects undergo are extremely slow (at least on the laboratory time scale) because they generally have activation energies that are much higher than 15 kcal. The major

degradation reactions of cellulose, possibly the most common material in museums, libraries, and archives, have activation energies in the range of 20-30 kcal.⁶ Such reactions double in rate with approximately every 5°C increase in temperature. Paper and other cellulosic materials are thus approximately twice as sensitive to temperature as they generally are regarded.

Multiple Reactions

The above rate equations and calculations apply if a single reaction is involved. Usually, however, it is not the rate of an individual reaction that is measured. Most of the tests used to assess degradation do not measure the rate or progress of individual reactions, but instead measure changes in properties that are affected by degradation. Often, the rate of change of a property is proportional to the rates of individual degradation reactions, at least for a while. (Any plot looks linear and can be fit to a straight line if you consider a small enough section of it!) Such measurements of a property would be perfectly adequate to gauge the progress of an individual reaction if only the one reaction were occurring, or if the property were not affected by other reactions that were taking place. In general, though, most of the properties that are normally used to gauge degradation are affected by a number of the reactions that occur during aging. If, instead of measuring the rate of a single reaction, one monitors the rate of change of a property that is affected by more than one degradation reaction, then the plot thickens (no pun intended).

Consider the case where the property being measured changes linearly with the progress of each of two degradation reactions. The rate of change of the property is proportional to the sum of the rates of the two reactions:

$$k_{\text{total}} = k_1' + k_2' \quad (12)$$

$$= A_1' \cdot \exp(-E_1/RT) + A_2' \cdot \exp(-E_2/RT) \quad (13)$$

The apparent activation energies for changes in many of the properties of paper have been determined. The activation energies for some important cellulose degradation processes that involve only one type of reaction are very similar⁶, and some differ by less than the amount of experimental error. This is not entirely coincidence, for one would expect that the various reactions of importance in the degradation of a material would have similar activation energies. If not, then it is likely that some reactions would be much faster or slower than other reactions. If some reaction were too fast, it either would determine the course of degradation by causing the material to disintegrate, or it would run to near completion early in the life of the object (many of the natural yellow dyes in textiles have faded completely). If some reaction were extremely slow, then it likely would play only a minor role in the degradation process. Thus it is usually the reactions of "average" speed and activation energy for the material that determine the fate of the material. This has interesting consequences, for if the activation energies E_1 and E_2 in Equation 13 have the same value E , then Equation 13 becomes

$$k_{\text{total}} = A_1' \cdot \exp(-E/RT) + A_2' \cdot \exp(-E/RT) \quad (14)$$

$$= (A_1' + A_2') \cdot \exp(-E/RT) \quad (15)$$

As in the situation with one reaction, one can determine k_{total} at different temperatures while keeping other experimental conditions constant. An Arrhenius plot of this data will yield a straight line with a slope of $-E$ and a y intercept of $(A_1' + A_2')$. This allows one to determine E and the sum $(A_1' + A_2')$, but does not allow one to determine A_1' or A_2' . This means that, without additional data of another type, it is not possible to calculate the relative contribution of the two reactions. It is not even possible to determine if one of the reactions does not occur at all under the specific conditions used! Remember that A_1' and A_2' are functions of A_1 or A_2 and the reactant concentrations, and thus can depend on the aging conditions. Changing the conditions may alter the rates of one or both reactions. This cannot be detected if one considers only the activation energy, because the plot of $\ln(k_{\text{total}})$ versus $1/RT$ is still a straight line with a slope of $-E$. The plot is shifted, however, so that while it is parallel to the plot for the old conditions, its y axis intercept is the new value of $\ln(A_1' + A_2')$. For example, an analysis of experimental data for cellulose degradation that demonstrates a parallel shift of Arrhenius plots with a change in humidity has been reported.⁷ In this case, increasing the humidity increases the concentration of a reactant (water) that is involved in some of the cellulose degradation reactions. This increases the degradation rate at each temperature, and shifts the entire plot. The reason for this parallel shift becomes clearer if one can imagine doubling the amount of test material and thereby doubling the "rate" of reaction at each temperature. This shifts each point of the Arrhenius plot by the same amount, but does not change the slope. The slope is a measure of the amount of energy involved in the reaction of an individual molecule, and is not affected by the number of molecules that are reacting. Alternatively, one could double the reaction rate by increasing the number of possible reactions. This again shifts the plot without changing the slope, because the slope is still a function of the energy involved in the reaction of individual molecules, and does not differentiate between reactions with the same activation energy, even if the products are very different. A measurement of the activation energy alone can not be used to determine how many different reactions with that activation energy are taking place, or the relative rates of each one.

The argument above can be extended to any number of reactions with similar activation energies. Even if the activation energies are not equal, it still is difficult to use tests that are not reaction-specific to sort out the various reactions. Plots of $\ln(k_{\text{total}})$ versus $1/RT$ are still often linear within experimental error. The "activation energy" determined from the plot will be an "average" of the activation energies of the reactions. This can be demonstrated by looking at data calculated for hypothetical reactions with typical activation energies. Figure 1 shows a plot of $\ln(k)$ versus $1/RT$ for two reactions between 50 and 150°C. Reaction 1 has an activation energy E_1 of 20 kcal/mol, Reaction 2 an E_2 of 25 kcal/mol. A_1' and A_2' have been chosen so that the rates of the two reactions are the same at 100°C. The log of the sum of the two reaction rates, which one might determine by measuring a property affected by both reactions, is plotted at intervals corresponding to 10°C differences. The data points for the sum of the two reactions are nearly co-linear, and closely follow the plot for a third hypothetical individual reaction, Reaction 3, that has an activation energy E_3 of 22.34 kcal/mol. Data such as the plotted points are not sufficient to determine whether one or two (or more) reactions are occurring, much less to determine the relative rates of individual reactions. In addition, the activation energy determined from the data (22.34 kcal/mol) may be different from that of the reactions that are actually occurring. This makes predictions of the temperature dependence of a complex process less reliable than those for simple systems. In this case, the reaction that is slower at lower temperatures, Reaction 1, can become the predominant reaction at the higher temperatures often used for accelerated aging! The aging process for this system is different at

high and low temperatures, and no indication of this can be seen in the data points for the sum of the rates of Reactions 1 and 2 that are plotted in Figure 1. Simple reaction systems yield straight-line Arrhenius plots, but straight-line Arrhenius plots do not imply a simple system.

