Paper published in *Journal of Imaging Science and Technology*, Vol. 42, No. 2 (March/April 1998): 59-66.

# Use of Micro-Environments for the Preservation of Cellulose Triacetate Photographic Film\*

Jean-Louis Bigourdan, Peter Z. Adelstein and James M. Reilly
Image Permanence Institute, Rochester Institute of Technology
Frank Gannett Memorial Building
70 Lomb Memorial Drive
Rochester, New York 14623-5604

<sup>\*</sup> Presented at the IS & T 50<sup>th</sup> Annual Conference, Boston, MA, on May 19<sup>th</sup>, 1997.

## **Abstract**

Film archivists have the option of storing film in a climate controlled macro-environment or in a micro-environment. This paper evaluates the effectiveness of the latter to control the stability of cellulose triacetate base film in roll form. It does not consider other factors such as equipment cost, maintenance, labor expense and accessibility. The use of vented cans to reduce the acidity of degraded film was not effective in controlling "vinegar syndrome." The addition of buffered cardboard disks to adsorb acid is not recommended. Micro-environments in which the film was previously moisture conditioned to a low relative humidity, or else the addition of desiccants such as molecular sieves or silica gel did retard further degradation. The improvement obtained with molecular sieves and silica gel was due to both their moisture adsorbing and acid adsorbing properties. However, neither material was effective at reducing the acid level of already degraded film. Macro-environments have the potential to be of much greater benefit for film stability than the micro-environments evaluated in this paper. Micro-environments are of great value when it is not possible to obtain humidity control of the storage area.

## Introduction

This study investigates the impact of enclosures and various micro-environmental alternatives to macro-environment control in minimizing degradation of acetate film base. This three-year research project was funded by the National Endowment of Humanities, Division of Preservation and Access. Micro-environment situations that were evaluated include specific enclosure designs, the use of silica gel or molecular sieves and moisture conditioning of film rolls in sealed containers.

# **Background**

In the nineteen-thirties the increasing use of photographic film for archival records and the expanding entertainment industry stimulated interest in the issue of permanence. Cellulose triacetate film base, first introduced almost fifty years ago marked a major advance over nitrate because of its lower flammability. However, more recently its own rather poor chemical stability has become a preservation challenge for the film archivist. The importance of chemical stability prompted early comparative study of nitrate and acetate film supports using accelerated aging. Over the years a predictive approach was developed during further studies of the stability of cellulose triacetate (CTA) and polyethylene terephtalate (PET). 6-8

During the past decade, the recognized chemical instability of CTA film base prompted numerous investigations. These studies focused on the impact of either intrinsic factors (e.g., composition and nature of the plastic) or extrinsic factors (e.g., climate conditions, enclosures).

Among the various intrinsic factors, the contribution of the components of the photographic film such as the gelatin emulsion, the subbing layer (containing traces of cellulose nitrate) and the use of plasticizers in the base composition have been addressed in several papers. The degradation mechanisms of CTA film base were reviewed and the importance of the acid-catalyzed hydrolytic mechanism was emphasized. <sup>9, 11, 14-16</sup>

These contributions added greatly to our understanding of film preservation, but they did not address the control of extrinsic factors to extend film life. Subsequent large-scale studies quantified the relationship between climate conditions (i.e., temperature and relative humidity) and chemical stability of cellulose acetate base.<sup>8, 17</sup> These findings suggested two basic preservation strategies. The first reduces the rate of the chemical decay by controlling temperature and relative humidity.<sup>18</sup> The second is based upon the removal of the reaction catalyst (i.e., acetic acid). It must be recognized, however, that the latter is only relevant once the degradation process has already started.

In practical terms, these two routes may be implemented either by controlling the macro-environment or by creating a favorable micro-climate. The micro-environment principle is based on the fact that at constant temperature, the permanence of photographic film depends in large measure on the nature of the air immediately surrounding it. Both options require the control of temperature, but the implementation of a moisture controlled micro-environment might replace costly dehumidification equipment. Removal of the acid catalyst by an acid-scavenger inside a sealed film can might be more effective than macro-climate measures which benefit the overall storage areas such as increased ventilation and acid vapor adsorption (e.g., using activated charcoal filters). Theoretically by using sealed containers in conjunction with

moisture/acid adsorbing materials, or by selecting appropriate enclosures, the shelf-life of acetate film base might be significantly extended.

