

# *Effectiveness of Storage Conditions in Controlling the Vinegar Syndrome: Preservation Strategies for Acetate Base Motion-Picture Film Collections*

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## *Introduction*

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Since the evolution of the entertainment industry in the nineteen thirties, the recognition of the cultural value of motion-picture films and the increasing use of photographic film as an archival information-recording medium have stimulated interest in film permanence.<sup>1</sup> Despite the fact that major problems were recognized early on, and that extensive knowledge of film stability has been gained during the past two decades, the preservation of moving images on photographic film is still a major concern today.<sup>2,3</sup> The current challenge for the archival community, however, is not to further understand the film degradation process but rather to formulate practical preservation strategies for film collections.

Photographic film is susceptible to various types of degradation which can be grouped into three major categories: physical, biological, and chemical. Since its beginnings, the technology of photographic film has evolved continuously, and much has been learned about film stability. Nevertheless, photographic film continues to be threatened by the spontaneous chemical decay of its major components, most notably the plastic base and color dyes. Consequently, the control of chemical degradation is a vital challenge for film archivists. They periodically face practical dilemmas regarding climate assessment, enclosure choice, and, more recently, the use of either micro- or macroenvironmental control. The decisions they make may impact the useful life span of film collections in significant ways.

There has been evidence of vinegar syndrome in photographic collections around the world for several decades. The recent availability of tools for surveying acetate film collections may lead to an even darker picture of the extent of vinegar syndrome in film archives. Knowing the magnitude of the problem is fundamental to taking the most efficient steps to preserve our film heritage. In addition, several large-scale research programs have been conducted during the last decade, leading to new strategic approaches to film preservation.

The purpose of this paper is threefold. It will report recent findings on the effectiveness of practical storage situations involving the use of microenvironments. It will suggest a preservation approach for film archivists based on the recognized role of storage conditions in controlling film stability. Finally, it will describe the use of a simple survey tool such as acid-detector strips in assessing the extent of vinegar syndrome in acetate base film collections. The ultimate goal is to define the key points involved in the control of chemical decay in film collections. One of the unique features of this investigation is that recommendations are based on studies lasting up to five years at

room temperature. The quality of the storage environment, the state of preservation of acetate film collections, and the required longevity of the film materials are considered to be the major determining factors in implementing a rational preservation strategy.

Background information and data developed at the Image Permanence Institute (IPI) under a research grant entitled *Environment and Enclosures in Film Preservation*<sup>4</sup> funded by the National Endowment for the Humanities are reported. A-D Strips, acid-detector strips designed by IPI as a survey tool for acetate film collections are discussed.

### *Chemical Stability of Acetate Film Base*

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Cellulose triacetate (CTA) film base, first introduced in 1948,<sup>5</sup> marked a major advance over cellulose nitrate film base because of its lower flammability. Although its poor chemical stability was not recognized at the time, it has since become a major threat for film collections. The spontaneous chemical decay of CTA film base leads to the deacetylation and chain scission of the polymer. At or near room temperature conditions, significant acetate degradation may occur within three to four decades, or even less if storage conditions are adverse. Polyester film base, first introduced in 1955<sup>6,7</sup> and increasingly used today, provides a significantly more stable film support.<sup>8,9</sup>

The importance of chemical stability prompted an early comparative study of nitrate and acetate film supports using accelerated aging.<sup>10</sup> Over the years, a predictive approach was developed through further studies of the stability of cellulose acetate film base and polyester film base.<sup>8,9</sup> During the past fifteen years, the recognized chemical instability of CTA film base has prompted a number of investigations worldwide. These studies have focused on the impact of either intrinsic factors (e.g., composition and nature of the plastic) or extrinsic factors (e.g., climate conditions and enclosures). The contribution of such intrinsic factors as gelatin, subbing layer (containing traces of cellulose nitrate), and plasticizers has been addressed in several papers.<sup>11,12,13,14,15,16</sup>

The generation of acid has been identified as the first and most sensitive indicator of acetate degradation.<sup>15</sup> This characteristic has made possible the development of a monitoring method for acetate stability studies<sup>17</sup> and has led to the creation of film collection survey tools such as acid detectors. The literature has discussed the degradation mechanism of CTA film base and has emphasized the importance of the autocatalytic mechanism.<sup>18,19,20</sup> Acetic acid, a byproduct of deacetylation, catalyzes further decay of the polymer. The consequences are illustrated in Figure 1, which reflects the rate of degradation of acetate base. The acidity increase faithfully mirrors the advance of chemical decay. This phenomenon is illustrated by the two portions of the curve: (1) an induction period, and (2) a period of fast change beyond the so-called autocatalytic point. Based on this representation, it can be said that the internal acidity level of the film determines the degree of risk that film will become unusable because of shrinkage, physical deformation, or plasticizer exudation. Subsequent large-scale studies have quantified the relationship between climate conditions—i.e., temperature and relative humidity (RH)—and the chemical stability of cellulose acetate film base.<sup>21,22,23</sup> These findings suggest two basic principles for preserving acetate film base:

1. Proper climate control leads to significant improvement in chemical stability. Lower temperatures and dryer conditions slow the degradation rate.
2. Acetate base film that has already started to degrade decays further at an ever-faster rate. The stabilization of decaying film requires improved climate conditions.
3. The removal of acetic acid vapors, a degradation byproduct, retards further degradation by reducing the autocatalytic effect and also limits the risk of infectious behavior.<sup>23,24</sup>

Fifty years after the introduction of CTA film base, partially degraded film is common in a large number of film archives; therefore, all three of these principles are relevant to the articulation of a film preservation strategy.

### *Climate Control Options*

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#### THE MACROENVIRONMENT

The macroenvironmental approach to film preservation assumes that materials are in equilibrium with the macroclimate. Ambient conditions affect the whole storage area and ultimately control the rate of chemical decay. The relationship between temperature and RH and the rate of chemical decay has been established for both fresh and degrading acetate film base and, more recently, for chromogenic dyes.<sup>22,25</sup> These data sets are of great importance because they provide a quantitative estimate of the impact of a wide range of temperatures, RHs, and their combinations on acetate base and dye stability. In practice, temperature and RH determine the life span of photographic film. Proper control of these two components can greatly improve the chemical stability of acetate base film and color materials. Although the effect of temperature and RH is synergistic, lower temperature provides the greater benefit. These conclusions have been integrated into the ANSI and ISO standard recommendations for storage of photographic film.<sup>26,27</sup> In addition, controlling the air quality in the storage area using adsorbing purification systems minimizes the risk of acid contamination from degrading acetate film.

#### MICROENVIRONMENTS

Enclosures are used to provide physical protection, but, in a sense, they also create “microenvironments” which may have a positive or negative impact on the stability of film base, primarily by either allowing some ventilation or trapping degradation byproducts. It was this fact that led to the design of vented cans in the 1990s. At constant temperature, the permanence of photographic material depends in large measure on the nature of the air immediately surrounding it. Therefore, the creation of controlled microenvironments in sealed enclosures may be a sound alternative for photographic film preservation. Moisture-controlled microclimates may be used in place of dehumidification equipment. Using an acid adsorbent to remove the acid catalyst from inside a sealed film can is another option.

Several microenvironmental approaches have been suggested in the literature, such as the use of desiccants<sup>28,29</sup> and the implementation of the FICA system proposed by the Swedish Film Institute, which combines the merits of establishing a low moisture content in the film with the benefits of cold temperatures.<sup>30</sup> More recently, Eastman Kodak

Company introduced molecular sieves (zeolites) as an aid in controlling vinegar syndrome and dye fading.<sup>31,32</sup> The ability of such crystalline molecular “cages” to trap moisture and acetic acid vapor has prompted a renewed interest in microenvironmental approaches for the preservation of acetate film collections.

#### *Enclosure and Microenvironment Study*

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Only a few studies have investigated the role of enclosures and microenvironmental alternatives. These studies addressed the potential detrimental effects of enclosure materials on acetate degradation.<sup>12</sup> Until now, considerations for enclosure design have been based on common sense (e.g., open housings promote acid vapor removal) or on experimental data obtained in exaggerated situations (e.g., high incubation temperatures or free-hung samples versus samples in sealed bags).<sup>12,13,18,23</sup> In recent years, data have been obtained which clarify the roles of enclosures and microclimates in minimizing further decay of acetate film base in sheet and roll formats.<sup>4,31,33,34,35</sup> Theoretically, enclosures and microclimates can impact on film stability in several different ways, including facilitating ventilation, neutralizing acid, adsorbing acid vapors, and reducing film moisture content. These are summarized in Table I.

The behavior of a variety of enclosures and microenvironments was investigated at IPI. Results have been presented in several reports.<sup>4,34,35</sup> This paper reports additional related data developed at IPI. The following sections describe the experimental procedure.

