



Article: Strategies for the Storage of Cellulose Acetate Film

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Strategies for the Storage of Cellulose Acetate Film

Douglas Nishimura

Presented at the 2015 PMG Winter Meeting in Cambridge, Massachusetts.

Recent questions about the storage of deteriorating cellulose acetate film demonstrated that some of the information produced by the Image Permanence Institute regarding acetate film storage hasn't been reaching the people that need it. The common problem has been how to house deteriorating acetate film to get rid of the acetic acid being generated by the film.

The issue began with the recognition that the deterioration reaction that liberated the acetic acid was simply the reverse of the process that created the cellulose acetate in the first place. Knowledge of the reaction of an alcohol with an acid as a method of organic synthesis to form esters has been known into the 19th century so this wasn't a new discovery. Nor was the reverse reaction that would produce an alcohol and an acid from an ester by hydrolysis. However, given that the liberated acetic acid in the hydrolysis reaction was an acid and would therefore function as a catalyst, was problematic.

The long flat acidity level at the start of deterioration strongly suggests that the deterioration rate in the absence of significant concentrations of catalyst is very slow at controlled room conditions, 70 °F (21 °C) and 50% RH (Fig. 1) suggesting that there could be significant benefit from removing the acetic acid catalyst. This was the state of knowledge in 1991. Note that acidity is measured in terms of the number of milliliters of tenth normal sodium hydroxide that contains the equivalent number of molecules of sodium hydroxide as there are molecules of acetic acid in one gram of film base. So the critical acidity value of 0.5 where deterioration rate takes a dramatic acceleration occurs when a gram of film base contains the same number of molecules of acetic acid as there are molecules of sodium hydroxide in 0.5 ml of 0.1 N sodium hydroxide solution.

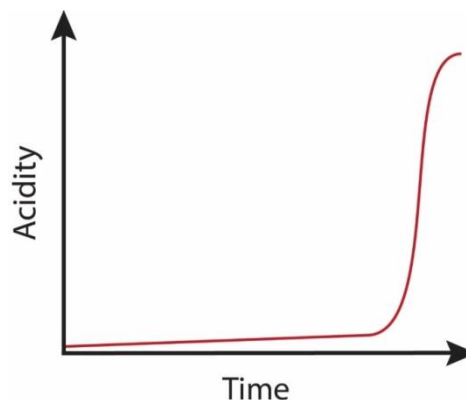


Fig. 1. Cellulose acetate base acidity over time (not to scale).

Add to this, the anecdotal claims that films found stored in a porous or open container such as a cardboard box or an open can are “always” in much better condition than similar films found stored in impermeable containers.

In 2006, Jean-Louis Bigourdan reported on experiments that he conducted on rolls of film that had been artificially deteriorated to the same level very close to the critical acidity at which autocatalysis takes over the deterioration rate. The film was divided into four groups with half in commercially available vented cans while the other half was in sealed cans. Half of each of these two groups were put into room condition storage at 21 °C and 50% to 55% RH while the other

half went into freezer storage at -16 °C and 50% to 60% RH. After 10.25 years, he found that all of the room temperature stored films were in much worse condition and comparison by acidity measurement showed no significant difference between the vented cans and unvented metal cans. The freezer-stored films all showed little significant change and no difference between the vented plastic cans and the unvented metal cans. (Bigourdan, 2006)

Other experiments tested the benefits of adsorbants such as zeolites and silica gel in sealed cans to see if adsorption of acetic acid in these materials helped beyond low humidity storage, since these materials are desiccants. Silica gel was used at 1.8% and 3.6% by mass of film. Zeolites were used at both 2.5% and 5% by mass of film. Kodak recommended 26.5 grams of zeolites per thousand feet of 35 mm film or a rate of about 1.8% by mass of film. A third set of samples was prepared in which the pre-deteriorated film was conditioned to 20% RH before being sealed in cans. It was demonstrated that both the silica gel and zeolites could adsorb acetic acid out of the cans of film with 5% zeolites removing the most. However, 5% zeolites performed the same as the film preconditioned to 20% RH. As desiccants, both the silica gel and the molecular sieves (zeolites) would dry out the environment in the cans.

Desiccants in sealed containers can work well for films in tropical environments, but can be problematic for films in good storage environments. Kodak recommends that the film cans either be sealed in polyethylene bags or taped with “moisture proof” tape. They further recommend using three-12.5 gram packages per thousand linear feet of 35 mm film so a 1000-ft can of 35 mm film would contain 37.5 grams of molecular sieves.

