IPI Storage Guide for Acetate Film
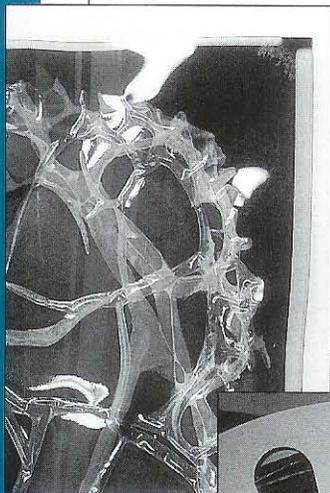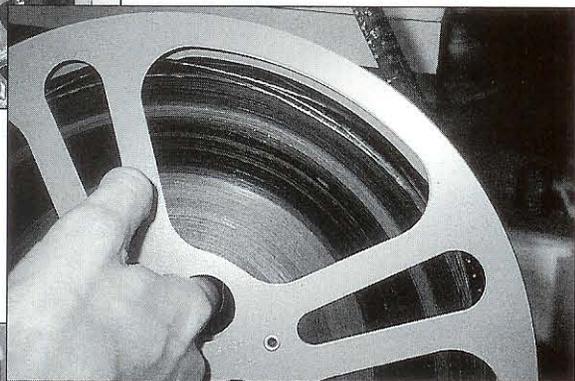
James M. Reilly • Director, Image Permanence Institute

Instructions for Using the Wheel, Graphs, and Table
Basic Strategy for Film Preservation

● The *IPI Storage Guide for Acetate Film* provides an overview of environmental specifications for film storage. It explains the relationship between temperature, relative humidity (RH), and "vinegar syndrome," the slow chemical decomposition of acetate plastics leading to loss of their value in a film collection.

● The main purpose of the *Guide* is to help collection managers evaluate the quality of the storage environment they provide for their film. *The Guide is not meant to predict the life of any individual film; it merely uses predicted life span as a yardstick to measure the quality of the storage environment.*

CONTENTS

The *IPI Storage Guide for Acetate Film* is a tool for evaluating and planning storage environments for acetate base photographic film, cinema film, and microfilms. This is a category that includes a great many films made between the 1920s and the present. (Refer to "History of Film Supports" on p. 21 for more information about which films in a collection are likely to be acetate and which are not.) Cellulose acetate is subject to a slow form of chemical deterioration known as the "vinegar syndrome." Nearly every sizeable collection of film has experienced losses due to vinegar syndrome, and many more losses are expected in the future. The main symptoms of this problem are a vinegar-like odor and buckling, shrinking, and embrittlement of the film. All acetate films are susceptible to such deterioration. Whether it happens within a few years or not for centuries depends on the storage conditions in which the film is kept.

The *IPI Storage Guide for Acetate Film* deals principally with one aspect of film storage: **the general relationship between storage RH, storage temperature, and the approximate number of years before the vinegar syndrome would become a serious problem for fresh, brand-new film.** While this is helpful information, it deals only with cellulose acetate plastic film base deterioration. Other important forms of film deterioration such as color dye fading, silver image fading, mold growth, physical damage, etc., have their own causes and their own relationship to the storage environment. There is more to the story of preserving film than preventing the vinegar syndrome, and there is more to the vinegar syndrome problem than just temperature and humidity conditions, although they certainly are key factors in the rate of deterioration. The section, "General Philosophy of Film Storage," beginning on p. 16, provides an overview of environmental considerations in film storage and puts the information specifically pertaining to vinegar syndrome into a broader context.

The *Guide* consists of four parts, as shown in Fig. 1: this booklet, the two-sided Wheel, Time Contours for Vinegar Syndrome (one for Fahrenheit, one for Celsius), and the Time Out of Storage Table. Each component presents information about film storage in a different format, providing slightly different approaches to the available data. The data in the *Guide* were obtained from experiments on triacetate base film, but they apply as well to diacetate, acetate
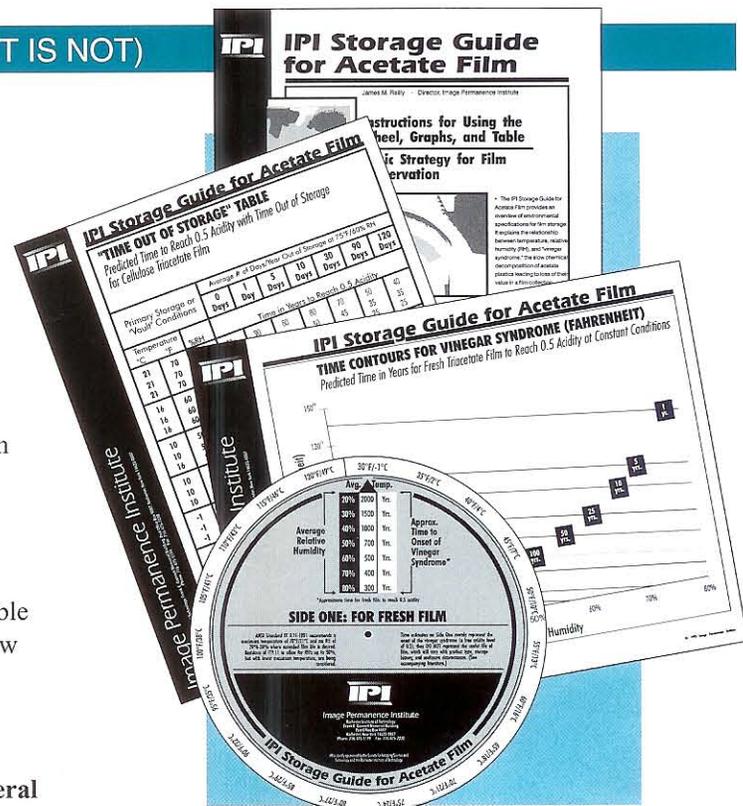

Fig. 1 Components of the *IPI Storage Guide for Acetate Film*.

butyrate, and acetate propionate film bases. In short, they are valid (to a first approximation) for all types of acetate film.

The Data in the *Guide*

The data presented in the *Guide* were gathered from accelerated-aging tests performed as part of an NEH-, NHPRC-, and Kodak-funded research project investigating the optimum storage conditions for film.[1,2,3] The end product of the project was a series of predictions for how long it would take for the onset of the vinegar syndrome at various storage conditions. (Bear in mind that the predictions are for *when vinegar syndrome reaches a threshold level*, not for the end of the useful life of the film.) Each prediction is associated with a particular temperature and RH combination and assumes that the conditions remain constant. The predictions represent the period of time in years that would be required for fresh acetate film to start experiencing noticeable levels of vinegar syndrome; at the end of that period, the film would smell of vinegar but would still be usable. At that point, however, the film would enter a stage in which the pace of deterioration increases markedly.

What Do the Predictions Predict?

One thing the *Guide* does *not* do is to predict the life span of individual pieces of film or specific collections of film. Because the Wheel, the Contours, and the Table all express life expectancies in years (nicely matched up with corresponding storage temperatures and RHs), there is a tendency to view the data as predictive of how long a given piece of film will "last." While such a prediction could turn out to be accurate, there are a number of good reasons why it cannot be relied on in any *individual* case.

The predictions are based on extrapolations from accelerated aging. They should be seen as a convenient way to quantify and express how good or bad a storage environment is for preventing the vinegar syndrome, not as literal predictions of how long a collection will last. (The *Guide* is not a fortune-teller—it only tells the relative benefits of one storage condition over another.) In order for the numbers to be taken as literal predictions of when vinegar syndrome would begin, the collection would have to reproduce exactly the circumstances under which the aging experiments were done; all film would have to be fresh, and it would have to be kept in a tightly sealed package at steady, unvarying conditions. In laboratory studies, such variables must be held constant throughout the duration of the experiment or the data would not clearly demonstrate the effect of those environmental factors.

Each individual film in a collection has a unique history and is in a state of preservation determined by how it has been stored throughout its whole existence up to the present time. If we are lucky, we may know the storage history of a film collection with some precision and then be able to more accurately estimate its state of preservation and its prospects for the future; usually, however, we have only a vague general idea.

Although the use of diagnostic tools such as A-D Strips (see p. 14) may provide an idea of how far down the path of deterioration a particular film has already travelled, it is still nearly impossible to predict exactly when a film will become unusable.

Importance of Acid Trapping by Enclosures

There is another important fact to know about vinegar syndrome besides its temperature and RH dependence: the "acid trapping" factor. The process of deterioration generates acetic acid (vinegar) inside the plastic film base. Under some circumstances, acidity either can leave the film by evaporating into the air or can become absorbed into storage enclosures. In other situations it can be trapped—prevented from escaping by the storage container. If trapped, it greatly accelerates the rate of deterioration. The predictions in the *Guide* were obtained from experiments in which the film was kept in tightly sealed foil bags, and so they represent a "worst-case" scenario where all the acid is trapped in the film.

Real-life storage may involve more opportunity for the acid to escape; if that is the case, it will take longer than predicted for vinegar syndrome to occur. However, most real-life film storage is more likely to be closed than open. Motion picture film is typically stored in closed cans, and sheet films are often kept in close quarters in a box or drawer. Though the "acid-trapping factor" can certainly make a big difference in how long film will last, if you evaluate film storage with the *Guide* (which assumes maximum acid trapping), you at least will not *over*estimate film permanence and probably will be close to the actual real-life behavior.

