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Stability of Acetate Film Base: Accelerated-Aging Data Revisited[1]

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Abstract. *This paper reports data on cellulose triacetate (CTA) film base stability obtained at 21 and −16 °C over a 10-year period. Results demonstrated the potential of subfreezing storage temperatures for stabilizing CTA films that have already started to decay. After over 10 years of storage at −16 °C, no change in free acidity was observed for film that had been predegraded to the onset of vinegar syndrome. Data obtained by natural aging at 21 °C, 50% relative humidity (RH) indicated that film acidity at least doubled within 5 years. These results were consistent with earlier predictions based on accelerated-aging tests and reaffirmed the inappropriateness of film storage at room conditions. Data on the effect of changing temperature and/or RH on CTA film base stability are reported. Results did not reveal that changing conditions caused unexpected extra CTA film base decay. The data reinforced the potential value of the time-weighted presentation index model in informing storage decisions. © 2006 Society for Imaging Science and Technology.* [DOI: 10.2352/J.ImagingSci.Technol.(2006)50:5(494)]

INTRODUCTION

Accelerated-aging data came into use to aid archivists who were facing the problem of information loss caused by irreversible decay in their collections. Since 1988, the Image Permanence Institute (IPI) has been engaged in a series of research projects involving the study of photographic material stability. IPI has focused on the development of preservation strategies and has produced a series of management tools for dealing with media collections, including the *IPI Storage Guide for Acetate Film*,[1] the *Storage Guide for Color Photographic Materials*,[2] and the *IPI Media Storage Quick Reference*.[3] These publications were designed as management tools for archivists to use in assessing the effectiveness of their storage conditions in controlling the decay of cellulose acetate film and color photographic materials or collections of mixed media. The vast majority of the information included in these publications is based on data produced by accelerated-aging tests, which were conducted primarily on photographic materials at steady elevated temperatures and at constant moisture content. In recent years, IPI has focused on developing data at lower temperatures. In an earlier paper, IPI published long-term data on the stability of nitrate, cellulose triacetate (CTA), and polyester film supports at 50 °C obtained from a 10-year incubation period.[4]

This paper revisits common accelerated-aging procedures used for the study of film stability, reporting data obtained by natural aging at room and subfreezing temperatures, and under changing temperature and relative humidity (RH) conditions. Common accelerated-aging practices and limitations are discussed first.

ACCELERATED AGING STUDIES—BACKGROUND

Using High Temperatures

Accelerated aging at high temperature was used in early comparative studies of nitrate and acetate film supports.[5] Later, a predictive method, based on the approach advanced by the Swedish chemist Svante Arrhenius,[6] was developed through successive studies of the stability of photographic film. Adelstein pioneered the use of the method to quantify the stability of color dyes.[7] Later accelerated aging studies on nitrate,[8,9] acetate,[4,10–15] and polyester[16,17] plastic supports, and on color dyes[18,19] further demonstrated the relevance of the Arrhenius equation for investigating photographic film stability. Through extrapolation of Arrhenius plots, these studies made it possible to quantify the relationship between temperature and the rate of degradation of materials at various humidity levels. In practice, some measurement of the rates of chemical reaction, e.g., free acidity or physical property changes during CTA film decay,[12] is determined at several temperatures and constant film moisture content. The logarithm of those rates is plotted versus the reciprocal of the absolute temperature (K). The data obtained at elevated temperatures can be used to estimate the rate of decay at other temperatures.[20] Thus, the method 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 21 °C, 50% RH. The International Organization for Standardization (ISO) has standardized this method.[21] The method has been useful for developing effective preservation strategies for film and color materials. Data published in the *IPI Storage Guide for Acetate Film*[1] and in the *Storage Guide for Color Photographic Materials*[2] were obtained using this type of data analysis.

A legitimate and frequently expressed concern is the possible distortion of the real-life behavior of the test mate-

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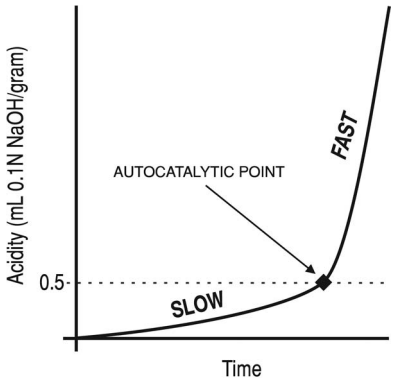

Figure 1. Free acidity change vs time for acetate film.

rials through the use of accelerated-aging conditions. The studies mentioned above were commonly conducted at high temperatures (70 °C and above). Can artificially created aging conditions reflect the materials' natural behavior? One response to this concern is to use only moderately accelerated conditions or even room conditions for testing material decay rate. However, this requires longer incubation periods, which can be impractical.

