Optimizing Nitrate Film Storage

PETER Z. ADELSTEIN

Because of many instances of severe degradation of cellulose nitrate base photographic film, over the years the recommendation has been to duplicate all nitrate film onto cellulose triacetate base. However, it is no longer considered a reasonable policy to duplicate all nitrate films in an archive simply because they are on nitrate base, unless safety or other considerations are paramount. That recommended procedure is not being followed by many archives and libraries for very good reasons.

1. It is very costly.
2. Duplication results in some degradation of the recorded images.
3. Duplicating onto triacetate base may actually be copying onto a less stable material. (However this is no longer a problem since polyester base films and digital imaging have now largely replaced triacetate base films as copy media.)

An alternate approach is to store the nitrate film in a cold environment where degradation is extremely slow. This is a preferable conservation procedure and is the one being used or being planned by many institutions, such as the George Eastman House in Rochester, NY, USA, the National Archives of Canada in Ottawa, Canada and the Danish Film Institute, Copenhagen, Denmark. However, a key question is the recommended cold storage environment for nitrate base photographic film. This is the topic of this paper.

HISTORY

Although the main focus of this paper deals with the recommended conditions to store photographic film on nitrate base, a brief review of the history of this film base will provide pertinent background.

Nitrate base photographic film is looked upon today as a source of concern about its flammability and long-term stability. However, we should not lose sight of the fact that the development of the photographic industry was very dependent upon the existence of this material. While there were many attempts at using various materials for a transparent base, film only became a widely accepted and commercial success with the introduction of cellulose nitrate as the base[1]. It was very coincidental that cellulose nitrate was one of the first commercially manufactured plastics and it had many of the required properties for a flexible transparent film support.

The first cellulose nitrate base film was marketed in 1878. Sheets of the plastic were cut from solid blocks and subsequently emulsion coated for use as dry plates. A decade later a manufacturing process was developed to manufacture long lengths of cellulose nitrate and this made possible the motion picture film industry as we know it today.

The main drawback to this plastic was its very high flammability. It was a serious fire hazard and there were many instances of major conflagrations [2, 3, 4]. There were also many examples of base degradation although this was not a consistent problem. Efforts were made by the Eastman Kodak Co., even before World War I, to develop an alternate film base. Consequently in the 1920s and 30s, cellulose diacetate, cellulose acetate propionate and cellulose acetate butyrate were manufactured for amateur movie film, professional sheet film, and x-ray film[1]. However, those materials did not have adequate physical properties to meet the requirements for repeated projections of motion pictures. It was not until 1948 that Kodak introduced cellulose triacetate base for professional motion picture film[5] . This marked the end of cellulose nitrate base film as a commercial photographic film product.

The early studies of cellulose triacetate clearly showed it to be much less flammable than cellulose nitrate and it was called “safety base” for this reason. It was a tremendous advance in film technology. Early studies also concluded that it had greater chemical stability than the cellulose nitrate[5].

NITRATE STABILITY

Our knowledge about the chemical stability of nitrate film base has evolved over the years. The early conclusions that cellulose nitrate is an inherently unstable material were based on dry incubation studies at 100°C, which was the incubation temperature employed by the National Bureau of Standards in the United States[6]. Incubations at this condition indicated the cellulose triacetate base was more stable than the cellulose nitrate. After ten days incubation, the cellulose nitrate base film had 0% fold retention whereas the cellulose triacetate base film had over 90% retention[5]. Other investigations had also used high temperature incubations to evaluate the relative stability of various nitrate formulations[6, 7]. Consequently it was concluded at the time that triacetate had a twofold advantage over the cellulose nitrate, namely lower flammability and greater chemical stability.

The experimental procedures to evaluate film base stability have changed since the 1950s. It was recognized that the relative stability of materials at high temperatures may not reflect relative behavior under use conditions. Consequently an Arrhenius-type treatment has been employed by many investigators. The logarithm of time to a given property change is plotted on the ordinate against the reciprocal of the absolute temperature on the abscissa[8]. A linear relationship is frequently obtained which allows extrapolation to lower temperatures.

Very little laboratory work was done on the stability of nitrate film between 1950 and 1990. In the latter year, Edge et al.[9] obtained Arrhenius plots at 50% RH, using incubation temperatures as low as 60∞C. A life expectancy of only ten additional years was predicted for the cellulose nitrate base motion-picture film that they studied. This is consistent with the earlier studies.

However, in recent decades the widely accepted viewpoint that cellulose nitrate is basically a very unstable material began to be questioned[10]. Nitrate films have been found that are in good condition after 50 years, while others showed complete decomposition after only five years. This was attributed to either differences in storage conditions or to the inherent stability of the cellulose nitrate as manufactured. This behavior was also observed during the 1933-50 period by regular examination of films in theatrical exchanges (projection prints circulating to the theaters) and in storage vaults (negatives and inactive prints). Occasional rolls showed obvious degradation after one to two years, while other films appeared unchanged after ten to twenty years. Additional evidence was found at the Oakland Museum in California, USA[11]. Cellulose nitrate film in this archive appeared excellent after many decades and in much better condition that some of the cellulose triacetate base materials stored in the same environment.