#### *Experimental*

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##### TEST PROCEDURE

The experimental approach was aimed at quantifying the effectiveness of various housing situations in retarding further degradation of partially degraded CTA film in roll form. The film was brought to the point of onset of vinegar syndrome prior to the experimentation. Given this initial acidity level, it was possible to evaluate the effectiveness of acid ventilation, neutralization, and adsorption provided by a variety of storage configurations.

##### MEASUREMENTS

Since acidity is the most sensitive indicator of acetate decay, the chemical degradation of the film was monitored by measuring film acidity. Film acidity values are expressed as milliliters of 0.1M NaOH. Brand-new film has an acidity value of about 0.05, while severely degraded film can reach 10.0 or more. The water-leaching method was used exclusively in this study.<sup>17</sup> Duplicate determinations were made at three locations along the length of a 100-foot roll (at 10, 50, and 90 feet).

##### ACID DIFFUSION RATE

A high diffusion rate is fundamental to the control of vinegar syndrome by means of catalyst removal. Figure 2 illustrates the impact of film configuration and winding tension on acid diffusion when degraded CTA film was exposed to 21°C, 50% RH. The film was pre-degraded prior to exposure in two formats: 7-inch strips and 100-foot rolls.

Film A was tightly wound. Film B was loosely wound. The acid diffusion rate was significantly slower for the film rolls than for the strips for both Film A and Film B. Film A in roll form did not display significant acidity loss after three months of exposure. During the same period of time, the acid content in the Film B roll decreased; it took almost six months, however, for the acidity to reach the level of 0.1, despite the fact that the film was loosely wound and not in an enclosure. These data indicated that the tension applied during the preparation of the rolls altered the acid diffusion rate. This supports the following observations:

1. The slow rate of acid diffusion might limit the benefit of any housing situation.
2. Since acid diffusion is a limiting factor and is very temperature-dependent, the incubation temperature used for microenvironment studies should be as close as possible to room temperature to reflect real-life situations. For this reason, temperatures between 21°C and 40°C were chosen for the study. The importance of this condition was discussed in an earlier paper.<sup>34</sup>
3. Film rolls used for enclosure and microenvironment studies must be wound at a moderate and constant tension.

#### MICROENVIRONMENTS

Microenvironments were created in sealed metal cans for the purpose of the study. Three basic effects were evaluated: (1) moisture control through use of a desiccant or through moisture pre-conditioning, (2) acid removal through addition of an acid scavenger, and (3) acid neutralization through the introduction of buffered cardboard disks. Activated silica gel grade 43 was used for its moisture adsorption property. Molecular sieves provided by Eastman Kodak Company were used for their ability to adsorb both moisture and acetic acid vapors. Cardboard disks containing calcium carbonate were included to evaluate the way in which buffering contributes to the neutralization of acid vapors.

#### *Results*

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##### EFFECTS OF ENCLOSURES

The impact of various enclosures was studied by placing 100-foot pre-degraded CTA film rolls in several types of housing. The behavior of enclosure materials (tin-plated steel cans, polypropylene boxes, and boxes made from cardboard containing 5 wt % calcium carbonate) and of different system designs (open versus closed or sealed) was studied. Figure 3 illustrates the acidity of 100-foot rolls kept in various enclosures for one year at 40°C, 50% RH. Significant acidity increases were observed inside unsealed metal cans and unsealed plastic microfilm boxes. Open systems (metal cans without lids, drilled plastic boxes, and buffered cardboard boxes) showed lower acidity levels. Previous data indicated that the lower acidity in the cardboard boxes could be attributed to the porosity of the material rather than to the alkaline buffer in the cardboard.<sup>34</sup> These results demonstrate that tight enclosures have a greater detrimental effect than open ones. However, it was not known if the “ventilation effect” would have a significant role at lower temperatures. This was investigated in a repeat experiment conducted at room temperature for three years.

Figure 4 reports acidity changes in pre-degraded 100-foot film rolls kept at 21°C in various enclosures. Because acidity increase is small at this temperature, each acidity level was corrected by subtracting the initial acidity value of the individual rolls. There was a significant acidity increase inside sealed containers (taped metal cans and taped plastic boxes), while open systems (metal cans without lids, cardboard boxes) showed lower acidity levels. Drilled plastic boxes minimized acidity increase in the film, though to a smaller degree than the open systems. These data confirm the detrimental effect of sealed containers at room temperature. It should be noted that open enclosures did not *lower* the acid content of partially degraded film after three years of storage. These results prompted several observations:

1. Tight enclosures have a detrimental effect on the stability of film that has already started to degrade. This behavior was observed in sealed cans, even at room temperature.
2. At 21°C, pre-degraded film stored in sealed metal cans and sealed polypropylene boxes decayed further at a similar rate.
3. Open enclosures did slow further decay but did not lower the acid content of degraded film to acceptable levels after three years of storage. Enclosures do not provide a definitive method for controlling vinegar syndrome but are a secondary factor.
4. Further decay of partially degraded acetate film base occurs at room conditions. Acidity changes achieved in sealed enclosures through natural aging at 21°C agree with earlier predictions based on accelerated aging. This finding increases the degree of confidence in previously published conclusions regarding the relationship between climate conditions and degradation rate.<sup>22</sup>

#### EFFECTS OF MICROENVIRONMENTS

There are four approaches that are based on the possible benefits of microenvironments. They are: (1) moisture control by pre-conditioning the film at a low RH; (2) moisture control through the addition of activated silica gel; (3) moisture control and acid adsorption through the use of zeolites; and (4) acid adsorption and acid neutralization through the use of buffered cardboard disks in sealed containers.

For the study, CTA film in 100-foot rolls was pre-conditioned at 50%, 35%, and 20% RH at 21°C and enclosed in sealed metal cans. Film rolls were also pre-conditioned to 21°C, 50% RH prior to being sealed in metal cans with activated silica gel, molecular sieves, or buffered cardboard disks. The rate of degradation was monitored by acidity determination for each pull time. The film rolls were incubated for three years at 35°C. Another series of rolls have been stored for four and a half years.

#### Study at 35°C

Figure 5 illustrates the effect of moisture pre-conditioning on the stability of degrading CTA film. Comparison of the acidity changes curve with the control curve (i.e., film conditioned to 21°C, 50% RH) shows the marked benefit of low RH pre-conditioning. Figure 6 illustrates the benefit obtained by the addition of activated silica gel (3.6 wt %) and zeolites (2.5 and 5 wt %—approximately the recommended level and twice the recommended level, respectively). Both materials benefited film stability at 35°C. Increasing the percentage of zeolites had a marked impact.

It is of particular interest that two distinct approaches—moisture pre-conditioning at 21°C, 20% RH and addition of 5 wt % zeolites—lead to a similar degree of stability improvement. The moisture pre-conditioning procedure reduces only the moisture content of the film; molecular sieves act as both desiccant and acid scavenger. The benefits of these two mechanisms have been previously assessed and discussed.<sup>34</sup> Zeolites alter the rate of acetate degradation by adsorbing both moisture and acid vapors. The moisture adsorption property of zeolites is recognized as the main factor in retarding further chemical decay of the acetate base.

### Study at 21°C

Repeat experimentation at room temperature confirmed that storing film with zeolites, with activated silica gel, or after low RH pre-conditioning retards further chemical decay. Figure 7 reports data obtained at room temperature using zeolites or activated silica gel in sealed cans. Using either zeolites or silica gel retarded further decay of the film. Increasing the percentage of adsorbents increased the benefits. Pre-degraded film rolls stored with 5 wt % zeolites did not display any acidity increase, while the acidity of pre-degraded film stored without adsorbents displayed more than twice the initial acidity level after the same period. It should be noted, however, that the use of zeolites did not reduce the initial acid content in film. Figure 8 indicates the beneficial effect of low moisture pre-conditioning observed at room temperature. These results confirmed previous data obtained at 35°C (Figure 5).

The use of cardboard disks (containing calcium carbonate or calcium carbonate and zeolites) was also investigated. Previously reported data obtained at 40°C indicated a detrimental effect caused by the introduction of additional moisture into the container by the cardboard disks.<sup>34</sup> Repeat experimentation conducted at room temperature using buffered cardboard disks in sealed cans did not support any significant benefit to film stability (Figure 9). Therefore, the use of cardboard disks is not recommended.

Data obtained at room temperature (Figures 4, 7, and 8) indicated that controlled sealed microclimates using either 5 wt % molecular sieves or moisture pre-conditioning at 21°C, 20% RH are slightly more beneficial than open enclosures at 21°C 50% RH.

### COMPARISON OF MICROCLIMATES TO MACROCLIMATES

Archivists must consider the relative merits of the macroenvironment approach versus the microenvironment approach. The former has equipment and operating costs, while the latter involves significant material and labor costs.