Several micro-environmental approaches have been suggested. Over fifty years ago the use of desiccants (e.g., activated silica gel) to control the moisture content of non-processed photographic film was investigated. Although never widely used, this was recommended as a preservation practice for motion-picture film and procedural guidelines were provided to film archivists. In 1981, the Swedish Film Institute proposed a conditioning apparatus (FICA system) which combined the merits of establishing a low moisture content in the film with cold storage temperature. This was accomplished by freezing the film after it was vacuum-sealed in moisture-proof packaging. In 1993, Eastman Kodak Co. introduced the use of molecular sieves as an aid to control the so called "vinegar syndrome". Although the interest in such crystalline molecular "cages" using natural or synthetic compounds to selectively adsorb gaseous components goes back to the nineteen-sixties, their ability to trap moisture and acetic acid vapor from cellulose triacetate film base prompted a renewed interest in micro-environmental approaches for film preservation.

While the merits of low temperature and dry conditions have been clearly identified and assessed, were few studies have investigated the role of micro-environment alternatives to control acetate film stability. The considerations for enclosure design have been based either on common sense (open system should promote acid removal from the film) or upon experimental data obtained under exaggerated situations. For instance, the harmful effect of acid-trapping was documented by measuring the degradation rate of free hung film samples compared to samples kept in the worst situation—i.e., samples in vapor-proof packaging. However, these data did not quantify the improvement that might be obtained under various real-life storage situations.

The main thrust of this paper is to evaluate various micro-climate situations for roll films including several alternative enclosure choices, the use of additional materials inside sealed containers (i.e., molecular sieves, silica gel, buffered cardboard) and moisture pre-conditioning prior to sealing the film in a micro-environment. This paper presents the experimental procedure, results, and the implications for current strategies in acetate film preservation.

# **Experimental**

The experimental approach was aimed at determining effectiveness of various storage configurations in minimizing further degradation of pre-incubated (and partially degraded) CTA film base. Film in roll form was used in order to reflect as closely as possible real-life storage situations. Because moderate temperatures were used (40°C, 35°C and 21°C), the film was brought to the onset of vinegar syndrome prior to the experimentation. This approach had two advantages (1) significant acidity changes could be observed in less than two years even at those moderate temperatures and (2) the initial free acidity in the base presented a situation which could evaluate the effectiveness of acid-scavengers.

# Film sample

Fujicolor Positive Film (Type 8816) on CTA base was used for this study. After standard Eastman Color Print (ECP-2) processing, the film was first pre-degraded in order to bring the material to the onset of vinegar syndrome. This was achieved by

incubating 1000-ft. rolls in heat-sealed aluminum foil bags for a pre-determined period at 90°C 50% RH. Subsequently, 100-ft. rolls of this pre-degraded film were prepared as sample units for subsequent studies.

#### **Enclosures**

The impact of various enclosures was studied by placing 100-ft. pre-degraded film rolls in one of the five following containers: buffered cardboard box, untaped metal can, metal can without lid, untaped plastic microfilm box and a drilled plastic microfilm box.

## **Micro-environments**

These were obtained by the use of sealed metal cans. Three basic approaches have been tested: (1) moisture control by use of a desiccant or by moisture pre-conditioning, (2) acid removal by the addition of an acid-scavenger and (3) acid neutralization by the introduction of cardboard containing calcium carbonate buffering. These three mechanisms may be additive in some situations.

Silica gel Grade 43 (14-20 mesh) with color indicator was used for its moisture adsorption property. Prior to use, individual packets of silica gel were re-activated in a dry oven at 110°C for 24 hours. Molecular sieves (zeolites) provided by Eastman Kodak Co. have the property to adsorb both moisture and acetic acid vapors. This feature of a carefully chosen type of zeolites [Ram 1994] has been reported to minimize further deterioration of acetate film base which is catalyzed by the acidic byproducts. Cardboard disks containing 5% by weight of calcium carbonate (and some also containing zeolites) were included in order to evaluate the contribution of a common buffer in neutralizing the generated acid vapors. This aspect was also explored in a parallel study on acetate base sheet films.<sup>4</sup>

#### Measurements

The chemical decay of the film was determined by measurement of film acidity. Early studies showed that the free acidity is the most sensitive indicator of acetate degradation. A method based on water-leaching was exclusively used during this study. Duplicate determinations were made on three locations along the length of the 100-ft. roll (10, 50, 90 ft.). Separate film rolls were used for each pull time. When appropriate, analysis was augmented by monitoring the moisture content (for film and desiccant) using a gravimetric approach.