"Activation Energy" of Multiple Reactions

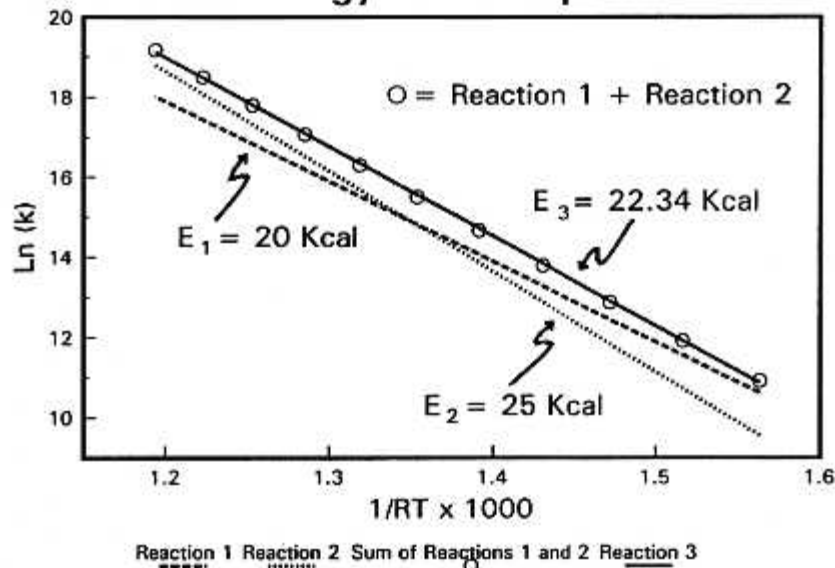


Figure 1. A process consisting of two reactions with different activation energies can yield data consistent with a single reaction with an activation energy of intermediate value.

The above discussion required a number of simplifying assumptions. Actual aging processes generally are more complex. A specific degradation process may consist of a sequence of reactions. Increasing the rate of the slowest reaction in a sequence may speed up the entire process, but only until that reaction is no longer the slowest, or rate-limiting, step in the sequence. Degradation products may themselves undergo reaction. Portions of cellulose (such as the non-crystalline regions) may react completely so that reactions involving them stop, causing data plots that are initially linear to curve or change slope as aging continues. In fact, it is quite unusual for plots of measurements of degradation to remain linear for the entire aging process. Most of these problems and complexities could be avoided by monitoring individual reactions rather than properties dependent on more than one reaction. The extent to which different reactions occurred under different aging conditions then could be compared directly; there would be no need to manipulate the data or to make assumptions as to which kinetic model best fit the data.

Determining the concentrations or relative quantities of degradation products is one means of following the individual reactions that produce them. If changing the aging conditions (from "natural" to "accelerated", for example) causes changes in the types, amounts, or proportions

of degradation products, then the reactions producing the products must not have occurred to the same extent. The aging conditions are not comparable. If, on the other hand, changing the aging conditions causes little change in the degradation product mixture, then the net aging process that produces the products has not been affected. A series of experiments with different sets of aging conditions would determine the degree to which aging conditions can be changed without affecting the aging process, and define a range of valid aging conditions. One also could determine the factor by which a set of aging conditions speeds up the aging process by comparing the amount of time required to produce an equivalent mixture of degradation products. Knowing how changing the aging conditions affects the rate and process of aging would allow one to predict more confidently how changing storage and display conditions would affect the preservation of collections.

This paper reports the use of analyses of the concentrations of a number of degradation products of a cellulosic paper to determine the effects of changes in temperature and humidity on the aging process.

EXPERIMENTAL

Aging Conditions

Seven sets of ten samples each of two types of paper were aged under seven different conditions of temperature and RH. Samples of each paper were removed from each aging chamber after varying lengths of time (the aging of some samples continues). Complete descriptions of the sample papers and aging conditions have been reported previously, along with results of the analyses of color changes as a function of aging conditions.⁹ This paper reports for Whatman #1 filter paper the results of chemical analyses of extractable degradation products for samples aged as listed in Table II as well as the results of stress-strain measurements of samples aged for varying times at 80°C at 32% or 77% RH.

Table II. Aging conditions for chemically analyzed samples of Whatman #1 paper.

Temperature, °C	RH, %	Days of aging
90	50	34, 49, 69, 105, 278
80	77	34, 49, 69, 105, 278
80	32	106, 581, 861
70	50	106, 581, 861
60	80	106, 581, 861

Analysis of Degradation Products

Gas chromatographic analyses of the extractable water-soluble degradation products of the paper samples were conducted. The general method has been described previously.⁹ The potential soluble degradation products of cellulose include sugars (especially glucose) and their oxidation, dehydration, and fragmentation products, as well as small fragments of the cellulose chain. The analytical conditions used for this work are able to detect sugars and sugar-like

compounds up to 4 monosaccharide units long. The monosaccharide compounds detected include glucose, a 6-carbon sugar that is the building block for cellulose, and other monosaccharides such as xylose, a 5-carbon sugar found in large quantities in wood and in smaller quantities in other forms of cellulose. Glucose oligomers 2, 3, and 4 units long also were found. In continuing work that will be reported elsewhere, other degradation products of sugars, such as oxidation and scission products, have been identified and followed.

The procedure consists of the following: approximately one gram portions of the aged paper samples are extracted with water, and the solutions are evaporated. The dried extracts first are treated to convert carbonyl groups to oximes, and then are converted to the per-trimethylsilyl (TMS) derivatives. Conversion to the oxime reduces the possible number of peaks each sugar might produce (due to the possible presence of each sugar in several different forms, such as the open chain form or different anomers of the hemiacetal form). The resulting TMS-oximes are volatile enough to be separated and analyzed by gas chromatography. The analyses reported here are the result of gas chromatographic separation on a moderately polar DB-17 (bonded polyphenylmethylsiloxane) column. Components are quantified through the use of an internal standard of known concentration. Amounts of each compound are calculated and reported in terms of micrograms per gram of paper. A correction was made for the "weight" added during derivatization. This correction is based on the weight change for glucose, other weight changes would be similar. Predictable components such as xylose, glucose, and glucose oligomers were identified by comparisons of their retention times with those of reference standards. Gas chromatography/mass spectrometry was used to identify other compounds. These results will be reported elsewhere. Neither complete nor even partial identification of specific compounds represented by specific chromatographic peaks, though, is needed to calculate and follow the amounts of the individual compounds during aging.