Based on the information obtained at 35°C shown in Figures 5 and 6, the respective merits of various microclimates can be quantified. Once film reaches the autocatalytic stage of vinegar syndrome (an acidity level of 0.5 or higher), the rate of chemical decay is significantly faster. As a result, film may become unusable within a short period of time. For this reason, an acidity level of 1.0 has been chosen as a relevant end point. However, previous studies have indicated that even at this stage of decay the physical properties of the acetate film base were not significantly altered. Film is still usable for a period of time that is ultimately dependent on the storage conditions. Table II reports, for each microenvironment investigated, the time required for an initially pre-degraded CTA film to double its acid content (an increase from 0.5 to 1). At 35°C, microclimates created by

using 5 wt % molecular sieves or by moisture pre-conditioning at 21°C, 20% RH increase the life of the film by a factor of 3 to 3.5 as compared to the control film pre-conditioned at 21°C, 50% RH.

An earlier study quantified the benefits of macroclimate control on film stability, based on data obtained under accelerated conditions and using the Arrhenius method.<sup>21</sup> Table III reports a few of the predictions taken from that study, the results of which were published in the *IPI Storage Guide for Acetate Film*.<sup>22</sup> These data indicate the factor of improvement obtained by lowering the temperature, lowering the RH, or lowering both parameters. The comparison of the effects achievable using either microclimate or macroclimate options led to the following conclusions:

1. The earlier Arrhenius study predicted that an improvement factor of 3 can be gained by lowering the RH from 50% to 20% at 35°C. More recent data verified that pre-conditioning the film at 20% RH leads to a similar improvement in film stability. This increases the degree of confidence in earlier predictions.
2. The improvements that can be achieved with microenvironments can also be achieved by lowering the temperature and/or lowering the RH. (As the experiments showed, there are three ways to increase the film stability by a factor of 3: addition of 5 wt % zeolites, lowering the RH from 50% to 20%, or lowering the temperature from 35° to 25°C.)
3. Microenvironments created by using adsorbents or moisture pre-conditioning can provide a benefit of the same magnitude as that provided by low macroenvironmental RH. The benefit provided by microclimates, like that of low RH, is added to the benefit gained from storage at low temperatures.
4. Most importantly, the benefit of low-temperature storage far exceeds that of either microenvironments or low macroenvironmental RH. Table III illustrates the great potential improvement provided by cold temperature.

### *Preservation Strategies*

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The data reported above indicate that open enclosures or sealed microenvironments alone are of less benefit than the macroenvironmental approach using low temperatures. Therefore, the priorities for photographic film storage are clearly defined. Colder temperatures and low RH have been consistently recommended. Almost thirty years after the pioneering paper by P. Z. Adelstein, et al.,<sup>36</sup> recent film stability studies have reinforced the need for cold storage for long-term preservation. Long-term preservation of both new and old film materials requires a climate that is colder than room temperature. This is even more critical if the film is already beginning to degrade.

### MONITORING THE EXTENT OF VINEGAR SYNDROME

The potential benefits of the microenvironmental and macroenvironmental approaches discussed in the previous sections depend upon the current condition of the film. A film in an advanced state of decay, i.e., with an acidity level beyond the autocatalytic point (see Figure 1), requires better storage conditions than a non-degraded film to have the same given life span. As degradation progresses, the rate of chemical decay increases, and better storage is needed to further postpone the time at which the material becomes

unusable. In addition, contamination of non-degraded film by degradation byproducts (e.g., acetic acid vapors) has been demonstrated in earlier studies.<sup>23,24</sup> This phenomenon has prompted recommendations for either segregation of degrading acetate base film or removal of degradation byproducts in order to avoid contamination. These behaviors emphasize the importance of evaluating the current film condition prior to implementing a preservation plan.

In practice, several actions may be undertaken to extend the life span of degrading acetate base film and to minimize the risk of contamination. Improvement of the macroclimate conditions, segregation of degrading films, implementation of microenvironments using adsorbents, control of air quality using an air-filtration system in the storage area, and duplication are among the options available for film preservation management. Therefore, monitoring the extent of vinegar syndrome is essential for recognizing the problem at its early stages and choosing the option that best fits the situation. Knowing the collection's state of preservation makes it possible to bring about suitable improvements in the storage conditions and to prioritize the duplication of films in an advanced state of decay before they become unusable. Continuous monitoring of film collections for signs of vinegar syndrome recently has been recommended by the European Broadcast Union in their document entitled *EBU Technical Recommendation*,<sup>37</sup> which deals with motion-picture film storage conditions.

The generation of acid is the first and most sensitive indicator of acetate base degradation. Acidity determination methods have been extensively used in laboratory research into film stability. Several diagnostic tools for use in film archives have been developed (e.g., Film Decay Detector Sensor®, Dancan's Danchek®, IPI's A-D Strips). These tools employ various acid-base indicators that change color when exposed to acid vapors.<sup>38,39</sup> These monitors vary in response time, color scale, interpretation, and uses. This paper does not compare these products but focuses on the use of A-D Strips.

A-D Strips are paper strips coated with an acid-base indicator (bromocresol green) in combination with sodium hydroxide. In practice, a strip is placed with film in a confined environment (e.g., inside a film can). After exposure, the strip's color shift is evaluated using a color-reference scale. Depending on the film condition, the color of the strip may shift from blue (its original color) to green or yellow. These color changes reflect the acid content of the film, i.e., its state of preservation. The strips are calibrated to differentiate four levels: level 0 (no deterioration or 0 to 0.1 acidity), level 1 (deterioration starting or a level of 0.2 acidity), level 2 (advanced deterioration or level of about 1 acidity), and level 3 (critical state or an acidity level equal or greater than 2). In a study done at IPI, determinations performed by various evaluators indicated that A-D Strip level readings may vary by half a level depending on the color perception of each evaluator. Half-level errors are not large enough to cause an archivist to miss the important landmarks in the progress of film decay nor to draw incorrect conclusions concerning the need for improved storage conditions or film duplication. At room conditions, 24 hours is the recommended minimum exposure time to achieve an accurate evaluation. Exposures of a few days to several weeks can be used when needed. Testing at low temperatures and low RH requires longer exposures prior to evaluation. Tests performed at near-freezing temperatures and low RH have indicated that minimum

exposure for low temperatures should be extended (e.g., two weeks at 2°C). Further recommendations regarding the use of A-D Strips under various climate conditions will be provided in a revised edition of the *User's Guide for A-D Strips*, the instruction booklet that is packaged with the product.

A-D Strips are specifically designed and calibrated to be a semi-quantitative measure of internal film acidity, and therefore they provide a means not only of detecting the vinegar syndrome in its early stages, but also of determining the state of preservation of the film in a collection. Is the film approaching the autocatalytic point? Has it reached that point or passed it? This information is essential for decision-making about how to preserve the film from now on. Prior to the autocatalytic point, the decay rate is slow. Beyond that point, the rate of deterioration increases greatly, and *action* should be taken to ensure a long life for the film. Together, A-D Strips and the *IPI Storage Guide for Acetate Film* supply the information necessary for obtaining a realistic prediction of film life expectancy, namely, the film's current state of decay and the effect of storage conditions on decay rate. It can be determined, for example, that a film roll that has degraded to the autocatalytic point (half way between levels 1 and 2, i.e., an internal acidity of 0.5) might reach an advanced state of decay (level 2) within a few years, if kept at room conditions. Acetate film collections that have already started to decay may still last for a long period of time if stored at optimum environmental conditions. By reducing the storage temperature from room conditions to 4°C at 50% RH, the life span of acetate base film that has already degraded to the autocatalytic point would be extended by a factor of ten. Moreover, films found to be actively degrading may be earmarked for duplication.

There is now hard evidence that decaying films kept at room temperature will continue to decay at an unacceptable rate. Storage at cold temperatures will stabilize these decaying films, as clearly demonstrated by the results reported in Table IV. After five years, the acidity of film kept at room temperature increased by a factor of 2 to 3. During the same period of time, the acidity of film kept at subfreezing temperatures did not display any significant change. This information is of great practical importance.

An item-by-item evaluation using acid-detectors can identify actively degrading films (i.e., from level 2 to level 3). Such materials should be stored in cold or freezing temperatures while awaiting duplication. Depending on the size of the collection, there are three recommended options:

1. For small collections, it may be practical to store actively degrading films in a separate refrigerated space.
2. A portion of a larger collection could be isolated in individual sealed containers with adsorbents and stored at cold temperature.
3. Institutions with large collections may choose to provide cold temperatures and air-quality control to the entire holdings, thus improving the overall quality of the storage environment and minimizing the risk of contamination by removing degradation byproducts from the air.