## **Results**

#### **Acid diffusion rate**

Fundamental to the control of vinegar syndrome by means of catalyst removal is the rate of acid diffusion from the degrading film to the surrounding environment. In an earlier study, cellulose acetate butyrate sheet films were incubated at 50°C 50% RH in contact with interleaving non-buffered paper. After one year, it was found that less than 20% of the acid generated in the base had migrated into the adjacent paper-receptor. These data suggested a slow acid-diffusion rate compared to the degradation rate, even when the contact area between the sheet film and paper receptor was optimized and the temperature was elevated.

Film rolls have a less advantageous situation than sheet film. The exposed area of the film is physically limited by the shape of the roll. Figure 1 illustrates the impact of film configuration on the acidity-loss when degraded CTA film was exposed at 21°C 50% RH. The film was pre-degraded to an acidity level of 0.4 (ml NaOH 0.1M/gram of film) prior to exposure in two distinct formats—i.e., in strips and in 100-ft. roll. The acid diffusion rate was significantly slower for the film roll compared to the strips. After three months at 21°C 50% RH, the acidity level remained the same in the roll whereas a significant decrease was observed for the strips. These data prompted two conclusions:

- 1. Diffusion of acid from the film must occur first in order to realize benefit from vented enclosure designs or acid adsorption effects provided by an enclosure.
- 2. Because the acid diffusion from a roll is so slow, the effectiveness of ventilation or acid adsorption depends upon the rates of both acid generation and acid diffusion. It is important that the experimental conditions produce the same relative rates between these two processes as are found under practical conditions. For this reason, it is possible that high temperature incubation may lead to suspect conclusions. Consequently, the incubation temperature should be as low as possible and therefore temperatures between 21°C and 40°C were chosen in this study.

# Effect of enclosure design

This part of the study compared the behavior of different enclosure materials (tinplated iron, polypropylene, buffered cardboard) and design. Figure 2 illustrates the acidity of 100-ft. film rolls kept in various enclosures after eight months at 40°C 50% RH. A significant acidity increase over the initial acidity level (0.1-0.2) was observed for the tightest sealed enclosure (i.e., untaped plastic box) whereas the buffered cardboard box displayed the lowest acidity level. This can be attributed to the porosity of the cardboard, allowing acid escape. In this case, as for the can without a lid, it seems that the "ventilation effect" reduces the acidity levels at 40°C. It also seems that tighter enclosures lead to higher acidity levels. These observations are consistent with previous analysis, however, further monitoring is still in progress. It is not known if the "ventilation effect" improvement is significant at room temperature because a higher temperature (40°C) promotes a greater acid diffusion from the film than would exist under normal conditions.

At 21°C, the same experimental configurations did not display significant differences after two years of monitoring (see Table I). This study is continuing.

## Effect of cardboard addition to micro-environments

Pre-degraded 100-ft. film rolls were first conditioned to 21°C 50% RH prior to incubation at 40°C in sealed metal cans with (1) cardboard containing 5 wt % calcium carbonate, (2) cardboard containing calcium carbonate and zeolites and (3) molecular sieves. Figure 3 illustrates the benefit obtained using 5 wt % molecular sieves, whereas both types of cardboard caused a significant *increase* of film acidity. This behavior is explained by the fact that molecular sieves adsorbed moisture, but the cardboard disks introduced extra moisture into the sealed can. The latter detrimental effect has been documented in an earlier study. It is interesting that the same buffered cardboard (5% CaCO<sub>3</sub>) used either as an enclosure material or as additional disks inside the sealed film

container lead to opposite behaviors. In the former case the "ventilation effect" dominated and in the latter it was the increased moisture.

The benefit obtained with 5 wt % molecular sieves encouraged further study on this micro-environment option.

# Effect of molecular sieves, silica gel and moisture pre-conditioning

Seven different micro-environments were subsequently investigated. They correspond to three alternative approaches: (1) moisture control and acid adsorption by using molecular sieves, (2) moisture control by the addition of activated silica gel and (3) moisture control by moisture pre-conditioning at low RH.

The 100-ft. film rolls were first conditioned to 21°C 50% RH prior to being sealed in metal cans. For each adsorbent, two percentages were tested (i.e., 2.5 and 5 wt % of molecular sieves; 1.8 and 3.6 wt % of silica gel). Film rolls were also pre-conditioned to 50, 35 and 20% RH at 21°C prior to being enclosed in sealed cans without additional materials. Separate film rolls were used for each pull time and incubation extended for 18 months at 35°C. The degradation rate was determined by monitoring the acidity of every roll at three locations for each pull time as previously described.