Given all these qualifications, what good, then, are the data? The real value of the data is in enabling us to understand in a general way how temperature and humidity affect the *rate* of film base degradation. The data describe major trends but do not predict the specific behavior of individual samples of film. In this respect, they are like an actuarial table for a life insurance company; the company has no idea when any given individual man or woman will die, but it has a very good idea how long the majority of people will live.
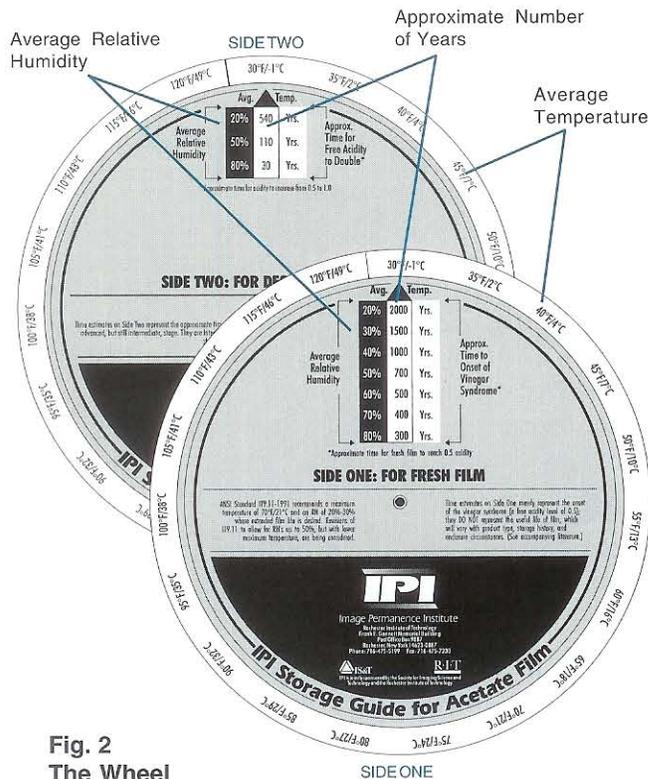
Fig. 2
The Wheel

The Wheel presents the research results about vinegar syndrome in a format that makes it easy to evaluate the effect of a particular storage environment on the life expectancy of acetate film. It makes it possible to compare the rate of deterioration at a wide range of conditions, to determine which of several existing storage environments is better for film, or to consider the various combinations of temperature and RH that would yield a specified life expectancy. The Wheel, as noted, has two sides (see Fig. 2). Side One is based on the approximate number of years it would take *fresh* (new) acetate film to start degrading (to reach 0.5 acidity—see p. 14) at various storage conditions. Side Two is based on the approximate number of years it would take *partially degraded* film (film that has already reached 0.5 acidity) at various storage conditions to reach an acidity level of 1.0. Printed on each side, around the circumference of the larger disk, is a range of temperatures from 30°F/-1°C to 120°F/49°C. Beside the window on Side One of the Wheel is printed a range of humidity levels from 20% to 80% RH in 10% increments. Side Two has only three increments: 20%, 50%, and 80% RH. The predicted number of years at each temperature/humidity combination is displayed in the window on each side.

Evaluating a Storage Condition

Suppose, for example, that a collection of fresh acetate film is kept in an air-conditioned room where it's comfortable for people: 70°F (21°C), with an RH of 50%. (We'll assume these conditions are maintained year round—not always an easy thing to do.) The question is, how good are these conditions for the film? To find the answer, consult Side One of the Wheel (the blue side). Rotate the smaller disk until the arrow points to the temperature in question—in this case, 70°F. A column of numbers will appear in the window. Next, select the RH of interest—in this case, 50%. Reading across on the same line, we find in the window the predicted number of years for that set of storage conditions—in this case, 40. (See Fig. 3)

At each temperature on Side One, the predicted number of years until vinegar syndrome begins to be a problem are shown for seven different humidity values. Notice that lower RHs (dryer conditions) have longer predicted times, while higher RHs (more humid conditions) have shorter predicted times. This is always true, regardless of temperature, because the room humidity controls how much water will be absorbed by the film. The water content of the film plays an essential role in the reactions of deterioration; therefore, the higher the RH, the faster the degradation.

Note in Fig. 3 the difference between the predictions at 50% RH and 20% RH. Generally, film degrades only about one third to one half as fast at 20% as it does at 50% RH. It's not a good idea to go lower than 20% RH, though, because film dries out too much and becomes brittle. Likewise, it's not a good idea to store film at RHs above 50%. As Fig. 3 shows, the predicted time at 70°F, 80% RH is considerably shorter than that at 70°F, 50% RH. In addition, high humidity not only promotes vinegar syndrome, it also can allow mold to grow (if RH is kept at 70% RH or above for sustained periods), leading to irreversible damage to the gelatin emulsion.

The prediction for room temperature (70°F/21°C) and 50% RH in our example may seem surprisingly short—only about 40 years. Nearly every film archivist knows of film that is 40 years old and still in good condition. (And many archivists also know of 40-year-old film that is not so good.) To understand the 40-year prediction, remember that it is the approximate number of years to the *onset* of measurable deterioration, and not the number of years it would take for film to
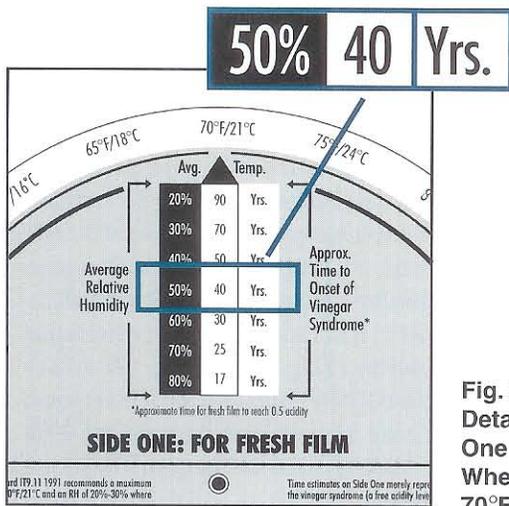
Fig. 3
Detail of Side
One of the
Wheel set for
70°F/21°C.

reach the later stages of deterioration, when it would become shrunken and brittle. Remember also that the predictions assume maximum acid trapping and that real-life films have usually experienced a changing environment, not a steady one. In spite of all these qualifications, and although the evidence is anecdotal and not rigorous, there does exist enough actual keeping experience with acetate film to confirm the general trends in the *Guide*. Film kept in warmer than room-temperature conditions does degrade in about 30 years, and film kept at cooler than room-temperature storage for 50 years shows no signs of degradation. The general trends in the IPI data have been confirmed by similar laboratory studies at Kodak[4,5,6] and Manchester Polytechnic in the U.K.[7,8,9,10] So, while the predictions should not be taken literally, neither are they unrealistic. However, their importance is that they can be relied on to quantify in a relative manner how much better or worse one storage condition is than another.

Using the Wheel to Plan a New Film Storage Environment

The Wheel is also useful for planning a new film storage environment. For example, let's assume an institution has the opportunity to build a new storage area for its photographic collection—one that consists of a variety of materials, including film, glass plates, color and black-and-white prints, etc. Since the collection has sizeable amounts of acetate film in the form of black-and-white sheet films and color transparencies, prevention of vinegar syndrome is one of several goals for the new storage area.

The first thing to do is to decide how long the institution wishes to retain its film collections. This will allow the use of the *Guide* to determine which storage conditions would provide the desired number of years before the onset of vinegar syndrome. In our example we will assume that the institution wants its acetate film to last a minimum of 100 years.

Is Room Temperature Good Enough?

If all the collection materials must coexist in one storage room, then because of the possible problems with glass plates at RHs lower than 25%[11] (see p. 19), an RH of 40% is decided upon. But what should the temperature be? The most convenient temperature is probably a comfortable room temperature of 72°F (22°C). Using Side One of the Wheel, find the temperature closest to 72°—in this case, it's 70°F (shown in Fig. 3). Although this is slightly cooler than the 72°F we're interested in, it's close enough. At 40% RH, 70°F, the predicted years to onset of vinegar syndrome is 50—only about half what the institution wants from their film. Clearly, room temperature is not a good choice to meet the preservation objectives of the institution, and somewhat cooler temperatures are required.

What Are the Choices?

To determine which temperature would yield the desired 100 years at 40% RH without danger of vinegar syndrome (remember the predictions on Side One of the Wheel are for fresh, undeteriorated film), rotate the smaller disk of the Wheel until 100 years or more appears in the window opposite 40% RH. At 60°F we find the desired 100 years (Fig. 4, left). If the collection contains older films with a questionable storage history, leading the collection manager to suspect that deterioration is already starting (even though obvious
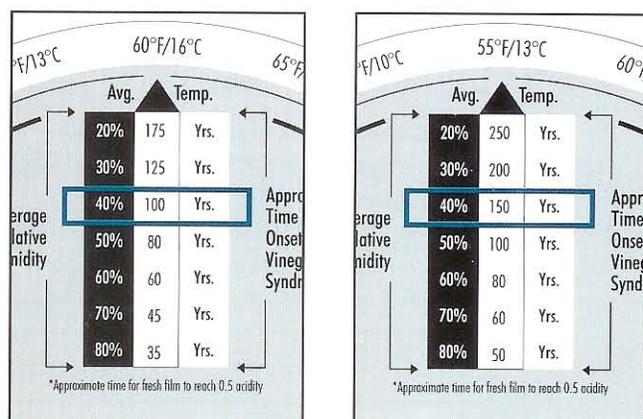

Fig. 4   Details of Side One of the Wheel set for 60°F (left) and 55°F (right).
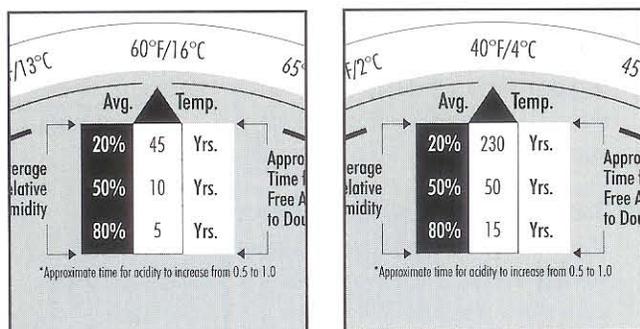
Fig. 5 Details of Side Two of the Wheel set for 60°F (left) and 40°F (right).

outward signs of it are not apparent), then somewhat cooler temperatures might be chosen to provide a little "cushion" on the 100 years. At 55°F, 40% RH, for example, the prediction for onset of vinegar syndrome for fresh film is 150 years (Fig. 4, right).

However, if there is evidence that film in a collection is indeed already deteriorating (odors, waviness on the edges of the film, etc.), then the situation is different. Can improved storage "stabilize" such film so that it may be kept around for a significant number of years? The answer is a qualified "yes," but colder temperatures are required to achieve a long life.