Using Moderately Accelerated Aging

With the above concerns in mind, investigators have used moderately accelerated aging conditions, either by extending the duration of investigation or by modifying the preparation of test samples. IPI's long-term collection of data on film supports[4] is an example of the former approach; its investigation of the role of microenvironments in controlling vinegar syndrome is an example of the latter.[22]

IPI incubated test materials at 50 °C for 10 years in order to evaluate earlier LE predictions for nitrate, acetate, and polyester film supports. The data from these tests, reported by Adelstein,[4] are important because they can be superimposed onto the initial Arrhenius plots, which were based on higher temperatures (70 °C and above). These results provided a preliminary answer to the question of whether the earlier LE predictions were realistic. In fact, the data obtained to date at 50 °C do not conflict with the previous LE predictions in any way, giving them added credence. Data published in the *IPI Storage Guide for Acetate Film* are consistent with the latest long-term aging investigation, which provides new grounds for long-term film storage recommendations and underscores the benefit of cold storage to film chemical stability.

To study the benefits to CTA film base stability of microenvironments created by adding acid scavengers (silica gel and molecular sieves) to sealed enclosures, incubation temperatures as low as 35 °C were used. The method involved predegrading the CTA film by incubating it for a short time at 90 °C prior to incubation at 35 °C. This approach was based on earlier research, which had demonstrated (1) that film acidity level is the best indicator of CTA film decay and (2) that, beyond an acidity level of 0.5 mL 0.1 NaOH per gram of film, the rate of deterioration progresses at an ever faster pace. That acidity level characterizes the autocatalytic point of acetate base chemical decay. Figure 1 illustrates the relationship between film free acidity and time. It also reflects the evolving condition of the film. Any increase in film acid content reflects the advance of CTA film base chemical degradation. As illustrated in Fig. 1, the rate of decay is slower before the autocatalytic point than it is after that critical point is reached. This behavior was the basis for predegrading the film samples prior to incubation at moderately accelerated conditions. The condition of newly processed CTA film was thermally altered at 90 °C until the film acidity reached the autocatalytic point. The newly processed film was initially moisture conditioned to 21 °C, 50% RH and then was enclosed inside two sealed aluminum-foil bags prior to the first incubation at 90 °C. This approach was successfully used to investigate the effectiveness of adsorbents (silica gel and molecular sieves), film enclosures, and moisture preconditioning to low RH in controlling acetate film base degradation. The method produced telling results at 35 °C and reduced the required incubation length to less than two years.[23] Further data were obtained at 21 °C, using the same methodology.[23]

Natural Aging of Collections

Surveying media collections may be the best way to quantify the effects of environment on film stability. In recent years, survey techniques for acetate base collections have been significantly improved by the use of acid detectors such as A-D Strips.[24] Such tools can identify materials in various states of deterioration, but they also can provide a general view of the state of preservation of large collections, on the basis of which efficient preservation strategies can be determined. It is recognized that knowing the condition of a collection is a necessary step in understanding the environmental needs of that collection. By definition, condition survey results reflect how fast acetate collections are naturally decaying. The attention given recently—since diagnostic tools such as A-D Strips have become available—to assessing the state of preservation of collections on acetate film base has provided strong evidence that most holdings are in part actively decaying if they have been kept in an inappropriate environment for several decades. This situation is consistent with predictions based on accelerated-aging data, which suggest that 40-year-old acetate materials may now be at the autocatalytic point of acetate degradation if they have been stored at room conditions (21 °C, 50% RH). Accelerated-aging data also suggest that collections stored at colder temperatures are in better condition than those stored in warmer temperatures. Unfortunately, pre-existing, and often current, storage climate conditions are guesses at best, and they are rarely fully documented. Anecdotal evidence from the field, only partially documented, suggests that colder temperatures postpone further acetate base chemical decay. In reaction to these uncertainties, IPI has been monitoring the condition of a series of acetate-base film rolls kept at both room and subfreezing storage temperatures.

Table I. Experiment configuration, initial film acidity, and acidity levels after 5, 6.5, and 10.25 years of storage at room temperature (21 °C) and in frozen storage (−16 °C). All samples were CTA-base motion picture film. Film free acidity expressed as mL 0.1 N NaOH/g of film.