Figure 4 illustrates the effect of the various micro-environments on the stability of degrading CTA film base. By comparing the acidity changes to the control curve (i.e., film conditioned to 21°C 50% RH incubated without adsorbent) one can evaluate the relative benefit of each configuration. Film conditioned to a lower RH than 50%, or stored in presence of silica gel and molecular sieves displayed an improved stability to various degrees.

Increasing the percentage of molecular sieves (from 2.5 to 5 wt %) had a marked impact. The same behavior was observed with silica gel. It is also of interest that two basically distinct options (i.e., pre-conditioning to 21°C 20% RH, and addition of 5 wt % of molecular sieves) lead to a similar stability improvement. Neither configuration displayed any significant acidity increase. However, the beneficial mechanisms involved are different. The moisture pre-conditioning procedure reduced only the percent moisture content of the film. Molecular sieves altered the micro-environment by adsorbing both moisture and acid vapors.

## Mechanisms involved in micro-environments

To understand the relative importance of moisture level and acid adsorption on reducing the acidity level, the percent equilibrium moisture content (%EMC) of the photographic film was determined gravimetrically. A 100-ft. film roll was conditioned successively to different relative humidities at 21°C and the weight increase over film that was oven-dried was plotted as a function of relative humidity. The resulting moisture equilibrium curve (see Figure 5) was then used to determine the equivalent equilibrium RH of each experiment discussed in the previous section. This was accomplished by measuring the weight of moisture extracted from film rolls at 21°C 50% RH which had been conditioned inside sealed cans with the same levels of each desiccant. Figure 6 reports the weight loss for rolls that were conditioned with these desiccants over a five-month period. Moisture equilibrium was reached in less than one month and the magnitude of the weight loss depended on both the nature and percentages of the desiccant. Based upon these weight losses (in Figure 6), the weight percent moisture was

calculated. These values were then translated into an estimated equilibrium RH for each desiccant experiment using the moisture equilibrium curve of Figure 5. For example, 2.5 and 5 wt % of molecular sieves resulted in respectively 40-45% and 30-35% equilibrium RH for the film. The equilibrium RH estimation was confirmed experimentally by using a temperature/relative humidity sensor inserted into the film can.

Based upon the above approach, the acidity levels reached after several incubation times were plotted against the equilibrium RH of the film. Figures 7 and 8 illustrate the results after 12 and 18 months incubation at 35°C. The line identified as "without additional material" shows the beneficial effect of only lowering the humidity (the data being obtained from Figure 4). The impact of acid adsorption is determined by comparing the acidity level obtained by the bars representing the different weight percent desiccant to the acidity obtained without additional material.

Based on Figures 7 and 8, it would appear that the advantages of molecular sieves and activated silica gel result from both moisture and acid adsorption. However, it must be recognized that this experiment was made at 35°C, which is considerably higher than room conditions. For this reason, the same experimental approach was repeated at 21°C. This temperature reflects practical conditions. However, it has the disadvantage that the acidity changes are small over the same period of time.

The separate film rolls used for each pull time had been pre-incubated to an acidity level of approximately 0.4. However, since the initial acidity levels were not absolutely identical and the changes observed were small, all acidity values were corrected for the initial level determined on the same film roll prior to incubation. The acidity increase over the initial stages of degradation is sufficiently linear with time to justify this correction. Consequently, the data reported in Table II are the acidity changes and cover a 20-month period of storage at 21°C. The film rolls pre-conditioned to 35 and 50% RH then sealed without additional material showed a consistent acidity increase. A similar trend was observed for the film stored with 1.8 wt % of silica gel although the differences were rather small. Film rolls pre-conditioned to 21°C 20% RH and stored with 3.6 wt % silica gel or 2.5 and 5 wt % molecular sieves remained at their initial acidity level. By comparison to the 50% RH control, the merit of molecular sieves and moisture preconditioning to 20% RH may be significant in postponing further degradation of the film. In other words, these levels of silica gel and molecular sieves appear to be effective in retarding further degradation, comparable to moisture conditioning at 20% RH. However, these data also indicated that acid-scavengers did not have a significant impact in lowering the acidity of the pre-incubated and slightly degraded CTA film. This latter observation casts some doubt regarding the effectiveness of molecular sieves for curative purposes. The experiment at 21°C is continuing.

