EFFECTS OF FLUCTUATING ENVIRONMENTS ON PAPER MATERIALS—STABILITY AND PRACTICAL SIGNIFICANCE FOR PRESERVATION

Jean-Louis BIGOURDAN and James M. REILLY
Image Permanence Institute
Rochester Institute of Technology
Rochester, New York, USA

ABSTRACT
The effect of changing environments on paper stability was studied using three types of paper (acid-processed 100% cotton, acid-processed groundwood, and buffered groundwood). The study was based upon three cycling situations. The effect of humidity cycling alone was investigated at 90°C, 70°C, and 50°C by exposing the paper samples to three humidity conditions: 60% RH, 80% RH, and cycling humidity between 40% and 80% RH (with a two-week cycle). The effect of temperature cycling was studied using two separate experimental procedures: 1) exposing the sample to constant RH and 2) keeping samples at constant moisture content in sealed bags. The temperature cycling included three incubation temperatures: 80°C, 70°C, and daily cycling temperature between 60°C and 80°C. The rates of paper deterioration were monitored using three indicators of decay: paper discoloration, MIT folds, and tensile properties. Data developed during this study indicated that the rate of paper decay was faster under cycling conditions than at the steady mid-range conditions of the cycles. The data also indicated that the paper decay rate was slower under cycling conditions than it was at the upper limits of the cycles. These observations were consistent for all sets of incubations investigated. These data failed to demonstrate that cycling environments are inherently detrimental to chemical stability in paper. Within the limited framework of this study, the deterioration rates observed with cycling conditions offer no evidence that transitions from one temperature to another or one RH to another provoke a new mechanism of decay or accelerate decay more than would be expected by current thermodynamic models.

KEY WORDS
Fluctuating environments, paper, permanence, TWPI, accelerated aging.

INTRODUCTION

Since 1998, the Image Permanence Institute (IPI) has been involved in a research project funded by the National Endowment for Humanities and the Institute of Museum and Library Services. This project has been investigating the effects of changing climate conditions on a wide variety of library and archives materials. The importance of climate conditions in the preservation of hygroscopic materials is well recognized. Temperature and relative humidity (RH) are the primary factors that govern the biological decay, chemical instability and mechanical damage of many types of information-recording media. With these risk categories in mind, people in the field have usually approached the control of temperature and RH in storage in terms of low and high limits, average levels, and magnitude of fluctuation. As a result of this approach, steady storage environments with tightly controlled temperature and RH set points have been recommended for most library and archives materials. These recommendations have always been based on the most current knowledge; hence, environmental preservation strategies have been periodically re-examined [Thomson (G), 1978; Erhardt (D), Mecklenburg (M), 1994; Michalski (S), 1994; Erhardt (D) et al., 1995; McCormick-Goodhart (M); 1996, Weintraub (S), 1996]. Although a steady environment has been considered the ideal storage situation, every collection is exposed to changing environments to a greater or lesser extent. Poorly controlled storage is not the sole cause of temperature and humidity fluctuations. Even materials stored in well-controlled special storage facilities experience climate changes induced by equipment failures or by transitions in and out of storage. It must be remembered that transitions between storage and use conditions also count as fluctuations. In fact, the colder the collection storage is (and therefore the better for chemical stability), the more extreme the transition to room conditions is for collection materials. Today, librarians and archivists have little guidance in determining how much fluctuation poses no risk and how much poses a great risk for the collection.

The objective of this research has been two-fold. The first goal was to determine if changing environmental conditions are inherently detrimental to paper stability by investigating the impact of temperature and humidity changes on collection materials. Toward that end, the question of whether changing environments cause *extra* chemical decay in common library and archives materials was addressed. Several papers and cellulose triacetate (CTA) base photographic film were chosen for this research. The second goal of the project was to measure the rate of moisture equilibration under changing temperature and humidity conditions in a wide range of materials. To do this required determining to what extent external environmental changes alter the microenvironments in which objects are kept and modify the moisture content of these objects. Earlier studies have underlined the importance of microenvironments in optimizing the life span of archival materials [Bigourdan (J-L), Adelstein (P), Reilly (J), 1998], most notably, their role in buffering temperature and RH changes, thereby mitigating the physical responses of stored organic materials [Weintraub (S), 1987; Daniel (V), 1993, Kamba (N), 1994; Toishi (K), Gotoh (T), 1994; Vos (M), 1994; Bigourdan (JL), Adestein (P), Reilly (J), 1997]. This research project has attempted to better understand the interaction between the macroenvironment and the objects themselves. This paper reports the project’s results related to the impact of changing conditions on paper chemical stability. Similar data developed for CTA film will be presented in another publication.

EFFECT OF CYCLING ENVIRONMENTS ON PAPER STABILITY

Previous studies

The effect of temperature and humidity on paper stability is well recognized [Browning (B), Wink (W), 1968; Byrd (L); 1970; Plooy (A), 1981]. Sebera’s isoperms has been proposed as a model to map the impact of climate on paper permanence [Sebera (D), 1989, 1994]. It has been demonstrated that heat and high humidity promote chemical deterioration of paper primarily through cellulose hydrolysis and oxidation. Because water is a reactant for hydrolysis, moisture content is directly related to the rate of paper decay. Heat increases the rate of chemical reactions; thus, it also increases the rate of paper deterioration. These relationships have been documented in earlier studies using accelerated-aging tests. These tests were conducted under various temperature and RH conditions depending on the nature of the paper tested and on the length of the study. These procedures were conducted mostly at steady temperature and either steady RH or steady paper moisture content. A few studies have investigated the effect of changing temperature or RH during accelerated aging. They are the first steps toward quantifying the risk to paper stability caused by changing environments. These studies have prompted interest and discussion because they seem to show faster rates of chemical decay under cycling climate conditions than can be explained by current theory. In other words, they imply that fluctuating environments may cause *extra* chemical decay as a result of some previously unknown mechanism or effect..

Shahani pioneered this type of investigation by exposing papers to cycling RH at constant temperature [Shahani (C), Hengemihle (F), Weberg (N), 1989]. Results led to the conclusion that cycling RH has the potential of increasing decay. This was based on the observation that sheets of two different papers incubated at 90°C and exposed to RH cycling between 40% and 60% (24-hour cycle) decayed faster than sheets exposed to steady 60% RH—i.e., to the upper limit of the humidity cycle—at the same temperature. No common thermodynamic model could explain that observation. In a study of the discoloration of paper materials, Hofenk de Graaff conducted several accelerated-aging experiments implementing both cycling RH and cycling temperature in order to reproduce behavior like that observed under real-life conditions [Hofenk de Graff (J) 1994]. Although the RH cycling implemented in that study failed to recreate the phenomenon observed under real-life conditions, results suggested that temperature cycling at constant RH could cause discoloration (i.e., yellowing). These issues were addressed in the IPI research through empirical paper stability studies.

Experimental

Paper samples

To obtain the maximum benefit from this study, various papers were considered representative of holdings in many libraries and archives. All papers tested were obtained from the American Society for Testing and Materials (ASTM) and were known in terms of composition and manufacturing procedure. Table I reports the composition of three papers tested during the project. They were made from various pulps and with and without alkaline fillers. The identifiers “Paper 5,” “Paper 7,” and “Paper 8” were assigned by ASTM at the time of manufacture.

Table I: Identification and composition of three papers tested.