### *Key Points in Implementing a Preservation Strategy*

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It is well established that preservation of photographic film is much more cost-effective than restoration, and frequently restoration is not possible. The only way to protect film from chemical decay is control of storage conditions. This can be accomplished by control of either the macroenvironment or the microenvironment. A film archivist must decide which approach is the most suitable for the institution, with respect to equipment expenditure, maintenance, accessibility and labor cost.

Macroenvironmental control has much greater potential for stability improvement if low temperatures are employed. Maximum longevity is obtained through the use of cold storage at subfreezing temperatures. This option maximizes the benefit of climate control on film base and chromogenic dye stability. The macroenvironmental approach using low temperatures can extend the useful life of acetate base film by a factor of one hundred even for film that has already started to degrade. This approach is recommended to preserve either old or new film materials.

At room temperature, tight enclosures have a detrimental effect on film stability. However, open enclosures do not significantly reduce the acid content of decaying acetate base film. Enclosures do not provide a definitive method of vinegar syndrome control.

The microenvironmental approach utilizes sealed containers. Using activated silica gel, molecular sieves, or low pre-conditioning RH can extend the longevity of film by a factor of three to four. The benefit provided by microenvironments, like that of low RH, is added to the benefit of storage at low temperatures.

Monitoring the extent of vinegar syndrome throughout the collections is believed to be an essential part of a proactive preservation strategy. Acid-detectors provide a simple way to identify degrading materials and evaluate the state of preservation of acetate film collections. With this information it is possible to estimate the remaining life span of film, and subsequently (1) to determine the required improvement in terms of storage conditions, and (2) to prioritize duplication of film in an advanced state of decay.

Risk of contamination may be addressed either by segregating actively degrading films or by controlling the concentration of acidic vapors in the air. Cold storage is the only alternative for stabilizing actively decaying acetate film base prior to duplication.

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*Table I: Potential functions of unsealed enclosures and microenvironments in sealed cans.*

Functions	Unsealed Enclosures	Microenvironments in Sealed Cans
<b>Reduce moisture content</b>	No effect	Addition of desiccants (zeolites, activated silica gel), or initial moisture pre-conditioning
<b>Facilitate ventilation</b>	Vented enclosures or porous enclosure material	No effect
<b>Neutralize acid</b>	Enclosure material containing alkali fillers (e.g., calcium carbonate)	Addition of cardboard disks containing alkali fillers (e.g., calcium carbonate)
<b>Adsorb acid</b>	Enclosure material containing acid adsorbents (e.g., zeolites)	Addition of acid adsorbents (e.g., zeolites)

*Table II: Approximate time required at 35°C to increase the acidity of 100-foot pre-degraded CTA film rolls from 0.5 to 1 and time factor of improvement for various microenvironments.*

Microenvironments in Sealed Cans	Time (Months)	Time Factor
Film conditioned to 21°C, 50% RH (control sample)	7	1
Film conditioned to 21°C, 35% RH	11.5	1.5
Film conditioned to 21°C, 50% RH with 2.5 wt % molecular sieves	10	1.5
Film conditioned to 21°C, 50% RH with 3.6 wt % activated silica gel	10	1.5
Film conditioned to 21°C, 50% RH with 5 wt % molecular sieves	21	3
Film conditioned to 21°C, 20% RH	25	3.5

*Table III: Benefit of macroenvironmental control. Effect of temperature and relative humidity on further CTA chemical decay from acidity of 0.5 to 1.0. Predictions based on accelerated aging.<sup>22</sup> Approximate time factor of improvement versus temperature and RH.*

Temperature	Time Factor at 50% RH	Time Factor at 20% RH
35°C	1	3
25°C	3	15
15°C	10	45
5°C	45	200
-1°C	110	540

## References

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1. J. G. Bradley, "Changing Aspects of the Film-Storage Problem," *J. SMPE* 15 (1938): 301-317.
2. Report of the Librarian of Congress, *Film Preservation 1993: A Study of the Current State of American Film Preservation*, 1-4 (Washington, DC: The Library of Congress, June 1993).
3. Report of the Librarian of Congress, *Television and Video Preservation 1997: A Study of the Current State of American Television and Video Preservation*, 1-5 (Washington, DC: The Library of Congress, October 1997).
4. 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 # PS 20802-94, September 15, 1997.
5. C. R. Fordyce, "Improved Safety Motion Picture Film Support," *J. SMPE* 51 (1948): 331-350.
6. D. R. White, J. G. Charles, and W. R. Holm, "Polyester Photographic Film Base," *Journal of the SMPTE* 64 (1955): 674-678.
7. C. Weyn, "New Film Supports," *Progress in Photography 1955-1958*, (New York: Focal Press, 1959) 88-90.
8. P. Z. Adelstein and J. L. McCrea, "Permanence of Processed Estar Polyester Base Photographic Films," *Photographic Science and Engineering* 9 (1965): 305-313.
9. P. Z. Adelstein and J. L. McCrea, "Stability of Processed Polyester Base Photographic Films," *Journal of Applied Photographic Engineering* 7 (1981): 160-167.
10. J. R. Hill and C. G. Weber, "Stability of Motion Picture Films as Determined by Accelerated Aging," *J. SMPE* 27 (1936): 677-690.
11. K. A. H. Brems, "The Archival Quality of Film Bases," *SMPTE Journal* 97 (1988): 991-993.
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 (1988): 194-198.
13. 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 (1988): 199-203.
14. A. T. Ram and J. L. McCrea, "Stability of Processed Cellulose Ester Photographic Films," *Journal of SMPTE*, 97 (1988): 474-483.
15. 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 (1992): 336-346.
16. 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*, N. S. Allen, et al., eds. (London: Royal Society of Chemistry, 1992) 138-150.
17. 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 (1995): 281-291.
18. 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 (1989): 345-362.
19. A. T. Ram, "Archival Preservation of Photographic Films—A Perspective," *Polymer Degradation and Stability* 29 (1990): 3-29.
20. 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 (1992): 4-12.
21. 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 (1992): 347-353.
22. J. M. Reilly, *IPI Storage Guide for Acetate Film* (Rochester, NY: Image Permanence Institute, Rochester Institute of Technology, 1993).
23. 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 (1995): 439-447.

24. N. S. Allen, M. Edge, T. S. Jewitt and C. V. Horie, "Initiation of the Degradation of Cellulose Triacetate Base Motion Picture Film," *The Journal of Photographic Science* 38 (1990): 54-59.
25. J. M. Reilly, *Storage Guide for Color Photographic Materials*, (Albany, NY: The University of the State of New York, New York State Education Department, New York State Library, The New York State Program for the Conservation and Preservation of Library Research Materials, 1998).
26. *American National Standard for Imaging Materials—Processed Safety Photographic Films—Storage*, PIMA IT9.11-1997, revision and redesignation of ANSI/NAPM IT9.11-1993, (New York: American National Standard Institute, 1997).
27. *ISO 18911 Photography—Processed Safety Photographic Films—Storage Practices* (formerly ISO 5466), International Organization for Standardization. Geneva, Switzerland.
28. C. J. Kunz and C. E. Ives, "The Use of Desiccants with Undeveloped Photographic Film," *J. SMPE* 46 (1946): 475-510.
29. Eastman Kodak Company, *The Book of Film Care*, Publication No. H-23, (Rochester, NY: Eastman Kodak Company, 1983).
30. R. Gooes and H.-E. Bloman, "An Inexpensive Method for Preservation and Long-Term Storage of Colour Film," *SMPTE Journal* 92 (1983): 1314-1316.
31. 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 (1994): 249-261.
32. A. T. Ram, D. F. Kopperl, and P. Miller, "Molecular Sieves for Film Preservation," *IS&T's 50<sup>th</sup> Annual Conference: Final Program and Proceedings* (Springfield, Virginia: The Society for Imaging Science and Technology, 1997).
33. 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, Edinburgh, Preprints* 2, (London: James & James, 1996) 573-579.
34. J.-L. Bigourdan, P. Z. Adelstein, and J. M. Reilly, "Use of Microenvironments for the Preservation of Cellulose Triacetate Photographic Film," *Journal of Imaging Science and Technology* 42 (1998): 155-162.
35. J.-L Bigourdan and J. M. Reilly, "Preservation Strategy for Acetate Film Collections Based on Environmental Assessment and Condition Survey," *Care of Photographic Moving Image & Sound Collections*, S. Clark ed., July 20-24, 1998, York, England (1999): 28-37.
36. P. Z. Adelstein, C. L. Graham, and L. E. West, "Preservation of Motion-Picture Color Films Having Permanent Value," *Journal of SMPTE*, 79 (1970): 1011-1018.
37. *EBU Technical Recommendation R101-1999. Storage conditions for preservation of motion picture film and accompanying magnetic sound material for broadcast organisations*, EBU (1999).
38. M. C. Fischer and J. M. Reilly, "Use of Passive Monitors in Film Collections," *Topics in Photographic Preservation* 6 (Washington, DC: AIC Photographic Materials Group, 1995) 11-40.
39. J. C. Harthan, M. Edge, N. S. Allen, and M. Bodnert, "The Development and Evaluation of a Sensory System to Detect Degradation in Cellulose Triacetate Photographic Film, Part II: Selection of a Solid Support for the Indicator and Field Trials on Indicator Performance," *The Imaging Science Journal* 45 (1997): 81-83.