Planning for Degrading Film

Side Two of the Wheel deals with storage conditions for already degrading film. The predictions on this side of the Wheel are based on the period of years necessary for the free acidity of film to double from 0.5 to 1.0. These numbers take a little explaining. (For more information, see p. 13 for a discussion of the course of the vinegar syndrome.) At the 0.5 free acidity level, film may smell of acetic acid, but it is still quite usable. At 1.0 free acidity the same is true, but the odor may be a little stronger; not until the free acidity reaches about 5.0 will changes (buckling, embrittlement) occur to render the film unusable.

All this is just to explain that the doubling of acidity to 1.0 doesn't mean that terrible things suddenly occur—it only indicates that deterioration has progressed. The acidity has doubled, but there is still some way to go before the film is ruined and useless. The important question is how storage conditions can be used to slow the progress of deterioration, and one can get a good idea of that from the predictions of time necessary for free acidity to go from 0.5 to 1.0.

Returning to our example of choosing storage conditions for a mixed collection, if some of the acetate film were already degrading, Side Two of the Wheel could be used to determine how the 60°F, 40% RH condition would affect the progression of deterioration in such film. Rotate the smaller disk on Side Two to point to 60°F, and locate the nearest RH value to the left of the window (Fig. 5, left). Side Two has only three RH values (20%, 50%, and 80% RH), so in this case we will have to interpolate between the 20% and 50% values. At 60°F, 50% RH the free acidity will double in ten years, at 20% RH, it will double in 45 years. Since 40% RH is closer to the 50% value, it will take about 20 to 25 years for free acidity to double in films kept at 60°F, 40% RH.

This is encouraging, but suppose the institution desired 100 years of useful life from already degrading film. (Remember that once channeled or embrittled, nothing can be done to reverse the course of deterioration—prevention is the only effective method of preservation.) Rotating the smaller disk on Side Two to 40°F shows that, at 50% RH, 50 years is predicted before free acidity doubles from 0.5 to 1.0 at that low temperature condition (Fig. 5, right). Interpolating to 40% RH, the prediction is for approximately 100 years. Thus the institution can reasonably expect that storage at 40°F, 40% RH would provide a century of additional useful life, even for film that was already in the initial stages of degradation (at an acidity level of 0.5).

Color Film

Of course, vinegar syndrome is only one consideration in the choice of a storage environment for a photographic collection. In our hypothetical example, color film is also included in the collection. Dye fading also has a strong temperature and RH dependence, but no "wheel" yet exists for color. A decision to choose temperatures cooler than room temperature will also benefit the color film and prints in the collection.[12] Many real-life institutions have opted for cold storage facilities to forestall simultaneously both dye fading and acetate base deterioration.

The Time Contours for Vinegar Syndrome (represented twice—for Fahrenheit and Celsius) give a broad overview of the relationship between temperature, RH, and the time in years for fresh film to begin deteriorating. (See Fig. 6.) Each sloping line on the graph is marked with a time period (one year, five years, etc.); any point on the line represents a temperature/RH combination for which the indicated life expectancy would be obtained. About 100 years of life expectancy, for example, could be obtained at 70°F, 20% RH, or at 48°F, 80% RH, or at any of a variety of intermediate combinations. This graph makes it possible to see the general trends at a glance—such as how short film life can be if stored in hot and humid places, and how long it can be kept under cold, dry conditions (15 centuries at 30°F, 20% RH).

It is important to realize that these time contours are useful for a quick approximation of the relation-ships between temperature, humidity, and the onset of the vinegar syndrome. Don't try to "read between the lines." On this type of graph, interpolation between the lines is difficult because the time intervals are not uniform; to find a life expectancy associated with a particular set of conditions, use the Wheel or the Time Out of Storage Table instead.

The Time Contours show the extreme range of life expectancies that are possible with acetate film. They range from very short (only one year at 130°F, 50% RH) to very long (more than 1000 years at 30°F, 50% RH). Even longer life expectancies are possible at still lower temperatures, but time periods of more than ten centuries seem a bit unreal to us—even though many objects survive that are three or four millennia old. The downward sloping lines of the Time Contours graph show how RH affects film life; at higher RHs the life expectancy of film is much shorter.
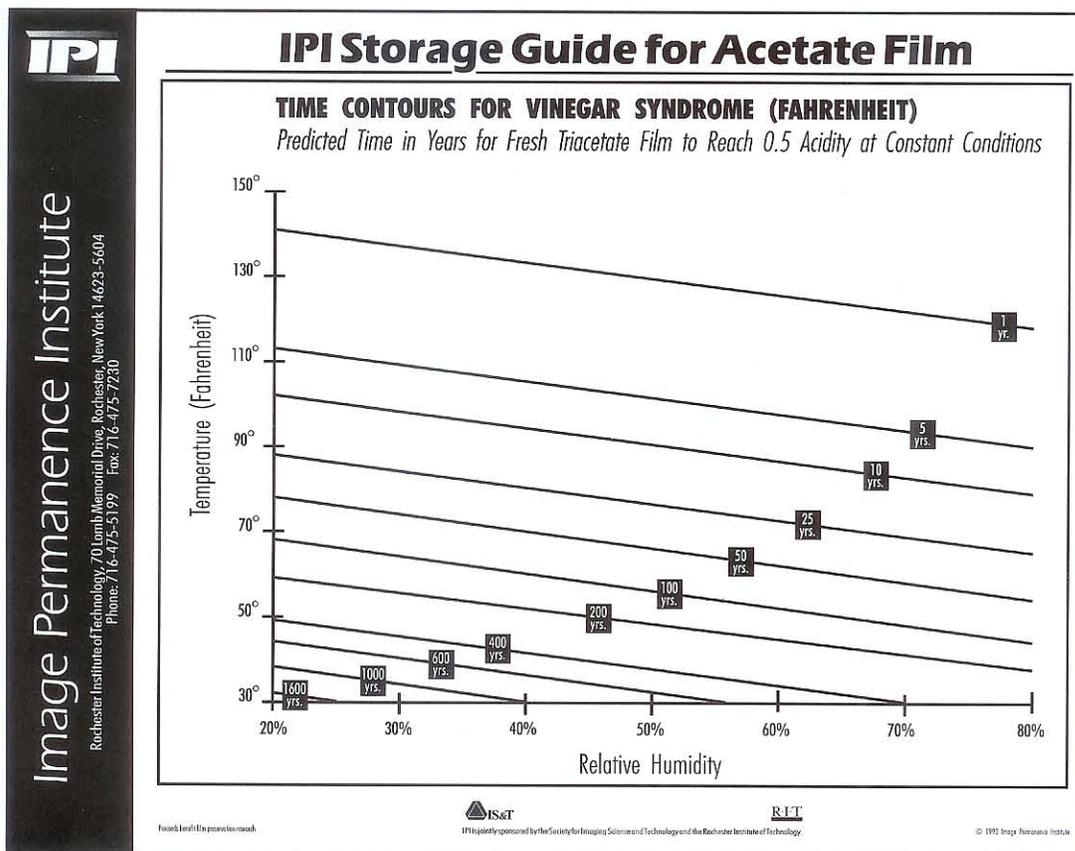

Fig. 6   Time Contours for Vinegar Syndrome

Even if a collection has a special environment such as a cold storage vault, objects do not always remain there. They may be brought out periodically for use, for maintenance of the vault, or for other reasons. Making use of an approach first suggested by Mark McCormick-Goodhart, a research scientist at the Smithsonian's Conservation Analytical Laboratory, the Time Out of Storage Table (Fig. 7) gives data similar to that found on the Wheel, but with the added dimension of "time out of storage" to show how film life expectancy is affected when film is taken from a storage vault and used at room temperature for a period of time. The effects of leaving the storage environment and spending varying amounts of time at office conditions (75°F, 60% RH) can be profound. Film life expectancy can be significantly diminished merely by removing film from special storage and keeping it for an average of 30 days each year at office conditions.

Using the Table

To use the Time Out of Storage Table, one must first locate the row that corresponds to the "vault" conditions. The Table is based on the assumption that, most of the time, film is stored in a primary storage area (referred to as the "vault," though it could be an ordinary room, a special vault, a refrigerator, or any other kind of physical storage arrangement). What matters is the temperature and RH of this primary storage or "vault" condition where film normally resides. The three left-hand columns of the Time Out of Storage Table are marked "Primary Storage or 'Vault' Conditions." The first two columns are temperature (shown for convenience in both Fahrenheit and Celsius), the third is RH.

Using the Time Out of Storage Table involves finding the row corresponding to the primary storage condition and then looking across the table at columns that refer to how much time the film is out of the vault and kept in an "office" condition of 75°F (24°C), 60% RH. This is meant to reflect the reality that film is often removed from a vault for use, for exhibition, for curatorial research, because of equipment failure, for maintenance, etc.

Each column heading is marked with the average number of days per year that film might spend out of the vault and in the "office" conditions. Thus the "120 Days" column means that film spends four months each

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"TIME OUT OF STORAGE" TABLE

Predicted Time to Reach 0.5 Aciditiy with Time Out of Storage for Cellulose Triacetate Film

Primary Storage or "Vault" Conditions			Average # of Days/Year Out of Storage at 75°F/60% RH						
			0 Days	1 Day	5 Days	10 Days	30 Days	90 Days	120 Days
Temperature									
°C	°F	%RH	Time in Years to Reach 0.5 Acidity						
21	70	20	90	90	80	80	70	50	40
21	70	40	50	50	50	50	45	35	35
21	70	60	30	30	30	30	30	25	25
16	60	20	175	175	175	150	100	60	50
16	60	40	100	100	100	90	80	50	45
16	60	60	60	60	60	60	50	40	35
10	50	20	400	350	300	250	150	70	60
10	50	40	200	200	200	175	125	70	50
10	50	60	125	125	100	100	90	60	50
4	40	20	800	800	500	400	200	80	60
4	40	40	450	450	350	300	175	70	60
4	40	60	250	250	200	200	125	70	50
-1	30	20	2000	1500	900	600	250	80	60
-1	30	40	1000	900	600	450	200	80	60
-1	30	60	500	500	400	300	175	80	60
-9	15	20	>3500	3500	1250	700	250	80	60
-9	15	40	3500	2500	1000	600	250	80	60
-9	15	60	1750	1500	800	500	250	80	60
-18	0	20	>>3500	>3500	1500	700	250	80	60
-18	0	40	>>3500	>3500	1500	700	250	80	60
-18	0	60	>3500	3500	1250	700	250	80	60
-26	-15	20	>>3500	>3500	1500	800	250	80	60
-26	-15	40	>>3500	>3500	1500	800	250	80	60
-26	-15	60	>>3500	>3500	1500	700	250	80	60

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Fig. 7   Time Out of Storage Table.

year in the office condition and eight months in the vault condition. The numbers in the columns are the predicted number of years for the onset of vinegar syndrome (defined as reaching 0.5 free acidity) in fresh acetate film; the predictions show the combined effects of being stored part of the time in the vault condition and part of the time in the office condition.