Paper Composition	Paper 5	Paper 7	Paper 8
Long-staple cotton fibers	100%	—	—
BNSWK (Bleached northern soft wood kraft)	—	20%	20%
BCTMP (Bleached chemithermomechanical pulp)	—	—	—
SGW (Stone-ground wood)	—	80%	80%
$CaCO_3$	no	no	5%
Starch	no	no	no
Alum	yes	yes	no

Accelerated-aging procedure

The study was based upon three different cycling situations. The effect of humidity cycling alone was studied under several constant incubation temperatures. It has been demonstrated that changing temperature induces changes in moisture content in organic materials such as cotton, paper, and photographic film, even when the humidity is kept constant [Urquhart (A), Williams (A), 1924; Ulm (R), 1938; McCormick-Goodhart (M), 1996; Adelstein (P), Bigourdan (J-L), Reilly (J), 1997; Bigourdan (J-L), Adelstein (P), Reilly (J), 1997]. In order to interpret the effect of temperature cycling, two sets of experiments were designed. The first investigated the effect of cycling temperature at constant RH. The second explored the effect of cycling temperature at constant moisture content in the paper materials. The series of incubation conditions investigated in this project are reported in table II.

Each segment of the research is based on three incubation conditions: (1) an incubation with either cycling temperature or cycling RH, (2) an incubation at a steady condition corresponding to the middle point of the cycle, and (3) an incubation at a steady condition corresponding to the upper limit of the cycle. This approach provides a way to directly compare the rates of material degradation under changing and steady conditions. Each paper tested was prepared in stacks of one hundred 20.3 cm x 24.5 cm sheets and moisture-conditioned at 21°C, 50% RH (see figure 1).

After conditioning, each stack used in the study of cycling RH at constant temperature and cycling temperature at constant RH was enclosed in an archival drop-front cardboard box and incubated. Moisture-permeable enclosures were used for these samples to insure full moisture equilibration during the experiment (see figures 2 and 3).

The investigation into the effect of temperature cycling at constant moisture content used a slightly different approach. After being moisture-conditioned to 21°C, 50% RH, each paper stack was enclosed inside moisture-proof packaging (two heat-sealed aluminum-foil bags) prior to incubation (see figure 4).

Table II: Effect of cycling environments on the chemical stability of paper—incubation conditions.

Study	Incubation Conditions
Effect of cycling RH at constant temperature	50°C, 60% RH
	50°C, 80% RH
	50°C, RH cycling between 40% and 80% with a two-week cycle
	70°C, 60% RH
	70°C, 80% RH
	70°C, RH cycling between 40% and 80% with a two-week cycle
	90°C, 60% RH
	90°C, 80% RH
	90°C, RH cycling between 40% and 80% with a two-week cycle
Effect of cycling temperature at constant RH	80°C, 50% RH
	70°C, 50% RH
	Cycling temperature between 60°C and 80°C with a one-day cycle at 50% RH
Effect of cycling temperature at constant moisture content	80°C (Paper conditioned to 21°C, 50% RH prior to insertion in a moisture-proof enclosure.)
	70°C (Paper conditioned to 21°C, 50% RH prior to insertion in a moisture-proof enclosure.)
	Temperature cycling between 60°C and 80°C with a one-day cycle (Paper conditioned to 21°C, 50% RH prior to insertion in a moisture-proof enclosure.)

Property measurements

The rate of chemical decay of the paper samples was monitored based on physical property changes and discoloration. For each pull, two sheets of paper were withdrawn from the middle of the stack and tested for MIT folds, tensile properties, and paper appearance.

MIT folds (TAPPI T511)

MIT folding endurance was determined based on the TAPPI Standard with one modification: the tension of the test specimen was varied for each type of paper in order to obtain between 400 and 700 MIT folds as the initial value for a given paper. Once determined by testing the non-incubated paper, the tension was kept constant for all other determinations (see table III). The MIT test was performed on 11 specimens (15 mm x 100 mm) cut in such a way that the length was in the machine direction of the paper. The retention of MIT folding endurance was determined using the average MIT folds value and expressed in percent. The variability of MIT folds evaluation was assessed on non-incubated paper specimens. The results, reported in table III, indicated a high variability. Nevertheless, MIT fold determinations were found to provide a good way of monitoring paper deterioration during the study and were a reliable indicator after significant properties changes occurred. It was observed that the variability of the method decreased as a function of MIT folding endurance loss.

Table III: Variability and baseline values obtained for MIT folds determination. Each determination was based on the evaluation of two sheets of paper.

	Paper 5	**Paper 7**	**Paper 8**
Tension (in grams)	700	400	400
Number of determinations	10	10	10
Number of folds (mean)	669	582	651
Standard deviation	78	129	46

Tensile measurements using TAPPI T494

This test determines the tensile energy absorption (TEA), the tensile strength at break, and tensile strain at break. Determinations were made using an Instron tensile machine. The test was performed on 11 specimens cut as described above. Because this size was smaller than the testing conditions described in TAPPI T494, the crosshead speed was reduced from 25 to 14 mm/min in order to keep the rate of strain as specified in the TAPPI standard. The average values were used for data analysis. Despite the fact that tensile measurements are a less sensitive indicator than MIT folds, the evaluation of TEA provided consistent results.

Paper appearance

This was measured using a Color Mate HDS-45 Spectrophotomer. Values of L*, a*, b*, and whiteness were obtained using Illuminant A. The increase in yellowness reflected by b* values is a good indicator of paper discoloration. The data reported in table IV show the variability of the b* determinations on a series of paper specimens having different levels of yellowing after incubation. Consequently, b* change was used to quantify the rate of paper discoloration caused by the different environments.

Table IV: Variability of color determinations. b values determined on various paper samples.*

	Sample A	**Sample B**	**Sample C**	**Sample D**	**Sample E**
Number of determinations	10	10	10	10	10
Average b* (Illuminant A)	0.14	12.11	21.23	24.20	26.41
Standard deviation	0.04	0.14	0.08	0.22	0.44

Results

Effect of cycling RH at constant temperatures

The impact of changing RH was investigated at 90°C, 70°C, and 50°C. Three humidity conditions were tested at each temperature: 60% RH, 80% RH, and cycling between 40% and 80% RH with one week at each humidity level (see figure 5). The rates of decay obtained at the two static humidity conditions were compared to the rate of decay observed under cycling conditions. Results for each type of paper are reported in the following sections.

Paper 5 (acid-processed 100% cotton)

Figure 6 illustrates the effect of constant temperature and cycling humidity conditions on paper discoloration, using b* change as the parameter. Although the thermal effect is obvious—greater temperature caused faster paper yellowing (see figure 6)—no significant difference was observed between the rates of discoloration obtained under cycling RH and at both steady humidity conditions. This behavior was observed at 90°C, 70°C, and 50°C. Very slight b* changes were observed at 50°C. Thus, the testing of Paper 5 did not provide any information regarding the impact of fluctuating RH on paper decay. The degradation was essentially thermally driven.

Paper 7 (acid-processed groundwood)

The difference in stability between Papers 7 and 5, due to their individual composition (see table I), is reflected in the different rates of discoloration as measured using b* value (see figures 6, 7, and 8). Figures 7 and 8 report the changes in b* obtained at 70°C and 50°C under the three humidity conditions described in figure 5. Significant b* changes were measured at 50°C during the 23-month incubation period. Notably, data obtained at 70°C and 50°C for Paper 7 indicated that humidity cycling caused a faster rate of decay than that caused by the steady mean RH of the cycle (60%). However, the rate of decay caused by cycling RH was slower than that caused by the upper RH limit of the cycle (80%). Data obtained at 90°C were inconclusive due to the instability of Paper 7 at this incubation temperature; in less than two cycles, maximum discoloration was achieved under all three humidity conditions. Tensile property changes and MIT folding endurance provided consistent information. However, the data for physical property changes varied more than those for paper discoloration, especially before significant property changes occurred. This behavior was seen in preliminary testing and therefore was expected. Figure 9 reports the change in MIT folding endurance observed at 70°C, expressed as a percentage of retention. Figure 10 illustrates the decrease of TEA over incubation time at 70°C. Both graphs indicate similar weakening of the paper as chemical decay progressed over time. The fastest decay was observed at 80% RH, and the slowest was seen at 60%. These results are consistent with those for paper discoloration (see figures 7 and 8).