Stress-strain Measurements

Stress-strain measurements were conducted on strips of paper samples by applying small strains (approximately .007), allowing the sample to stress relax, and repeating to failure. The time allowed for stress relaxation, one minute, was empirically determined to yield results the same as those for longer periods of stress relaxation. The technique has been used and described previously.¹⁰ Stress-strain curves were plotted and used to determine loss of strength and change in modulus as a function of time of aging.

RESULTS

Chemical Analyses

Figure 2 is a gas chromatogram of the degradation products extracted from the sample aged at 80°C and 77% RH for 278 days. The major peaks are identified. Xylose, glucose, and glucose dimer (cellobiose) were identified by comparison with reference standards. Glucose trimer and tetramer are identified by their later elution and the improbability of any other high molecular weight material being present in such quantity.

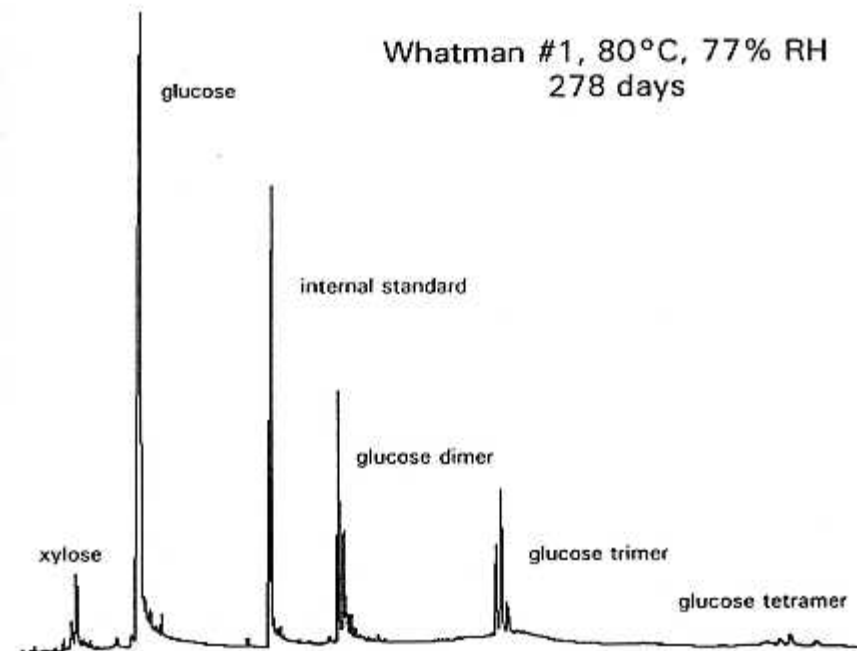


Figure 2. Gas chromatogram of extractable degradation products in Whatman #1 paper aged at 80°C and 77% RH for 278 days. Over a hundred peaks are present, with the larger ones due to cellulose chain fragments produced by hydrolysis.

Over a hundred different peaks were observed for the various samples. Many were detectable starting in the early stages of aging for all conditions, others only in later stages of aging, and others have not yet appeared in samples aged in the conditions of lowest temperature and RH. In some cases, peaks corresponding to major products (such as glucose) become large enough to swamp or obscure smaller peaks. The indications are, though, that the differences in products produced in the range of conditions studied are ones of the quantities, rather than the type, of products. Earlier work had shown that aging at very high temperature (150°C) yielded substantial amounts of products found only in much smaller quantities at lower temperatures (120°C and below).⁹

Each peak was quantified, and the concentration of that component calculated in terms of micrograms per gram ($\mu\text{g/g}$) of paper. Plots of quantity versus aging time were made for each peak for each aging condition. Of the peaks analyzed, approximately thirty or so "behaved" well, producing plots that increased consistently over time for each aging condition. Others had more complex behavior, ranging from inconsistent increases to increases followed by decreases to completely erratic (especially for compounds present in amounts near the detection limit). The actual number of compounds is somewhat less, since some of them will produce more than one peak.

Activation Energies and Dependence of Reaction Rate on Temperature

Figure 3 plots the concentration of glucose as a function of time for each of the aging conditions. Figure 4 plots the concentration of glucose in terms of $\ln(\text{concentration})$ versus time for the 50 and 77-80% RH data. Such plots often yield linear relationships. This is true for this data, at least through most of the aging process. The linearity breaks down only well into the aging process, probably when much of the cellulose is altered considerably. Figure 5 plots the initial, linear portions of the data for glucose. Linear regression plots for the data also are shown. The ratios of the slopes of these lines are ratios of the reaction rate for each set of aging conditions. For two sets of conditions that differ only in temperature (i.e. the same RH), the rates and temperatures can be substituted into Equation 11 and the energy of activation calculated for the reaction. Energies of activation for the production of xylose, glucose, and glucose dimer and trimer were calculated for 50% RH conditions using the data for 70 and 90°C, and for 80% RH conditions using the data for 60 and 80°C. The results are listed in Table III. Results for glucose tetramer are not listed since it was not detectable until late in the aging process and did not yield enough data points for regression analysis.