# Curative applications for acid adsorbers

While the previous experiment indicated that acid adsorbers offer advantages in retarding further base degradation, they do not lower the acidity of already degraded film to an acceptable level. To further evaluate possible curative applications, a very seriously degraded film with an acidity level of 1.6 was exposed in a sealed container in the presence of molecular sieves. In this experiment, the diffusion rate was optimized by placing the film on a processing reel which allowed total exposure of both sides. Although this configuration did not reflect the reality of a film roll, it served the purpose

of this experiment. Figure 9 reports the acidity change of 10 grams of pre-degraded film. The addition of 10 wt % molecular sieves produced only a small decrease in acidity even after one year.

The same experimental approach was repeated using a much higher percentage of molecular sieves and activated silica gel, namely 12.5 grams of adsorbent and 10 grams of degraded film inside a sealed can. In addition the "ventilation effect" offered by the film without an enclosure and the impact of a Tyvek packet was also tested. The results are reported in Figure 10 and showed a similar acidity loss when the film was either in the presence of molecular sieves or activated silica gel. This confirmed that silica gel may also play a role as acid-scavenger as indicated by Figures 7 and 8. The greater acidity decrease obtained when the film was stored without a film can was not surprising because a very high surface area was exposed and the film acidity level was very elevated. Under these exaggerated conditions, the molecular sieves and silica gel displayed some acid-trapping capacity, but the acid levels remained relatively high. This suggests that the use of acid-scavengers even in large amounts can not reduce the acidity of degraded CTA film to acceptable levels.

These studies are all consistent and indicate that acid adsorption does not offer a practical method of reducing the acidity of degraded CTA film.

# **Implications to Current Strategies**

#### **Enclosures**

The information gained during this study documented the detrimental effect of tight enclosures. However, an improvement using "vented" enclosures was not observed at 21°C even after two years. This suggests that film enclosure design has only a secondary role compared to the marked effect of temperature and relative humidity in controlling the stability of CTA film base. <sup>18</sup>

## **Micro-environments**

Aside from considerations of equipment cost and power expenses for use of macro-environments and labor costs associated with micro-environments, the archivist must consider the benefit associated with each alternative. The option of using micro-environment featuring molecular sieves, silica gel or moisture pre-conditioning at low RH should be compared to the benefit of the macro-environmental approach. Based on the information obtained at 35°C reported in Figure 4, the effect of 2.5 wt % molecular sieves can be estimated. By choosing an acidity end point of 1, the addition of 2.5 wt % molecular sieves improved the base stability by approximately a factor of two (i.e., from 10 to 20 months). Based upon Arrhenius predictions, only a 5°C decrease at 50% RH should have a similar effect. In the future, additional data may provide a better quantitative assessment of the respective benefit in terms of life expectancy. However, the benefit of low temperature macro-environment storage far exceeds those of micro-environmental storage at room temperature. However, micro-environments are viable options for controlling the moisture content of film in sealed cans as a substitute for dehumidification equipment.

# **Conclusions**

- 1. At 40°C, the detrimental effect of vapor tight enclosures on the stability of cellulose triacetate base film was documented. After two years at 21°C, however, the merit of open enclosures in lowering the acidity of degraded CTA film was not demonstrated.
- 2. The use of buffered cardboard disks in sealed film cans is not recommended based upon its detrimental effect at 40°C.
- 3. Micro-environments creating a lower film moisture content benefit the stability of cellulose triacetate base film. This can be obtained by pre-conditioning the film to 21°C 20% RH or by the addition of molecular sieves or silica gel.
- 4. The acid-adsorption property of 5 wt % molecular sieves made a significant contribution in minimizing further degradation of cellulose triacetate base film at 35°C. This preventive benefit was also observed after 20 months storage at room temperature, comparable to that obtained by lowering the equilibrium RH to 20%.
- 5. Molecular sieves had minimal impact on reducing the acid content of cellulose triacetate base film that had already started to degrade. In such situations, cold storage is recommended until the film can be duplicated.
- 6. The use of micro-environments is highly recommended when it is not possible to control the macro-environment. However, the benefit obtained by micro-environments do not equal those obtained by temperature and humidity control of the storage area.

# Acknowledgments

This investigation was conducted under a grant from the Office of Preservation and Access, National Endowment for the Humanities, with additional support from Fuji Photo Film Co. Ltd. and Eastman Kodak Co..