Zeolites rise very sharply in equilibrium water content from nominally 0% water by weight at equilibrium with a 0% RH environment to about 20% water by weight at equilibrium with an 8% RH equilibrium environment. Here, the curve levels off almost completely, barely rising to about 23% water by weight at 100% RH equilibrium humidity. At equilibrium with a 50% RH environment, the zeolites contain roughly 21.5% water by weight. At 21 °C and 50% RH, there is about 9.2 grams of water per cubic meter of free air or 0.26 grams per cubic foot of free air so the water in the free air space in the can is negligible. Fully activated molecular sieves should remove roughly eight grams of water from the film. In two years, the molecular sieves will be replaced and the film will lose another eight grams of water. During the third replacement cycle between six and eight years of storage, the film will fall below the minimum recommended water content where film is expected to suffer from permanent distortion due to excessive curl and stress relaxation. So the use of molecular sieves requires reconditioning film. Now since much of its benefit is derived from the low RH inside the can, the film shouldn't be reconditioned to 50% RH, which would undo the RH effect of the molecular sieves, but rather 25% RH or so, although this would have to be done every two years.

This amount of labor might be okay for a few cans of film (or a few bags of sheet film), but not for a moderate to large sized collection.

Six conclusions came out of this research:

1. Microenvironments creating a lower film moisture content benefit the stability of cellulose triacetate base film. This can be done by preconditioning the film to low relative

humidity or by the addition of moisture adsorbents such as molecular sieves or activated silica gel.

2. Both molecular sieves and activated silica gel were observed to have acid-adsorption properties. However, moisture adsorption is the main factor in controlling the degradation of cellulose triacetate base film.
3. The use of 5 wt % molecular sieves made a significant contribution in minimizing further degradation of cellulose triacetate base film at 35 °C. The preventive benefit was also observed after 20 months of storage at room temperature, comparable to that obtained by moisture preconditioning the film to 21 °C, 20% RH.
4. Acid adsorbents had a minimal impact on reducing the acid content of already degraded cellulose triacetate base film. At best, impractical quantities of acid-adsorbents would be required to reduce the acid content of the film to acceptable levels. In such a situation, cold storage is recommended until the film can be duplicated.
5. The benefits of microenvironments using moisture and acid adsorbents such as molecular sieves and activated silica gel do not equal those obtained by lowering the temperature of the storage area.
6. The use of microenvironments is recommended when it is not possible to prevent high humidity in the storage area. (Bigourdan, 1997, 50)

While the actual experiments were carried out using cellulose triacetate film, the conclusions apply to all cellulose acetate film supports.

So adsorbents fail to greatly improve the deterioration of acetate film, other than what can be accomplished with low storage humidity. However, it's no big surprise. Consider Figure 2.

This is the essentially the same as Figure 1. Time runs along the x-axis while film acidity runs along the y-axis. During the early life of the film, the increase in acidity in the film is very slow so a small decrease in acidity can set the clock back for the film by decades. See for example, a film at point A in its life. If a small amount of acidity can be removed, then the effective age of the film goes from A to B. At point A, the film is pretty indistinguishable from a fresh film reaching point B on the graph. So by losing a bit of acidity, a film at point A can return back to its state when it first reached point B. The difference is equivalent to a few tenths on our acidity scale, but given that a film can theoretically get up to 92, the difference in the cellulose acetate polymer between A and B is insignificant. Clearly during the early few decades, a very small loss of acidity can translate into decades of additional life for the film.

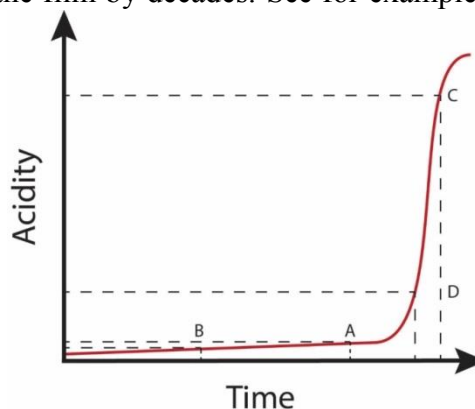


Fig. 2. Gain in life of acetate base for a given loss of base acidity at two times.

So it's no surprise that film archivists have observed that films that spent their lives in open or porous containers survived hydrolytic deterioration much better than films that were stored in sealed containers from the beginning.

Film that is obviously deteriorating by smell, will be on the steep part of the deterioration curve in Figures 1 and 2. Along this region of the curve, even a moderately large decrease in acidity doesn't affect the remaining life of the film very much. This can be seen by the large loss of acidity from point C to point D and the small gain along the time axis. Can buffered paper envelopes act as an alternative to cold storage at this condition? We don't think so. It has been demonstrated that unbuffered paper can adsorb some acetic acid and therefore directly affect the film. It has also been shown that sheets of film interleaved with paper buffered either with precipitated calcium carbonate or with dolomite, will reduce the rate of acid build-up in sealed bags, to a higher degree than unbuffered paper. Unfortunately, interpreting the results from bagged, accelerated tests and extrapolating the results to real-life storage situations is complicated and difficult. For one thing, collections would normally have no reason to put negatives in envelopes and then into vapor-proof packages unless they were using the packaging for humidity control in cold storage. Possibly one might consider it as a way of segregating deteriorating film from non-deteriorating film, but there should be cheaper and easier ways to segregate film. So the accelerated testing method doesn't extrapolate to real-life very well. Chemically, the combination of a sealed package with high temperature incubation is intended to make things happen faster, but it disproportionately accelerates the acetate deterioration more than any of the other processes that we might be interested in. However, the fact that film interleaved with buffered paper performs better than film interleaved with unbuffered paper provides at least evidence for proof of concept.