Consider an example of a vault that is operating at 40°F, 40% RH (Fig. 8). This is an excellent storage condition that should provide a very long life for films. If film were always kept in the vault, then the predicted time before the onset of vinegar syndrome in fresh film would be 450 years. The column in the Time Out of Storage Table marked "0 Days" repeats the same predictions as Side One of the Wheel—this simply means the film never leaves the vault. Looking across the row, the predicted number of years drops off sharply from 450 down to 60 as the average number of days per year *out* of the vault increases.

At 30 days per year out of the vault, the predicted time is only 175 years, less than half of the value for 0 days. It isn't difficult to imagine circumstances in which film would average 30 days per year out of a cold storage vault, considering all the possible reasons for intentional or unintentional removal or equipment

shutdown. If the film is out an average of 120 days per year, the predicted time is only 60 years, about 13% of the life expectancy if it never left the vault.

What Happens to Film Out of Storage?

The longer the time out of the vault, the more the warmer condition "takes over" in determining the overall life expectancy of the film. Note that in reading down the column marked "120 Days" out of storage (Fig. 7), there is little or no benefit from having a film vault any colder than 50°F. The time spent at the "office" condition is determining the life expectancy of the film. No matter how much colder than 50°F the vault condition may be, the four months per year at 75°F, 60% RH dictates that only 60 years will pass before the predicted onset of vinegar syndrome.

The impact on film life expectancy of the *combined effects* of a storage vault and an office (i.e., use) condition will of course depend on the temperature and RH of both areas. The Time Out of Storage Table is predicated on an office condition of 75°F (24°C), 60% RH. The predictions in the Table will be different for other office conditions. IPI can, if desired, calculate a customized Time Out of Storage Table based on a different use environment; institutions can have this done on a consulting basis by contacting IPI.

Primary Storage or "Vault" Conditions			Average # of Days/Year Out of Storage at 75°F/60% RH						
			0 Days	1 Day	5 Days	10 Days	30 Days	90 Days	120 Days
Temperature			Time in Years to Reach 0.5 Acidity						
°C	°F	%RH							
4	40	20	800	800	500	400	200	80	60
4	40	40	450	450	350	300	175	70	60
4	40	60	250	250	200	200	125	70	50

Fig. 8   Detail of the Time Out of Storage Table showing a primary storage condition of 40°F.
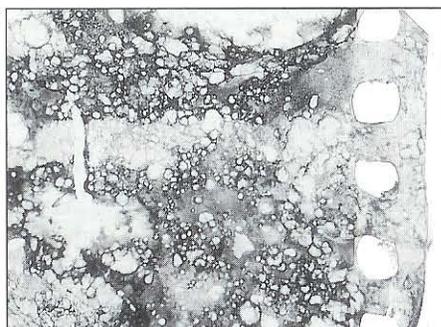
Fig. 9 Ruined gelatin in degraded 35mm nitrate motion picture film.

Chemical Deterioration of Nitrate

Many archivists are familiar with the slow chemical deterioration of cellulose nitrate film,[13,14] but they have assumed that cellulose acetate (so-called "safety" film) is something entirely different. It turns out that cellulose nitrate and cellulose acetate both share a built-in propensity to degrade; both these plastic materials are modified forms of cellulose, and both have a regrettable tendency to become "un-modified" by the same kinds of chemical pathways. To make nitrate plastic in the first place, nitro (NO_2) groups are grafted onto the long molecular chains of native cellulose.[15]

As long as these "side groups" stay put, all is well. But in the presence of *moisture, acids, and heat* they tend to become detached, liberating the nitro groups.[16] The nitro groups are very harmful substances to let loose—they are strongly acidic and strongly oxidizing in nature. They fade silver images and make gelatin soft and sticky; their highly acidic fumes rust film cans and embrittle paper enclosures.[17] This, however, is nitrate—a sad tale, but one already told many times. How does acetate degradation differ from nitrate degradation, and where does the vinegar syndrome come in?

Acetate Film and Vinegar Syndrome

Vinegar syndrome is a problem that affects only cellulose *acetate* plastic materials.[18] In acetate film the "side groups" are not nitro (NO_2) but *acetyl* (CH_3CO—see Fig. 10). As with nitrate, all is well as long as these acetyl groups remain grafted onto the cellulose molecules. Detachment of the acetyl groups also can occur in the presence of moisture, heat, and acids—only, in this case, free *acetic acid* is liberated.

The acetic acid is released inside the plastic, but it gradually diffuses to the surface, causing a familiar sharp odor—the odor of vinegar (which in fact is a 5% acetic-acid solution in water). The amount of acetic acid that can be generated by degrading film is surprisingly large; expressing it in terms of teaspoonfuls of household vinegar, in advanced stages of deterioration there can be nine teaspoonfuls or more of vinegar for every four feet of 35mm movie film. A typical 1000-ft. can of 35mm film can generate enough acetic acid to be equivalent to 250 teaspoonfuls of household vinegar!

So, to restate, cellulose nitrate film and cellulose acetate film are somewhat similar in that they are both modified forms of cellulose, and both can slowly decompose under the influence of heat, moisture, and acids. Not surprisingly, the conditions of storage that are good for nitrate are also good for acetate, and vice versa.[1,2] However, the symptoms of deterioration, when it does occur, are rather different in the two film types.

The Effects of Free Acetic Acid

The oxidizing and highly acidic nature of liberated nitro groups has been described above, but what are the effects of free acetic acid? In some ways, they are much more benign. Acetic acid is not a strong acid (it won't aggressively rust cans unless present in large amounts). It is not a strong oxidizer, so the silver image is not faded to orange-red as is often the case in nitrate decomposition. In extreme cases, vinegar syndrome can lead to softening of gelatin, but in general the emulsions of degrading acetate films remain in much better shape than nitrate film emulsions do. There is not much color film on nitrate base, but one effect of acetic acid generation in acetate film is to accelerate the fading rate of some color dyes in color film.
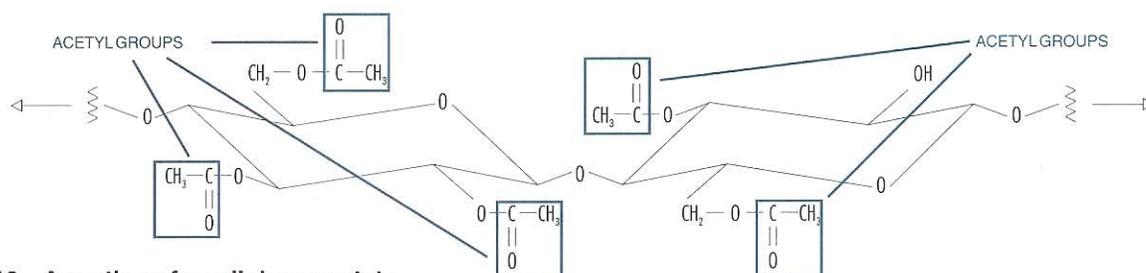

Fig. 10   A portion of a cellulose acetate chain. Two units shown; molecule goes on.

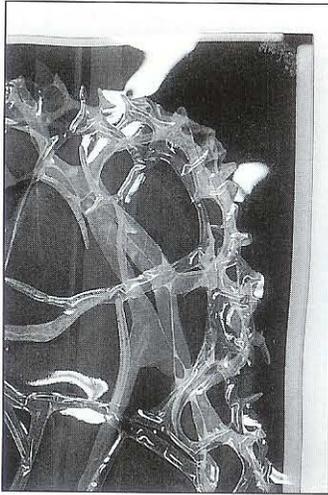Fig. 12 Shrunken, embrittled 35mm acetate microfilm.

Fig. 11 Shrinkage due to deterioration in acetate sheet film leads to severe buckling of the emulsion away from the plastic film base.

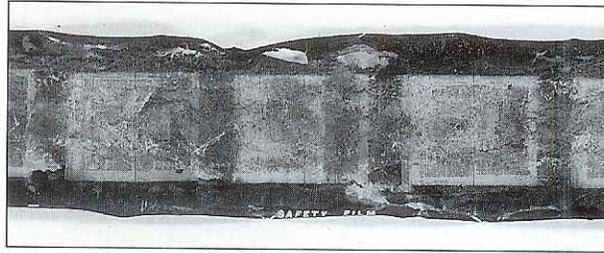Fig. 13 Shrunken, embrittled 16mm acetate motion picture film.

Recognizing Vinegar Syndrome

Vinegar Odor

The vinegar smell is perhaps the most obvious symptom of acetate base deterioration, but it is not the only one; if an unpleasant odor were the only consequence of degradation, many ruined films would still be with us. Unfortunately, other chemical and physical changes take place in acetate film as the acetyl side groups are split off. The vinegar odor is a warning that chemical deterioration is progressing in the acetate film base.

Embrittlement

One of the physical changes that occurs in the advanced stages of deterioration is the embrittlement of the plastic base, in which a formerly supple and strong material is changed into a weak one that easily shatters with the slightest flexing. This is a consequence of the fact that cellulose acetate is made up of long chains of repeating units (i.e., it is a long-chain polymer). When acetic acid is liberated as the acetyl side groups come off, the acid environment helps to break the links between units, shortening the polymer chains and causing brittleness.

Shrinkage

Another consequence of acetate-base decomposition is shrinkage. With the polymer chains breaking into smaller pieces, and with the side groups splitting off (literally making smaller molecules), the plastic film base begins to shrink. Film can shrink for other reasons than deterioration (some small amount of shrinkage occurs over time through loss of solvents from the base), but really destructive shrinkage is a result of vinegar syndrome. Shrinkage greater than about 1% is enough to cause real trouble for cinema films.