IPI STABILITY STUDIES

As a result of this inconsistent behavior, additional laboratory studies were done by the Image Permanence Institute[12] between 1988-1990. Arrhenius type studies indicated that the tensile break stress retention gave a predicted life of a cellulose nitrate film at 20∞C 50% RH which was of the same order of magnitude as the acetate-type cellulosic films that were studied. This Arrhenius plot is reproduced in Figure 1. Nitrate film had the fastest degradation rate of all the films in this study at the *high* temperatures of 90 and 100°C, agreeing with the earlier findings of Hill and Weber [6] and Fordyce[5]. However, when data from all the temperatures were plotted, the Arrhenius line had a strong temperature dependence (i.e. a steep slope), and the extrapolated time for the nitrate film to lose one-third of its original tensile strength was approximately 250 years at room temperature. This was the same as the triacetate film.

Since this behavior was observed on only a single sample of nitrate film, IPI undertook a second more extensive investigation in 1991[13]. This program featured the incubation of five cellulose nitrate base films manufactured between 1930 and 1941. Four were motion picture products and one was a sheet film. All films were at least 50 years old prior to testing. Incubations were at the six temperatures of 50, 60, 70, 80, 90 and 100°C after moisture conditioning to 20, 35 and 50% RH. Some of these incubations have now been extended to times over 5 years. This gives greater credence to the Arrhenius projections of life expectancy.

Figure 2 shows the Arrhenius type projections based on the base acidity for two of the films in this study. The sheet film from the Arizona Historical Society, USA is considerably less stable than the motion picture film from the British Film Institute, UK. This difference is more dramatic from the Arrhenius projections calculated from the tensile toughness data (Figure 3). Table I gives a summary for all five materials evaluated in this study. The extrapolated life varies between 10 and 2,700 years at 20°C 50% RH depending upon the property measured and the particular film. This wide variation in behavior is consistent with observations made under practical conditions. The four motion picture films had excellent projections of life expectancy at 20°C, particularly considering that all films had aged for 50 years prior to testing. However, the Arizona sheet film had a relatively low predicted life when based on times for the film toughness levels to decrease to a 66% retention level. However, even at this 66% level, the film still has considerable physical integrity. Extended incubation studies have shown that the toughness decreases relatively slowly after an initial more rapid change.

The beneficial effect of reduced humidity is shown in Table II. Storage at 20% RH considerably extended the useful life of the sheet film.

It is recognized that only five nitrate base films were evaluated in the 1991 study. However, this investigation is the only source of quantitative data on which to recommend a storage environment.

SURVEY OF EXISTING NITRATE FILMS

It is evident that the environmental conditions suitable for a nitrate film vault will be very dependent upon the condition of the film to be stored. If the film is similar to the 1933 motion picture film from the British Film Institute, storage at 20°C 50% RH will provide a useful life of over 500 years. This condition would not be satisfactory for film that is similar in stability behavior to the Arizona Historical Society sheet film.

It is obviously impossible to know the condition of films that are in existing archives. However, some general indication of the condition of cellulose nitrate films now in storage can be made from an IPI survey conducted in 1990[13]. Forty-four samples were obtained from a number of archives and libraries. Measurements were made of both the base acidity and toughness on the film as received without any incubation. There was a general relationship between these properties as shown in Figure 4. Of the eight films which had low toughness values, seven had acidity measurements of 0.5 or greater. This is 16% of the films in the survey which is a significant percentage. By way of comparison, the film from the British Film Institute had an acidity value of only 0.02 while the less stable Arizona film was 0.08.

STORAGE RECOMMENDATIONS

The tremendous range in the inherent stability of nitrate films poses a problem in recommending the storage environment for a film vault. If all the film in an archive was similar to the film from the British Film Institute, then Table I indicates that a storage condition of 20° 50% RH should be satisfactory. However, this is not a prudent assumption. In matters of conservation, it is essential to be conservative and assume that a significant percent of the collection is less stable than the BFI material.

One assumption is that the least stable film in the collection is similar in behavior to the Arizona sheet film. Figure 5 shows the Arrhenius-type plot for toughness retention that was obtained on this film. When moisture-conditioned to 50% RH, the predicted life is only ten years at 20°C, but 500 years at -10°C. (This plot is identical to Figure 3 with the addition of data obtained at the lower humidity). When this film was moisture-conditioned to 20% RH, incubations at the high temperatures surprisingly showed faster degradation than at 50% RH. However, at 50°C this was no longer true. Extrapolations indicated a 160-year life at 20°C and many centuries at still lower temperatures. (The predictions at the very low temperatures cannot be considered quantitative because the extrapolations are so very extended). This beneficial effect of lower humidity is consistent with previous Arrhenius studies on photographic film stability[12]. Since both low temperatures and low humidities are beneficial to film stability, a higher storage temperature can be compensated for by a lower storage humidity. This is the rationale in recommending several storage conditions, namely -10°C 50% RH or 2°C 30% RH. This environment gives a predicted life expectancy of at least 500 years if the acid level is no greater than 0.08. For films with lower acid levels, these conditions are extremely conservative.