Paper 8 (buffered groundwood)

Paper samples were incubated for periods of time up to two years. Figures 11 and 12 report data obtained at 50°C and 70°C. The behavior of Paper 8 was consistent at both temperatures, and conclusions similar to those for Paper 7 were reached. Although, due to the presence of alkaline fillers, Paper 8 discolored more slowly than Paper 7, it responded similarly to the various humidity conditions. The fastest yellowing was observed at 80% RH, and the slowest was observed at 60% RH at both incubation temperatures. The monitoring of MIT folding endurance indicated the same behavior. Figure 13 reports data developed at 70°C. The paper weakened faster at the upper limit of the humidity cycle (80% RH) than under cycling humidity or at the mean RH of the cycle (60% RH). As for Paper 7, data obtained for Paper 8 at 90°C were inconclusive due to high variability in the measurements and to the rapid rate of paper decay.

At this point, results obtained in this study indicate that decay occurs faster under cycling humidity conditions than at the steady mean RH of the cycle. However, none of the data developed in this project confirm the assumption that cycling RH may cause faster decay than the steady maximum RH of the cycle. This is based on the consistent and repeated observations reported above: the rate of decay measured under cycling relative humidity—between 40% RH and 80% RH with one week at each condition—was no faster than the rate obtained at a steady 80% RH. This behavior occurred at both 50°C and 70°C. Consequently, this observation does not support the assumption that fluctuating environments may cause extra chemical deterioration. Cycling RH between the high and low limits of the cycle did not cause faster decay than steady conditions at the upper limit of the RH cycle.

Effect of cycling temperature at constant RH

The impact of changing temperature at 50% RH was studied during an incubation period of one year. Stacks of one hundred 20.3 cm x 24.5 cm paper sheets enclosed in cardboard boxes were incubated under three temperature conditions: constant 70°C, constant 80°C, and daily cycling between 60°C and 80°C (see figure 14). The humidity was kept at 50% RH for all three temperatures. The much shorter length of the cycle used for this part of the investigation—one day versus two weeks for the RH cycling study—was chosen based on the fact that thermal equilibration is much more rapid than moisture equilibration. Thermal equilibration occurs in hours, while moisture equilibration takes days or weeks, depending on materials and configurations. In all cases, it was found that the rate of paper decay at fluctuating temperatures was faster than the rate of decay at the steady mean temperature of the cycling profile (70°C). Decay indicators also showed that decay occurred more slowly at cycling temperature than it did at the upper limit of the temperature cycle (80°C). Data obtained for the various papers tested showed consistent behavior. Figures 15-17 illustrate the rates of discoloration for Paper 5, Paper 7, and Paper 8 using b* as the decay indicator. Figures 18-20 report the changes in MIT folding endurance for the same papers incubated under identical conditions. The observed behavior was similar for all three papers, regardless of the decay indicator used (either paper discoloration or MIT fold).

Based on current theories of chemical aging, this result was expected. During cycling, time spent at the worst condition—the upper limit of the cycle (80°C)—had a greater impact on samples than time spent at the best condition—lower limit of the cycle (60°C). As a result, the paper incubated under cycling temperature conditions decayed faster than the paper incubated at the constant mean temperature of the cycle (70°C). This is supported by the data reported in figures 15-20. In addition, data obtained in this study do not demonstrate the earlier assumption that fluctuating temperature causes extra chemical decay. Temperature cycling between the high and low limits of the cycle did not cause faster decay than steady conditions at the upper limit of the temperature cycle.

Earlier studies investigating the relationship between temperature, RH, and moisture content in paper have indicated that at constant RH, temperature changes cause equilibrium moisture changes. Each of three series of paper samples was incubated at 50% RH at a different temperature condition. Each set of samples had a different moisture content that depended upon its particular incubation temperature. Samples incubated at higher temperature contained less moisture than samples incubated at lower temperature. Results indicated that despite the fact that there was higher water content at lower temperature, it was the thermal effect that was predominant in determining the rate of paper decay. Higher temperature led to faster paper decay.

Effect of cycling temperature at constant moisture content

After moisture-conditioning at 21°C, 50% RH, paper samples were placed in moisture-proof enclosures prior to incubation at three temperature conditions: 70°C, 80°C, and daily cycling between 60°C and 80°C. The only variable in this situation was temperature. The moisture content of the paper was constant. The monitoring of paper color provided the most telling results. The data reported in figures 21 and 22 for Papers 7 and 8 indicate behavior similar to that observed under cycling RH and cycling temperature at constant RH. The rate of decay under cycling temperature conditions is shown to fall between the rates of decay under both steady temperatures explored in this study.

Although this experiment was designed to investigate only the impact of cycling temperature at constant water content, the experimental procedure used (enclosing moisture-conditioned paper in a sealed bag) introduced new factors of decay. Comparison of the decay rates at constant moisture content in the paper samples and at constant RH showed behavior that could not be explained by the effects of temperature alone. The paper enclosed in sealed bags after initial moisture conditioning to 21°C, 50% RH—in other words, kept at constant moisture content during incubation—decayed faster than the samples enclosed in cardboard boxes and incubated at constant 50% RH. This was observed at all three incubation temperature conditions: 70°C, 80°C, and daily cycling between 60°C and 80°C.

The explanation for this different behavior can be found in the two experimental procedures that were used, and the behavior can have at least two causes. First, the moisture content in the paper samples enclosed in cardboard boxes at 50% RH was always less than the moisture content in the samples incubated in sealed bags after moisture preconditioning at 21°C, 50% RH. It has been demonstrated that, at a given RH, increasing temperature decreases the water content in paper. Paper samples in equilibrium with room conditions (21°C, 50% RH) can hold 30% more water than the same samples in equilibrium at 80°C, 50% RH [Canadian Conservation Institute, 1998]. Consequently, the paper samples incubated in the sealed bags contained more water than the samples incubated inside cardboard boxes at 50% RH and any of the test temperatures (70°C, 80°C, or cycling between 60°C and 80°C). In the porous enclosures at constant RH, the amount of water in the paper was determined by temperature, which caused the moisture equilibrium curves of the papers to shift. Thus, we can assume that the faster decay rate in the sealed samples was caused in part by the greater moisture content of the paper.

In addition, the sealed enclosure configuration may have caused a greater rate of decay by trapping deterioration by-products. Such a phenomenon was observed in an earlier study comparing the rate of decay of single sheets of paper to that of sheets incubated in book format [Shahani (C), Hengemihle (F), Weberg (N), 1989].

In the end, the procedure implemented in this study provided a valid assessment of the impact on paper chemical deterioration of fluctuating temperature at constant moisture content in the paper. The results agreed with those reported above for the other cycling conditions tested.

Discussion

Accelerated-aging procedure

The data developed during this project were consistent. Only the study of the effect of cycling RH at 90°C provided inconclusive data. The fast rate of paper decay masked any potential differences in behavior while samples were incubated at 90°C under three humidity conditions. The rates of decay obtained at constant RH are not directly comparable to those observed at constant moisture content, since the water content of the paper was significantly higher when the samples were incubated inside sealed bags after moisture preconditioning than when they were incubated inside cardboard boxes at constant RH. However, the effect of cycling temperature could be assessed vis-à-vis steady incubation temperatures for both sets of experiments.