## References

- 1. J. G. Bradley, Changing Aspects of the Film-Storage Problem, *J. SMPE*, **15**: 301 (1938).
- 2. C. R. Fordyce, Improved Safety Motion Picture Film Support, *J. SMPE*, **51**: 331 (1948).
- 3. D. G. Horvath, *The Acetate Negative Survey: Final Report*, University of Louisville, Louisville, KY, 1987.
- 4. J. L. Bigourdan, P. Z. Adelstein and J. M. Reilly, Acetic Acid and Paper Alkaline Reserve: Assessment of a Practical Situation in Film Preservation, *ICOM-CC*, *11th Triennial Meeting Edinburg*, *Preprints*, **2**: 573 (1996).
- 5. J. R. Hill and C. G. Weber, Stability of Motion Picture Films as Determined by Accelerated Aging, *J. SMPE*, **27**: 677 (1936).
- 6. P. Z. Adelstein and J. L. McCrea, Permanence of Processed Estar Polyester Base Photographic Films, *Photographic Science and Engineering*, **9**: 305 (1965).
- 7. P. Z. Adelstein and J. L. McCrea, Stability of Processed Polyester Base Photographic Films, *Journal of Applied Photographic Engineering*, 7: 160 (1981).
- 8. 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 Journal*, **101**: 347 (1992).
- 9. M. Edge, N. S. Allen, T. S. Jewitt, J. H. Appleyard, and C. V. Horie, The Deterioration Characteristics of Archival Cellulose Triacetate Base Cinematograph Film, *The Journal of Photographic Science*, **36**: 199 (1988).
- 10. 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 Journal*, **101**: 336 (1992).
- 11. A. T. Ram, J. L. McCrea, Stability of Processed Cellulose Ester Photographic Films, *SMPTE Journal*, **97**: 474 (1988).
- 12. N. S. Allen, M. Edge, T. S. Jewitt, J. H. Appleyard, and C. V. Horie, Degradation of Historic Cellulose Triacetate Cinematographic Film: Influence of Various Film Parameters and Prediction of Archival Life, *The Journal of Photographic Science*, **36**: 194 (1988).
- 13. Y. Shinigawa, M. Murayama, and Y. Sakaino, Investigation of the Archival Stability of Cellulose Triacetate Film: Effect of Additives on Cellulose Triacetate Support, *Polymers in Conservation*, Eds. N. S. Allen and al., Royal Society of Chemistry, 1992, p. 138.
- 14. M. Edge, N. S. Allen, T. S. Jewitt, and C. V. Horie, Fundamental Aspects of the Degradation of Cellulose Triacetate Base Cinematograph Film, *Polymer Degradation and Stability*, **25**: 345 (1989).
- 15. A. T. Ram, Archival Preservation of Photographic Films—A Perspective, *Polymer Degradation and Stability*, **29**: 3 (1990).
- 16. N. S. Allen, M. Edge, T. S. Jewitt and C. V. Horie, Degradation and Stabilization of Cellulose Triacetate Base Motion Picture Film, *Journal of Imaging Science and Technology*, **36**: 4 (1992).

- 17. 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 Journal*, **104**: 439 (1995).
- 18. J. M. Reilly, *IPI Storage Guide for Acetate Film*, RIT/Image Permanence Institute, Rochester, NY, 1993.
- 19. C. J. Kunz, and C. E. Ives, The Use of Desiccants with Undeveloped Photographic Film, *J. SMPE*, **46**: 475 (1946).
- 20. Eastman Kodak Publication No. H-23, The Book of Film Care, 1983.
- 21. R. Gooes and H.-E. Bloman, An Inexpensive Method for Preservation and Long-Term Storage of Color Film, *SMPTE Journal*, **92**: 1314 (1983).
- 22. A. T. Ram, D. F. Kopperl, R. C. Sehlin, S. Masaryk-Morris, J. L. Vincent, and P. Miller, The effects and Prevention of the "Vinegar Syndrome," *Journal of Imaging Science and Technology*, **38**: 249 (1994).
- 23. D. W. Breck and J. V. Smith, Molecular Sieves, Scientific American, 200: 85 (1959).
- 24. D. W. Breck, Crystalline Molecular Sieves, *Journal of Chemical Education*, **41**: 678 (1964).
- 25. E. Roland and P. Kleinschmit, Zeolites, *Ullmann's Encyclopedia of Industrial Chemistry*, **A28**: 475 (1996).
- 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 Journal, 104: 281 (1995).