There should be a word of caution about this predicted life expectancy. It is based on Arrhenius extrapolations and it can be seen from Figure 5 that these are very extended extrapolations. Only a slight change in slope of the Arrhenius line at the elevated temperatures can cause a very significant effect at subzero temperatures. Another concern is the paucity of Arrhenius-type information available for nitrate films. The 1991 study involved only a limited number of films. This was because of the expensive nature of this investigation and the difficulty in obtaining nitrate films that archives would be willing to donate from their collections. Moreover, tests on the Arizona sheet film gave results which were quite variable. This is attributed to the fact that this film had already started to degrade and the degradation was not uniform throughout the collection. However, there is no alternative to utilizing the only information that is available. There is also no doubt that storing in a colder and drier environment will increase film life. What is more problematic is the accuracy of the projected life expectancies.

A second and alternate assumption is that a significant portion of the nitrate film collection has acid levels that are at a level higher than that of the Arizona film. This was found for many of the films in the 1990 survey. Therefore it is recommended that archivists examine representative portions of their collection for evidence of high film curl, silver image degradation, metal can corrosion, base discoloration or other signs of degradation. If there are any signs of these problems, then more stringent environments are suggested. For that situation, storage recommendations are -5°C 30% RH or -16°C 50% RH. Obviously data does not exist for estimates of the life expectancy under these environments since this is so very dependent upon the condition of the film. However, all Arrhenius studies have consistently shown that these very low temperatures, as well as reduced humidity, are extremely beneficial.

In addition to the Arrhenius extrapolations, laboratory data supporting this conclusion were obtained by J.-L. Bigourdan at IPI[14]. He found absolutely no increase in the acidity of partially degraded cellulose triacetate film when stored for 5 years at 16°C 50% RH. There are no corresponding data for nitrate base films but there are many anecdotal examples of arrested degradation of other organic materials at subzero temperatures, for example the excellent preservation of human remains found after many decades in the Arctic region.

Table III summarizes the two sets of storage recommendations for nitrate base film. The appropriate recommendations depend upon whether there are any indications of incipient degradation. This table also gives the storage recommendations that are now published in existing ISO standards. The nitrate storage recommendations for film that appears in good condition are identical to those given for the preservation of photographic color images[15]. The 2°C 30% RH condition is also identical to that made independently by the Society of Motion Picture and Television Engineers and standardized by ISO[16]. These nitrate recommendations are colder than those standardized for the preservation of cellulose triacetate base film. However, the recommendations given in this paper are for nitrate films that are at least 50 years old. In addition, they may also have shown some initial signs of degradation as observed for the Arizona film. In contrast, the acetate recommendations are for fresh undegraded film. The SMPTE/ISO 10356 standard is not considered sufficiently cold for nitrate films that have any physical indication of change.

All the storage recommendations in Table III give a range for the relative humidity. The minimum humidity specified is 20% RH. While some films may exhibit brittle behavior at this humidity, flexibility is restored when the humidity is raised. However, at still lower humidities, the gelatin-emulsion layer exerts an increased contracting force on the plastic base. This can cause a permanent deformation in the base. For motion picture film, this is manifested as ”spoking.”

The question has been raised whether freezing photographic film can cause permanent damage. In other words, does the water in the emulsion layer crystallize at temperatures below 0°C? Calhoun[17] conclusively showed that this does not occur, even at temperatures of -70°C. Subsequent work at Kodak[18] investigated freeze/thaw daily cycling of motion picture films at -15°C for 6 months. This is of interest since films would be periodically removed from cold storage. However no effects were found.

PRACTICAL CONSIDERATIONS

It must be recognized that when film is removed from a cold storage environment to a work environment, the film must be acclimatized. The reason is that air holds less water at lower temperatures than at higher temperatures. (the temperature at which air will start to condense water is known as the dew point of the air). When cold film is brought to room temperature, the air in contact with the film is cooled below its dew point. There is danger of moisture condensing on the film surface if the film is below the dew point of the air at room conditions. In order for films to be safely exposed to the air in a darkroom or viewing area, the film must be above the dew point temperature of the room. There are two common methods used to safely move film from a cold storage environment to a use environment without causing condensation. One approach is to warm up the film stepwise by placing it in a staging environment. However, a second approach can be used if only a limited number of films will be removed at any one time. The film may be kept in a closed container and allowed to warm up in the container at room temperature. This procedure requires less capital expenditures. Suitable sealed containers are taped film cans or placing the film in a closed plastic bag. The warm up times are very dependent upon the size of the film roll but generally four hours is adequate.