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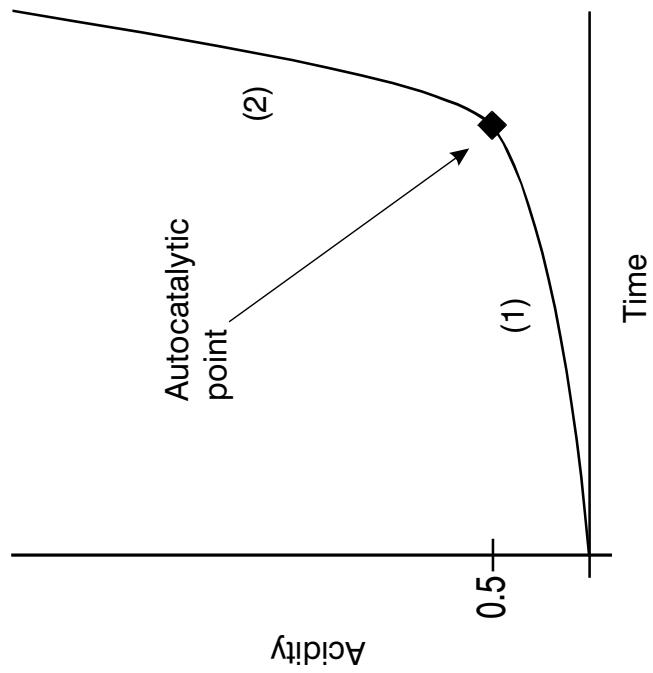
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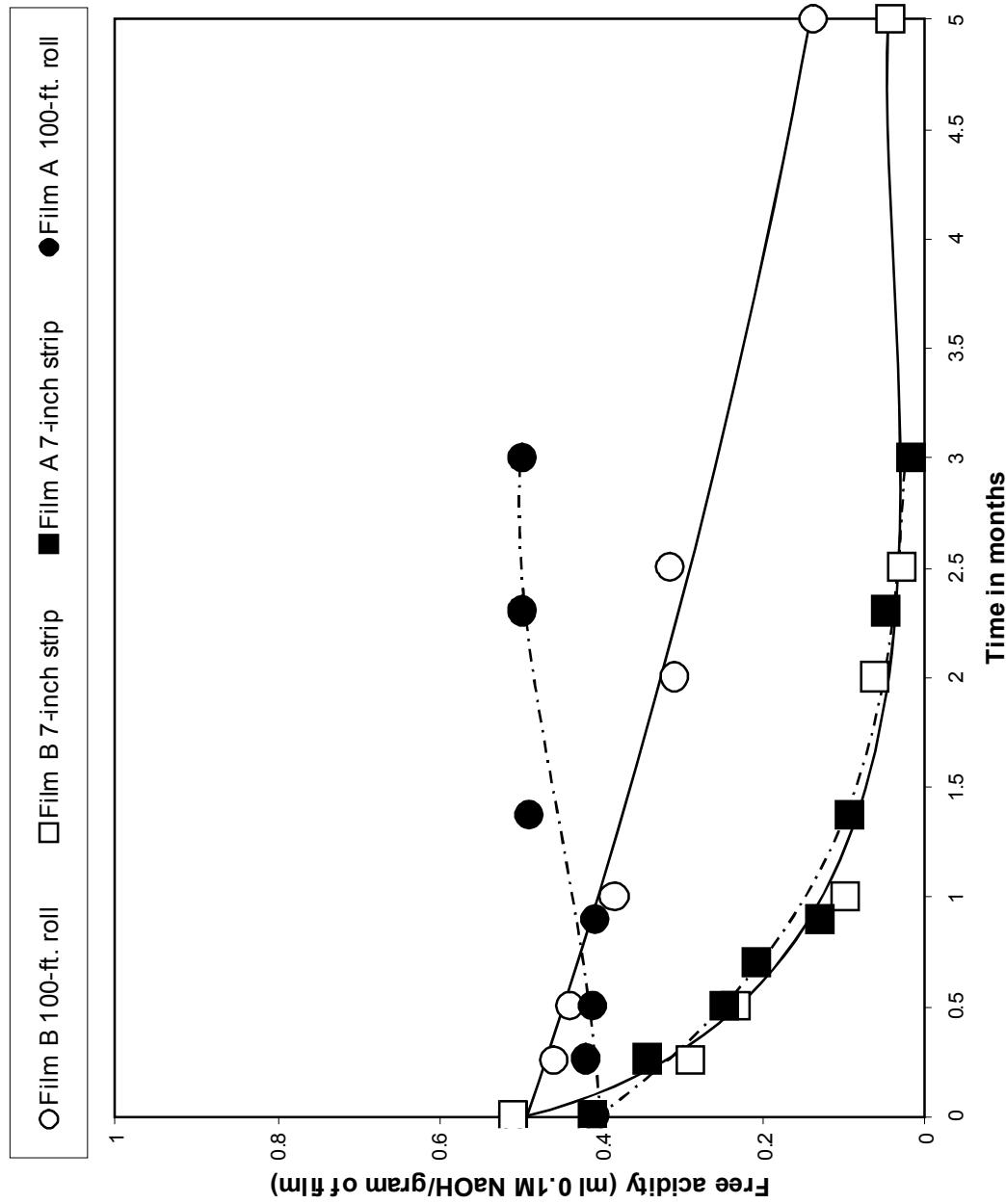
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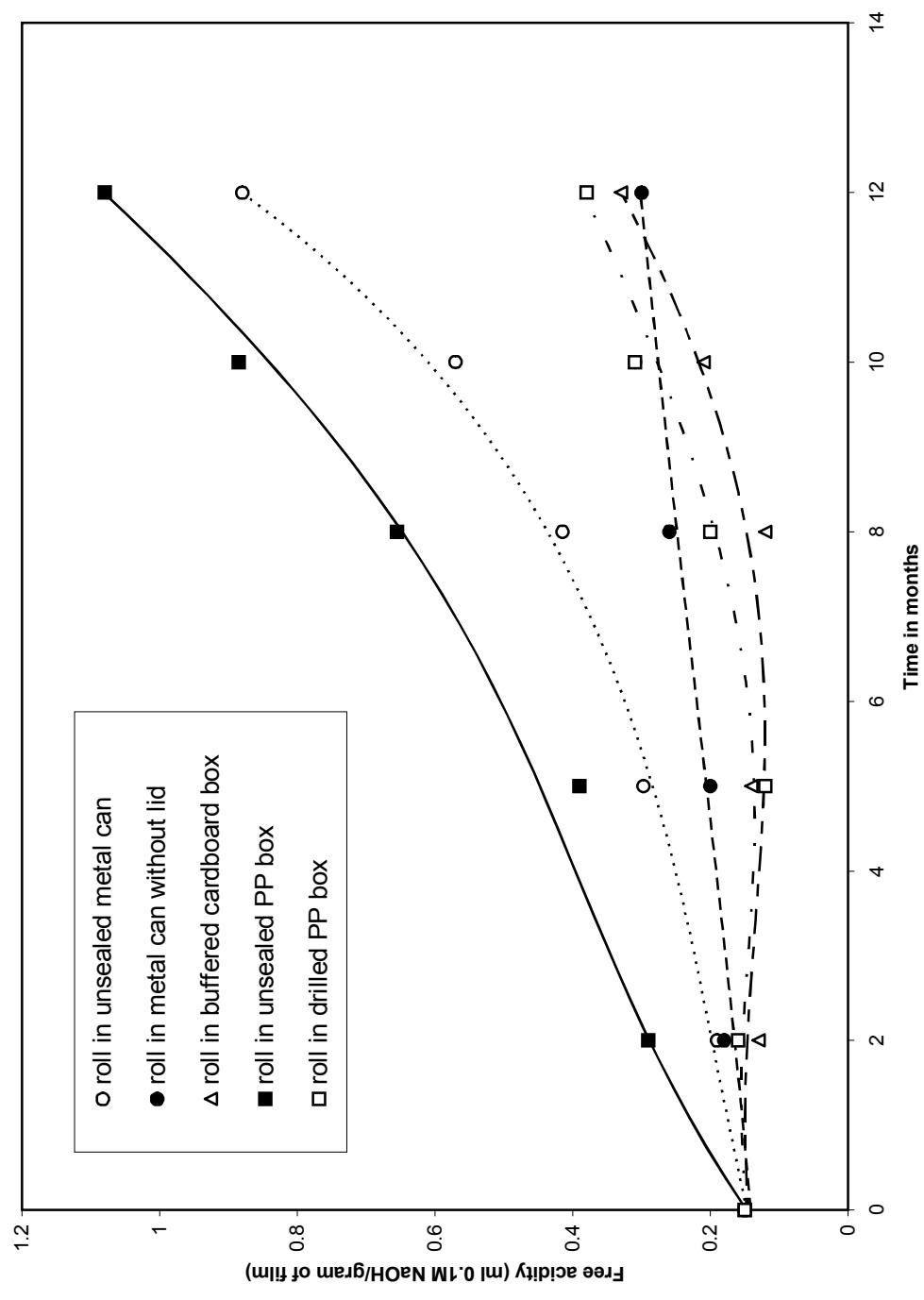
*Figure 1: Free acidity change versus time for acetate film.*