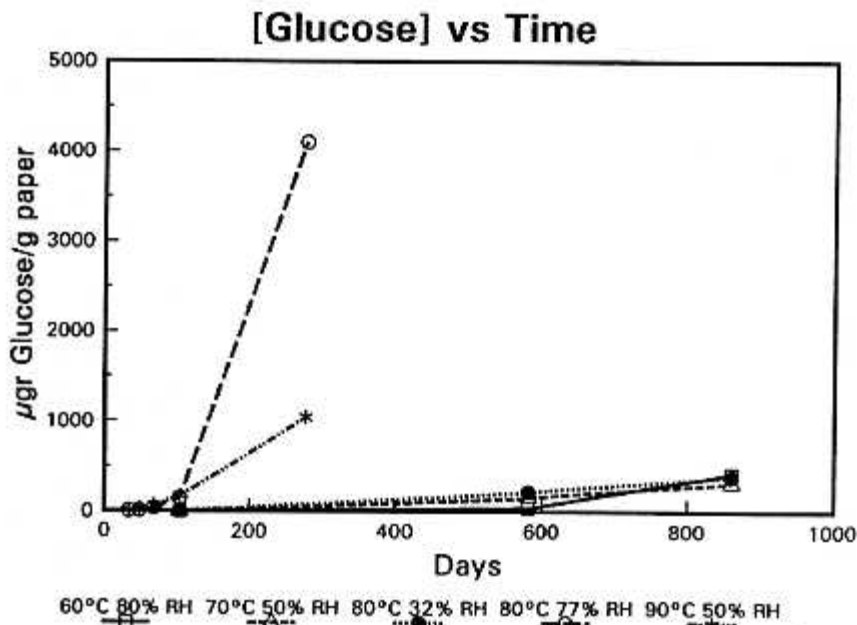


Figure 3. Concentration of glucose in Whatman #1 paper as a function of time and aging conditions.

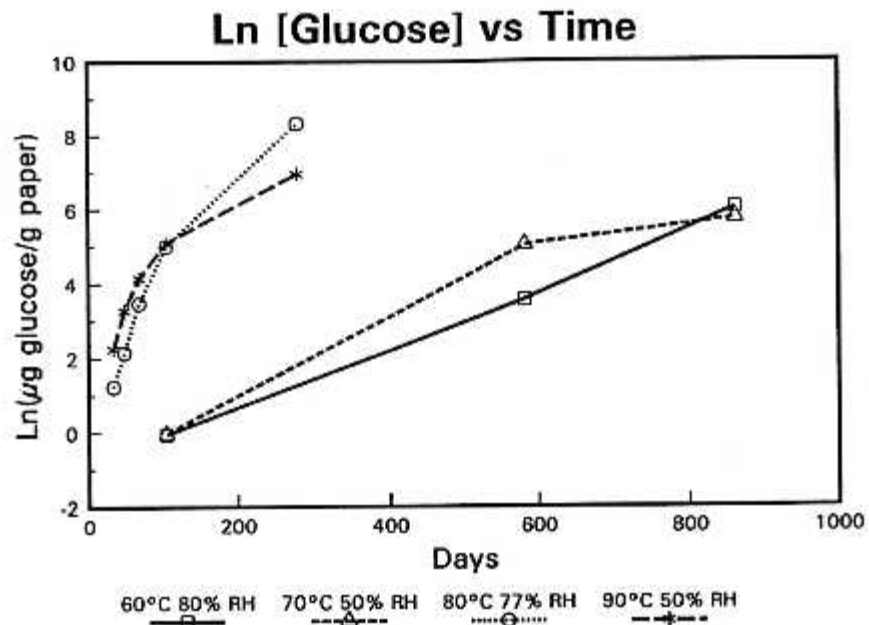


Figure 4. Logarithm of glucose concentration as a function of time and aging conditions.

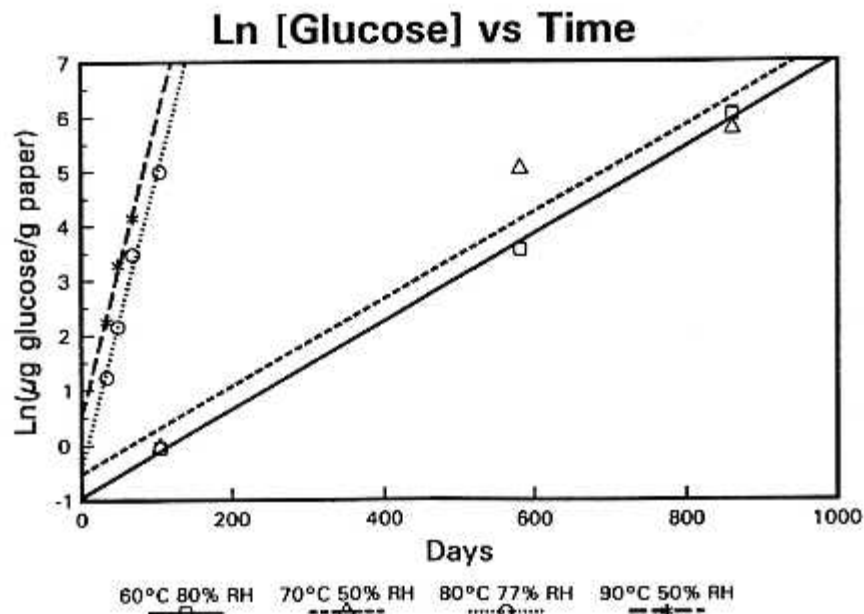


Figure 5. Linear regression plots for initial linear glucose concentration data.

Table III. Activation energies for reactions resulting in major soluble products of aged paper.

Reaction product	Activation energy (kcal)	
	50% RH	77-80% RH
Glucose	23.8	23.5
Glucose dimer	21.0	22.7
Glucose trimer	22.7	22.7
Xylose	29.1	26.8

Dependence of Reaction Rate on RH

The results for 50% RH at 70 and 90°C were used to calculate the reaction rates expected for 80°C and 50% RH. These calculated rates are plotted in Figure 6 with the measured rates for 80°C at 32 and 77% RH as a function of RH. The rates of the reactions that produce these products are highly dependent on RH, increasing sharply above 20% RH. Linear plots fitted to these points reach zero at around 25-30% RH. Power curves fitted to the data are shown in Figure 7. The plots depend on RH to powers ranging from 2.1 to 3.1. (Michalski¹¹ fitted such a curve to the data reported by Graminski, Parks, and Toth¹² for strength loss and found a dependence on RH to the power 1.35.) These plots have non-zero rates for all non-zero values of RH, but still reach very low values below about 20-30% RH. This agrees with earlier work, in which it was shown that only minimal amounts of glucose were produced during dry oven aging (90 to 150°C, less than 2% RH)⁹.