Storage conditions	Sample	Enclosure	Initial acidity	Acidity after 5 years	Acidity after 6.5 years	Acidity after 10.25 years
−16 °C 50%–60% RH	A	Vented plastic can	0.71	0.69	0.75	0.75
	B	Vented plastic can	0.72	0.64	0.51	0.58
	C	Vented plastic can	0.49	0.53	0.55	0.53
	D	Vented plastic can	0.38	0.41	0.51	0.42
	E	Vented plastic can	0.44	0.50	0.55	0.54
	F	Metal can	0.42	0.42	0.43	0.43
	G	Vented plastic can	0.40	0.39	0.41	0.42
	H	Vented plastic can	0.76	0.69	0.73	–
21 °C 50%–55% RH	I	Vented plastic can	0.50	1.55	2.21	6.83
	J	Vented plastic can	0.50	1.51	1.98	6.18
	K	Vented plastic can	0.39	1.31	1.83	5.82
	L	Metal can	0.71	1.76	2.40	6.68
	M	Metal can	0.57	1.16	1.72	4.79
	N	Metal can	0.57	1.48	2.11	5.90

NATURAL AGING STUDY

Experiment

A series of fourteen 400 ft. 35 mm color motion picture print rolls on CTA support were preincubated in order to initiate the vinegar syndrome. The film was first moisture conditioned to 21 °C, 50% RH and then enclosed in two heat sealed aluminum-foil bags. It was then preincubated at 90 °C for long enough to produce an acidity level near the autocatalytic point of acetate base decay. Using the water-leaching determination method,[25] the initial acidity level for each 400 ft. film roll was determined by titration. Each film roll was placed inside either a metal can or a vented polypropylene can. Eight samples were stored inside a frost-free freezer (average temperature: −16 °C). Six samples were kept at room conditions (21 °C, 50%–55% RH).

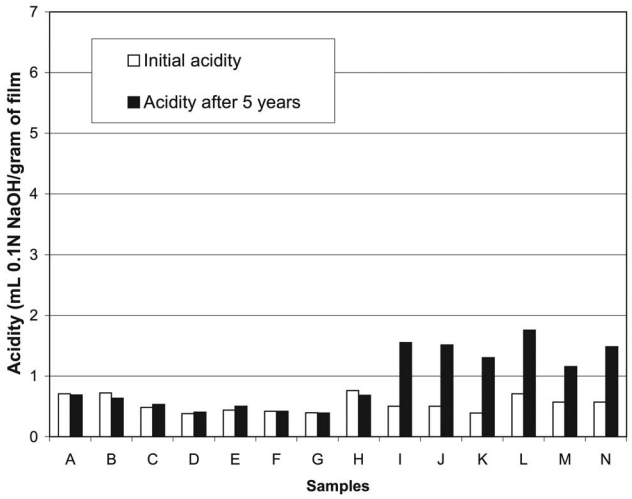

Figure 2. Film initial acidity and acidity level after 5 years of storage for CTA-based photographic film rolls. Samples A–H were kept inside a frost-free freezer (−16 °C). Samples I through N were kept at room conditions (21 °C, 50%–55% RH).

Results

Effect of Storage Temperature

The acidity of each roll was measured after 5 years of storage, after 6.5 years of storage, and again after 10 years and 3 months of storage. Each roll was tested in three locations (10, 200, and 390 ft. from the end of the roll). The values listed in Table I are average acidities based on these three measurements. All of the acidity measurements were made using the same method.[19] Figures 2–4 report the initial acidity levels and illustrate the acidity changes observed after 5, 6.5, and 10 years and 3 months, respectively.

No significant change in film free acidity was detected in the samples kept in frozen storage. The variations observed in the results reflect only the variability of the determination method. By contrast, all film rolls kept at 21 °C, 50%–55% RH displayed major acidity increases. After just 5 years, the acidity levels had increased by a factor of 2 or 3. Data obtained after 6.5 years of storage at room conditions indicated that the deterioration had progressed further at an even faster rate. After more than 10 years of storage at

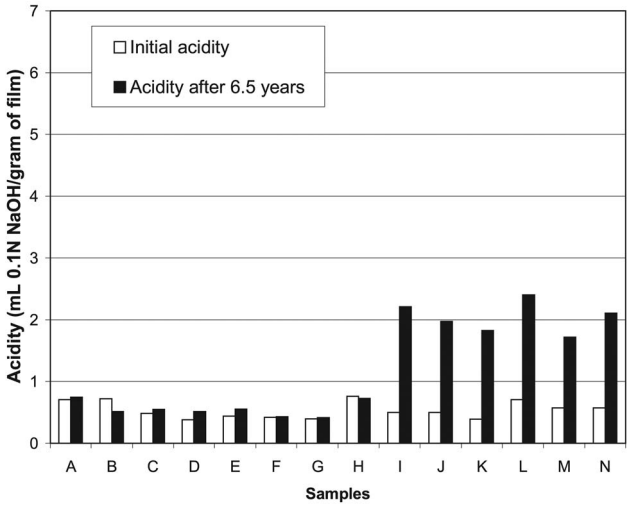

Figure 3. Film initial acidity and acidity level after 6.5 years of storage for CTA-based photographic film rolls. Samples A–H were kept inside a frost-free freezer (–16 °C). Samples I through N were kept at room conditions (21 °C, 50%–55% RH).