Effect of cycling RH

The data obtained at 70°C and 50°C are summarized in table V. Incubation times in days to reach 50% b* maximum change are reported for each paper. The rate of paper decay under cycling RH was faster than at the steady mid-range RH of the cycle. Based on current thermodynamic theories, this result was expected. During cycling, time spent at the worst humidity condition (80% RH) had a greater impact than time spent at the best humidity condition (40% RH). As a result, paper samples incubated under cycling humidity discolored faster than the samples at the steady mid-range of the humidity cycle (60% RH) but more slowly than those at the 80% RH level. Similar observations were made in an earlier study [Shahani (C), Hengemihle (F), Weberg (N), 1989] at 90°C using a greater RH cycling frequency (i.e., daily cycling between 40% and 60% RH versus two-week cycling between 40% and 80% RH). Although these earlier data were believed to be the result of incomplete moisture equilibration during the cycling experiment, this cannot be said about the recent findings. One week at each humidity at all incubation temperatures caused a significant change in paper moisture content. (Data developed at IPI indicated that at 35°C, a stack of paper sheets reached 90% equilibration after four days of moisture conditioning.) The conclusion is that cycling humidity is not inherently detrimental to paper stability. On the contrary, these data illustrated a behavior that several prediction models, such as IPI's Time-Weighted Preservation Index (TWPI), had introduced to monitor the impact of changing environments on chemical decay of organic materials [McCormick-Goodhart (M), Mecklenburg (M), 1993; Reilly (J), 1993; Reilly (J), Nishimura (D), Zinn (E), 1995; Reilly (J), 1997; Reilly (J), 1998; Nishimura (D) *et al.*, ND]. The calculation algorithm used for TWPI emphasizes the determinant impact of bad conditions (e.g., high RH) versus good conditions (e.g., low RH) on the rate of chemical decay.

These data do not confirm earlier results [Shahani (C), Hengemihle (F), Weberg (N), 1989] obtained by incubating free-hung samples under cycling humidity at 90°C. The earlier results indicated that cycling had the potential to promote extra deterioration. However, the recent observations at lower temperatures failed to demonstrate the same detrimental behavior.

Effect of cycling temperature

The data obtained at constant RH and constant paper moisture content led to a similar conclusion (see table V). Although the two experimental procedures produced different rates of decay, both approaches indicated that the rate of decay under cycling temperature was (1) faster than the rate measured at the steady mid-range of temperature cycle, and (2) slower than the rate measured at the steady upper limit of the temperature cycle. These observations are similar to those made in the study of the effect of cycling RH. The data show that time spent at the worst temperature condition (80°C) had a greater impact on the stability of the paper samples than time spent at the best temperature condition (60°C).

Table V: Effect of cycling environments on the rate of paper yellowing as measured by the incubation time required to reached 50% b change under various incubation conditions.*

	Incubation conditions	Approximate time to 50% b* change (in days)	
		Paper 7	**Paper 8**
Cycling RH at 70°C	70°C, 60% RH	55	145
	70°C, 60%±20% RH (two-week cycle)	35	75
	70°C, 80% RH	20	25
Cycling RH at 50°C	50°C, 60% RH	560	660
	50°C, 60%±20% RH (two-week cycle)	280	200
	50°C, 80% RH	180	120
Cycling temperature at constant RH	70°C, 50% RH	50	130
	70°C±10°C, 50% RH (daily cycle)	40	70
	80°C, 50% RH	25	45
Cycling temperature at constant moisture content	70°C.*	30	115
	70°C±10°C (daily cycle).*	20	75
	80°C.*	15	40

*Paper conditioned to 21°C, 50% RH prior to insertion in a moisture-proof enclosure.

Practical significance

PRACTICAL SIGNIFICANCE

One of the main objectives of this study was to investigate the possibility that cycling environments might cause even faster decay in paper than that observed at the upper limit of the temperature or RH cycle. Data developed during this project have demonstrated that this is not the case. Within the limited framework of this study, the deterioration rates observed with cycling conditions offer no evidence that transitions from one temperature to another or one RH to another provoke a new mechanism of decay or accelerate decay more than would be expected by current thermodynamic models. In essence, the overall rate of chemical decay under changing conditions is independent of the number and frequency of transitions. What matters is the amount of time spent at each condition along the way.

The practical significance of this result is profound, but should not be taken as evidence that environmental fluctuations are unimportant or always benign. Paper and book collections are subject to forms of decay due to mechanical stresses induced by inappropriate RH levels or excessively large RH fluctuations. This study considered only those manifestations of decay in paper (discoloration and loss of mechanical properties) that result from spontaneous *chemical* change. It did not consider other forms of decay that are in fact dependent on the frequency and magnitude of RH transitions. Chemical, biological, and mechanical forms of decay all must be considered when setting storage conditions in practice.

However, it is a commonly held belief that steadiness in temperature and RH is desirable in every practical storage situation, with every collection. The results of this study show that for chemical forms of decay in paper, steadiness is no more desirable than any other profile of temperature and RH that yields the same overall rate of decay. There is no reason to put a premium on avoiding fluctuations from the chemical decay perspective. While mechanical stresses must certainly be considered in practice, book and paper collections are at much greater risk from slow chemical change that leads to embrittlement, discoloration, red rot, and other common ills. If we take a view of paper storage conditions that emphasizes steadiness at the expense of overall chemical decay rate, we run the risk of missing out on significant opportunities to improve the preservation of collections.

Ideally, of course, storage environments for paper should combine the best of both worlds—steadiness at appropriate RH levels for mechanical decay and temperatures low enough to assure a slow rate of chemical change. The data from this study show that we should not choose steadiness for its own sake when an alternative profile having changing conditions would yield a slower chemical decay rate without creating excessive risk of mechanical damage. The TWPI model [Reilly (J), 1995] allows for analysis of dynamic environments to obtain an overall measure of chemical decay rate, enabling evaluation of actual conditions and simulations of new designs. The data show that we can use dynamic modeling of chemical decay rates to inform storage decisions without fear of unexpected decay from temperature and RH transitions.

AKNOWLEDGEMENTS
This study was part of a three-year research project conducted under grants from the Division of Preservation and Access of the National Endowment for the Humanities (NEH), a federal US agency, and by The Institute of Museum and Library Services (IMLS). The project received additional support from ASTM Institute for Standards Research. Thanks go to Kijoo Kim, Nyla Schroeder, Kim Sennett, Edward Zinn, and Karen Santoro for their assistance in this project.

REFERENCES

Adelstein P., Bigourdan J.-L., Reilly J. Moisture relationships of photographic film. *JAIC*, vol. 36, 1997, p. 193-206.

Bigourdan J.-L., Adelstein P., Reilly J. Moisture and temperature equilibration: Behavior and practical significance in photographic film preservation. In *La Conservation: Une Science en Evolution—Bilan et Perspectives*, Actes des troisièmes journées internationals d'études de l'ARSAG, Paris, 21 au 25 avril 1997. Paris: ARSAG, 1999, p. 154-164.

Bigourdan J.-L., Adelstein P., Reilly J. Use of microenvironments for the preservation of cellulose triacetate photographic film. *Journal of Imaging Science and Technology*, vol. 42, n°2, 1998, p. 155-162.

Browning B., Wink W. Studies on the permanence and durability of paper: I. Prediction of paper permanence. *TAPPI*, vol. 51, April 1968, p. 156-163.

Byrd L. The effects of humidity on paper. *Chem 26 Paper Processing*, vol.7, 1970, p. 30-35.

Canadian Conservation Institute, ASTM/ISR research program on the effects of aging on printing and writing papers: Accelerated aging test method development: Annual research report year II, 1998. In *ASTM/ISR Research Program on the Effects of Aging on Printing and Writing Papers: Year III—Project Report*. West Conshohocken, PA: ASTM Institute for Standards Research, 1999, p. 107-127.

Daniel V., S. Maekawa S. Hygrometric half-lives of museum cases. *Restaurator*, n°. 14, 1993, p. 30-44.

Erhardt D, Mecklenburg M. Relative humidity re-examined. *Preventive Conservation Practice, Theory and Research*, IIC Congress, Ottawa, September 1994, p. 32-37.

Erhardt D., Mecklenburg M., Tumosa C., McCormik-Goodhart M. The determination of allowable RH fluctuations. *WAAC Newsletter*, vol. 17, n°. 1, 1995, p.19-23.

