Film archivists face a variety of challenges in their efforts to preserve film collections. Dealing with highly flammable nitrate film base, witnessing the decomposition of nitrate, observing the spread of the so-called “vinegar syndrome” in acetate film collections, and discovering dramatically faded color prints in their vaults are common experiences for film archivists. Some aspects of this continuing struggle were reviewed in an earlier paper.1

During the last two decades the chemical deterioration of photographic film has become a major concern and prompted numerous film stability studies around the world.2 Since 1988, the Image Permanence Institute (IPI) has been involved in a series of research projects investigating the stability of photographic film. IPI has focused on developing preservation strategies, such as the determination of key factors controlling chemical decay, the assessment of the effectiveness of storage conditions in minimizing vinegar syndrome and color dye fading, and the development of survey tools with which to evaluate the condition of acetate base film collections. Data and tools developed through several successive research projects have made possible the articulation of practical approaches for preserving motion-picture film collections. The elaboration of a strategic preservation plan at the Danish Film Institute (DFI) Film Archives is a recent example of the methodology developed at IPI.3, 4 IPI has gathered long-term data on the stability of nitrate, triacetate (CTA), and polyester film supports over a ten-year incubation period and also has obtained data on acetate base stability at both moderately accelerated incubation conditions and room temperature. Since 1998, IPI has been involved in a research project funded by the U.S. National Endowment for the Humanities and the Institute of Museum and Libraries Services to investigate the impact of changing environments on a wide variety of library and archives materials. The impact on these materials of cycling temperature and humidity was assessed. The objective of this paper is to update the results of IPI’s ongoing film stability studies.

LONG-TERM AGING STUDIES
Accelerated-Aging Studies
The importance of the chemical stability of photographic film prompted an early comparative study of nitrate and acetate film supports using accelerated aging.5 Over the years, a predictive method, based on the approach advanced by the Swedish chemist Svante Arrhenius,6 was developed through successive studies of the stability of acetate and polyester supports and color dyes.7, 8, 9, 10 The use of high incubation temperatures was shown to produce measurable material property changes within a
practical length of time. The Arrhenius approach provides a way to analyze the experimental data and translate them into terms of life expectancy (LE) for the tested materials, expressed in years stored at 20°C, 50% RH. The International Standards Organization (ISO) has standardized this method. Data published in the IPI Storage Guide for Acetate Film and in the Storage Guide for Color Photographic Materials and those at the core of IPI's Preservation Calculator were obtained using this type of data analysis.

It is recognized, however, that there are situations in which this type of interpretation does not work. The study of the effect of the microenvironmental housing on the rate of acetate base decay is one such situation. Here, it is not solely a chemical reaction but the rate of diffusion of degradation byproducts that determines the extent to which the microenvironmental housing approach can control vinegar syndrome.

Another legitimate and frequently expressed concern regards the possible distortion of the real-life behavior of the test materials through the use of accelerated-aging conditions. Can artificially created aging conditions reflect the materials' natural behavior? The only basis for confidence in the results of the film stability studies, and their interpretation, are anecdotal evidence gathered by film archivists and the systematic approach that was taken in carrying out the laboratory studies. One definitive response to this concern is to use only moderately accelerated conditions or even room conditions for testing film decay rate. However, this option requires longer incubation periods that can easily become impractical for investigators.

**LE Based on Long-Term Aging**

IPI has been continuously incubating test materials for a period of ten years in order to evaluate life expectancy predictions made earlier for nitrate, acetate and polyester film supports. These data, reported by Adelstein, are important because they can be superimposed onto the initial Arrhenius plots, which were based on higher temperatures and/or shorter incubation times. These latest results provide a preliminary answer to the question of whether the earlier life-expectancy predictions were realistic. In fact, the data obtained to date at 50°C and 20°C do not conflict with the previous LE predictions in any way, giving them added credence. The LE values reported in Table I reflect the relative stability of film supports at 20°C, 50% RH. The stability of nitrate film base was found to be highly variable, however the data are based on a limited number of samples. At room conditions, the LE of triacetate film base is only 40 years. Under the same circumstances, polyester base has an LE greater than 1,000 years. The superior chemical stability of polyester over triacetate and nitrate is consistent with earlier studies.