In advanced stages of deterioration, shrinkage can be as much as 10%—a huge amount. The acetate base gets much smaller, but the gelatin emulsion frequently does not (it isn't undergoing deterioration, so it stays the same size). The result is that something has to give; eventually the bond between the emulsion and base lets go in some areas, thus relieving the stress caused by base shrinkage. The emulsion is now buckled up in a way that archivists describe as "channeling." Cut sheet films (4 x 5, 8 x 10, etc.) quite often are severely channeled in the later stages of acetate degradation (see Fig. 11). Sometimes the emulsion actually tears as it buckles. Sheet films have gelatin on both sides of the base; the gelatin on the non-emulsion side is there primarily to control curl. When shrinkage occurs, the gelatin will buckle up and channel just as the emulsion does.

Because the gelatin emulsion usually stays intact through the degradation process, for sheet films it is possible to save the image by dissolving the emulsion away from the shrunken base using solvents. Once it has been freed from its original support, it can be made flat and photographed, or else transferred to a new support. This is a delicate and (because of the solvents used) a potentially hazardous undertaking. It certainly is expensive to do with a large film collection. Degraded motion picture films cannot be restored this way, but sheet films often can. Even torn emulsions can be dealt with successfully. For very important images, the cost of this kind of restoration can be justified; unfortunately, for most images the cost is too high.

Fig. 14 Degraded acetate sheet film showing channeling and circular bumps of crystallized plasticizer under the gelatin emulsion.
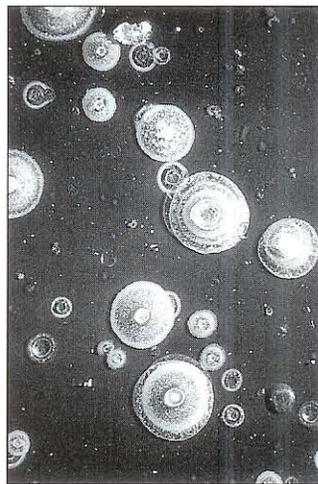

Fig. 15 Close-up view of circular bumps of solid, crystalline plasticizer as typically found on degraded acetate sheet film.

Fig. 16 Bubbles of liquid plasticizer that have formed under the emulsion on degraded acetate sheet film.

Crystals or Bubbles on the Film

Another consequence of base deterioration is the appearance of crystalline deposits or liquid-filled bubbles on the emulsion.[18] This is evidence of *plasticizers,* additives to the plastic base, becoming incompatible and oozing out on the surface. They can appear on either the base or emulsion side of the film. Plasticizers are chemical additives that are mixed in with the cellulose acetate during manufacture; normally they are distributed throughout the whole plastic support.[5]

Plasticizers make up about 12% to 15% by weight of the film. Their purpose is twofold. Their main job is to slow down the rate of burning of the film, should it ever catch on fire. The awful tragedies that occurred because of the high flammability of nitrate film (fires that consumed film vaults, sometimes killing many people) made the photographic industry very careful about the burning properties of "safety" film.[19,20] The high plasticizer content of acetate films reflects a desire to make film as non-flammable as possible. The second function of plasticizers is to reduce the dimensional instability of film due to solvent loss or humidity change. All cellulosic films will shrink under dry conditions and expand under damp conditions; minimizing this behavior is an important role of plasticizer additives. (Nitrate film also contains plasticizers that exude onto the surface as deterioration progresses.)

At the time of manufacture, acetate films readily retain the incorporated plasticizers. However, if chemical deterioration should occur later on, the capacity of the base to retain the plasticizer is reduced, and the plasticizer exudes out of the base and crystallizes on the surface. Most commonly this takes the form of needle-like crystals which melt away under mild heat and which re-form when the heat is taken away. In some films, the plasticizer is exuded as a liquid; bubbles form under the emulsion, typically in the center of the film. The exudation of plasticizers is associated with more advanced stages of degradation.

Pink or Blue Colors on Deteriorated Sheet Films

Still another consequence of vinegar syndrome is the appearance of pink or blue colors in some sheet films.[18] This is caused by dyes incorporated into the gelatin layer on the back side. Such dyes are called *antihalation* dyes because they prevent "halos" in the image.* These dyes are supposed to have been made colorless when the film was processed, but when acetic acid is formed during deterioration, the acid environment makes the dyes go back to their original pink or blue color. (Pink colors are found in some Kodak films, while blue colors are found in some Agfa and Ansco films.)

* "Halos" are unwanted circles of light that show up around a bright object in the image—a street lamp in a night scene, for example. This is a disturbing, unreal effect caused by light reflecting off the film base during exposure. The gelatin coating on the back side of sheet films is a convenient place to put some dyes that would absorb this unwanted light and keep it from forming halos in the image.

It is useful to understand the progression of acetate deterioration so that the condition of a film collection can be assessed more knowledgeably. Of all the changes brought about by degradation, the first sign is usually the vinegar odor. Fig. 17 shows how acidity builds up in film base over time. It is the *shape* of this curve that is important, because it describes how acidity is at first almost non-existent, then for a long time builds up gradually, little by little. Then, after the acid level increases to a certain point, the increase suddenly becomes very rapid. Before this point, acidity rises slowly. After it, large amounts of acid are generated in a short time.

How Storage Conditions Influence the Course of Deterioration

The reason why degradation follows this course is easy to understand. Recall that acetic acid is formed when the acetyl "side groups" are split off from the cellulose molecules (Fig. 10). There are three factors that induce such changes: heat, moisture, and acid. In the early stages (the "induction period," before the sharp turn upward) there is little acid present, so **the reaction rate is determined primarily by heat and moisture.** During this long, slow buildup, the storage environment plays the decisive role. The temperature of the storage room determines how much heat energy is available to push deterioration along. Likewise, the amount of moisture present in the film is governed by the relative humidity of the storage area. Thus environmental factors can influence whether the induction period is long (perhaps centuries) or short (just a few decades).
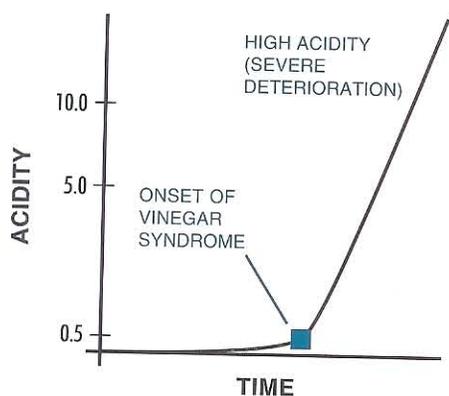

Fig. 18 Later stages of acetate deterioration involve brittleness and channeling of the emulsion, but the silver image usually remains in good condition.

Autocatalytic Behavior in Deteriorating Film

The sharp bend in the time-versus-acidity curve represents the point when acidity becomes another major factor, along with heat and moisture, in determining the rate of deterioration. Although the environment still influences the rate of degradation, **the more advanced deterioration becomes, the more the reaction rate is influenced by the presence of acidity.** The reason is that the reaction is now "feeding on itself"—displaying what scientists call *autocatalytic* behavior. A catalyst is a substance that speeds up a chemical reaction but is not consumed by it. When a reaction is catalyzed by acids as it is in acetate film, and acid is a product of the reaction itself, you have an autocatalytic system. The acetic acid that is liberated as the acetyl groups split off catalyzes the removal of other side groups, and the whole process snowballs.

Free Acidity—The Best Way to Measure Deterioration

The sharp upward turn in the time-versus-acidity curve in Fig. 17 is called the *autocatalytic point*. It's labeled with the value 0.5, which takes some explanation. The number 0.5 is a measure of the "free acidity" in the film base; free acidity is not the same as a pH value. It represents the total amount of acid present in the film base.* ANSI Standard IT9.1-1992 specifies the method used to obtain free acidity measurements. The ANSI

Fig. 17 Time-versus-acidity curve for acetate film. The autocatalytic part of the curve occurs at about 0.5 free acidity, the point chosen as the basis for predictions of the onset of vinegar syndrome in the *Guide*.

*The free acidity values actually are derived from the volume of alkali that is necessary to completely neutralize the acidity of the film base.
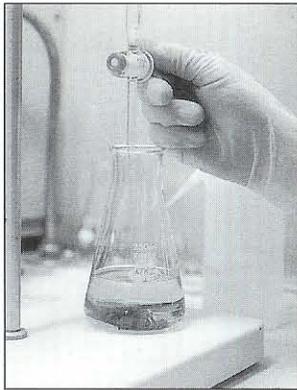
Fig. 19 Measuring free acidity in the laboratory.

method was the way in which free acidity was measured in the film base during IPI's research project on acetate deterioration. All the parts of the *Guide* (the Wheel, the Time Contours, and the Time Out of Storage Table) are based on free acidity measurements. Free acidity appears to be the most sensitive and reliable measure of acetate degradation, and that is why the *Guide* is based on it.

Some landmarks on the free acidity scale are 0.05 (the very low level of free acidity typically found in freshly manufactured films) and 0.5 (which we've already seen is approximately at the autocatalytic point). Advanced stages of deterioration (which are marked by very strong odor, shrinkage, buckling, and plasticizer exudation) often have free acidity levels of 5.0 to 10.0 and sometimes even higher (see Fig. 17). At the 0.5 free acidity level, the film will smell of vinegar, but it may not have any other symptoms of degradation and will be perfectly usable. However, it will degrade rather quickly from then on unless kept in low-temperature, low-RH storage, as shown on Side Two of the Wheel.

The Goal of Good Film Storage: Keeping Free Acidity at Low Levels

Side One of the Wheel, the Time Contours, and the Time Out of Storage Table are based on predictions, derived from accelerated aging, of the number of years (at constant temperature and RH) before fresh film will reach a free acidity level of 0.5. Knowing the importance of the 0.5 autocatalytic point in the overall course of degradation helps to put the meaning of the Wheel's predictions in perspective. **The goal of good storage is to keep the film from ever getting to the 0.5 autocatalytic point in the first place, because once there, its useful life from that point on (at least if kept at room temperature) will be short.**

The same kinds of predictive mathematical models that were used on the accelerated-aging data to predict the number of years until fresh film reaches 0.5 free acidity also can shed some light on how fast things will happen after the 0.5 acidity point is reached. (Predictions for doubling of free acidity from 0.5 to 1.0 are given on Side Two of the Wheel.) The best inferences

that we can make from the accelerated-aging tests indicate that film in the early stages of deterioration still can be preserved for many years by improved storage. Although nothing can bring back severely degraded, channeled film, something *can* be done for film that is still in the early stages of deterioration.