A second practical consideration is the consequence of removing film from the cold storage vault. The longer the time out of the vault, the longer the effect of the warmer temperature with possible decrease in the film life. The importance of this effect is very dependent upon the condition of the film. For nitrate film having very low acidity, its expected life at room temperature is greater than 500 years (Table I). For such material, one week/year out of storage should not cause significant changes. However, for films that have started to show some acidity increase, this is no longer true. Such a film may only have a ten-year life at 20°C (Table I). Quantitative data is not available as to the extent of degradation for limited times at this temperature, but tighter restrictions on time out of storage should be followed.

Another important consideration in the design of a cold storage vault is the temperature and humidity tolerances. It can be seen from Figure 5 that the Arrhenius slopes are very steep. If the proposed -10°C 50% RH increased to -5°C 50% RH, the predicted life expectancy would decrease from 500 to 250 years. In other words, maintaining the temperature at or below the recommended levels is fairly critical. However, temperature fluctuations themselves are not critical as long as the highest temperature is not greater than that recommended. Moderate cycling of the humidity is not important, as the moisture conditioning of film is very slow at these low temperatures. This is illustrated by the moisture conditioning times shown in Table IV[19]. Motion picture film would not re-equilibrate to any short-term cycling humidity.

CONCLUSION

It is recommended that a visual examination first be made of the physical condition of a representative portion of the nitrate film collection. If there is no evidence of possible degradation, storage conditions of -10°C 50% RH or 2°C 30% RH are recommended. However, if there are any indications of physical change, more stringent conditions of 16°C 50% RH or -5°C 30% RH should be considered.

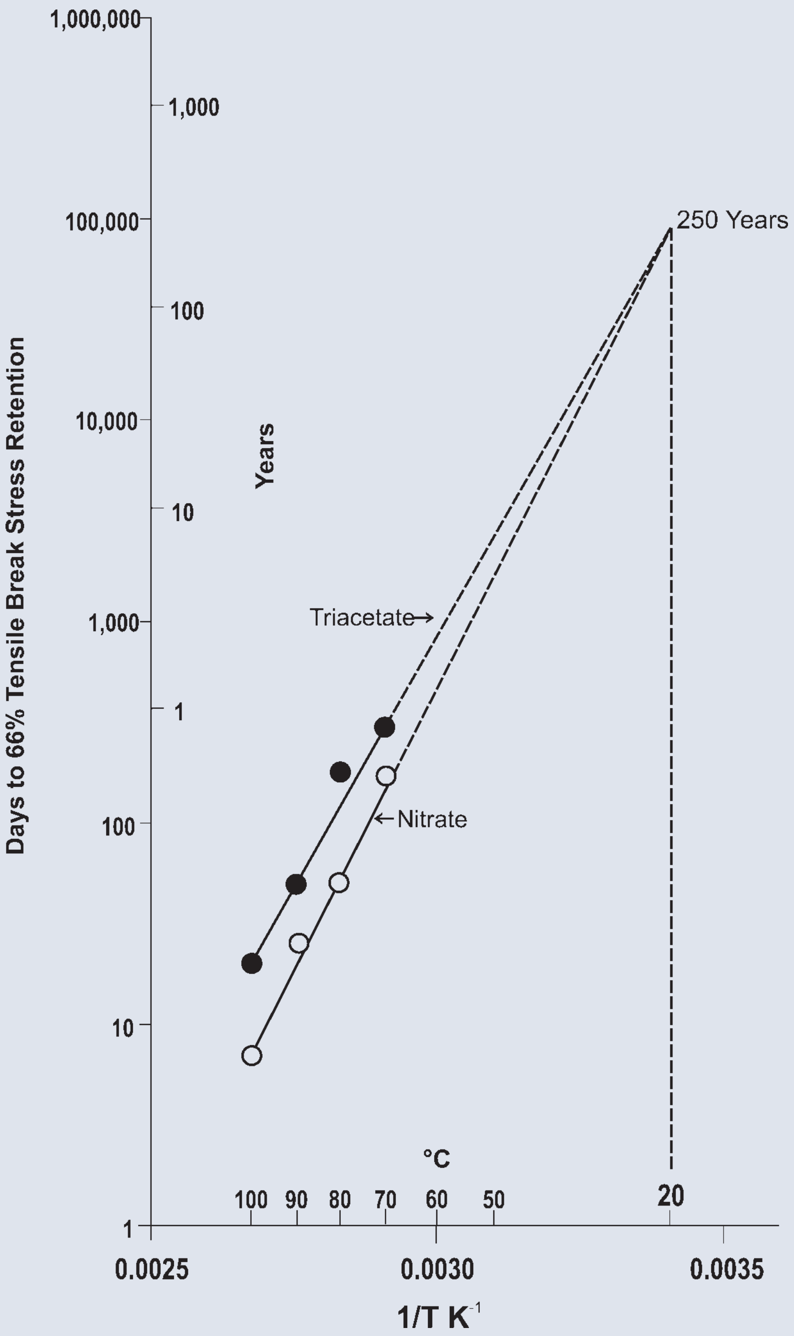

Figure 1. Arrhenius-type plot for tensile break stress of motion-picture film. Specimens preconditioned to 21°C, 50% RH, then heated in sealed bags.