<table>
<thead>
<tr>
<th>Film Support</th>
<th>LE at 20°C, 50% RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate</td>
<td>10 to 500 years</td>
</tr>
<tr>
<td>Triacetate</td>
<td>40 years</td>
</tr>
<tr>
<td>Polyester</td>
<td>1,000 years</td>
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</tbody>
</table>

Table I. Life Expectancy (LE) predictions for nitrate, triacetate, and polyester film.
Significance of Long-Term Data for Film Storage Recommendations
The data obtained from long-term aging reaffirms the great potential of colder temperatures and lower RH in maximizing the stability of photographic film supports. The LE values in Table I demonstrate that nitrate and acetate base film collections will not last long if stored at room conditions (room temperature and moderate RH). Contingent to this conclusion is the fact that the long-term aging data for nitrate and triacetate indicate that these materials, which decay rapidly at room conditions, could last several hundred years if kept in cold storage. Data published in the IPI Storage Guide for Acetate Film illustrate the critical relationship between temperature, RH, and the chemical decay rate of acetate film base. Such data sets are consistent with the latest long-term aging investigation, which provides new ground for long-term film storage recommendations. These guidelines are reiterated by Adelstein.

Defining a Strategic Preservation Plan for Film Collections
Today, articulating a best-fit strategic plan for film collections can and should go beyond choosing the standard storage recommendations as the ultimate goal. For their recommendations, standards organizations assume that films are newly processed and, implicitly, that film collections are homogeneous in nature. In reality, nearly all collections include materials of various ages, types, and conditions. Each collection poses a unique problem to collection managers whose work it is to optimize the preservation of mixed holdings. For instance, one collection may need a colder storage environment than another to achieve the same useful life.

The aforementioned DFI project demonstrated the need for a systematic methodology that (1) assesses the current storage situation, (2) evaluates the state of preservation of the collections, (3) uses this information to estimate the risk of information loss over time, and (4) customizes the requirements for an adequate storage facility and preservation policy. In practice, the response to a given storage situation may vary from institution to institution. However, a reasonable preservation program will be one that balances the investment in a proper storage facility with a commitment to a prioritized duplication program. The strategic plan for the DFI collections discussed in this publication offers an insight into this methodology.

CHANGING ENVIRONMENTS STUDY—OBJECTIVES
Although steady environmental conditions have been consistently recommended as the ideal storage situation, every collection is exposed to temperature and RH changes to a greater or lesser extent. A poorly controlled storage climate is not the sole cause of temperature and RH fluctuations. Even materials stored in a well-controlled storage space can experience environmental changes due to equipment failures or transitions in and out of storage. (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 the film.) This raises two questions: (1) how can the overall long-term effect of changing environments on the rate of chemical decay be predicted, and (2) to what extent are macroenvironmental changes transmitted to the microenvironments, ultimately causing changes in the materials themselves? For the answers, an
assessment of the mitigating effect of enclosures or other housing systems commonly used to store information-recording materials is required.

IPI addressed the first question by developing prediction predictive models, such as a time-out-of-storage prediction table for decay of acetate film base\cite{12} and color dyes \cite{13} and as an extension of this, the more generic time-weighted preservation index (TWPI).\cite{18, 19} These are calculation models that quantify the impact of changing environments on chemical stability. They are based on the knowledge that temperature and moisture content govern the chemical degradation of organic materials based on recognized thermodynamic principles.

Few studies have looked at the impact of cycling environments on decay rate. An earlier investigation of paper behavior seemed to indicate that cycling environments cause decay mechanisms that cannot be explained by commonly recognized thermodynamic principles. The study data shows that at 90°C paper decays faster under cycling RH than at the steady upper limit of the given humidity cycle.\cite{20} These paper test results prompted a reevaluation of paper and photographic film behavior. It was judged important to determine if changing temperature and RH conditions are inherently detrimental to the stability of archives materials. Toward that end, the question of whether changing environments cause extra chemical decay in paper and triacetate film base was addressed. The behavior of several papers and triacetate film base was studied; the paper results have been reported.\cite{21} Data obtained on triacetate base photographic film are discussed in the following sections. The data developed in this study documents the relevance of the TWPI model.

**Effect of Cycling Environments on Film Stability**

Although the stability of cellulose triacetate film base has been extensively studied at various constant temperature/RH conditions, the effect of cycling conditions on film base stability had not been investigated. The present study was conducted primarily to investigate (1) the effect of cycling RH at constant temperature and (2) the effect of cycling temperature at constant moisture content. A third approach exploring the effect of an increasing number of temperature cycles was conducted by implementing three different cycle times within the same incubation period.

**Film Samples**

The material tested was processed 35mm motion picture film on cellulose triacetate base. In order to conduct the investigation at the lowest temperature as possible, the film was thermally predegraded prior to incubation. This approach was implemented successfully in previous acetate base stability studies and offers the advantage of providing meaningful results within a practical period of time. Film in the form of several solid 1,000-ft. rolls was first moisture-preconditioned to 21°C, 50% RH and then placed in sealed bags and preincubated at 90°C. After preincubation, the 1,000-ft. rolls were broken down into several series of 100-ft. rolls, all displaying similar acid content. Free acidity levels were determined by using the IPI-developed water-leaching method.\cite{22}
EFFECT OF CYCLING RH AT CONSTANT TEMPERATURE

Three series of predegraded 100-ft. rolls were incubated in this portion of the study. Preliminary testing was done to determine the best enclosure type and cycle length for achieving a significant moisture-content change during each RH cycle. Archival cardboard boxes were selected because, being porous, they would provide optimum moisture equilibration between the film material and the cycling environment. Three series of predegraded 100-ft. rolls were incubated in this portion of the study.