Table I: Free acidity level (in ml NaOH 0.1M/gram of film) of CTA film rolls stored in various containers at 21°C 50% RH; acidity values were determined in duplicate on three locations in the roll (10, 50, 90 ft.)

enclosure and initial acidity range	3 months	6 months	10 months	15 months	20 months	24 months
metal can	0.59	0.66	0.71	0.82	0.63	0.67
0.55-0.65	0.62	0.67	0.69	0.80	0.64	0.63
	0.58	0.67	0.72	0.88	0.66	0.67
metal can w/o a lid	0.36	0.37	0.40	0.46	0.47	0.54
0.35-0.50	0.40	0.42	0.425	0.48	0.50	0.44
	0.40	0.41	0.44	0.45	0.51	0.41
cardboard box	0.43	0.37	0.39	0.42	0.33	0.46
0.35-0.45	0.48	0.48	0.40	0.51	0.46	0.33
	0.48	0.48	0.41	0.46	0.48	0.49
plastic box	0.60	0.52	0.54	0.61	0.67	0.77
0.40-0.60	0.55	0.49	0.55	0.60	0.69	0.64
	0.57	0.48	0.54	0.62	0.67	0.75
roll in drilled	0.55	0.65	0.68	0.77	0.53	0.98
plastic box	0.56	0.65	0.70	0.77	0.83	0.76
0.55-0.65	0.54	0.66	0.71	0.76	0.70	0.90

Table II: Free acidity change (in ml NaOH 0.1M/gram of film) of CTA film rolls stored in sealed cans at 21°C in various micro-environments; acidity values were determined in duplicate on three locations in the roll (10, 50, 90 ft.)

micro-environmental alternatives	3 months	6 months	10 months	15 months	20 months
2.5 wt % molecular	+ 0.02	0	0	+ 0.05	+ 0.09
sieves	+ 0.02	+ 0.05	+ 0.05	+ 0.06	-
	+ 0.01	+ 0.02	+ 0.01	- 0.04	+ 0.10
5 wt % molecular	0	+ 0.02	+ 0.03	+ 0.02	+ 0.01
sieves	- 0.01	+ 0.02	- 0.02	+ 0.01	-
	+ 0.02	+ 0.02	+ 0.02	+ 0.02	+ 0.03
1.8 wt % silica gel	+ 0.01	+ 0.05	+ 0.04	+ 0.07	+ 0.12
	+ 0.01	+0.05	+ 0.06	+ 0.07	-
	+ 0.02	+ 0.04	+ 0.04	+ 0.12	+ 0.15
3.6 wt % silica gel	- 0.01	- 0.04	+ 0.02	+ 0.12	+ 0.03
	- 0.02	- 0.01	+ 0.02	+ 0.02	-
	+ 0.01	- 0.04	0	+ 0.04	+ 0.03
pre-conditioning to	+ 0.03	+ 0.06	+ 0.13	+ 0.16	+ 0.29
21°C 50% RH	+ 0.03	+0.07	+ 0.12	+ 0.15	-
	+0.04	+ 0.07	+ 0.10	+ 0.15	+ 0.37
pre-conditioning to	+ 0.04	+ 0.03	+ 0.07	+ 0.17	+ 0.16
21°C 35% RH	+0.07	+ 0.04	+ 0.08	+ 0.08	-
	+0.05	+ 0.03	+ 0.11	+ 0.14	+ 0.16
pre-conditioning to	0	- 0.01	+ 0.01	+ 0.03	+ 0.02
21°C 20% RH	+ 0.01	+ 0.01	+ 0.01	+ 0.05	-
	+0.07	- 0.01	+ 0.01	+ 0.02	+ 0.03

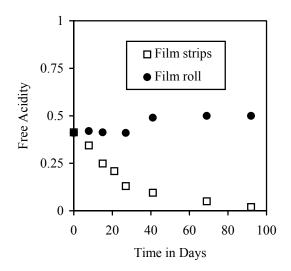


Figure 1: Acidity of degraded CTA film when exposed at 21°C 50% RH in two film formats (i.e., strips and roll).

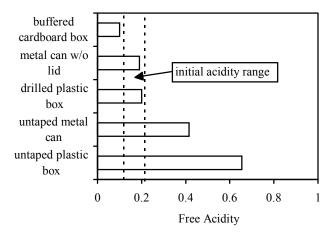


Figure 2: Effect of enclosure designs on the acidity of degraded CTA film rolls determined after 8 months incubation at  $40^{\circ}\text{C}$  50% RH.