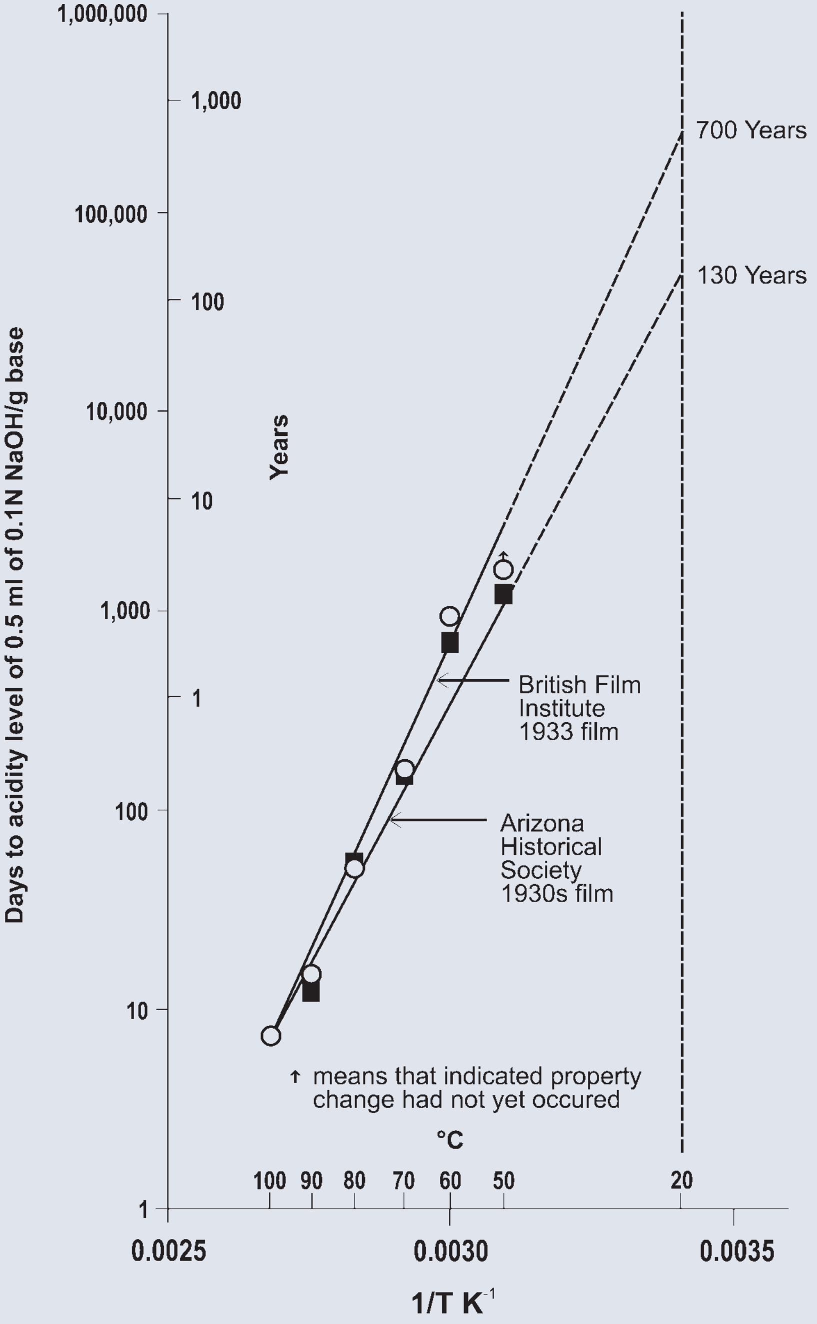

Figure 2. Arrhenius-type plot for acidity of nitrate base film. Specimens preconditioned to 21°C, 50% RH, then heated in sealed bags.