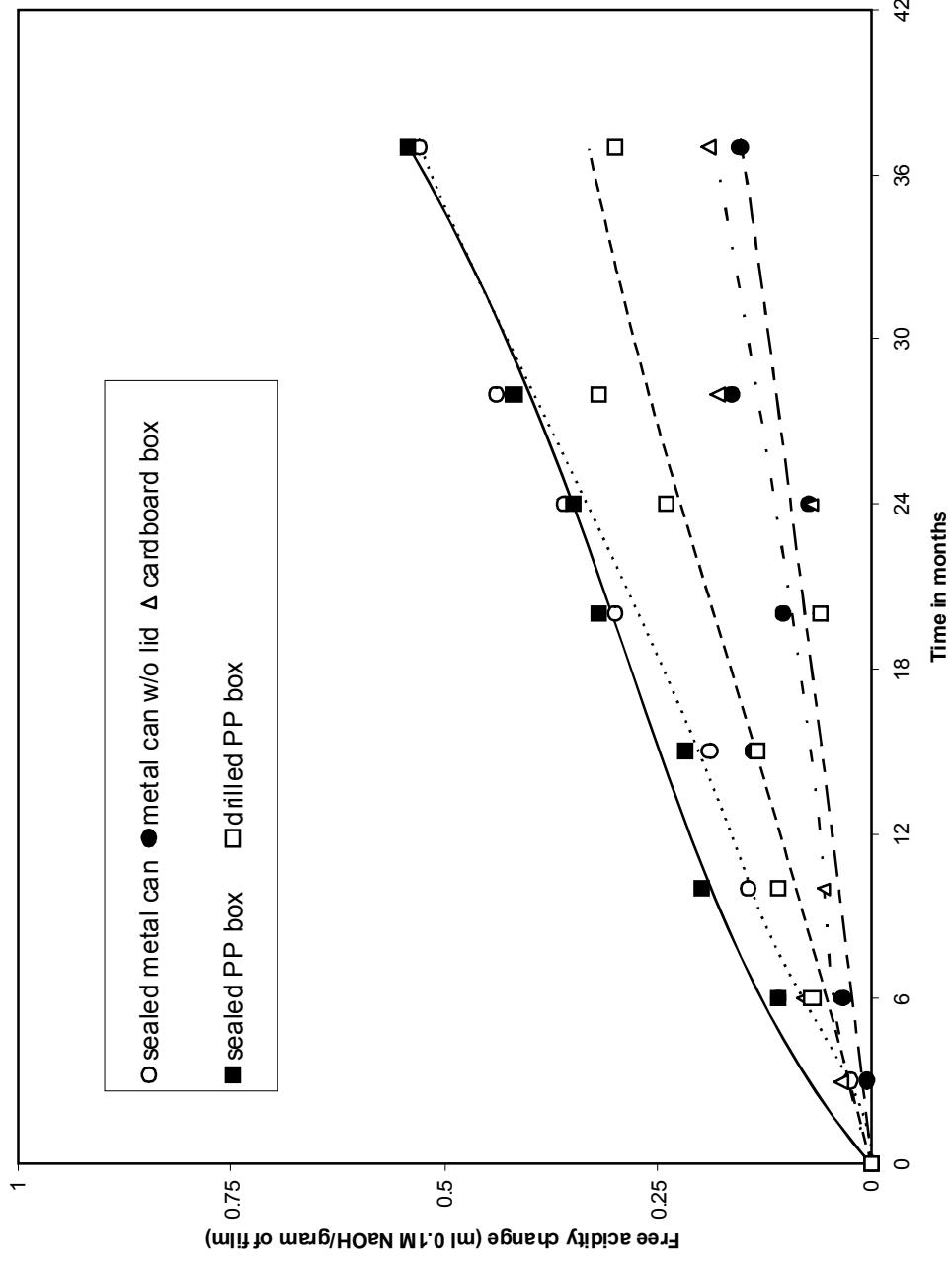
*Figure 2: Acidity of degraded CTA film exposed to 21°C, 50%RH in two formats (100-foot roll and 7-inch strip). Film A was tightly wound. Film B was loosely wound. Film samples were exposed without enclosures.*



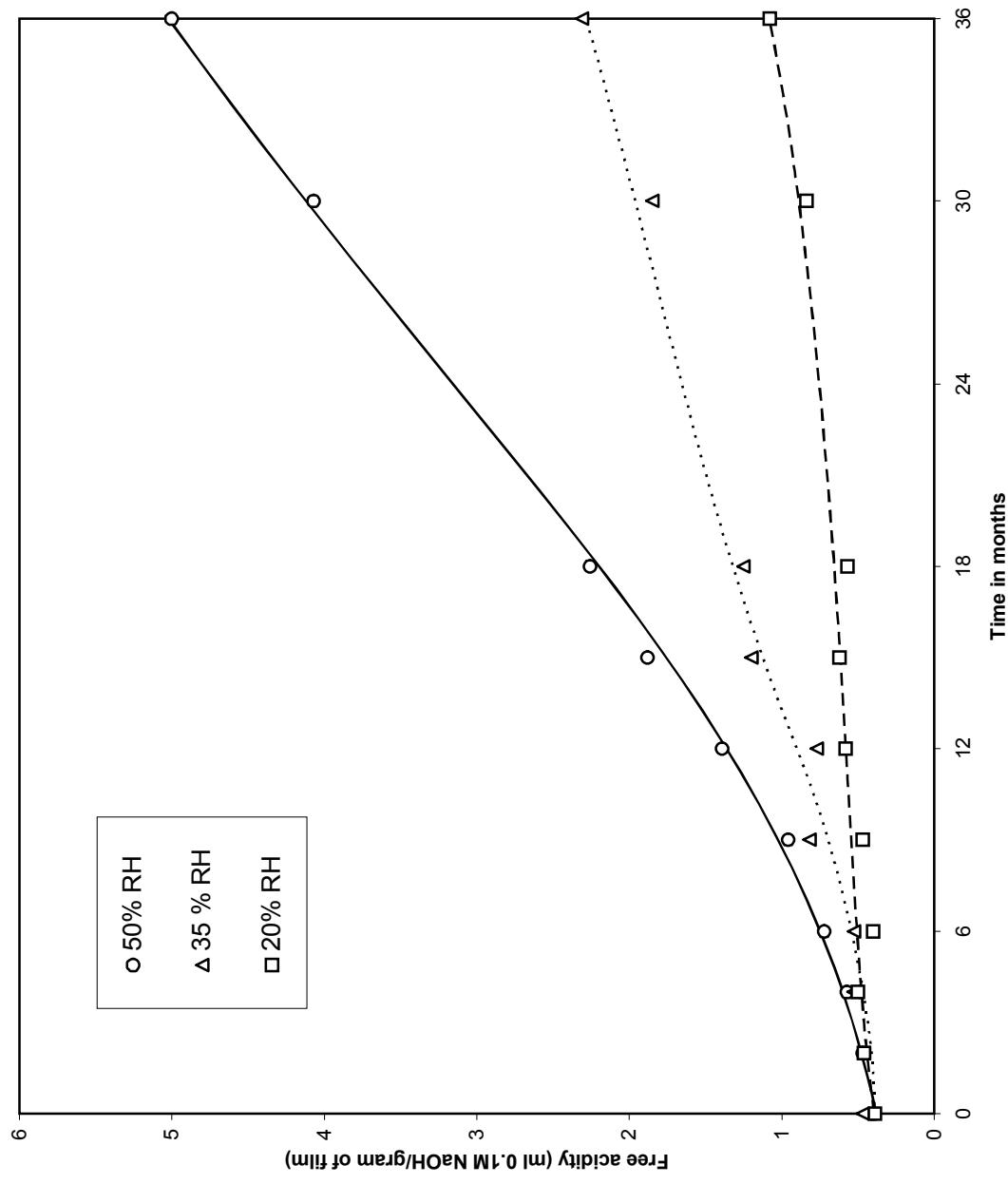
*Figure 3: Acidity for 100-foot rolls of pre-degraded CTA film incubated at 40°C, 50%RH in various enclosures. Film initially conditioned to 21°C, 50%RH.*