Erhardt D., Mecklenburg M., Tumosa C., McCormik-Goodhart M. A discussion of research on the effects of temperature and relative humidity on museum objects. *WAAC Newsletter*, vol. 18, n°. 3, 1996, p. 19-20.

Hofenk de Graaff J. Research into the cause of browning of paper mounted in mats. In *Contributions of the Central Research Laboratory to the Field of Conservation and Restoration*. Amsterdam, Netherlands: Central Research Laboratory for Objects of Art and Science, 1994, p. 21-42.

Kamba N. Performance of wooden storage cases in regulation of relative humidity change. In *Preventive Conservation Practice, Theory and Research*, IIC Congress, Ottawa, September 1994, p. 181-184.

McCormick-Goodhart M. The allowable temperature and relative humidity range for the safe use and storage of photographic materials. *Journal of the Society of Archivists*, vol. 17, n^{o}. 1, 1996, p. 7-21.

McCormick-Goodhart M, Mecklenburg M. Cold storage environments for photographic materials. *Final Program—Advance Printing of Paper Summaries, IS&T 46th Annual Conference, Boston*. Springfield, VA: IS&T, 1993, p. 277-280.

Michalski S. Relative humidity and temperature guidelines: What's happening? *CCI Newsletter*, n^{o}. 14, 1994, p. 6-8.

Nishimura D, Reilly J, Zinn E, Bigourdan J-L. TWPI and mold risk factor algorithms for interpreting temperature and relative humidity data in libraries, archives, and museums. Submitted for publication in *JAIC*, May 1, 2002.

Plooy A. The influence of moisture content and temperature on aging rate of paper. *Appita*, vol. 34, 1981, p. 287-282.

Reilly J. *IPI storage guide for acetate film.* Rochester, NY: Image Permanence Institute, Rochester Institute of Technology, 1996.

Reilly J. Preservation and the economics of information access in institutions, libraries, and archives. In *La Conservation: Une Science en Evolution—Bilan et Perspectives*, Actes des troisièmes journées internationals d'études de l'ARSAG, Paris, 21 au 25 avril 1997. Paris: ARSAG, 1999, p. 70-76.

Reilly J. *Storage guide for color photographic materials.* Albany, NY: The University of the State of New York, New York State Education Department, New York State Library, The New York State Program for the Conservation and Preservation of Library Research Materials.

Reilly J., Nishimura D., Zinn E. *New tools for preservation: Assessing long-term environmental effects on library and archives collections.* Washington, DC: The Commission on Preservation and Access, 1995.

Sebera D. A graphical representation of the relationship of environmental conditions to the permanence of hygroscopic materials and composites. In *Proceedings of Conservation in Archives: International Symposium, Ottawa, Canada, May 10-12, 1988*. Paris: International Council on Archives, 1989.

Sebera D. *Isoperms: An environmental management tool*. Washington, DC: The Commission on Preservation and Access, 1994.

Shahani C., Hengemihle F., Weberg N. The effect of variations in relative Humidity on the accelerated aging of paper. In *Historic Textile and Paper Materials II*, ACS Symposium Series 410, Zeronian S., Needles H., eds. Washington, DC: American Chemical Society, 1989, p. 63-80.

Thomson G. *The museum environment*, Butterworth-Heinemann, 1978 (second edition 1986).

Toishi K., Gotoh T. A note on the movement of moisture between the components in a sealed package. *Studies in Conservation*, vol. 33, n^{o} 2, 1994, p. 265-271.

Ulm R. Influence of atmospheric humidity and temperature on the moisture content of paper board. *Paper Trade Journal* vol. 8, 1938, p.108.

Urquhart A., Williams A. The moisture relations of cotton: The effect of temperature on the absorption of water by soda-boiled cotton. *Journal of the Textile Institute* vol. 15, 1924, T559.

Vos M. Heat and moisture diffusion in magnetic tape packs. *IEEE Transactions on Magnetics*, vol. 30, n^{o}. 2, 1994, p. 237-242.

Weintraub S. Revisiting the RH battlefield: analysis of risk and cost. *WAAC Newsletter*, vol. 18, n^{o}. 3, 1996, p. 22-23.

Figure 1. Paper stacks were moisture-conditioned at 21°C, 50% RH prior to incubation under various conditions.

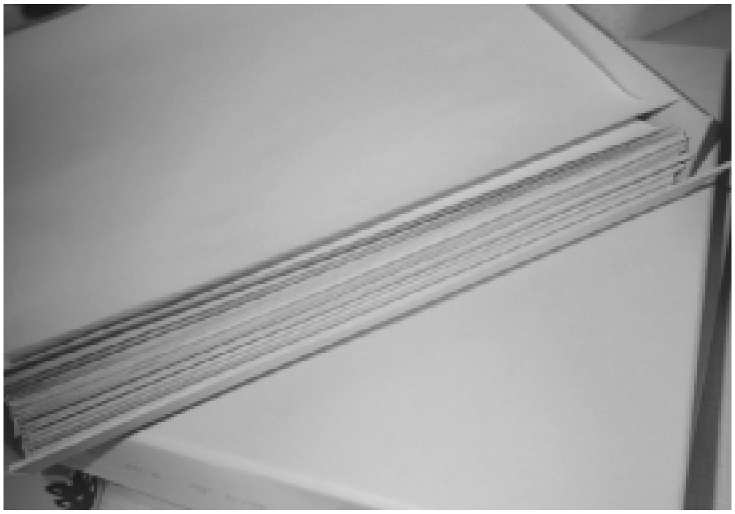

Figure 2. One-hundred-sheet stacks of paper were enclosed in drop-front cardboard boxes to study the effect of cycling RH at constant temperature and cycling temperature at constant RH. Measurements were made on sheets pulled from the middle of each stack.

Figure 3. Papers were incubated in cardboard boxes under various conditions.

Figure 4. After moisture conditioning, 100-sheet stacks of paper were heat-sealed inside two aluminum foil bags and incubated under three different temperature conditions to study the effect of cycling temperature at constant moisture content.

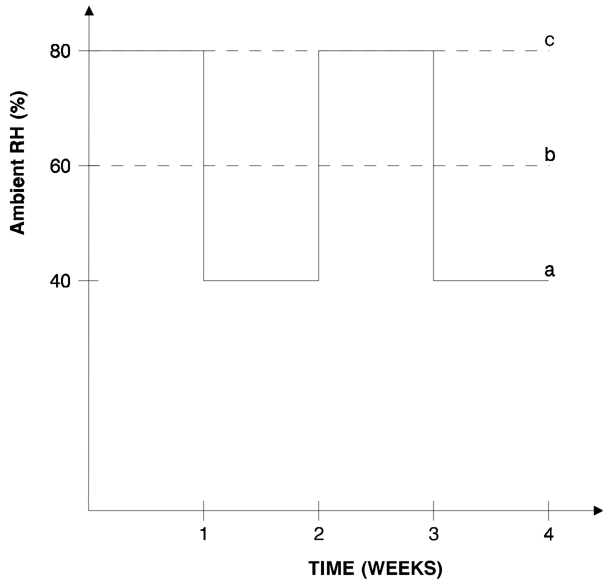

Figure 5: Humidity cycling conditions. (a) Cycling between 40% and 80% RH. (b) Static at 60% RH. (c) Static at 80% RH.