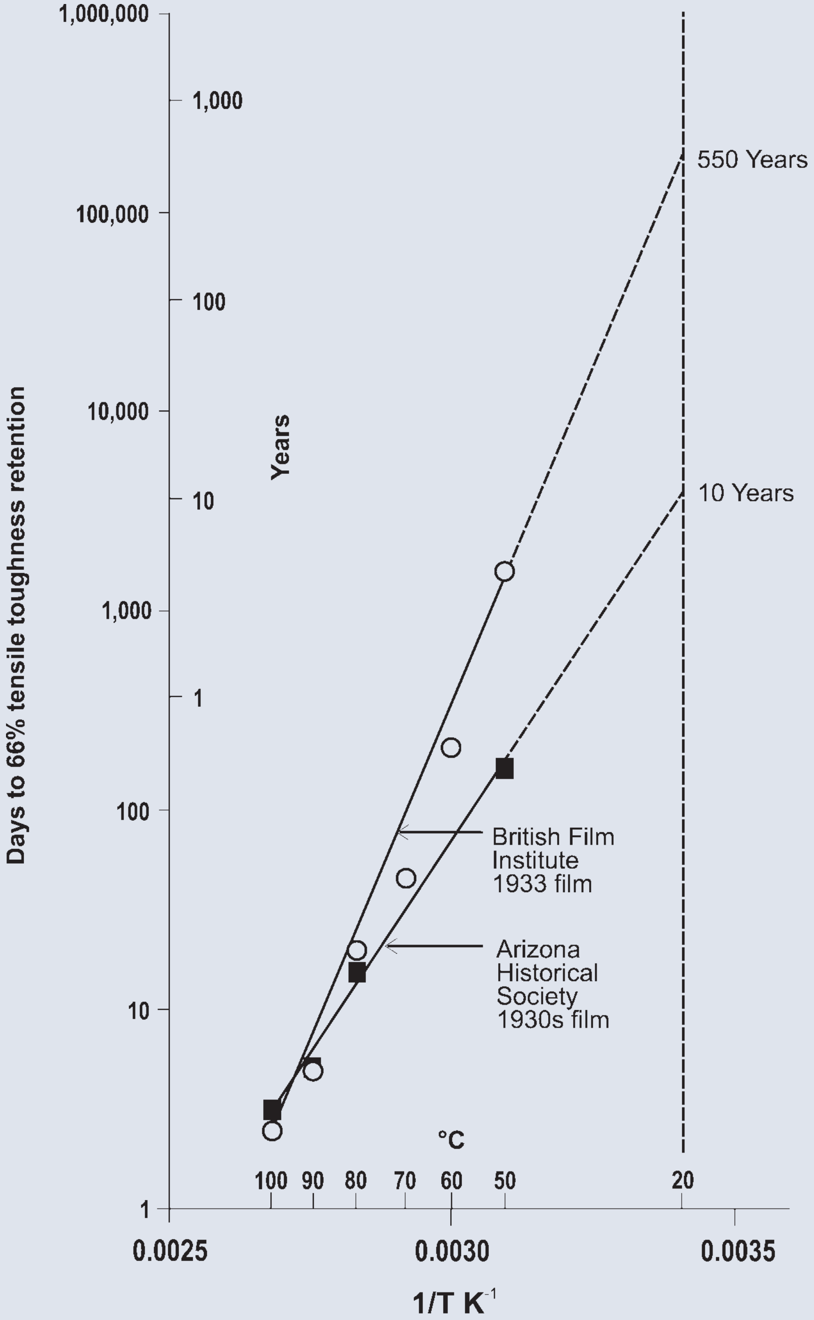

Figure 3. Arrhenius-type plot for toughness of nitrate base film. Specimens preconditioned to 21°C, 50% RH, then heated in sealed bags.

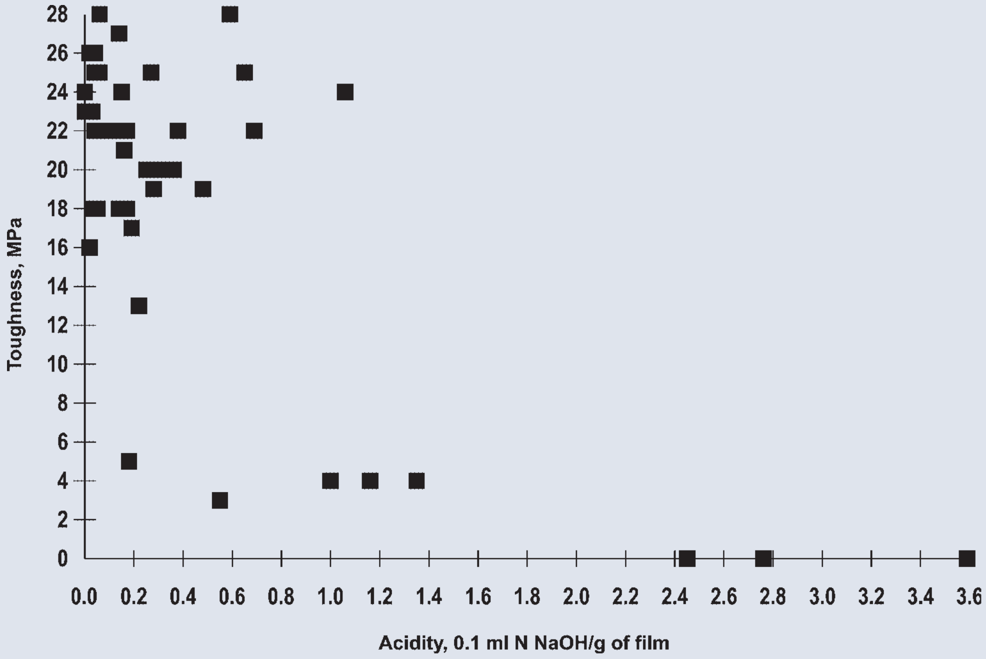

Figure 4. Relationship between film toughness and acidity for naturally aged nitrate base.