Storage Strategies for Degrading Film

One of the primary strategies for dealing with nitrate film in collections has been to segregate it from the other film materials. This has been done for two reasons: because of the potential fire hazard[21] and because the acidic and oxidizing fumes from degrading nitrate film may infect other, still healthy, films.[17] Does this make sense to do with degrading acetate? The available evidence on this point is limited. While in some circumstances deterioration appears to have spread from film to film, one cannot be sure of the extent to which absorption of acid vapors helped to trigger the degradation.

Laboratory experiments show that acetic acid vapors are readily absorbed by fresh film, and this will lead to faster deterioration. In practice, however, it's quite difficult to judge when a threat actually exists. Where at all practical, films showing vinegar syndrome should be segregated. However, this is not always possible, and having a little degraded acetate film in a large, well-ventilated room may not infect other materials. In such cases the measurable acetic acid concentration in the room may be very low. On the other hand, having some strong-smelling film inside a closed container with good film will likely cause faster deterioration in the good film, because the concentration inside the box can be rather high. More research is needed to explore the practical aspects of this phenomenon, but until then, film archivists will have to use their own best judgment about when and how degrading acetate film should be segregated from the rest of a collection.
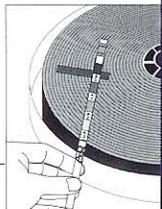
DOES THE *GUIDE* APPLY TO NITRATE FILM?

In the section on chemical deterioration of film bases, we mentioned the chemical similarities between cellulose nitrate and cellulose acetate and pointed out that the same factors (heat, moisture, and acids) govern the rate of deterioration in both materials. Do the data in the *Guide* therefore apply to nitrate film as well as acetate? In a general sense, yes. Trends similar to those seen in the effects of temperature and RH on the rate of acetate deterioration are seen for nitrate deterioration as well. At this time, IPI has limited data on the behavior of nitrate films, so a "wheel" for nitrate does not exist.

IPI's 1988-1990 study of film-base deterioration included a 50-year-old sample of nitrate motion picture film; its response to the storage environment (and therefore its predicted life expectancy) were much the same as that of acetate film.[1,2] This somewhat surprising result also occurred with some of the samples in a follow-up study at IPI. But there is an important difference between nitrate and acetate that also showed up in IPI's follow-up study. Nitrate film is like the little girl of the old nursery rhyme: "When she was good she was very, very good, but when she was bad she was horrid."

Samples of nitrate seemed to divide into two groups: those that were in apparent good shape and performed similarly to fresh acetate, and those that were in apparent good shape but degraded very quickly in the accelerated-aging tests. Some of the nitrate film samples* used in the research had slightly more acidity initially, and these degraded faster. An attempt was made to seek out nitrate samples in as good a condition as possible, but differences necessarily will exist among such older materials.

IPI's experiences with nitrate confirm what many film archivists already knew about nitrate film: it surprises you both with how long it can last and how quickly and utterly it can deteriorate. Nevertheless, the positive outcome of IPI's research is that some nitrate film can have a very long life—as long a life as acetate—if stored well. The *Guide* can offer insights on what kind of storage environment is best for nitrate film: the cooler the better, with RH not lower than 20% or higher than 50%. The further nitrate film has already progressed along the path of deterioration, the more essential it is to store it at low temperatures. Many collections have opted for near- or below-freezing temperatures for their nitrate film materials.

* Since nitrate film hasn't been manufactured for forty years, all the nitrate samples were at least a half-century old.
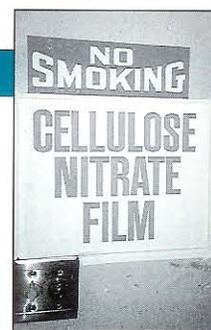
POLYESTER BASE FILM

Polyester films, introduced in the mid-50s, now comprise a significant fraction of archival film collections (p. 22 has more information on which films are likely to be on polyester supports). Polyester film base is inherently more chemically stable than either cellulose nitrate or cellulose acetate.[2,4,5] With nearly 50 years of manufacturing and keeping experience behind it, polyester film support has shown exceptional chemical stability and overall good physical performance. When there is a choice between polyester and acetate film supports, polyester is clearly the best one for archival use.

Although polyester base is also subject to chemical deterioration (nothing lasts forever), accelerated-aging tests show that it will last five to ten times longer than acetate under comparable storage conditions.[2,4] Such testing shows temperature and humidity dependence in polyester base deterioration, so good storage is still important to get the longest life from polyester film. To date, there have been no reported cases of chemical deterioration of polyester base in archival collections. When such deterioration does occur, brittleness and loss of tensile properties will likely be among the symptoms.

The excellent chemical stability of polyester film base offers the opportunity to create photographic records of unparalleled permanence, even at room temperature conditions. Gelatin emulsion layers have the potential to last for centuries; together, polyester base, gelatin emulsion layers, and the correct choice of image substance will yield a pictorial recording medium that should survive five centuries or more at room temperature and moderate RH. Although conventionally processed silver images are not equipped to withstand the slow attack of atmospheric pollutants, they can be chemically treated to become virtually unalterable.[27] Thus black-and-white films on polyester base, together with appropriate stabilizing treatment of the silver image, can provide an extraordinarily long-lived pictorial record.

Vinegar syndrome is only one consideration in determining the best storage conditions for film. The needs of other film components—the gelatin emulsion, and the silver or dye image—must be taken into account as well. Beyond the physical and chemical nature of film as an object, storage conditions also have implications for how a collection can be accessed and used. Good storage can be costly, so it's vital to be clear about the necessity of a proper environment from a technical point of view. A brief review of the needs of each film component will help establish a context in which to place the issue of vinegar syndrome. The principal factors in the storage environment that affect film are temperature, RH, and pollutants. Acting alone, or more typically, acting in combination, they can have significant effects on the deterioration of gelatin, silver, and dyes.

Temperature

Heat energy makes chemical reactions happen faster. The higher the temperature, the more vigorously atoms and molecules vibrate and move around, colliding with each other with greater force, thus becoming more likely to react. The common forms of film deterioration—vinegar syndrome and color dye fading—are chemical reactions occurring in the plastic or dye molecules. Temperature plays a key role in determining the rate of chemical reactions, and that is the basis for the simple truth that cooler conditions (all other things being equal) are always better for film than warmer ones.

How Big a Difference Does Temperature Make?

In other words, how much improvement in deterioration rate can be obtained by low temperature storage? Can deterioration reactions be completely stopped? Only at absolute zero (definitely not a recommended storage condition!) are all chemical reactions stopped. Otherwise, the reactions will have some finite rate, however slow. The good news is that very dramatic improvements in deterioration rate are possible, especially when compared to room temperature.

The Wheel and Table in the *Guide* show that the reactions of vinegar syndrome will take about 17 times longer at 30°F than at 70°F. There is no single "ideal" storage temperature for film, no one temperature where film is "happiest." The deterioration reactions that occur in its gelatin emulsion, plastic base, or color dye image are always moving forward, sometimes

faster, sometimes slower, according to the amount of heat energy available. It is up to us to decide whether the storage temperature we are providing for film is low enough to ensure the life expectancy we require. The purpose of the *Guide* is to provide the link between environmental conditions and the rate of the vinegar syndrome, so that—at least as far as this one form of deterioration is concerned—we know what conditions we must have to make film last as long as needed.

Silver Images

Black-and-white images do fade (rather a lot), and chemical reactions involving metallic silver are the root cause. However, temperature plays only a limited role in silver image fading.

Dye Images

Because of the problem of dye fading, we have to worry much more about storage temperature with color film.[12] Some organic dyes are stable, others are not. Textile dyes usually won't fade in the dark within a few decades, but photographic dye images do. Many people are familiar with the "purple" cast in some old color movies or prints. This is due to the fact that the image is really made up of three different dyes—cyan, magenta, and yellow—and the magenta (reddish-purple) dye typically lasts the longest. After the other two fade away, all that's left is the magenta dye.

The dyes in color film are complex organic molecules that lose their color if structural rearrangements occur. The heat energy present at room temperature is enough to cause significant fading, so cold storage is recommended for color photographic films. ANSI Standard IT9.11-1991 cites a *maximum* temperature of 2°C (35°F) for "extended term" storage of color film. Older color products (pre-1980) had less inherent dye stability than contemporary films, so collections of older color material are hit with a "double whammy;" the color has only about 20 to 30 years at room temperature before fading becomes significant, and the film is already approaching that age. Low temperature storage must become a top priority for institutions serious about keeping color film in good condition.

The good news about color film is that cold storage can slow dye fading to such an extent that centuries of life are possible. The act of thawing and re-freezing film does not harm it.[22] Ice crystals do not form in the film as it is frozen, and concerns over

damage from taking film in and out of cold storage have not been borne out by experience. Many institutions and organizations have had success with cold storage, in small and large installations alike. However, cold storage has pitfalls; for example, condensation on the film when bringing it from cold storage must be avoided. Frost buildup inside cold storage areas can cause damage in some circumstances. Practical aspects of cold storage are outside the scope of this publication; it is a complex subject, daunting at times, but quite manageable if properly planned.[23] Any institution seeking to implement cold storage should get help from qualified preservation and engineering professionals.

Relative Humidity

Relative humidity is a second decisive factor, but one with complex effects which take a little more explanation. What really matters is the amount of available water in the film base or in the gelatin. Water is a necessary reactant in vinegar syndrome and image fading. Removing all the water would seem a simple and effective way to preserve film, but unfortunately it isn't a desirable thing to do. Without some water present, gelatin and acetate film would contract and become so brittle that they might crack when handled.