Film was also put into envelopes made from the same buffered and unbuffered papers. These envelopes were stood vertically in the chambers and incubated under the same conditions without the sealed bag. After 12 months, there was no significant difference between the films in buffered versus unbuffered envelopes. (Bigourdan, 1996) However a comparison of the acidity after 12 months of the four configurations shows a trend.

Table 1
Film Acidity after 12 Months

	Buffered	Unbuffered
Sealed	2.8	5.5
Open	0.78	0.93

All of the films started out as fresh samples so nominally 0.0 acidity initially. One obvious observation is that the buffered paper resulted in a lower average acidity whether in a sealed bag or freely exposed to the air versus unbuffered paper. It is also apparent that whether stored either in buffered or unbuffered envelope or interleaved with buffered or unbuffered paper, storage in a sealed package performs worse than storage with free exposure to the air. One might argue that interleaving with paper was less effective than a true paper envelope, but given that the air is pressed out of the bags before sealing, the only real difference would be the adhesive seam which is unlikely to make such a significant difference. However, the experiment does support the anecdotal evidence that film that spends its entire life in open or porous containers perform better than similar film stored entirely in sealed containers.

It would certainly be possible to remove substantial acetic acid from film by washing it, although as the film deteriorates, the risk of water causing emulsion loss also increases. One might also festoon roll films over clothes lines or hang individual sheets of film from a clothes line, but neither method is particularly practical.

In addition, there are other complications associated with trying to control deterioration rate by removal of acetic acid. According to thermodynamics, the reaction should go forward until some critical ratio of activities (concentrations) of products and reactants is reached, at which point, the reaction has reached equilibrium and stops. The presence of catalyst won't affect this since it changes the kinetics rather than the thermodynamics of the reaction. So as long as the acetic acid product is removed, the reaction will tend to move forward.

The second, and more serious complication is that acetic acid occupies space in the film, whether it exists as an acetate group on the polymer chain or as free acetic acid trapped in the base.

As far as we know, this was first demonstrated by the Florida State Archives, although at the time, no one really understood the significance of their observation. Their sheet films were stored standing vertically on shelves like books in a library and quite tightly packed. Back in the early 1990s, they pulled some film off the shelves and put them on a table a few feet away with the intent of retrieving the film soon to print or copy. When they came back, the formerly pristine looking film had shrunk and distorted enough that it formed channels where the emulsion and anti-curl layers had lifted from the shrinking base, in effect, forming pleats. They had been away only about 20 minutes when this occurred and they were horrified. Another negative was pulled that they watched as it curled, shrunk, and popped as the emulsion and anti-curl layer lifted in channels. A final negative was pulled, but this time, they started timing it from the moment it left the shelf. Every 30 minutes, they drew a circle around the areas where the emulsion had lifted. The negative was then put into an overnight courier envelope and shipped to IPI with a circle, date, and time indicating the extent of channeling right before they sealed the envelope.

At first it was assumed that the film had been forced to stay flat by the tight packing of the shelves and time off the shelf simply allowed the internal stresses to relax, but later experiments in the lab showed that badly degraded film produced by incubation in a tightly confining container also resulted in good looking film initially, but as the acetic acid diffused to the surface of the negative and evaporated, the film shrunk and channeled.

A more formal study was performed using a larger body of deteriorating films. A film archivist intern made dimensional measurements using a film shrinkage gauge as well as acidity measurement on the films. The films were then allowed to air-out before the size and acidity were remeasured. Indeed, the dimensional loss (shrinkage) correlated quite well with the decrease in acidity.

As conservators, you're caught between the devil and the deep blue sea. Either changing the enclosures to something more porous does nothing significant towards extending the life of the enclosed film, or it does and you shorten the useful life of the film by causing it to shrink and channel faster.

At this time, it appears that the enclosure plays a secondary role in the stabilization of actively deteriorating negatives, although they serve a primary role in the protection of films from dirt, dust, and a certain amount of handling damage. Cold storage remains the best method of preserving film collections for long-term keeping.

For additional assistance with film care collections, the Image Permanence Institute has unveiled a new on-line tool called Filmcare.org. The web tool is expected to have two major sides. For the casual user, there are resources to help calculate survey size, identify film base type, and teach about common forms of damage and deterioration. For the more serious user, free registration is required. The reason for the registration is to password protect collection information.

This side of the web site helps the user to answer key preservation questions for their collection:

- What is in the film collection?
- What condition is it in?
- How good is the storage environment?
- If practical improvements can be made to the storage environment, what can be done?
- How does one make environmental improvements?
- How does one continue to monitor the collection into the future?

It is our hope that Filmcare.org proves to be of great benefit to collections having to deal with film preservation.

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