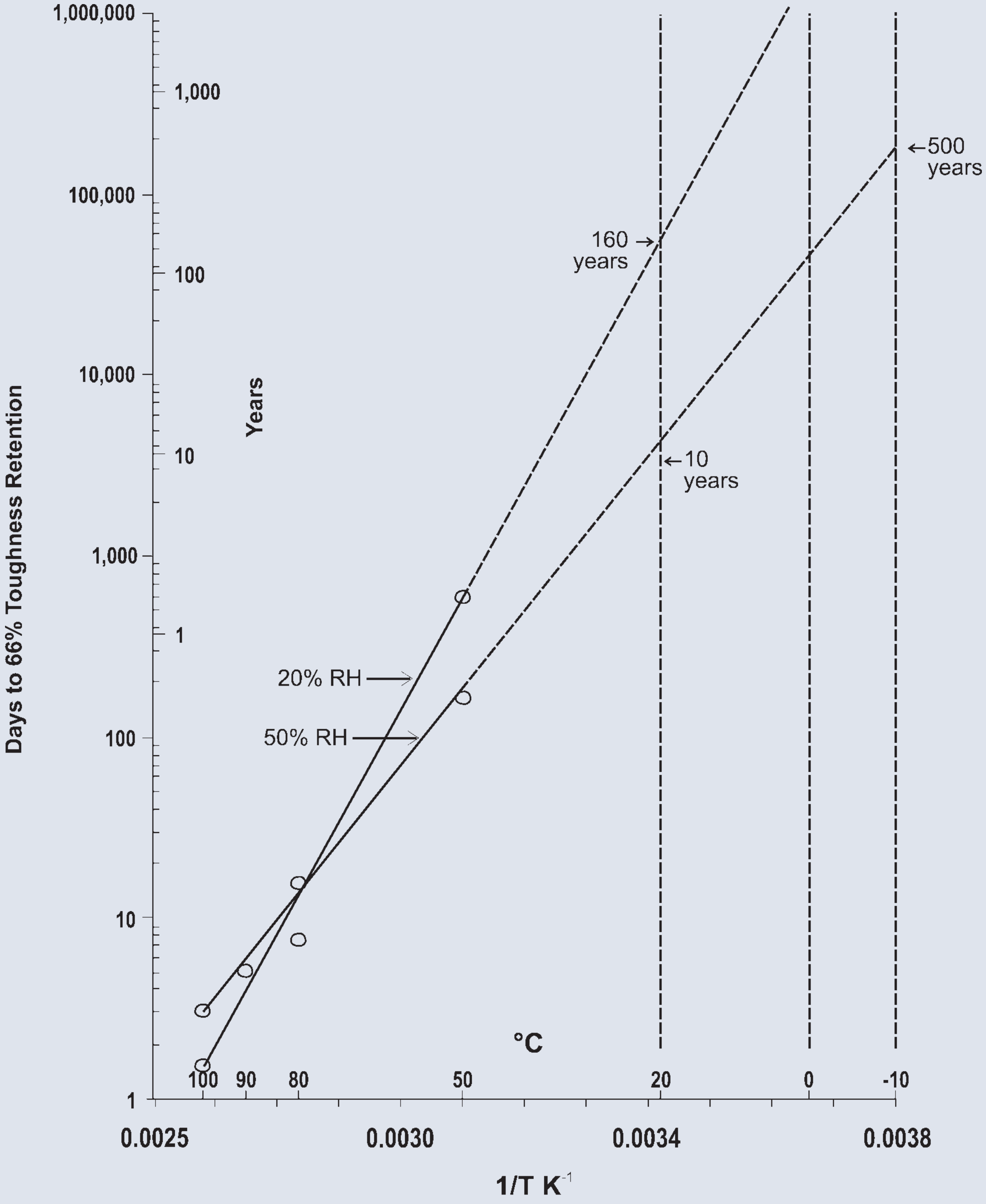

Figure 5. Arrhenius-type plot for toughness of cellulose nitrate film with an acidity value of 0.08. Film specimens preconditioned to 21°C and indicated RH and heated in sealed bags.

				Life Expectancy years at 20 °C 50% RH	
Format	**Source**	**Approx. Year of Mfr.**	**Film Manufacturer**	**Acidity (end point of 0.5 ml N NaOH)**	**Toughness (end point 66% 0.1 retention)**
Sheet	Arizona Historical Society, USA	1930s	Kodak	130	10
Motion Picture	Library of Congress, USA	1941	Kodak	2700	800
Motion Picture	Library of Congress, USA	1932	Kodak	950	500
Motion Picture	Library of Congress, USA	1932	DuPont	800	800
Motion Picture	British Film Institute, UK	1933	Kodak	700	550

Table I. Extrapolated Life of Nitrate Base Film

Film Manufacturer	Kodak	Kodak
Approx. year of mfg.	1930s	1933
Format	Sheet film	35mm motion picture
Source	Arizona Historical Society, USA	British Film Institute, UK
	Years for acidity level to show 0.5 ml 0.1 N NaOH/g base	
20% RH	550	_
35% RH	570	1600
50% RH	130	700
	Years to show 66% toughness retention	
20% RH	160	2700
35% RH	-	1200
50% RH	10	550