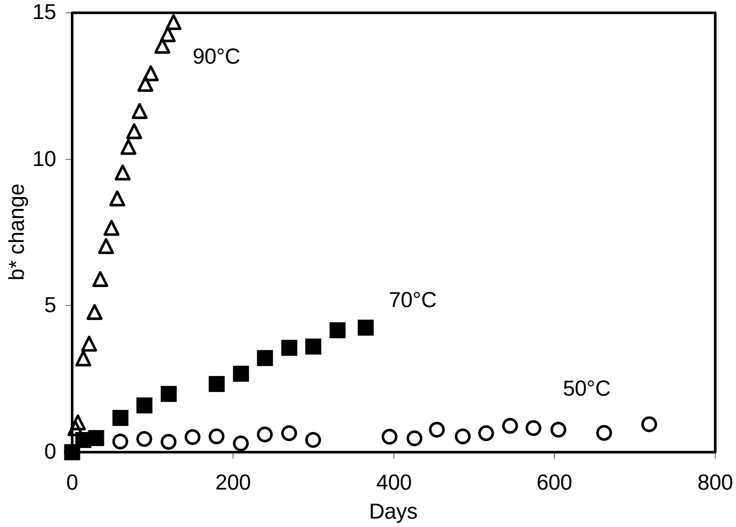

Figure 6: Effect of temperature on Paper 5 discoloration at 50°C, 70°C, and 90°C under cycling humidity conditions between 40% RH and 80% RH (two-week cycle). b change versus incubation time. Initial b* value: -1.*

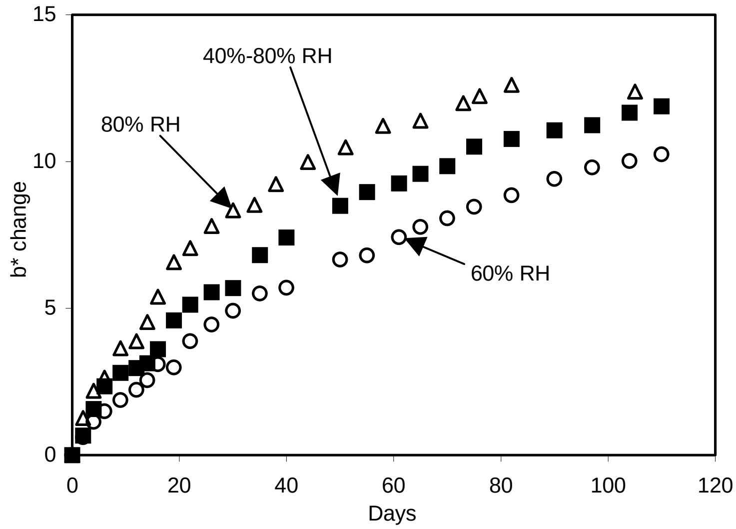

Figure 7. Effect of cycling RH at 70°C on Paper 7 discoloration. b change versus incubation time. Initial b* value: 12.1.*

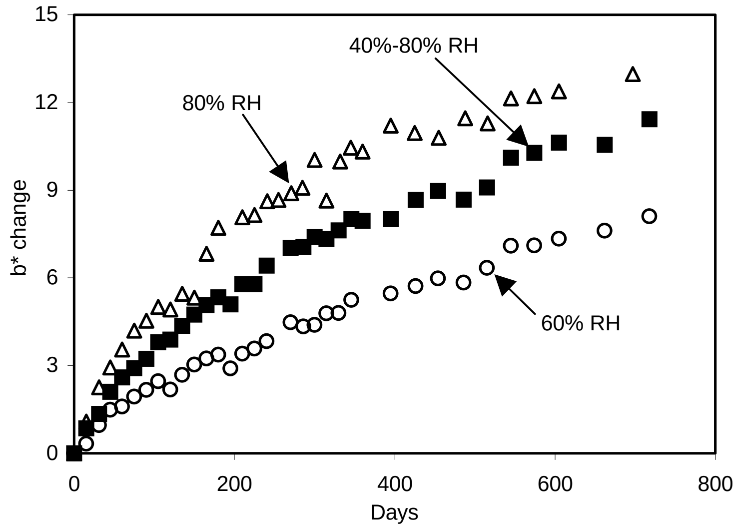

Figure 8. Effect of cycling RH at 50°C on Paper 7 discoloration. b change versus incubation time. Initial b* value: 12.1.*

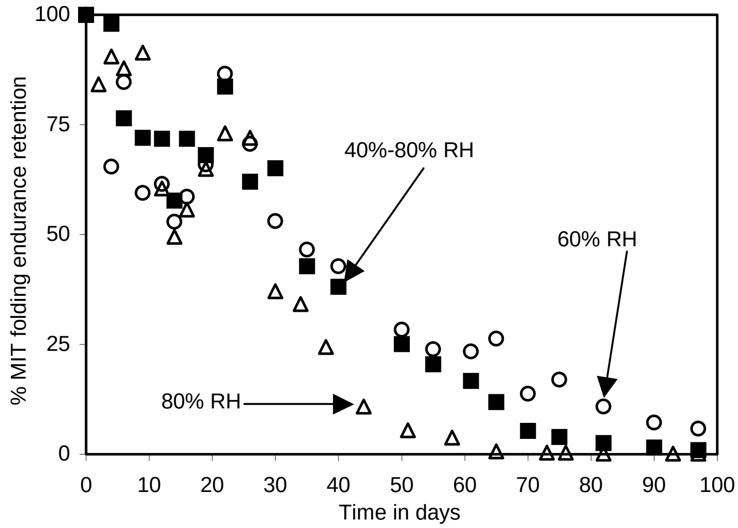

Figure 9. Effect of cycling RH at 70°C on MIT folding endurance of Paper 7. Percent retention versus incubation time.

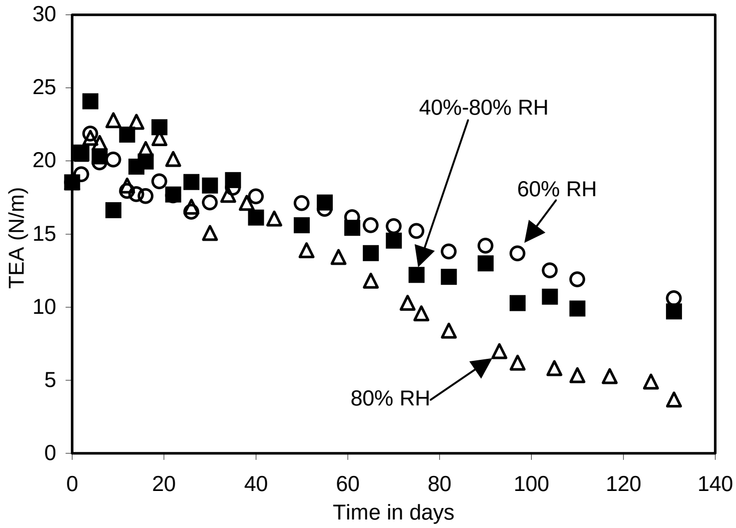

Figure 10. Effect of cycling RH at 70°C on tensile absorption energy (TEA) of Paper 7.

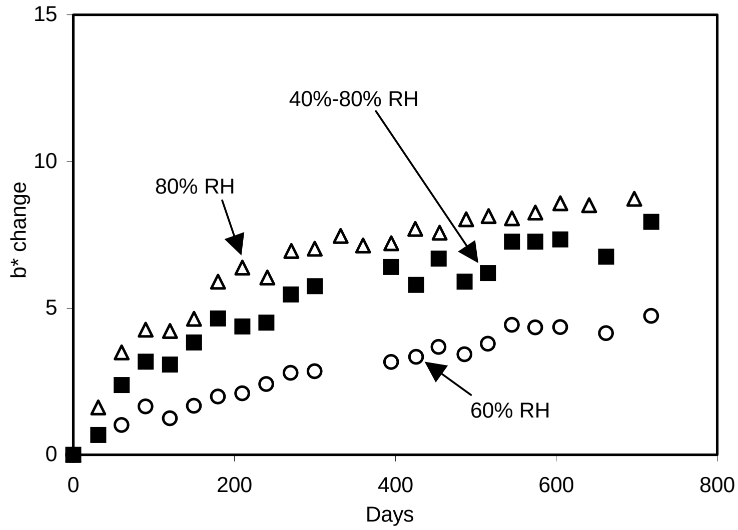

Figure 11. Effect of cycling RH at 50°C on Paper 8 discoloration. b change versus incubation time. Initial b* value: 11.2.*