Figure 1. Humidity conditions used at 35°C. (a) Cycling between 40% and 70% RH. (b) Static at 55% RH. (c) Static at 70% RH. Rolls of film enclosed in archival cardboard boxes.

Figure 2. Moisture equilibration for 100-ft. roll of 35mm motion-picture film on CTA base initially conditioned to 21°C, 20% RH and exposed to 50% RH at 21°C and 35°C.

Ambient RH (%) vs. Time (weeks)

Figure 2. Moisture equilibration for 100-ft. roll of 35mm motion-picture film on CTA base initially conditioned to 21°C, 20% RH and exposed to 50% RH at 21°C and 35°C.
humidity conditions were selected: steady 55% RH, steady 70% RH, and cycling between 40% and 70% RH with a two-week cycling time (see Figure 1). The 55% RH level corresponds to the mid-range of the RH cycle, and the 70% RH level corresponds to the upper limit of the cycle. Incubation temperature was set at 35°C. Figure 2 illustrates the effect of temperature on the rate of moisture equilibration of photographic film. Data obtained at 35°C indicates that 90% equilibration was reached after five days of conditioning. The relevance of these data is independent of the range of the one-time RH change. One week each at the upper and lower limits of the RH cycle resulted in a significant change in film moisture content during the cycle.

The film’s degradation rate was determined by monitoring its free acidity over time. (Acetate base stability studies have consistently demonstrated that the increase of free acidity in film provides the best indicator of decay and reflects the rate of decay over time.) Results were analyzed by comparing the rates of acidity increase obtained under the three humidity conditions. Figure 3 illustrates that comparison by plotting the acid content in the film versus incubation time under the three RH conditions. Incubations were conducted for almost two years. Each data point corresponds to one sample pull and reflects the free acidity of an individual roll, as measured at three locations along the length of the roll (i.e., 10, 50, and 90 ft.).

As expected, the highest rate of decay was observed at the highest steady humidity condition, i.e., at 70% RH, the upper limit of the RH cycle profile. This reflects the fact that high water content in the film has a detrimental effect on acetate base stability. Film incubated at a steady 55% RH and at cycling humidity between 40% and 70% RH (with a two-week cycle time) degraded at slower rates. The data seem to indicate a slightly faster rate of degradation under cycling RH conditions than under steady 55% RH (the mid-range of the RH cycle). This can be seen in the rise in acidity for the cycled film after 500 days of incubation. Measured changes in film acid content remained
Figure 4. Temperature conditions used at constant moisture content in the film roll. (a) Cycling between 20°C and 50°C. (b) Static at 35°C. (c) Static at 50°C. Roll of film enclosed in sealed metal can.

Figure 5. Effect of cycling temperature on CTA film base stability at constant moisture content. 100-ft. film rolls incubated inside sealed metal cans. Film initially conditioned to 21°C, 50% RH. Film free acidity expressed in ml 0.1N NaOH/gram of film.
small throughout the entire incubation period, and therefore the results were variable. This experiment did not indicate that the decay rate at cycling RH conditions was greater than at the upper limit of the RH cycle profile.

EFFECT OF CYCLING TEMPERATURE AT CONSTANT MOISTURE CONTENT

Three series of preincubated 100-ft. rolls were moisture-preconditioned to 21°C, 50% RH and enclosed in sealed metal cans prior to incubation at three temperature conditions: steady 35°C, steady 50°C, and daily cycling between 20°C and 50°C. These incubation conditions are illustrated in Figure 4. Because of the small free space in the sealed cans and, thus, the small moisture absorption capacity in the air compared to the total water content in the one hundred feet of film, the incubations were conducted essentially at constant film moisture content. The short one-day cycle time was chosen based on previous demonstrations that thermal equilibration is a much faster process than moisture conditioning. Full temperature equilibration occurred within two hours for a 100-ft. roll of 35mm film enclosed in metal can.\textsuperscript{23, 24}

Film samples were incubated for various periods up to almost two years at 35°C. For each temperature condition, the rate of decay was determined by monitoring the free acidity of the film, using the approach described in the previous experiment. Figure 5 illustrates the acid content in the film versus incubation time under the three temperature conditions studied.