The amount of water present in the film is determined by the relative humidity of the storage environment. For example, consider film which has resided a long time in a room at 50% RH and is then brought to another room where the RH is only 20%. At the new, low RH, moisture leaves the film and evaporates into the air. At the same time that water is leaving the film, some few water molecules are also being absorbed by the film from the air, so that both evaporation and absorption are going on simultaneously. But because the air is at low RH, much more water is evaporating than being absorbed, and the net flow is from the film into the air. As the process continues, the film begins to dry out; it's holding less moisture now, so the rate of evaporation begins to slow down. Eventually an *equilibrium* is reached when continued water absorption from the air is perfectly matched by continual evaporation of water into the air.

Regardless of what the temperature is, it's the RH that is going to govern how much water remains in the film after the equilibrium is attained. At low RH, there will be very little water absorbed by the film; at high RH the equilibrium point will shift, and the moisture content of the film will be much higher.

Mold

Nearly all film has an emulsion layer of gelatin. Gelatin has proven to be a durable substance except under prolonged damp conditions, when it is prone to attack by mold. Gelatin is an ideal nutrient for mold growth. Although some antifungal additives are used in photographic films, the photographic industry so far has not developed a way to prevent mold. Any time the ambient RH remains above 70% RH or so for several days, mold growth is possible. Good air circulation greatly reduces the chances of mold damage. There are no satisfactory remedial treatments for mold damage to gelatin (mold releases enzymes which soften and dissolve gelatin and also cause stains). Prevention is the only practical answer. Mold spores are almost omnipresent; whenever there is enough moisture, they will propagate and grow.

Chemical Attack

Gelatin is also subject to slow chemical attack by acids, alkalies, and oxidizing air pollutants, leading to loss of strength and ultimately to softening and inability to withstand immersion in water. Such chemical attack is influenced by the moisture content of gelatin (i.e., by ambient RH), but it generally takes so much longer to happen than other forms of deterioration (such as acetate base degradation or fading of color dyes) that it is not even noticed. However, in the case of polyester film (the base of which is very stable at room temperature),[4,24,25] the base may last long enough that the slow chemical deterioration of gelatin becomes the limiting factor in the survival of film. This presumes, of course, that the image component survives that long as well. In the case of nitrate film, gelatin can be attacked by the strong acids and oxidants released by degrading nitrate film base.

Physical Damage

In addition to mold and slow chemical degradation, gelatin may experience physical damage under excessively dry conditions (RH less than 15%). At such dry conditions, the gelatin emulsion may be too brittle for the film to be safely handled. Another result of low humidity is the increase in film curl. This causes motion picture film to show "spoking" (a deformation of a roll of film that resembles spokes on a wagon wheel).

In summary, the gelatin component of film is best stored at an average RH between 20% and 50%, a range in which there is enough moisture to avoid brittleness yet not enough to accelerate chemical deterioration or to grow mold.

RH and Silver Images

The image component of film can be either metallic silver (in the case of black-and-white film) or organic dyes (in the case of color film). The response of silver and dyes to the storage environment is radically different. Let's consider silver images first. RH is a critically important environmental factor in silver image fading because it facilitates the oxidation (corrosion) of metallic silver. The effect of humidity is particularly important in the presence of pollutants (see below). Without moisture present, silver images would not oxidize and, hence, would not fade.

Dye Images

The rate of most dye fading reactions is governed in part by the moisture available in the emulsion layer—which, of course, is determined in turn by the ambient relative humidity. Water actually is a reactant in some types of dye fading, and so there is also a strong humidity dependency to dye fading.[26] In like manner with silver images, the effect of RH is specially important when pollutants are present. Although dye stability is optimum at near total dryness, some moisture (as noted above) must be present for flexibility of the gelatin.

Pollutants

Pollutants originating from either the overall environment or from storage enclosure materials have a very strong effect on silver and dye images, although they are not usually a significant factor in chemical deterioration of film bases.

Silver Images

Contaminants in the air (peroxides, ozone, sulfides, etc.), and contaminants arising from poor-quality storage enclosure materials are the substances that actually react with black-and-white images to cause fading.[27] How much damage they can do is determined mainly by the RH of the storage environment. Without the presence of water, even the most aggressive pollutants don't have much effect on silver. The higher the RH, the more water is absorbed by the gelatin emulsion (where the silver is), and the greater the chances that contaminants—if they are around—can react with the silver.

Another aspect of the importance of RH in silver image fading is the fact that gelatin shrinks at low RH and swells at high RH. When swollen (as it is at RHs above 60%), the gelatin offers no resistance to the diffusion of contaminants through the emulsion. However, at RHs below about 50%, gelatin becomes an increasingly effective barrier to the diffusion of gases, thus protecting the image against the attack of contaminants.[28] So, while we always seek to keep the atmosphere of the storage area clear of pollutants and always try to use inert, non-reactive storage envelopes and boxes, we rely on an RH of 20% to 50% to be our primary line of defense against contaminants.

Dye Images

Color dyes are quite susceptible to attack by oxidizing air pollutants such as ozone and nitrogen dioxide.[29] Recent studies at IPI have shown that the severity of this attack is also RH-dependent, partly because of the barrier properties of gelatin. Sulfur dioxide and hydrogen sulfide have much less effect on color images than oxidizing pollutants.

The Best RH Range for Film Storage

In deciding what is the best RH for film storage, we must take the following into account:

1. The needs of the plastic base.
2. The needs of the gelatin emulsion.
3. The needs of the silver image or of the three dye images (cyan, yellow, and magenta).

In the discussion of all the humidity-dependent forms of deterioration (dye fading, vinegar syndrome, silver image fading, slow chemical deterioration of gelatin) we have suggested an RH range of 20% to 50% as desirable and acceptable. However, whether storage is at the low end of this RH range (20% to 30%) or at the relatively higher end of this RH range (40% to 50%) can make a significant difference in the long term, especially with vinegar syndrome and dye fading. The data in the *Guide* show about a three-fold improvement in life expectancy (years to onset of vinegar syndrome) at 20% RH over 50% RH. Generally similar improvements exist with dye fading in most color films. This difference is definitely not trivial, and this is why the ANSI standard for film storage currently specifies 20% to 30% RH where maximum film life is required.

Establishing the Optimum RH within the 20% to 50% Range

It is possible to "trade off" temperature and RH to achieve a desired deterioration rate; for any given temperature, the slowest deterioration will be at 20% RH, but the equivalent life expectancy could be achieved at any RH up to 50% by lowering the temperature. The *Guide* shows which conditions are equivalent for controlling the rate of vinegar syndrome in acetate film.

The issue of storage RH has several practical dimensions, however, which may influence where in the "acceptable" 20% to 50% RH range a given storage area is operated. Because of geographic location or the type of HVAC (heating, ventilating, and air conditioning) equipment in place, it may not be possible to operate a storage area at 20% to 30% RH. Another concern is mixed collections, in which film has to share a storage space with other kinds of materials. Some glass plates with gelatin emulsions may suffer delamination from the glass support at RHs below 25%.[11] Other non-photographic materials may be present which cannot safely tolerate 20% RH. In this event, the best choice will be to provide a higher average RH, not exceeding 50%, and as cool a temperature as is consistent with the needs of all the objects in the room.

Cycling of Temperature and RH

The use of the adjective "average" with RH is not accidental. What counts most in a film storage environment is not the instantaneous humidity value but the long-term average RH ("long-term" being on a scale of weeks or months), because this will determine the moisture content of the film. Even when they're "in control," all HVAC systems oscillate somewhat in temperature and RH—it's in the nature of controls to always cycle up and down to some extent. Normally we don't notice these oscillations because they are too small. The question is, how large can the magnitude of such cycling get before it causes problems with the film?

The key point to bear in mind is that temperature equilibration (film coming up or down to a new air temperature) is rather fast—usually a matter of a few hours. Humidity equilibration, on the other hand, is usually rather slow—a matter of days, weeks, or months.[12] Changes in temperature per se (i.e., simple temperature changes that do not result in drying out of the film) do not cause any physical damage to film.

Slowness of Humidity Equilibration

Humidity equilibration is slower because moisture must diffuse through the walls of boxes, through gaps in the lids of boxes or cabinets, and through any other enclosures in which the film might be stored before it can be absorbed by the film itself.[30] If a single strip of film were freely hanging in the room on a clothesline, RH equilibration would be substantially complete within eight hours. Film wrapped on a roll and stored in a can or box, might require three months to equilibrate at room temperature. In cold storage, diffusion is

slower, so equilibration takes even longer.

Considering the slowness of humidity equilibration in most real-life storage circumstances, it is easy to see why cycling of RH up or down 10% in the period of an hour or a day hardly matters. The film inside its packaging has not experienced the change in RH because it has been buffered by the storage enclosures and cabinets.[30] Fast cycling between extremes of RH (a difference greater than 30% or so) and particularly fast drying out of a film should be avoided. But in most practical circumstances, the storage enclosures of film slow down the rate of humidity equilibration enough that cycling is not a concern.

Summary of Temperature and RH for Film Storage

The summary of how environmental conditions can be used to control chemical deterioration in film might be stated as follows:

Make the temperature as low as you can, and preferably make the average RH 20% to 30%. RHs up to 50% will do no special harm; they will only result in a faster rate of vinegar syndrome and dye fading than would occur at 20% RH.

Volatiles in the Film Vault Atmosphere

An important aspect of creating a storage environment for film is recognizing and managing volatile substances that may originate from the film itself. These arise from three main sources:

1. Residual casting solvents and other materials introduced during manufacture.
2. Residual cleaning solvents used on processed film.
3. Volatile degradation products such as acetic acid (from decomposing acetate film) and nitrogen oxides (from decomposing nitrate film).

The table on p. 20 gives a partial list of volatiles that might be encountered in film vaults, together with their possible sources.

Although only a few studies of film vault atmospheres have been done,[31] the limited available data suggest that the substances found in highest concentration are usually cyclohexane, methylene chloride, and n-butanol. The cleaning solvent 1,1,1-trichloroethane is also commonly encountered. Slow evaporation of solvents is a normal behavior of acetate and nitrate film collections, and typically the observed concentration

of volatiles is extremely low, posing no health risks. As long as the acetate or nitrate film base is not deteriorated, there will be no acetic acid or nitrogen oxides in the film vault atmosphere.