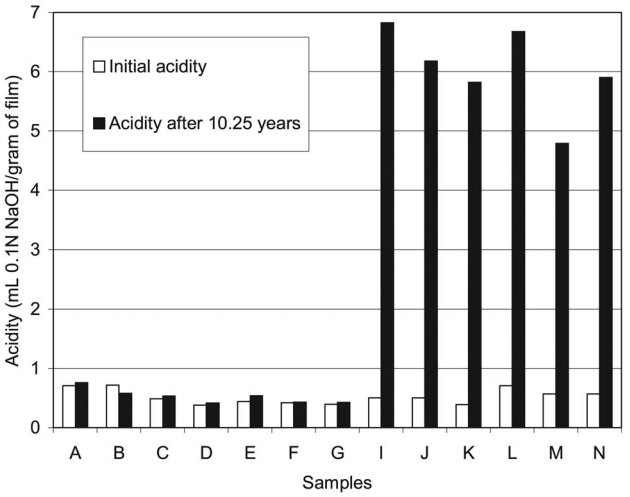

Figure 4. Film initial acidity and acidity level after 10.25 years of storage for CTA-based photographic film rolls. Samples A–G were kept inside a frost-free freezer (–16 °C). Samples I through N were kept at room conditions (21 °C, 50%–55% RH).

21 °C, the film acidity was found to be 9–13 times greater than the initial acidity levels. These results are strong evidence of the impact of temperature on CTA film base stability. Table II underscores the real benefit of frozen storage in postponing further chemical degradation of acetate materials. Furthermore, these empirical results are consistent with predictions based on accelerated-aging data for degrading acetate film base published in the *IPI Storage Guide for Acetate Film*, i.e., that film acidity at the autocatalytic point (i.e., 0.5 mL 0.1 NaOH per gram of film) would double after 5 years of storage at 21 °C, 50% RH.

Effect of Film Enclosures

Since no significant acidity change was detected in frozen storage, only the data obtained at room temperature were of interest for assessing the impact of enclosure design on CTA film base stability. Figure 5 illustrates the film acidity increase over time for each test sample stored at 21 °C. Films stored in metal cans and vented plastic cans alike displayed drastic acidity changes. Films in both types of containers decayed rapidly at room conditions and displayed no significant condition change in frozen storage after more than 10 years. These data indicate that the type of enclosure plays only a marginal role in controlling vinegar syndrome, confirming findings from earlier research.[17]

Table II. Effect of room and frozen storage on film free acidity after 5, 6.5, and 10.25 years.

	Film Free Acidity	
	Room storage at 21 °C	Frozen storage at –16 °C
After 5 years	2 to 3 times greater	No change
After 6.5 years	4 to 5 times greater	No change
After 10.25 years	9 to 13 times greater	No change

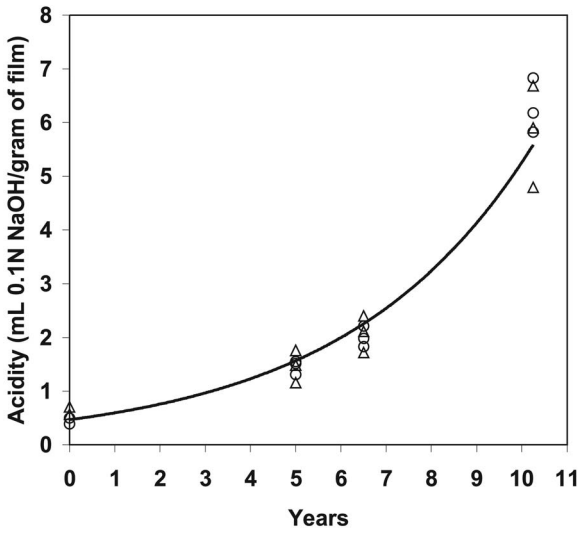

Figure 5. Film free acidity increase over time. Test samples were enclosed either inside metal cans or polypropylene vented containers. All samples were kept at 21 °C, 50%–55% RH for 10 years and 3 months.

Practical Significance

This study is of great practical importance because it shows that actively degrading films can be successfully stabilized in frozen storage while awaiting duplication or reformatting. These data demonstrate that acetate films that have started to decay will be in an advanced state of decay after only a few years of storage at room temperature, and will likely be damaged. This is a strong argument for using cold storage temperatures for the benefit of all film materials. The data also show that materials that have started to degrade can be stabilized for many decades. The stability of materials show-

ing no signs of chemical decay will be optimized and those materials will last for hundreds of years. As stated above, the type of enclosure plays no significant role in preventing vinegar syndrome. Providing cold storage is the best option for protecting vulnerable photographic film from chemical decay.