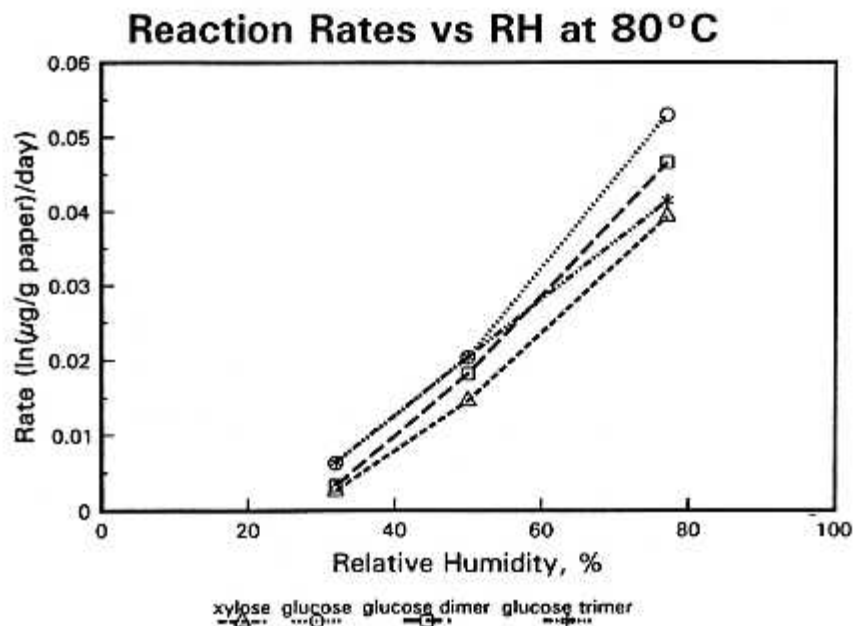


Figure 6. Reaction rates vs RH at 80°C for major reaction products in Whatman #1 paper.

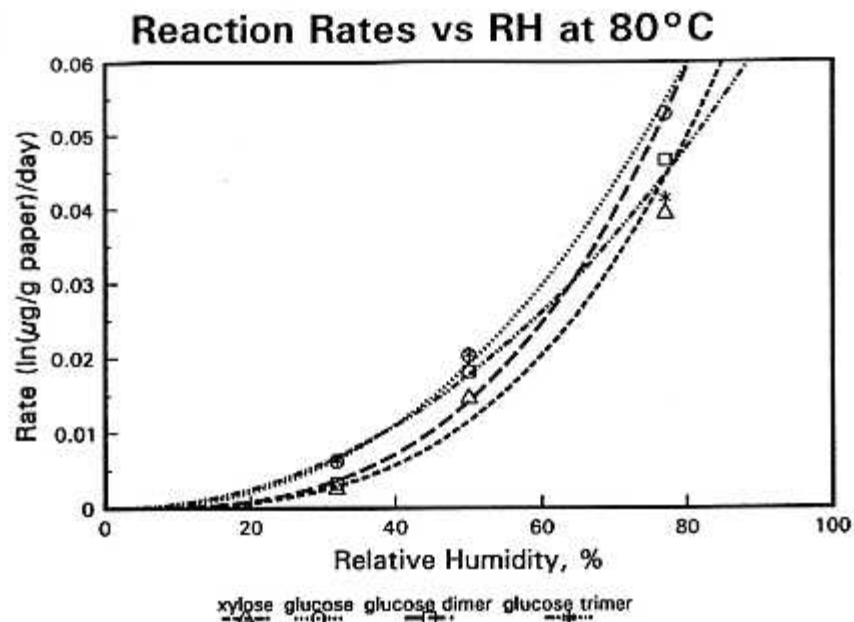


Figure 7. Power curves fitted to data for reaction rate vs RH at 80°C for major reaction products in Whatman #1 paper.

Product Distribution

Gas chromatographic analysis shows that the distribution of reaction products changes over time for any specific set of aging conditions. Thus, in order to compare product distributions as a function of aging conditions, one must compare product distributions for samples that have reached similar stages of aging. One way to do this is to use the concentration of glucose as an indicator of aging. Figure 8 shows the portions of the gas chromatograms in which monosaccharides appear for five samples aged under different conditions but at about the same intermediate stage of aging. All except one have glucose concentrations of between 147-216 μg/g paper. The one exception is the 60°C, 80% RH sample which has a concentration of 35 μg/g paper (the next longer aged sample had a much higher concentration). The chromatograms are scaled equivalently, with the glucose peak approximately 150% of scale for each. As mentioned before, the same peaks (reaction products) are produced for the entire range of aging conditions represented here. The product distribution does vary, however, with different amounts (peak sizes) for many of the reaction products in each chromatogram. The interesting aspect of these plots is that the differences seem to be more a function of relative humidity than of temperature. The plots for 80°C and 77% RH and 60°C and 80% RH are similar, but obviously different from the others. Likewise, the 50% RH plots (for 70 and 90°C) are similar, and seem to have characteristics intermediate between the low (32%) and high (77 and 80%) RH plots. The conclusion is that the product distribution, i.e. aging process, is a function of RH

rather than of temperature (at least up to 90°C). Changing the temperature while keeping the RH constant speeds up the aging process without appreciably altering it, allowing equivalent states of aging to be reached sooner. Changing the RH changes the aging process, so that equivalent states of aging (product distribution) are not reached at any time during aging. Even so, the differences within the range 30-80% RH are relatively small, and probably no more than would be produced by a range of natural aging conditions.