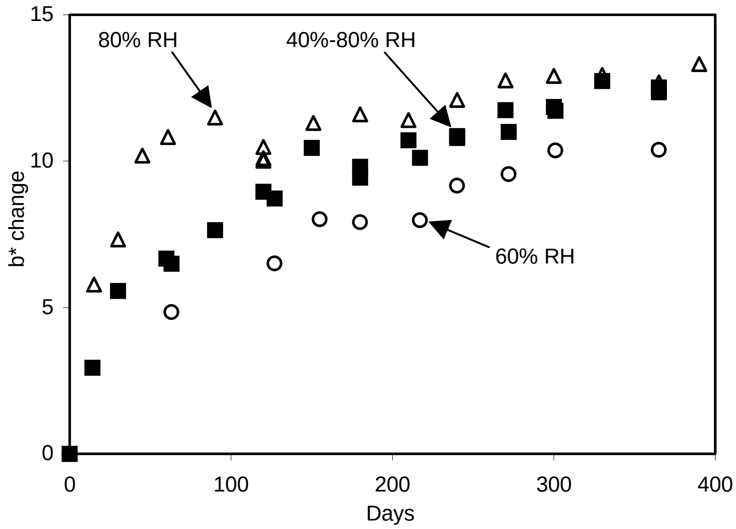

Figure 12. Effect of cycling RH at 70°C on Paper 8 discoloration. b change versus incubation time. Initial b* value: 11.2.*

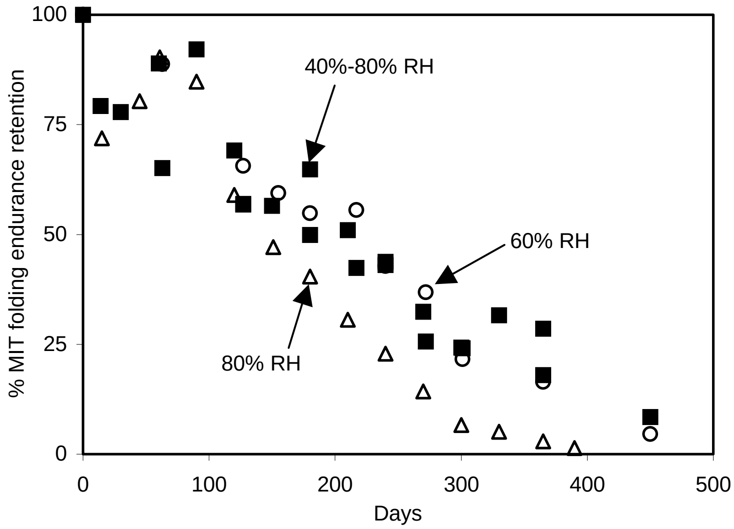

Figure 13. Effect of cycling RH at 70°C on MIT folding endurance retention of Paper 8. Percent retention versus incubation time.

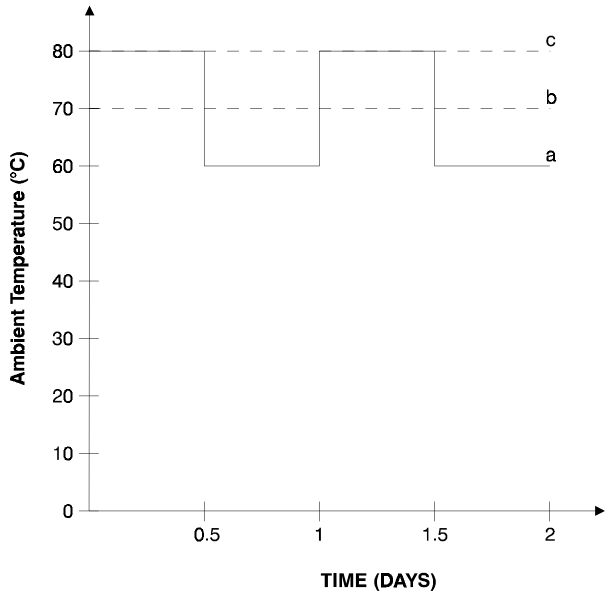

Figure 14. Temperature conditions. (a) Cycling between 60°C and 80°C. (b) Static at 70°C. (c) Static at 80°C.

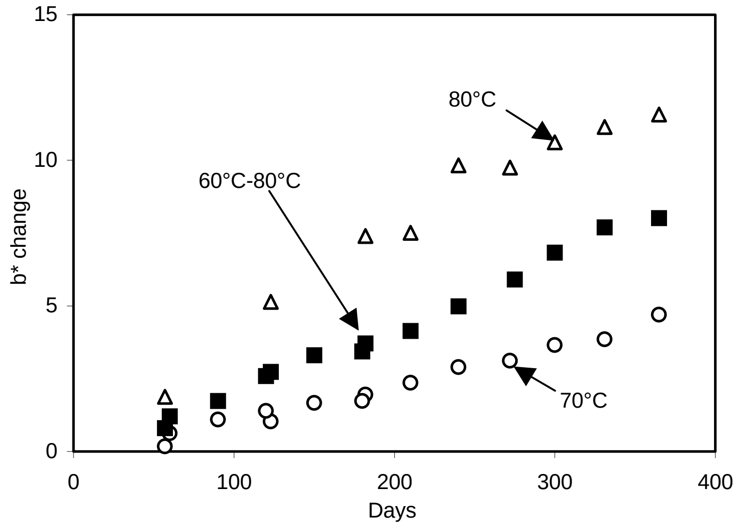

Figure 15. Effect of cycling temperature on Paper 5 discoloration at 50% RH. b change versus incubation time. Initial b* value: -1.*

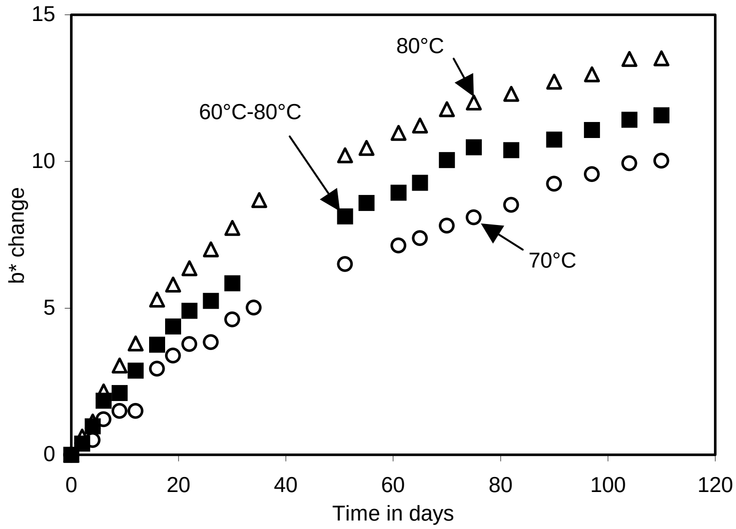

Figure 16. Effect of cycling temperature at 50% RH on Paper 7 discoloration. b change versus incubation time. Initial b* value: 12.1.*

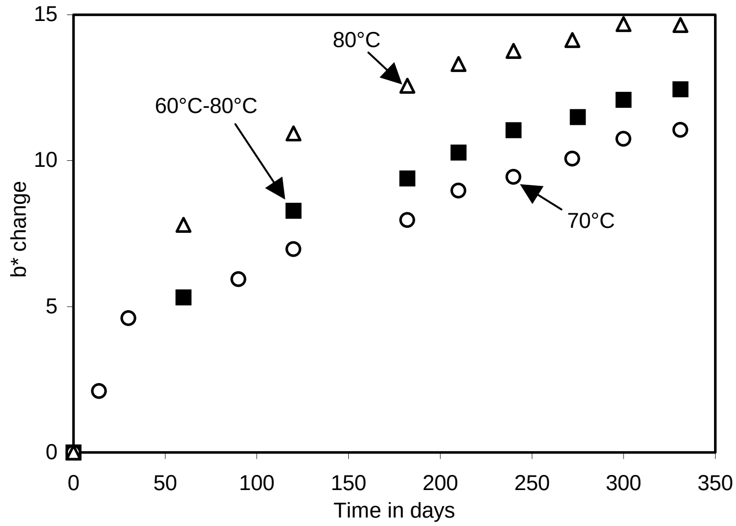

Figure 17. Effect of cycling temperature at 50% RH on Paper 8 discoloration. b change versus incubation time. Initial b* value: 11.2.*