As expected, the highest rate of decay was observed at the highest steady temperature condition, i.e., 50°C, the upper limit of the temperature cycle profile studied. This is illustrated in Figure 5 by the fast acidity increase at steady 50°C compared to the acidity changes observed at steady 35°C and at daily cycling temperature between 35°C and 50°C. The rate of decay obtained at cycling temperature conditions was greater than that obtained at the steady mid-range temperature but slower than that observed at the upper limit of the cycle.
Effect of the Number of Temperature Cycles

The objective of this part of the study was to assess the impact of the frequency of temperature cycles within a given period on the decay rate of CTA film base. Three series of pre-degraded 100-ft. film rolls were moisture-preconditioned to 21°C, 50% RH, enclosed in sealed metal cans, and then incubated. The film was incubated for a six-month period under temperatures cycling between 20°C and 50°C with three cycle times: one day, one week, and three months. After six months, the effects of 180 one-day cycles, 24 one-week cycles, and two three-month cycles were compared with respect to their impact on CTA film base stability at constant moisture content. Figure 6 reports no significant differences among the rates of acid generation caused by the three experimental conditions. These data do not support the assumption that increasing the frequency of temperature cycling might cause extra chemical decay in CTA film base. This investigation is being continued.

DISCUSSION

Neither set of experiments comparing the effects of cycling temperature/RH and the effects of steady temperature/RH supports the idea that environmental fluctuations cause extra chemical decay. Film samples did not decay faster under cycling conditions than at the steady high limit of the cycle. On the contrary, the rate of decay observed under humidity cycling between 40% and 70% RH was slower than that observed at steady 70% RH, the upper limit of the humidity cycle. The same behavior was observed in the study of temperature cycling. The rate of decay measured under temperature cycling between 20°C and 50°C was slower than the rate measured at steady 50°C, the upper limit of the temperature cycle.

It should be noted that in the RH-cycling investigation the relatively long time required for the film to reach moisture equilibrium mitigated the effect of changing RH. However, this is a situation that occurs in real life as well. Due to the rapid thermal equilibration of the film, the effect of temperature changes was mitigated to a lesser extent during the temperature cycling experiment. Despite these uncertainties, it can be concluded based on these two separate sets of data that neither cycling RH nor cycling temperature appeared to be inherently detrimental to CTA base stability.

These data do not invalidate the principle that forms the basis of prediction models like TWPI, which identify environmental conditions as the determining factor in the chemical stability of organic collections. The calculation algorithm used for TWPI emphasizes the determinant impact of bad storage conditions (i.e., high temperature and high RH) versus good storage conditions (i.e., cold temperature and low RH) on the rate of chemical decay. In the study of the effect of cycling temperature on acetate base stability, film samples spent an equal amount of time at each temperature. The fact that the rate of film decay was faster under cycling temperature than at steady 35°C, the mid-range temperature of the cycle, supports the principle that the worst condition has a greater impact than the best condition in determining overall film base stability. The time spent at 50°C had a greater impact on the rate of base degradation than the time spent at 20°C. In that regard, the TWPI model is consistent with the behavior observed in this study.

Investigation of the effect of cycling temperature with cycle times of one day, one
week, and three months indicated that decay rate is unaffected by the number of cycles within a given period of time. This suggests that the rate of degradation is dependent only on the total amount of time spent at each temperature of the cycle. Incubating the film samples through two, 24, and 180 temperature cycles between 20°C and 50°C over a period of six months produced no noticeable differences in the rates of degradation; free acidity increased at the same rate for all three sample series (see Figure 6). The total time spent at 20°C and 50°C was considered to be essentially the same for all three series. Therefore, we can conclude that the time spent at each temperature is the determining factor of the rate of decay. This observation further reinforced the validity of TWPI model, which is based on this premise.

CONCLUSIONS
The data presented in this paper reaffirm the importance of environmental conditions in preserving photographic film. Recent long-term aging data are consistent with the results of earlier studies and underscore the importance of storage at cold temperature and low RH to optimum film base stability. The main objective of this paper was to investigate the possibility that the temperature and humidity transitions in cycling environments might cause extra chemical decay in film supports. Within the framework of this study, the rates of decay observed under cycling RH and cycling temperature offer no evidence that transitions from one RH to another or from one temperature to another cause a new mechanism of deterioration or accelerate degradation more than would be expected by current thermodynamic models. Recently, similar observations were made regarding the chemical stability of paper. The overall rate of acetate base decay was found to be independent of the number and frequency of transitions but strongly governed by the amount of time spent at each condition. These data validate the TWPI model, by which the changing conditions in real-life storage environments can be analyzed to reach an overall estimate of the chemical decay rate in the collections. Further, the data reinforce the potential value of TWPI in informing storage decisions through the assessment of current situations or in simulating new storage spaces without neglecting unexpected chemical degradation caused by temperature and RH transitions.

ACKNOWLEDGEMENTS
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NOTES


14. IPI’s Preservation Calculator: software developed by Image Permanence Institute. Can be downloaded downloadable from the IPI following website: <www.rit.edu/ipi>