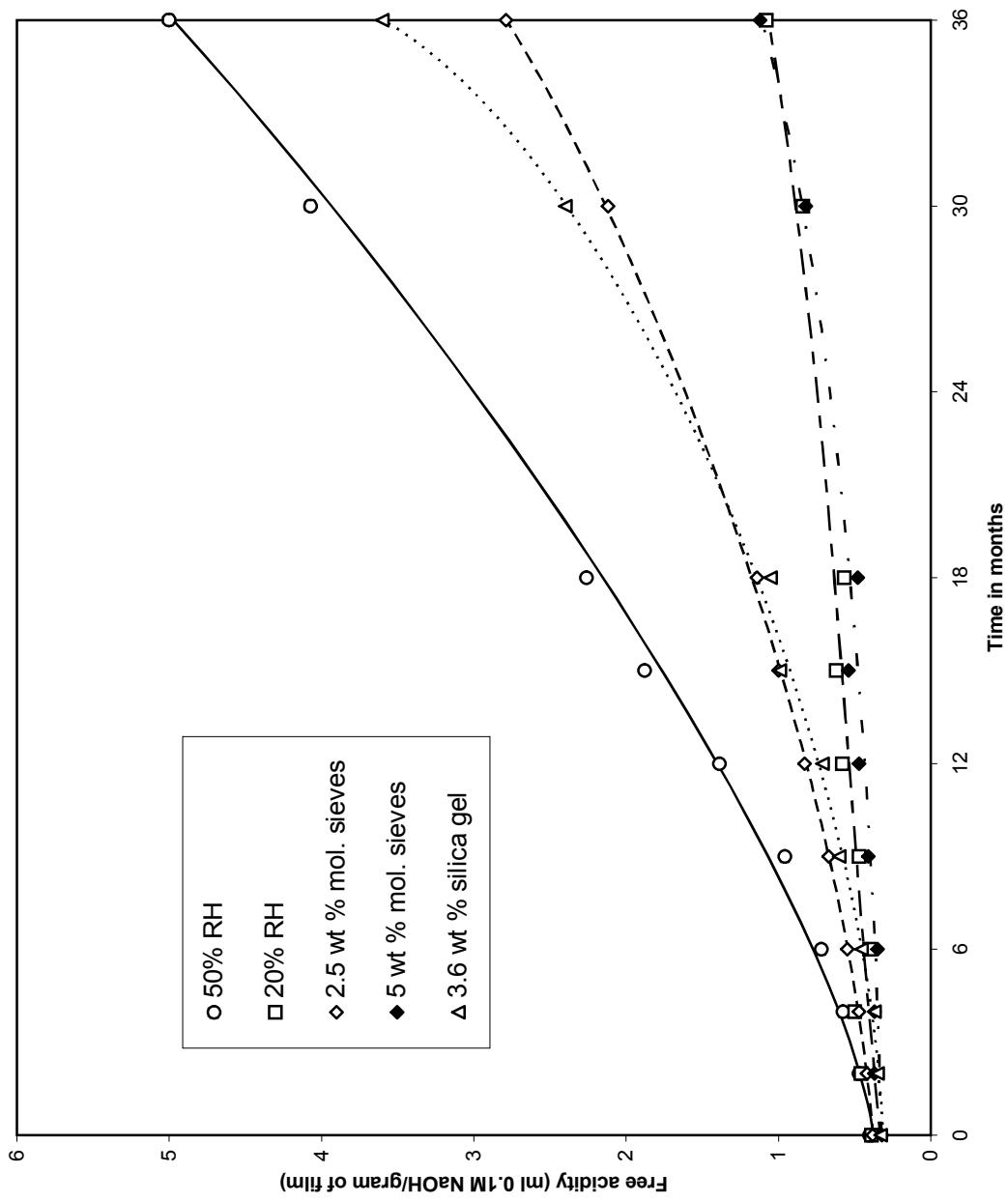
*Figure 4: Effect of enclosures at room temperature. Acidity change for 100-foot rolls of pre-degraded CTA film stored at 21°C, 50% RH. Initial film acidity 0.4 to 0.6. Film initially conditioned to 21°C, 50% RH.*



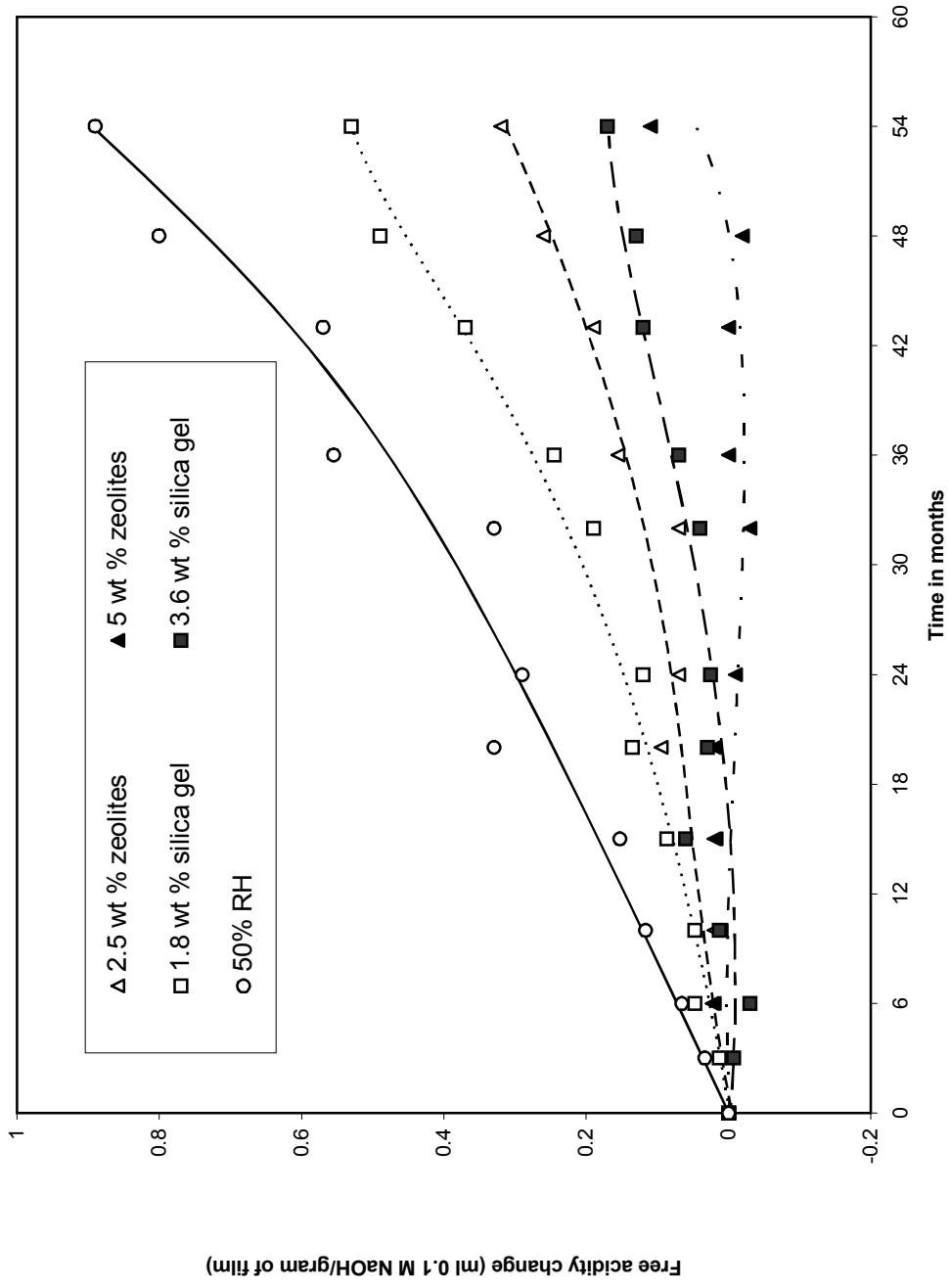
*Figure 5: Effect of moisture pre-conditioning. Acidity for 100-foot rolls of pre-degraded CTA film incubated at 35°C in sealed cans. Film initially conditioned to 50%, 35%, and 20% RH at 21°C.*