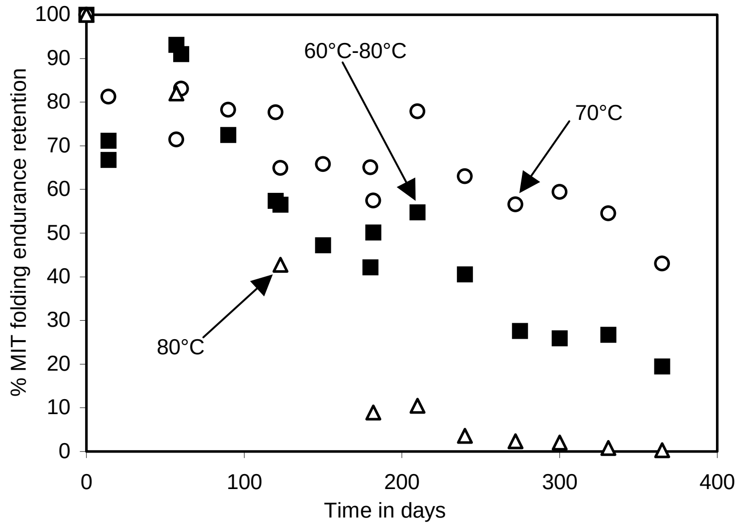

Figure 18. Effect of cycling temperature at 50% RH on MIT folding endurance of Paper 5. Percent retention versus incubation time.

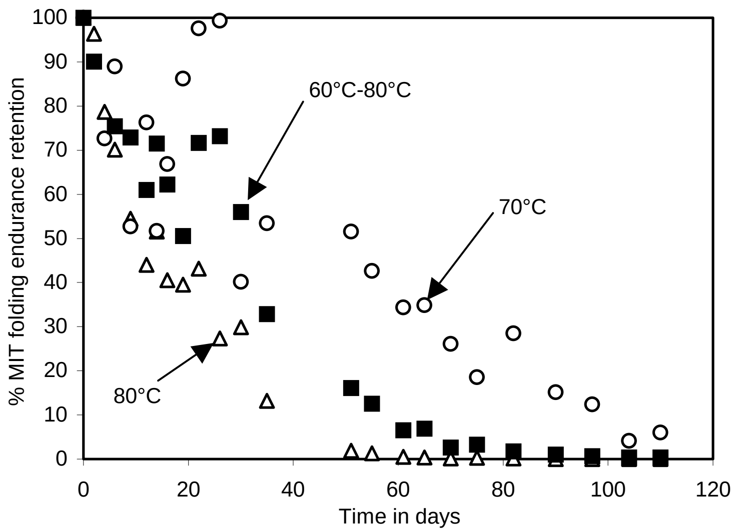

Figure 19. Effect of cycling temperature at 50% RH on MIT folding endurance of Paper 7. Percent retention versus incubation time.

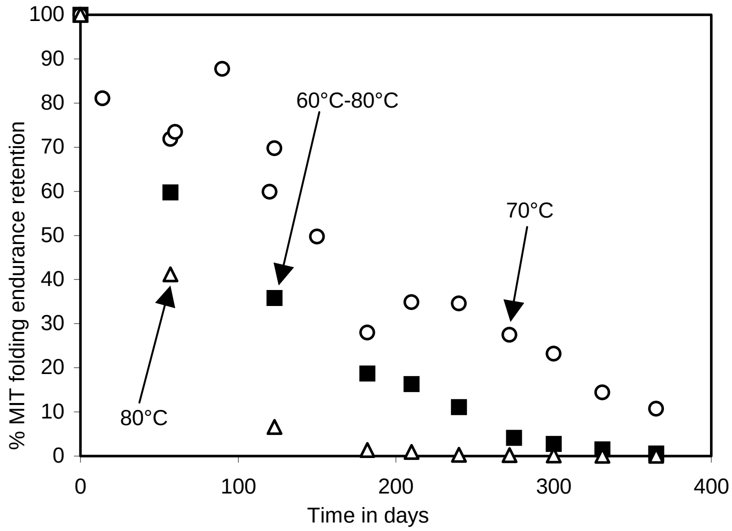

Figure 20. Effect of cycling temperature at 50% RH on MIT folding endurance of Paper 8. Percent retention versus incubation time.

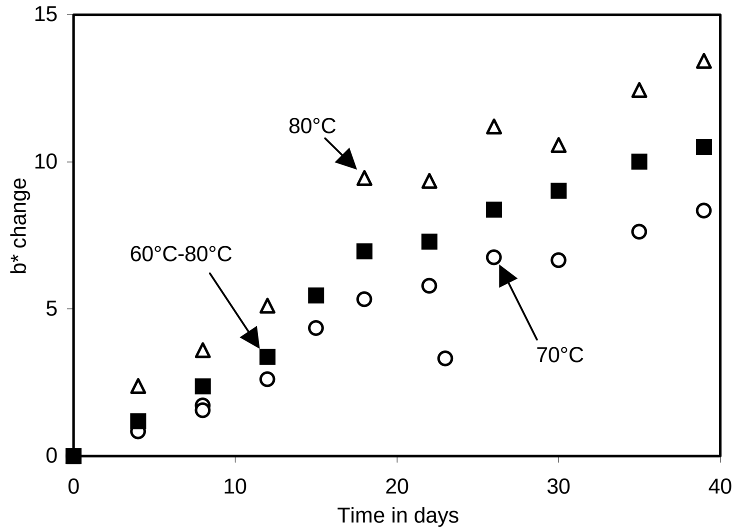

Figure 21. Effect of cycling temperature at constant moisture content on Paper 7 discoloration. Paper initially conditioned to 21°C, 50% RH. b change versus incubation time. Initial b* value: 12.1.*

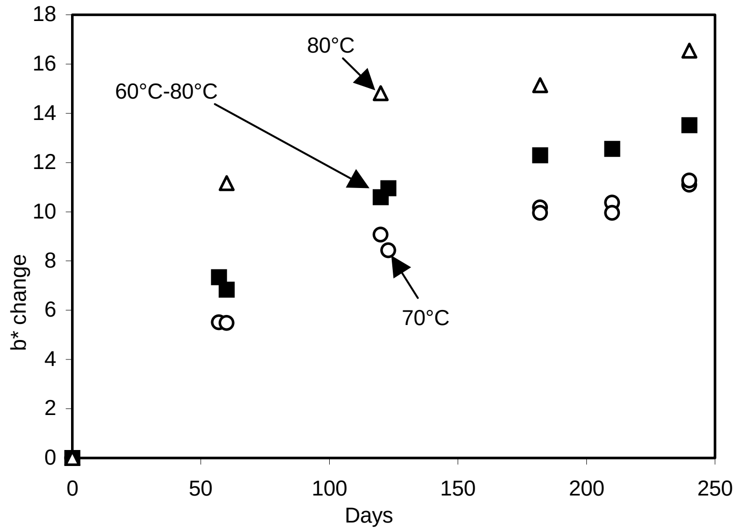

Figure 22. Effect of cycling temperature at constant moisture content on Paper 8 discoloration. Paper initially conditioned to 21°C, 50% RH. b change versus incubation time. Initial b* value: 11.2.*