EFFECT OF CYCLING ENVIRONMENTS ON CTA FILM BASE STABILITY

Changing Temperature and RH

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) To what extent are macroenvironmental changes transmitted to the microenvironments surrounding the collection materials within their enclosures, ultimately causing changes in the materials themselves? and (2) How can the long-term effect of changing environments on the rate of chemical decay be predicted? IPI has addressed the first question by developing data on thermal and moisture equilibration for a variety of situations. Some of the data have been reported.[26] IPI has addressed the second question both by developing predictive models for acetate film base[1] and color dye[2] decay and by creating the time-weighted preservation index (TWPI), a calculation model that quantifies the impact of changing environments on chemical stability.[27] All of these developments are based on the knowledge that temperature and moisture content govern the chemical degradation of organic materials according to recognized thermodynamic principles.

Few studies have looked at the impact of cycling environments on the rate of chemical decay. Shahani[28] pioneered this type of investigation by exposing paper to cycling RH at constant temperature. Results led to the conclusion that cycling RH has the potential for increasing chemical decay. This earlier investigation seemed to indicate that cycling environments cause decay mechanisms that cannot be explained by commonly recognized thermodynamic principles. The study data showed that at 90 °C paper decays faster under cycling RH than at the steady upper limit of the given humidity cycle. Hofenk de Graaff conducted several accelerated-aging experiments implementing both cycling RH and cycling temperature in order to study the discoloration of paper materials.[29] Results suggested that cycling temperature at constant RH could cause discoloration (i.e., yellowing). These paper test results prompted a re-evaluation 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 archived materials. Toward that end, the question of whether changing environments cause *extra* chemical decay in paper and CTA film base was addressed. The behavior of several papers and CTA film base was studied; the paper results have been reported.[30] Data obtained on CTA photographic film base are discussed in the following sections.

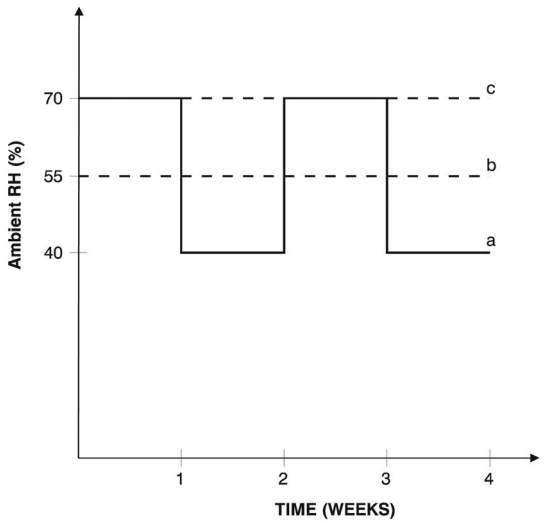

Figure 6. Humidity conditions used at 35 °C. (a) Cycling between 40% and 70% RH. (b) Steady at 55% RH. (c) Steady at 70% RH. Rolls of film were enclosed in archival cardboard boxes.

Although the stability of CTA film base had been extensively studied at 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.

Experimental and Results

Samples

The material tested was processed 35 mm motion picture film on CTA film base. In order to conduct the investigation at the lowest possible temperature, the film was thermally predegraded prior to incubation. Several solid 1000 ft. film rolls were first moisture preconditioned to 21 °C, 50% RH and then placed in sealed bags and preincubated at 90 °C. After preincubation, the 1000 ft. rolls were broken down into several series of 100 ft. rolls, all with similar acid content. Free acidity levels were determined by using the water-leaching method.[15]

Effect of Cycling RH at Constant Temperature

Three series of predegraded 100 ft. rolls were incubated in this portion of the study. Archival cardboard boxes were selected for the study because, being porous, they would provide optimum moisture equilibration between the film material and the cycling environment. Three humidity conditions were selected: steady 55% RH, steady 70% RH, and cycling between 40% and 70% RH with a 2-week cycling time (see Fig. 6).

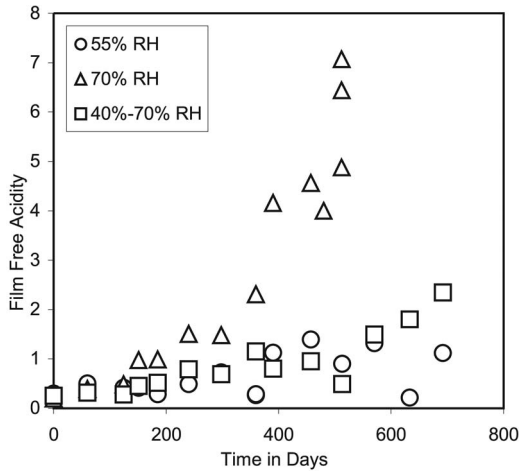

Figure 7. Effect of cycling RH on CTA film base stability at 35 °C. Film in 100 ft. rolls was incubated under three humidity conditions: 55% RH, 70% RH, and cycling RH between 40% and 70% with a 2-week cycle. Film acidity expressed in ml 0.1N NaOH/g of film.