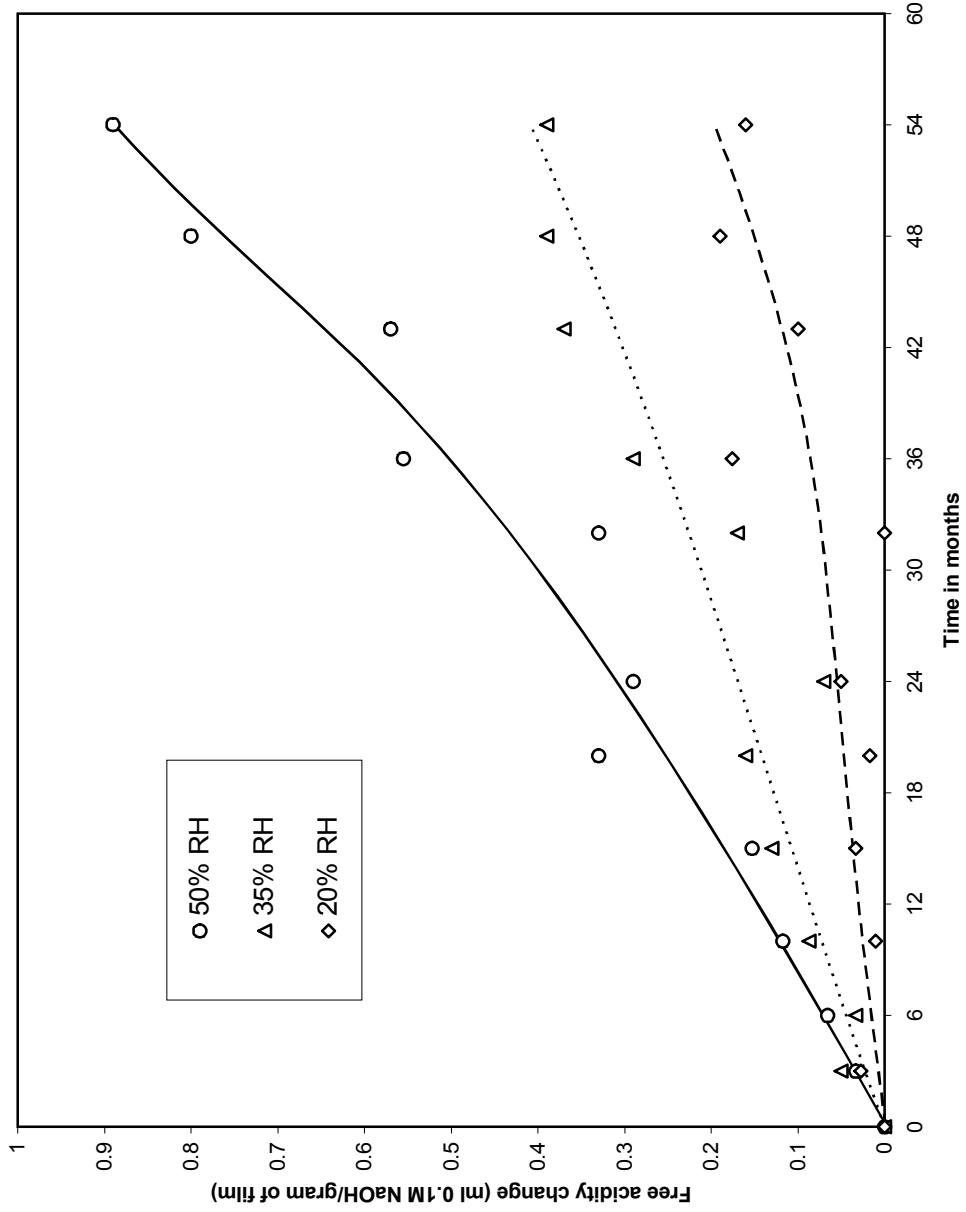
*Figure 6: Effect of adsorbents. Acidity of 100-foot CTA film rolls incubated at 35°C in sealed cans with zeolites or activated silica gel or after moisture conditioning at 21°C, 20%RH. Film conditioned to 21°C, 50%RH prior to addition of adsorbents.*



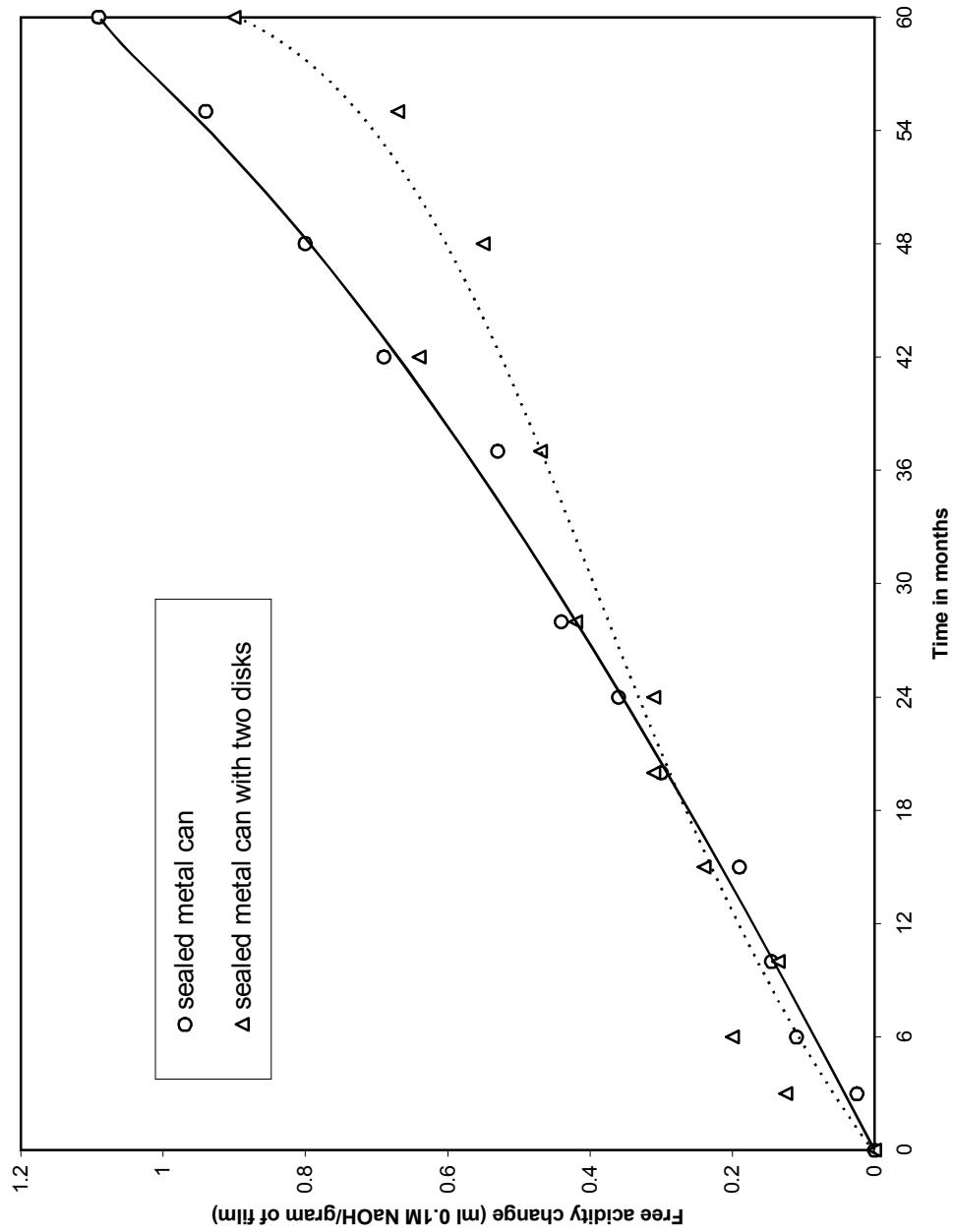
*Figure 7: Effect of adsorbents at 21°C. Acidity change of 100-foot CTA film rolls stored in sealed cans with molecular sieves or activated silica gel. Film initially conditioned to 21°C, 50% RH prior to addition of adsorbents. Film's initial acidity: 0.4.*



*Figure 8: Effect of moisture pre-conditioning at 21°C. Acidity change for 100-foot rolls of pre-degraded CTA film stored at room temperature in sealed cans. Film initially conditioned to 50%, 35% and 20% RH at 21°C.*



*Figure 9. Effect of buffered cardboard disks at 21°C. Acidity change of 100-foot CTA film rolls stored inside sealed metal cans with and without two buffered cardboard disks. Film initially conditioned to 21°C, 50% RH. Initial film acidity: 0.4 to 0.6.*



*Figure 10: Acidity change of 400-foot rolls of pre-degraded CTA film after five years of storage at 21°C, 50% or at -16°C, 50% to 55% RH. Initial acidity levels were from 0.4 to 0.7.*