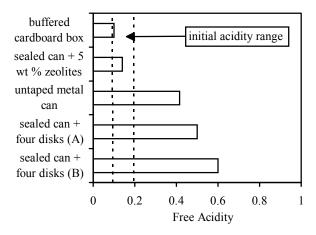


Figure 3: Effect of cardboard disks in sealed cans on the acidity of degraded CTA film rolls after 8 months incubation at  $40^{\circ}$ C 50% RH. Disks (A): cardboard with calcium carbonate and zeolites. Disks (B): cardboard with 5 % alkaline reserve.

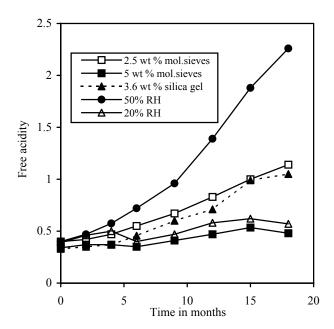


Figure 4: Acidity of 100-ft. CTA film rolls incubated at 35°C in various micro-environmental alternatives.

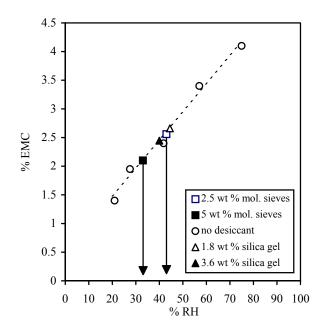


Figure 5: Moisture equilibrium curve for 35mm motion-picture film on CTA base and determination of equilibrium RH obtained by use of molecular sieves and activated silica gel.

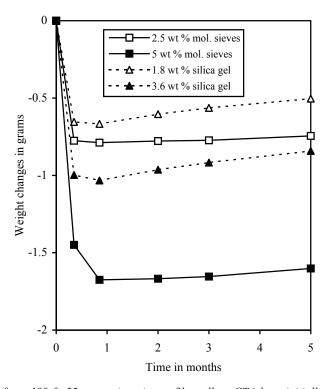


Figure 6: Weight change for a 100-ft. 35mm motion-picture film roll on CTA base initially conditioned to 21°C 50% RH then enclosed in sealed can with desiccants.

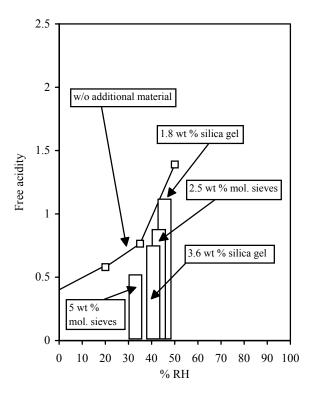


Figure 7: Acidity of CTA film rolls after 12-month incubation at 35°C in sealed cans with various desiccants.

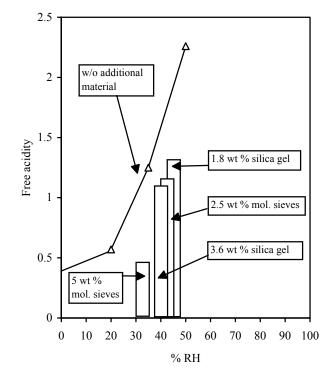


Figure 8: Acidity of CTA film rolls after 18 months' incubation at 35°C in sealed cans with various desiccants.

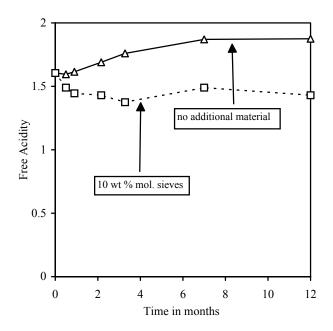


Figure 9: Acidity of degraded CTA film on reel enclosed in a sealed container without and with 10 wt % molecular sieves at 21°C.

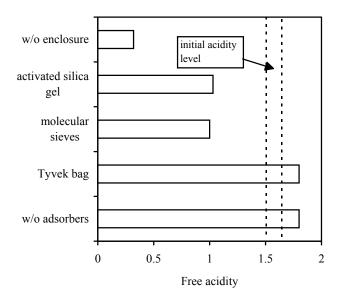


Figure 10: Acidity of 10 grams of degraded CTA film exposed on reel for 2.5 months at 21°C with 12.5 grams of molecular sieves and 12.5 grams of activated silica gel inside sealed cans.