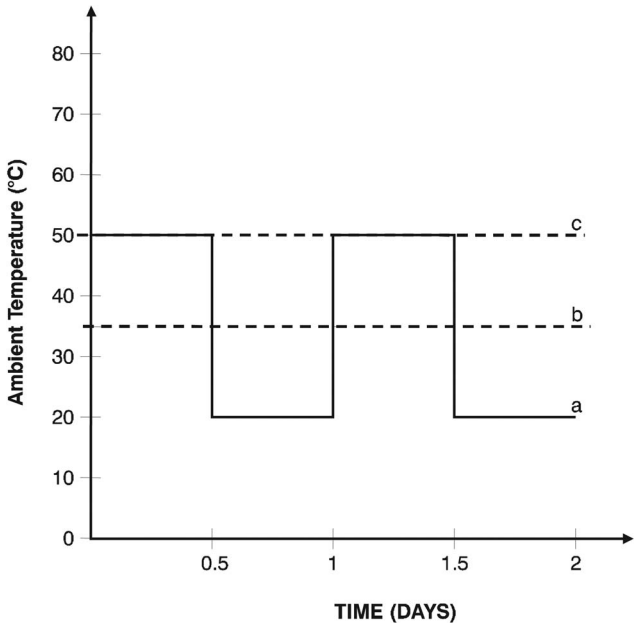

Figure 8. Temperature conditions used at constant moisture content in the film roll. (a) Cycling between 20 and 50 °C. (b) Steady at 35 °C. (c) Steady at 50 °C. Rolls of film were enclosed in sealed metal cans.

The 55% RH level corresponds to the midrange of the 40%–70% RH cycle, and the 70% RH level corresponds to the upper limit of the cycle. Incubation temperature was set at 35 °C, based on moisture equilibration data indicating that 90% equilibration can be reached after 5 days of conditioning at that temperature.[31] 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. Results were analyzed by comparing the rates of acidity increase obtained under the three humidity conditions.

The comparison is illustrated in Fig. 7, which shows the acid content in the film versus incubation time under the three RH conditions. Incubations were conducted for almost 2 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. from the end).

As expected, the highest rate of decay was observed at the highest steady humidity condition (70% RH, the upper limit of the RH cycle profile). This confirms that high water content in acetate film base has a detrimental effect on the film's stability. Films incubated at a steady 55% RH and at cycling humidity between 40% and 70% RH (2-week cycle time) degraded at slower rates. A slightly faster rate of decay was seen under the cycling RH conditions than at steady 55% RH (the midrange of the RH cycle) as shown by the rise in acidity in the cycled film after 500 days of incubation. Changes in film acid content were small throughout the entire incubation period, and therefore the results were variable. This experiment did not show that the decay rate under 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 and 50 °C. These incubation conditions are illustrated in Fig. 8. Because of the small free space in the sealed cans and the resulting small moisture absorption capacity of the air compared to the total water content in the film, the incubations essentially were conducted at constant film moisture content. The short 1-day cycle was chosen based on previous demonstrations that thermal equilibration is much faster than moisture equilibration. Full temperature equilibration occurred within two hours for a 100 ft. roll of 35 mm film enclosed in a metal can.[27]

Film samples were incubated for various periods up to almost 2 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 9 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 (50 °C, the upper limit of the temperature cycle profile studied). This is illustrated in Fig. 9 by the fast acidity increase at steady 50 °C compared to the smaller acidity changes observed at steady 35 °C and at temperatures cycling between 35 and 50 °C. The rate of decay under cycling temperatures was faster than that at the steady midrange temperature but slower than that at the upper limit of the cycle.

Effect of the Number of Temperature Cycles

The study was extended to include assessment of the impact of the frequency of temperature cycles within a given period on the decay rate of CTA film base. Film samples were ex-

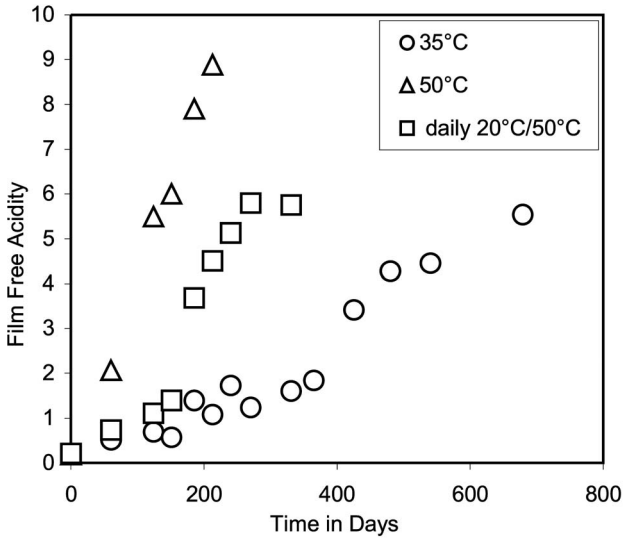

Figure 9. Effect of cycling temperature on CTA film base stability at constant moisture content. Film in 100 ft. rolls incubated inside sealed metal cans. Film initially conditioned to 21 °C, 50% RH. Film free acidity expressed in ml 0.1N NaOH/g of film.