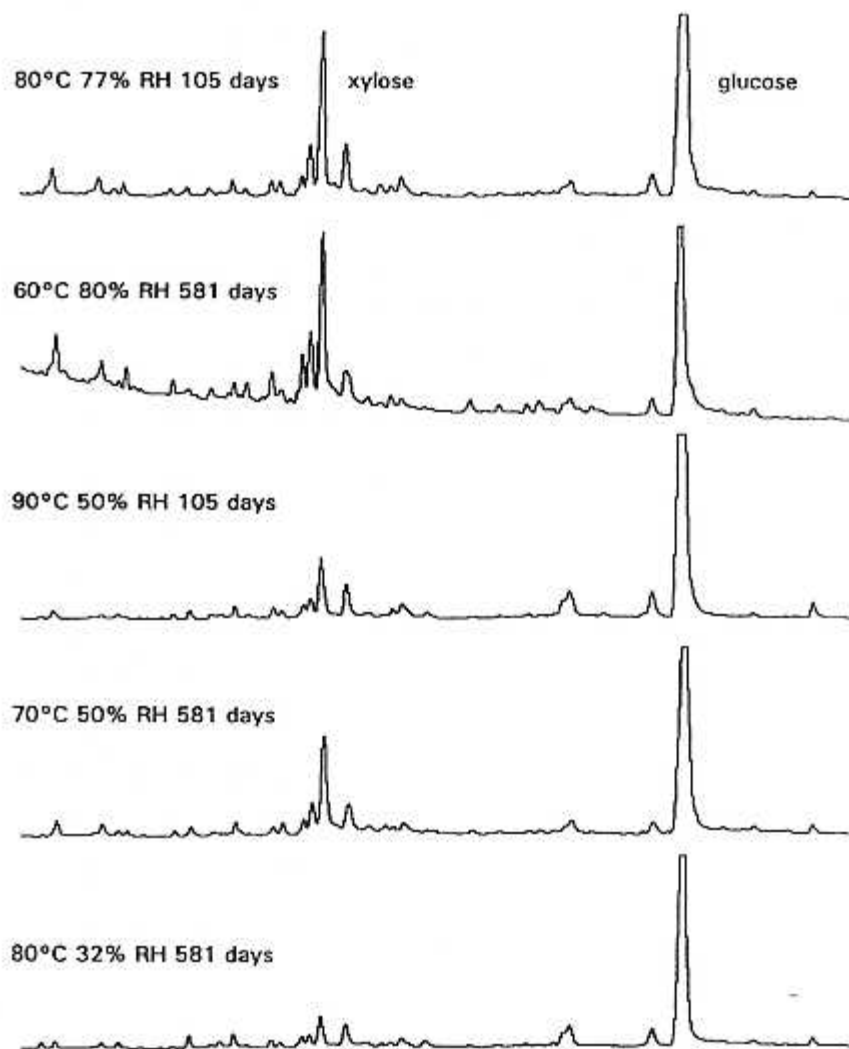


Figure 8. Portions of gas chromatograms of degradation products in Whatman #1 paper samples aged under different conditions but with similar concentrations of glucose.

These results are to be contrasted to results for dry oven aging reported previously.⁹ During dry oven aging at 90 to 150°C (with relative humidities below 2%), only small amounts of soluble products were produced even during late stages of aging when the paper was brown and all but crumbling. The product distribution also was very different, with glucose as a minor rather than the major product it is during aging in the range 30-80% RH. This is consistent with the current results, which indicate that the rates of production of hydrolysis products, including glucose, drop to very low levels at low RH.

Stress-strain Measurements

Stress-strain measurements for samples aged at 80°C and 77% RH are plotted in Figure 9. As is typical for measurements conducted so far, the shapes of the curves are similar for all aging times. The major effect of aging is a loss of strength, with the paper samples simply breaking sooner in the test. The stiffness, as measured by the modulus, or initial slope of the curves, does not change. Paper aged under these conditions is not "stiffer", but is weaker, breaking more easily with less force and deformation required. This loss of strength (% decrease in breaking stress) is plotted versus time in Figure 10 for conditions of 80°C and 77 and 32% RH. It was found that the loss of strength corresponded reasonably well to the increases in concentration of glucose and its oligomers. This is demonstrated in Figure 11, where the concentrations of glucose trimer are plotted with the loss in strength. This demonstrates a correspondence between strength loss and hydrolysis of the cellulose chain.

Stress-strain Curves

Paper aged at 80°C 77% RH

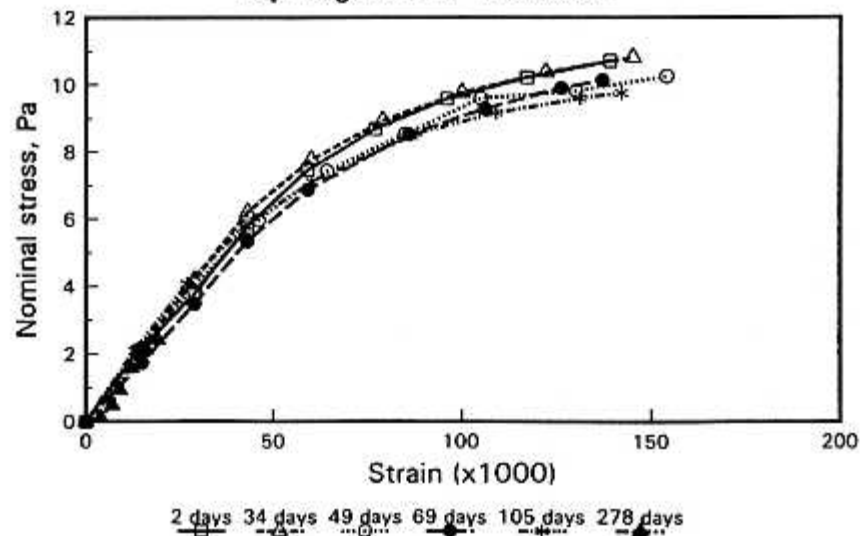


Figure 9. Stress-strain curves for Whatman #1 paper aged at 80°C and 77% RH for various lengths of time.