Table II. Extrapolated Life of Nitrate Base Film at 20°C

	Temperature, °C	**% Relative Humidity**
Nitrate film with good appearance	-10	20-50
	2	20-30
Nitrate film with possible degradation	-5	20-30
	-16	20-50
ISO 10356: 1996 for nitrate film (14)	2	20-30
ISO 18911 for color film (15)	-10	20-50
	-3	20-40
	2	20-30
ISO 18911 for acetate film (15)	2	20-50
	5	20-40
	7	20-30

Table III. Recommended Environmental Conditions for Long-Term Film Storage

	Temperature,°C	**Days**
35mm roll with one surface exposed	21	2
	-16	30
35mm roll in closed metal can	21	40
-16	>500	

Table IV. Time to Reach 50% Moisture Equilibration for Motion Picture Film.

NOTES

1. P.Z. Adelstein, “From Metal to Polyester: History of Picture-Taking Supports,” E. Ostroff, editor, *Pioneers of Photography,* SPSE The Society of Imaging Science and Technology, 1987, 30-36.
2. A.H. Nuckolls and A.F. Matson, “Some Hazardous Properties of Motion Picture Film,” *J. SMPE*, Vol. 27, 657-661, Dec. 1936.
3. J.W. Cummings, A.C. Hutton, and H. Silfin, “Spontaneous Ignition of Decomposing Cellulose Nitrate Film,” *J. SMPTE*, Vol. 54, 268-274, Mar. 1950.
4. J.M. Calhoun, “Old Nitrate Films are Dangerous,” *International Projectionist*, 8-18, May 1962.
5. C.R. Fordyce, “Improved Safety Motion Picture Film Support,” *Journal of Society of Motion Picture Engineers*, Vol. 51, 331-350, 1948.
6. J.R. Hill and C.G. Weber, “Stability of motion picture films as determined by accelerated aging,” *Journal of Society of Motion Picture Engineers*, vol. 27: 677-690, December, 1936.
7. G.L. Hutchison, L. Ellis, and S.A. Ashmore, “The Surveillance of Cinematograph Record Film During Storage,” *Journal of Society of Motion Picture and Television Engineers*, Vol. 54, 381-383, Mar. 1950.
8. ISO 18924-2000 *Imaging materials – Test method for Arrhenius-type predictions,* International Standards Organization, Case postal 56, CH-1211 Geneva 20, Switzerland.
9. M. Edge, N.S. Allen, M. Hayes, P.N.K. Riley, C.V. Horie, and J. Luc-Gardette, “Mechanisms of Deterioration in Cellulose Nitrate Base Archival Cinematograph Film,” *Eur. Polymer J*., 26:623-630, June 1990.
10. J.M. Calhoun, “Storage of Nitrate Amateur Still-Camera Film Negatives,” *J. Biological Photographic Assn*., 21:1-13, Aug. 1953.
11. D.H. Norris, “A Survey of the Photographic Collection at the Oakland Museum,” Jan. 1991, unpublished.
12. P.Z. Adelstein, J.M. Reilly, D.W. Nishimura, and C.J. Erbland, “Stability of Cellulose Ester Base Photographic Film: Part II – Practical Storage Considerations,” *Journal of Society of Motion Picture and Television Engineers*, Vol. 101, 347-353, May 1992.
13. P.Z. Adelstein, J.M. Reilly, D.W. Nishimura, and C.J. Erbland, “Stability of Cellulose Ester Base Photographic Film: Part IV – Behavior of Nitrate Base Film,” *Journal of Society of Motion Picture and Television Engineers*, 359-369, Jun. 1995.
14. J.L. Bigourdan and J.M. Reilly, “Effectiveness of storage conditions in controlling the vinegar syndrome: preservation strategies for acetate base motion-picture film collections,” Proceedings of the Joint Technical Symposium, Paris, Jan. 2000.
15. ISO 18911:2000 *Photography – Processed Safety Films – Storage Practices* (formerly ISO 5466), International Organization for Standardization, Geneva, Switzerland.
16. ISO 10356:1996 *Cinematography – Storage and Handling of nitrate-base motion-picture films*, International Organization for Standardization, Geneva, Switzerland.
17. J.M. Calhoun, “Cold Storage of Photographic Film,” *Photographic Science and Technique,* PSA Journal 18B, No. 3, Oct. 1952.
18. D.F. Kopperl and C.C. Bard, “Freeze/Thaw Cycling of Motion-Picture Films,” *SMPTE Journal*, 826-827, Aug. 1985.
19. J.-L. Bigourdan, P.Z. Adelstein and J.M. Reilly, “Moisture and Temperature Equilibration: Behavior and Practical Significance in Photographic Film Preservation,” Proceedings of Arsag Conference, Paris, April 1997.