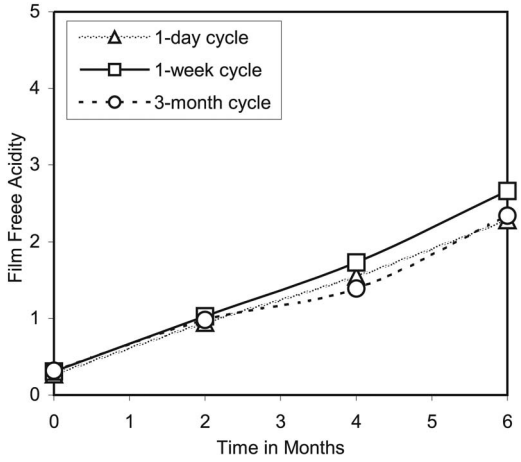

Figure 10. Effect of cycling temperature on CTA film stability. Film exposed to temperature changes between 20 and 50 °C with various frequencies. Film was initially moisture preconditioned to 21 °C, 50% RH and incubated in sealed metal cans. Film free acidity expressed in ml 0.1N NaOH/g of film.

posed to several temperature cycles. Three series of predegraded 100 ft. film rolls were moisture conditioned to 21 °C, 50% RH, enclosed in sealed metal cans, and then incubated for 6 months under temperatures cycling between 20 and 50 °C. Three cycle times were used: 1 day, 1 week, and 3 months. After 6 months, the effects of 180 1-day cycles, 24 1-week cycles, and two 3-month cycles were compared with respect to their impact on CTA film base stability at constant moisture content. Figure 10 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.

Discussion

The results of the experiments comparing the effects of cycling temperature and RH and the effects of steady temperature/RH do not support 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 under humidity that cycled between 40% and 70% RH was slower than 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 and 50 °C was slower than that 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 situation 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 sets of data, that neither cycling RH nor cycling temperature appeared to be inherently detrimental to CTA film base stability.

These data do not invalidate the principle that forms the basis of prediction models like TWPI. The fact that the rate of film decay was faster under cycling temperature than at steady 35 °C, the midrange 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. 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 1 day, 1 week, and 3 months indicated that decay rate is unaffected by the number of cycles within a given period of time. This suggests that the rate of decay 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 and 50 °C over a period of 6 months produced no noticeable differences in the rates of degradation; free acidity increased at the same rate for all three sample series (see Fig. 10). The total time spent at 20 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 reinforces 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. Data obtained under natural-aging conditions on CTA-base photographic film are consistent with earlier predictions based upon accelerated-aging studies. These latest data underscore the effectiveness of cold-temperature storage for stabilizing CTA film that has already started to decay and

foroptimizing film base stability overall. The second objective of this paper was to investigate the possibility that temperature and humidity transitions might cause extra chemical decay in CTA 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. These data validate the TWPI model, with which the changing conditions in real-life storage environments can be analyzed to reach an overall estimate of the chemical decay rate in 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.