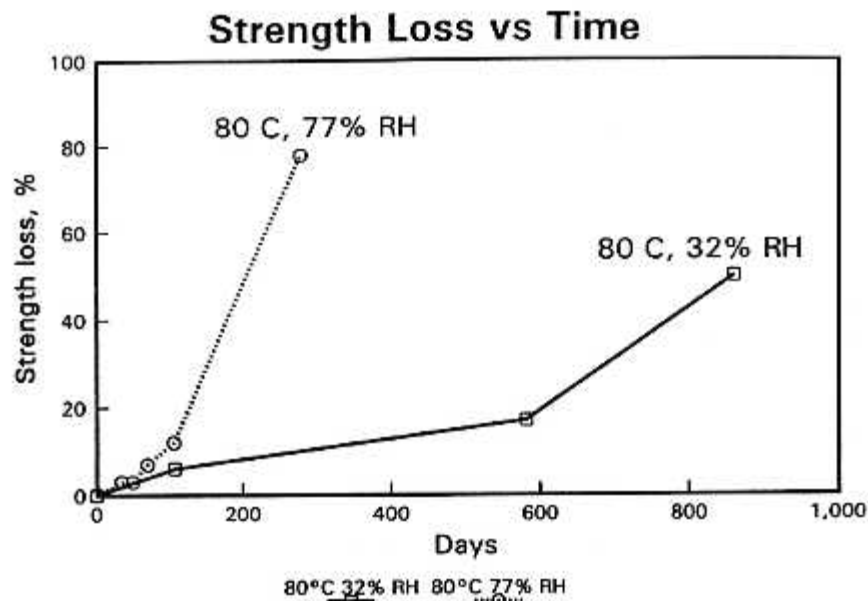


Figure 10. Strength loss vs time for Whatman #1 paper aged at 80°C and 32 or 77% RH.

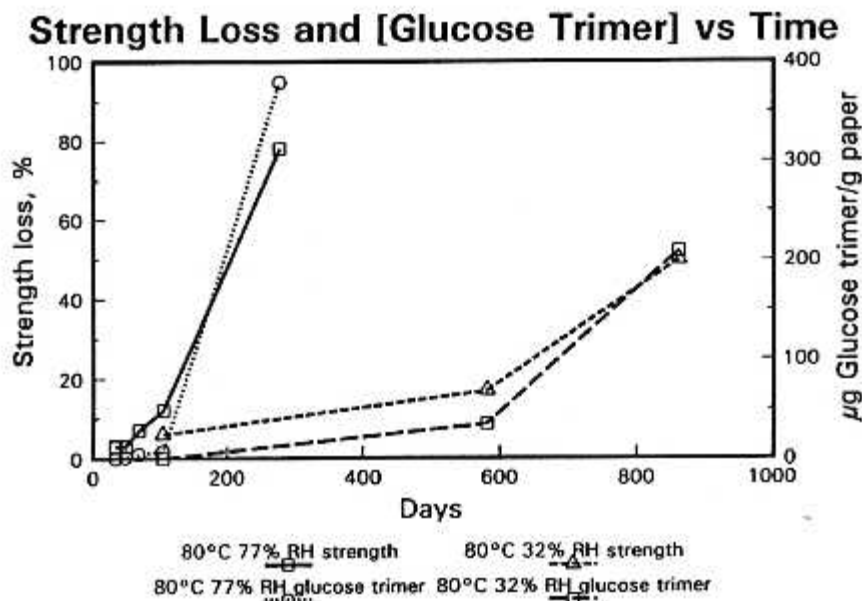


Figure 11. Strength loss at 80°C and 32 or 77% RH correlates with the concentration of glucose trimer produced by hydrolysis of the cellulose chain.

DISCUSSION

Accelerated aging conditions should be compared by determining to what extent different conditions change the aging process. This is most readily achieved by examining individual reactions that make up the aging process. This is the approach taken in this work in examining the effects of temperature and relative humidity on the aging process of cellulose. Analyses of the soluble degradation products of paper samples aged for varying lengths of time under different conditions of temperature and relative humidity were used to determine the major products, and the rates of the reactions producing them. The effects of temperature and relative humidity on the reaction rates were determined, allowing calculations of reaction rates for conditions other than the specific ones examined. The distribution of reaction products also was examined to determine how the overall aging process changes with conditions.

In many ways, the results are what might be expected. The overall aging process, as indicated by the distribution of reaction products, varies with changes in relative humidity. The activation energies, and temperature dependence, of the individual reactions are within the range of activation energies reported previously for related processes. The temperature dependence of the reactions examined is similar, so that changing the temperature while keeping the relative humidity constant speeds up each reaction by approximately the same factor. This observation seems to extend to other reactions not specifically examined in this work, since the product distributions at comparable stages of aging as indicated by gas chromatographic analysis seem to be relatively independent of temperature. Raising the temperature speeds up the aging process without fundamentally altering it. Changing the relative humidity alters the aging process itself, as indicated by changes in the distribution of reaction products. The differences in the RH range examined are relatively minor, however, and probably no more than would be produced by a range of natural aging conditions. Extreme (i.e. dry oven) conditions produce a distorted distribution of reaction products that probably is indicative of an aging process much different from that which occurs during natural aging.

These results are for a matrix of conditions spanning the range 60-90°C and 30-80% RH (and part of a continuing set of experiments that extends to 50°C). The basic question is whether the results and conclusions of this work apply to natural aging, including conditions typical of archives and museums. This would be true if the results can be confidently extrapolated to temperatures in the range 10-25°C, about 30-40° beyond the 30-40° wide range under study. The results so far support such an extrapolation. Within the range of conditions studied, there was little change in the aging process as a function of temperature, and no fundamental difference due to changes in RH. If these tendencies continue beyond the temperature range studied through a similar span of temperatures, then the results would be applicable to natural aging. Especially significant are the results indicating that the aging process does not change if the RH does not change. This means that the results of accelerated aging conducted at elevated temperatures at a specific relative humidity can be directly applied to natural aging at the same RH with no correction other than for overall rate. The (relatively) small differences found within the RH range 30-80% also indicate that the results of aging at 50% RH should be applicable to most conditions of natural aging in which other factors (light, pollution) do not play important roles.

CONCLUSIONS

Accelerated aging is an indispensable tool for the evaluation of long-term aging behavior. Critical to the relevance of accelerated aging results is whether the accelerated aging conditions yield the same results as natural aging would. While any relevant property can be used to measure the effects of accelerated aging, it is much harder to determine whether the results relate to natural aging. Aging is a complex process, involving a number of different reactions. For the results of accelerated aging to be relevant to natural aging, accelerated aging must speed up the aging process without fundamentally altering it. For this to be true, each reaction involved in the aging process must be speeded up by the same factor, so that relative rates of reactions remain reasonably constant. Considerations of reaction kinetics show that it is difficult to determine relative rates of individual reactions by following properties that are a function of more than one reaction. One way to follow individual reactions is to determine the quantities of reaction products that are produced.