When film collections are stored in areas designed for human occupancy, the ventilation rates usually are sufficient to keep volatiles at very low levels. If, however, film is stored in large quantities in specially built vaults, then air purification systems and/or sufficient fresh air exchange are necessary to ensure that volatiles do not build up too high. Some large cinema film vaults have experienced unpleasant odors, even though the film was in good condition and not degrading. Investigation showed that no health risks were involved, but the odors were sufficiently strong to make working inside the vaults quite unpleasant. Such cases have occurred in vaults purposely designed without any fresh air exchange in order to minimize operating costs.

Apart from the natural slow release of volatile solvents, when base deterioration begins to occur, additional volatile substances are introduced into the film vault atmosphere. Acetate film collections may release acetic, butyric, or propionic acids upon degradation. Since deterioration is acid-catalyzed, exposure to acid vapors is likely to accelerate deterioration in otherwise healthy films. Degrading nitrate films may introduce nitrogen oxides and/or nitric acid.[17] Strong oxidants from nitrate may cause fading of silver images and embrittlement of paper enclosures.

Health Risks from Degrading Film

The threat from substances originating from deteriorated film is not limited to collections, however. Human health risks are also present under some circumstances. Good ventilation is *essential* when handling or inspecting degraded films. Latex, polyethylene, or nitrile gloves should be worn when handling degraded film. Throat and skin irritations have been reported due to handling of deteriorated acetate and nitrate films.[32] Working for long periods in confined, poorly ventilated spaces with large amounts of degraded film definitely should be avoided.

Storage Enclosures for Film Collections

All films need some form of storage enclosure; in fact, most films have several levels of protective packaging. Enclosures are needed for physical protection against dust and handling damage, and they also serve to shield film from atmospheric contaminants and fast changes in environmental conditions. All enclosures should be chemically inert toward the components of film—the base, the gelatin emulsion, and the silver or dye image. Much damage has been done by reactive, poor-quality papers, adhesives, and cardboards. Any enclosure that is made from such materials must meet the general requirements outlined in ANSI Standard IT9.2-1991 and must pass the ANSI Photographic Activity Test (ANSI Standard IT9.16-1993). The PAT guarantees that the enclosure will not chemically interact with the film to cause staining or fading.

Table of Volatile Substances Possibly Found in Film Storage Areas

	Substance	Source
Solvents Used in Manufacture	Methylene Chloride	Acetate Film
	Acetone	Acetate Film
	N-Butanol	Acetate Film
	Cyclohexane	Acetate Film
Cleaning Solvent	1,1,1-Trichloroethane	All Film
Volatiles from Degrading Film	Acetic Acid	Acetate Film
	Butyric Acid	Acetate Film
	Propionic Acid	Acetate Film
	Nitrogen Dioxide	Nitrate Film

This brief summary of the types of plastic bases used in photographic, cinema, and microfilm products is designed to help collection managers know which films are likely to be on nitrate, acetate, or polyester base. This is only a general outline of historical trends; a full treatise on the history of film bases and methods to identify the various plastics is outside the scope of this publication.

Identifying Film Bases

Although several physical and chemical tests exist to identify film bases, most of the time the nature of the film supports in a collection can be determined by the age and historical context of the collection (i.e., from the historical generalities given below). On occasion, characteristic forms of base deterioration help make it clear which films in a collection are **nitrate** and which are **acetate**. (The nitrate will have sticky emulsions and lots of silver image deterioration, while the acetate will have channeling and smell of vinegar.)

The easiest method to distinguish **polyester** film from acetate or nitrate is by the use of crossed polarizers. Polarizing plastic sheeting (something like the lenses in polarized sunglasses) can be obtained from a scientific or photographic supply house. When polyester film is placed between two sheets of polarizing plastic and viewed by transmitted light, color fringes appear that resemble the colors formed by oil slicks on ponds. This phenomenon, known as "birefringence," occurs only in polyester film. Acetate or nitrate film will not form bands of color in crossed polarizers. This non-destructive method is very useful in positively identifying polyester film.

Another optical property of polyester makes it easy to tell which roll films in a collection are made on polyester base. (This is quite handy in microfilm collections, where acetate and polyester are likely to coexist.) Film must be wound on a core or on a spoked reel for this method of identification to work. When viewed "edge on" (holding the reel up to a light source and looking through the spokes of the reel), polyester film will transmit much more light than acetate or nitrate (see Fig. 20). Some light will "pipe" through the edges of the film with acetate, but polyester will look much brighter. A little experience with the appearance of the two types will allow for quick and unambiguous identification of polyester roll films.
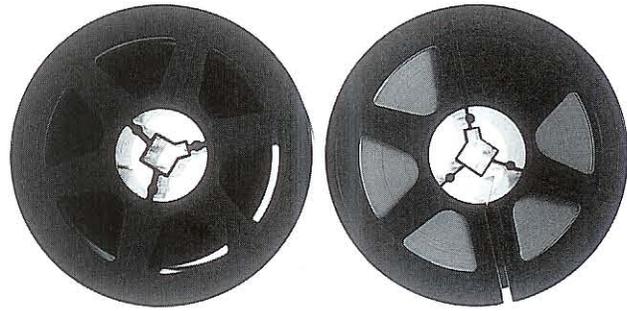

Fig. 20 When held up to a light source the polyester film "pipes" light through the edge of the film, while acetate and nitrate do not. (Polyester film shown at right.)

Historical Overview of Film Formats and Film Bases

Four main types of film formats can be found in archival collections:

1. Motion Picture Film—Perforated roll films typically found in 35mm, 16mm, and 8mm widths

2. Cut Sheet Films—Single-sheet, relatively thick pieces of film commonly found in sizes of 4 x 5, 5 x 7, and 8 x 10 inches.

3. Amateur Roll Films—Short rolls or cut single images on thin base. Used in hand-held cameras (formats designated by numbers such as 620, 616, 828, etc.) by amateurs and professionals. This category includes perforated 35mm still-camera negative and slide films.

4. Microfilm—Unperforated roll films in 35mm and 16mm widths, and 105mm-width microfiche.

Nitrate Base

Much nitrate base film is labeled on the edge with the word "Nitrate," which certainly makes it easy to identify. Films on cellulose nitrate support were first manufactured in the late 1880s, and nearly all films made between 1889 and the mid-1920s were nitrate.[13,33,34,35] So, any film manufactured before the mid-1920s, in any format, is likely to be nitrate.

Motion Picture Nitrate Film

All 35mm motion picture film is likely to be nitrate up to 1951, when it was replaced by triacetate. No 16mm or 8mm motion picture film was manufactured on nitrate base.

Cut Sheet Nitrate Film

All sheet films were made on nitrate base until the mid-1920s. Sheet films on nitrate base are uncommon after 1940.

Amateur Roll Nitrate Film

Amateur roll film camera negatives from 1890 to the mid-1940s are nitrate base. These include many postcard-sized film formats as well as smaller film widths. From the mid-1940s to 1950, some were nitrate, some acetate. No amateur roll films were on nitrate base after 1950.

Microfilm on Nitrate Base

Only the earliest microfilms (1920s to mid-1930s) were on nitrate base. It is quite uncommon to find nitrate base microfilms in library collections.

Acetate Base

Both acetate base film and more modern polyester base films are labeled with the words "Safety Film." Films marked "Safety" which were manufactured prior to 1955 are definitely acetate, not polyester. Although experiments with acetate film were conducted from about 1900 on, large-scale manufacture of cellulose acetate films did not commence until the mid-1920s, when the 16mm home cinema format became popular. Cellulose acetate makes up the largest fraction of film bases in most photographic collections.

Motion Picture Acetate Film

In general, cinema and amateur roll films marked "Safety" are likely to be acetate, regardless of format or age. Thus, collections of cinema film will consist largely of acetate (apart from 35mm cinema films made before 1951, which will be nitrate). At present, acetate continues to be the most commonly used base for motion picture films, though since the late 1980s the trend toward polyester is increasing.

Cut Sheet Acetate Film

Sheet films on acetate base were first introduced in the 1920s and appeared in quantity in the late 1930s. After 1940 nearly all sheet films were on acetate base. An exception is "film pack" sheet films (very thin sheets of film used in special holders where the photographer pulled a paper tab after each exposure to bring a new sheet of film into place); film pack films were last made (by Kodak) on nitrate base in 1949.[13]

Amateur Roll Acetate Film

If marked "Safety", all the amateur roll films are likely to be acetate, with a few exceptions of recent origin on polyester base. Nitrate amateur roll film was not manufactured by Kodak after 1950.

Microfilm on Acetate Base

Microfilm is a special application of film that appeared in the 1920s and grew rapidly during the 1930s and 1940s. At first, conventional cinema films were used as microfilm, but later on, products were manufactured expressly for use in document reproduction. The majority of microfilms produced since the late 1930s were made on acetate base, but during the 1980s, the use of polyester base increased rapidly.

Polyester Base

Polyester plastic film supports are quite different from acetate in their chemical and physical properties.[36] For example, polyester cannot be torn (except with tremendous effort) unless a nick or cut exists, while acetate and nitrate are fairly easy to tear. Polyester film is not prone to chemical decomposition in the same way that nitrate film and acetate film are.

Motion Picture Polyester Film

The first trials of motion picture polyester base film were made in the mid-1950s.[37] The acceptance of polyester base in cinema films has been slowed somewhat by difficulty in splicing on traditional splicing equipment. In the 1980s use of polyester base film began to increase, but it is still a small portion of the total film used.

Cut Sheet Polyester Film

Polyester base film, introduced in 1955, was first used in applications such as X-ray and graphic arts films where good physical properties and dimensional stability were prime requirements. During the 1960s and 1970s it gradually replaced acetate as the support for many types of cut sheet films. Some color transparency films are still manufactured on acetate base, but most other sheet films are on polyester.

Amateur Roll Polyester Film

Only a small amount of polyester film was manufactured for the amateur roll film formats, with the exception of some relatively recent 35mm still camera films.

Microfilm on Polyester Base

Today, nearly all microfilm is on polyester base. The reasons for switching to polyester support were the greater chemical stability of the base and the possibility of using thinner supports, thereby increasing the number of images on each roll.

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Cover photos, clockwise from left:

1. Buckling emulsion in deteriorated acetate sheet film.

2. Shrinkage and warping in deteriorated 16mm acetate motion picture film.

3. Residue of a glassine storage envelope stuck fast to the gelatin emulsion on a sheet film negative.

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