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REFERENCES

[1] J. M. Reilly, *IPI Storage Guide for Acetate Film* (Image Permanence Institute, Rochester Institute of Technology, Rochester, NY, 1993).
[2] J. M. Reilly, *Storage Guide for Color Photographic Materials* (University of the State of New York, New York State Library, Albany, NY, 1998).
[3] P. Z. Adelstein, *IPI Media Storage Quick Reference* (Image Permanence Institute, Rochester Institute of Technology, Rochester, NY, 2004).
[4] P. Z. Adelstein, J. M. Reilly, and F. G. Emmings, "Stability of photographic film: Part VI—Long-term aging studies," SMPTE J. **111**, 136–143 (2002).
[5] J. R. Hill and C. G. Weber, "Stability of motion picture films as determined by accelerated aging," J. SMPE **27**, 677–690 (1936).
[6] S. Arrhenius, "Über die Reaktionsgeschwindigkeit beider Inversion von Rohrzucker durch Säuren," Z. Phys. Chem. **4**, 226–248 (1889).
[7] P. Z. Adelstein, C. L. Graham, and L. E. West, "Preservation of motion-picture color films having permanent value," J. SMPTE **79**, 1011–1018 (1970).
[8] P. Z. Adelstein, J. M. Reilly, D. W. Nishimura, and C. J. Erbland, "Stability of cellulose ester base photographic film: Part IV—Behavior of nitrate base film," SMPTE J. **104**, 359–369 (1995).
[9] P. Z. Adelstein, "Optimizing nitrate film storage," *Preserve Then Show* (Danish Film Institute, Copenhagen, 2000, 52–66.
[10] A. T. Ram and J. L. McCrea, "Stability of processed cellulose ester photographic films," SMPTE J. **97**, 474–483 (1988).
[11] A. T. Ram, S. Masaryk-Morris, D. Kopperl, and R. W. Bauer, "Simulated aging of processed cellulose triacetate motion picture films, J. Imaging Sci. Technol. **36**, 21–28 (1992).
[12] P. Z. Adelstein, J. M. Reilly, D. W. Nishimura, and C. J. Erbland, "Stability of cellulose ester base photographic film: Part I—Laboratory testing procedures, SMPTE J. **101**, 336–346 (1992).
[13] P. Z. Adelstein, J. M. Reilly, D. W. Nishimura, and C. J. Erbland, "Stability of cellulose ester base photographic film: Part III—Measurement of film degradation," SMPTE J. **104**, 281–291 (1995).
[14] P. Z. Adelstein, J. M. Reilly, D. W. Nishimura, and C. J. Erbland, "Stability of cellulose ester base photographic film: Part II—Practical storage considerations, SMPTE J. **101**, 347–353 (1992).
[15] P. Z. Adelstein, J. M. Reilly, D. W. Nishimura, C. J. Erbland, and J.-L. Bigourdan, "Stability of cellulose ester base photographic film: Part V—Recent findings," SMPTE J. **104**, 439–447 (1995).
[16] P. Z. Adelstein and J. L. McCrea, "Stability of processed polyester base photographic films," J. Appl. Photogr. Eng. **7**, 160–167 (1981).
[17] M. Edge, M. Mohammadian, M. Hayes, and N. S. Allen, "Aspects of polyester degradation: Motion picture film and videotape materials," J. Imaging Sci. Technol. **36**, 13–20 (1992).
[18] R. J. Tuite, "Image stability in color photography," J. Appl. Photogr. Eng. **5**, 200–207 (1979).
[19] B. Lavedrine, C. Trannois, and F. Flieder, "Etude expérimentale de la stabilité dans l'obscurité de dix films cinématographiques couleurs," Studies in Conservation **31**, 171–174 (1986).
[20] J. M. Reilly, "Accelerated aging tests," *Research Techniques in Photographic Conservation* (Danish Film Institute, Copenhagen, 1995) 77–84 1996.
[21] ISO 18924-2000, *Imaging Materials—Test Method for Arrhenius-type Predictions* (International Organization for Standardization, Geneva, Switzerland, 2000).
[22] J.-L. Bigourdan, P. Z. Adelstein, and J. M. Reilly, "Use of microenvironments for the preservation of cellulose triacetate photographic film," J. Imaging Sci. Technol. **42**, 155–162 (1998).
[23] J.-L. Bigourdan and J. M. Reilly, "Effectiveness of storage conditions in controlling the vinegar syndrome: Preservation strategies for acetate base motion-picture film collections," *Proc. JTS*, (2000), pp. 14–34.
[24] www.imagepermanenceinstitute.org/sub_pages/8page9.htm.
[25] P. Z. Adelstein, J. M. Reilly, D. W. Nishimura, and C. J. Erbland, "Stability of cellulose ester base photographic film: Part III—Measurement of film degradation," SMPTE J. **104**, 281–291 (1995).
[26] J.-L. Bigourdan, P. Z. Adelstein, and J. M. Reilly, "Moisture and temperature equilibration: Behavior and practical significance in photographic film preservation," Proc. ARSAG 154–164 (1997).
[27] J. M. Reilly, D. W. Nishimura, and E. Zinn, *New Tools for Preservation: Assessing Long-Term Environmental Effects on Library and Archives Collections* (The Commission on Preservation and Access, Washington, DC, 1995).
[28] C. Shahani, F. Hengemihle, and N. Weberg, "The effect of variations in relative humidity on the accelerated aging of paper, Historic Textile and Paper Materials II," *ACS Symposium Series*, Vol. 410, edited by, S. Zeronian and H. Needles, (American Chemical Society, Washington, DC, 1989, pp. 63–80.
[29] J. Hofenk de Graaff, "Research into the cause of browning of paper mounted in mats," *Contributions of the Central Research Laboratory to the Field of Conservation and Restoration*, Central Research Laboratory for Objects of Art and Science, Amsterdam, Netherlands (1994), pp. 21–42.
[30] J.-L. Bigourdan and J. M. Reilly, "Effects of fluctuating environments on paper materials—Stability and practical significance for preservation," Proc. ARSAG 180–192 (2002).
[31] J.-L. Bigourdan and J. M. Reilly, "Environment and enclosures in film preservation," Final Report to the Office of Preservation, National Endowment for the Humanities, Grant No. PS 20802-94 (Sept. 15, 1997).