This work has determined how temperature and relative humidity affect a number of individual reactions involved in the aging process of cellulose. Individual reactions were followed over time by monitoring the concentrations of reaction products, and rates of reactions were determined as a function of temperature and relative humidity. The reactions studied were highly dependent on RH, perhaps to a greater extent than would have been expected. Activation energies were determined that can be used to calculate reaction rates for temperatures outside the range studied. The distribution of reaction products was found to be dependent on RH, but relatively independent of temperature. This implies that the aging process is more a function of RH than temperature. Raising the temperature while keeping the RH constant speeds up the aging process without fundamentally altering it, so that equivalent states of aging can be reached simply by aging for appropriate lengths of time. Changing the RH changes the relative rates of reactions and the distribution of reaction products, so that equivalent states of aging cannot be reached. Accelerated aging should be conducted at the same relative humidity as the conditions to which the results are to be applied.

Within the range of conditions studied (60 to 90°C, 30 to 80% RH), differences in the distribution of reaction products as a function of RH are ones of relative quantities, with the range of results probably no greater than would be encountered for "natural" aging conditions ranging from dry to wet climates. The very low values of relative humidity produced during dry oven aging, however, produce quite distorted distributions of reaction products that probably do not reflect natural aging. Thus, for cellulosic materials, aging within the moderate (30 to 80%) RH range of this study, and at temperatures at least up to 90°C, should produce results relevant to natural aging. Different relative humidities (and to a lesser extent, temperatures) within this range may produce different results, but the differences probably reflect what might be seen for a range of natural aging conditions. The presence of non-cellulosic materials such as lignin or inorganic fillers could alter the aging process and its dependence on temperature and RH. In such cases, the range of conditions that would be relevant to natural aging could be reduced.

It is often assumed that the degradation of cellulose is a roughly linear function of RH. This work shows that hydrolytic reactions are much more sensitive to RH. These results have important implications for the storage of cellulosic materials. For example, reducing the RH for storage of cellulosic materials to 30% from the commonly recommended 50% RH would

slow degradation by a factor of 0.60 assuming a linear relationship between degradation rate and RH, but by a factor of 0.2 to 0.3 based on reaction rates measured in this work. This represents a 2 to 3-fold difference from what would be predicted based on a linear dependence on RH, for a total 3 to 5-fold slowing of hydrolysis relative to 50% RH. The rate of reactions which are independent of RH would not be affected. Other reactions such as crosslinking increase in importance at very low RH, but probably not unless the relative humidity is lower than about 20-25%.¹³ Thus, the rates of hydrolytic reactions can be reduced to very low levels without lowering the relative humidity so much that reactive hydrophilic sites in the cellulose molecule are exposed by the loss of absorbed water. The RH at which the chemical deterioration of cellulose is minimized is probably somewhere between 20-30% RH when cellulose has absorbed only as much water as can be tightly bound by and is needed to cover reactive sites, but no excess water which would be more mobile and available for reaction.

In conclusion, this work has identified the major lower molecular weight products produced during the aging of cellulose, determined the temperature and RH dependence of the individual reactions of cellulose which produce them, and examined the distribution of products as a function of aging conditions and how the aging process is affected by temperature and relative humidity.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of interns Annette Owens, Cecile Politte, and Melissa Todd, who conducted the extensive mechanical testing of the paper samples.

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GENUINE VEGETABLE PARCHMENT PAPER: EFFECTS OF ACCELERATED AGING ON SOME PHYSICAL AND CHEMICAL PROPERTIES

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ABSTRACT

Characterization of paper provides information vital to the preventive care and conservation of vast collections of paper-based materials in museums, libraries, archives and research repositories. Tracing papers, a relatively cheap material used abundantly by folk artists and architects, pose particular problems because of reactivity and instability inherent in their compositions and structures. Previous research published in MRS investigated the aging properties and the impact of conservation treatments on natural, prepared, vellum, and imitation vegetable parchment tracing papers [1, 2]. An additional group that of genuine vegetable parchment papers, needs particular evaluation with respect to other tracing papers, since they are made by controversial production methods which while considered to be economically advantageous, are environmentally questionable. This technical study characterized three types of genuine vegetable parchment papers, assessing their relative degree of deterioration after aging and their reactivity to solvents commonly used with tracing papers to remove mounts and repairs. Tracing parchment papers were compared optically (fiber, surface, and cross-section morphology; colorimetric opacity, and gloss properties), chemically (FT-IR, SEM/EDS, and pH), and mechanically (tensile measurements) to provide baseline information on aging properties important to preventive care, storage and relative reactivity important to conservation treatment protocols. The effects of solvents used in conservation treatments (deionized water, ethanol, acetone, toluene, and ammonium hydroxide) were evaluated by comparing relative degrees of reaction (absorption).

INTRODUCTION

The Conservation Analytical Laboratory has since 1986 undertaken numerous technical studies characterizing paper found within the various libraries, archives and research collections of the world's largest museum, the Smithsonian Institution. Careful characterization of a wide range of papers can provide primary information pertaining to the preventive care of research collections, forestalling the need for future, intrusive conservation treatment. It can also provide valuable information about how to store, exhibit, and treat if necessary the many art and historical materials made from paper. Previous research has focussed, among other things, on the composition of papier-mache used for furniture, globes, etc. on pigment-coated papers found in card and book stock for use with photomechanical printing or meta-point drawing; and on tracing papers used for architectural drawings and designs [3]. The latter research covered natural, prepared, vellum, and imitation parchment tracing papers [1, 2]. The current study covers genuine parchment paper.

Tracing papers are used for art works, designs, architectural drawings, and an ever-increasing number of paper-based supports found in research and art collections in museums, libraries and archives. Such papers are inherently susceptible to damage and degradation upon aging (requiring potentially invasive conservation treatments to repair them) as a result of manufacturing processes used to make paper translucent, including overbeating of pulp, supercalendering or coating of sheets, or acid immersion [1, 2].

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