PHOTOGRAPHS

5.1 A Short Guide to Film Base Photographic Materials: Identification, Care, and Duplication

Monique Fischer
Senior Photograph Conservator
Northeast Document Conservation Center

INTRODUCTION

New technologies are adopted based on their advantages, and disadvantages are considered later or sometimes not at all. Preservation often involves working to mitigate those disadvantages and, in the case of photography, this means working to increase the stability of inherently unstable materials.

There are three broad types of film-based photographic materials: cellulose nitrate, cellulose acetates, and polyester. These materials have been used as a support for negatives, positive transparencies, motion pictures, microfilm, and other photographic products. Unfortunately, cellulose nitrate and cellulose acetates are unstable. The products of their degradation can severely harm and even destroy photographic collections, in addition to posing serious safety hazards.

IDENTIFICATION

Nitrate Film Base

In August 1889, Eastman Kodak began selling the first photographic negatives on cellulose nitrate flexible film support. This innovation was the foundation of an entirely new era in photography. The increased convenience of flexible films enabled professional photographers to take more photographs under a wider variety of conditions; it also created a new amateur market which quickly became the economic foundation of the photo industry. Nitrate film remained in production in various formats until the early 1950s.

As a photographic support, nitrate film had some serious disadvantages. The film was, and is, highly flammable, and it releases hazardous gases as it deteriorates. Large quantities of nitrate film have caused several disastrous fires. Due to the inherent instability of cellulose nitrate, much of our photographic legacy from this period is disappearing.

A photographic collection that contains any flexible, transparent film negatives from the time period of 1890-1950 is very likely to contain at least some nitrate film. Since these negatives need special attention, they should immediately be separated from other negatives. Deteriorated nitrate negatives are easy to identify, but nitrate negatives in good condition are almost visually indistinguishable from other types of transparent films. There are four ways to identify nitrate negatives.

1. Edge printing

Many manufacturers stamped professional sheet films with an identification along one border. The words generally identified the manufacturer and the type of film: nitrate or safety. Unfortunately, not all manufacturers adopted edge printing identification. It wasn't done on either early nitrate negatives or on some roll film formats. Amateur roll films were not marked but can be identified by their tendency to curl into very tight scrolls (later roll films were coated on both sides to prevent such curling). Notch codes can also identify sheet film as nitrate. A "V" notch code (first from the edge) will identify pre-1949 Kodak sheet film as nitrate while a "U" shaped notch (first from the edge) will indicate the Kodak film is acetate. Note that a nitrate negative may have been copied at some point and the edge printing from the original will appear on the copy. Therefore, just because you see the word "nitrate" does not guarantee that it is. See the section on testing to be sure.

Nitrate Kodak notch code (at right) and printing

Acetate Kodak notch code (at right) and printing

2. Dating Information

The dates Eastman Kodak stopped the manufacture of nitrate film are listed in the table below. If a negative can be accurately dated, either by subject or by the photographer's notes, it is possible to determine if it is nitrate film.

Type of Film (see notes)	*Last Year of Nitrate Manufacture*
X-ray films	1933
Roll films in 35mm (A)	1938
Portrait and Commercial sheet films (B)	1939
Aerial films	1942
Film Packs (C)	1949
Roll films in sizes 616, 620, etc. (D)	1950
Professional 35mm Motion Picture films (E)	1951

NOTES for Type of Film table

A. It has always been a common practice for photographers to purchase bulk rolls of 35mm motion picture film and re-spool it into cassettes for still camera use. It is possible to find still camera negatives on nitrate film for an additional 13-year period after this date.
B. Nitrate sheet film tends to have a very thick and rigid base. Additionally, professional sheet film negatives will have notches on one corner. These notches are used by photographers to determine the emulsion side in the dark.
C. Film pack negatives were produced in the same sizes as sheet film. Film packs used a much thinner and a very flexible based film. These negatives will feel like roll film. They lack a notch code, but may have a negative number, generally 1 through 12.
D. These sizes were called amateur roll film formats. Many families may have a small number of these negatives stored in their home with no idea of the hazard they represent.
E. Professional 35mm motion picture film is the most hazardous type. All nitrate 35mm motion picture film should be duplicated by an authorized laboratory. Then the nitrate motion picture film should be disposed of by the local fire marshal or a hazardous materials disposal service. NOTE: 16mm, regular 8, and super 8 movie formats were considered amateur formats and were always made on a safety film base.

Unfortunately, Eastman Kodak is the only manufacturer that has supplied any dates on nitrate film production. These dates do not apply to other manufacturers' films, nor do they give an indication of when Kodak started selling safety films. For example, nitrate sheet film production ended in 1939, but Kodak began test marketing safety based sheet film sometime in the mid-1920s. For most formats, there was a carryover period when both types of film were made.

3. Nitrate film base deterioration

A third method of film base identification is based on the observations of deterioration characteristics. Nitric oxide, nitrous oxide, and nitrous dioxide are all released as gases from the decomposition of cellulose nitrate. In the presence of atmospheric moisture, these gases combine with water to form nitric acid. The formation of nitric acid acts to further degrade cellulose nitrate film, and it can destroy enclosures in which the negatives are stored. It can even damage materials stored in close proximity to the collection.

Because of their extreme flammability, institutions should isolate and properly store cellulose nitrate materials—especially when those materials are in a deteriorated condition. They should be stored in a controlled environment of relatively low humidity, or ideally, in cold storage.

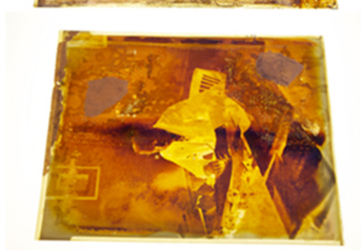
Cellulose nitrate decomposition can be very rapid. Deterioration is generally categorized in six progressive stages:

Level 1
No deterioration.

Level 2
The negatives begin to yellow and mirror.

Level 3
The film becomes sticky and emits a strong noxious odor (nitric acid).

Level 4
The film becomes an amber color and the image begins to fade.



Level 5
The film is soft and can weld to adjacent negatives, enclosures and photographs.

Level 6
The film degenerates into a brownish acid powder.

Most negatives will retain legible photographic detail into the third stage of decomposition. These negatives may become brittle, but—with careful handling—they can be duplicated. Negatives in the fourth, fifth, and sixth stages of decomposition generally have decreasing areas of legible image and should be either placed in cold storage or digitized before the image completely fades away.

4. Testing

Tests provide a more exact, but not completely definitive, way of identification. There are four tests, three of which are destructive; they require that a sample be taken from the film base material in question. Any destructive tests should be performed only after all other identification procedures have been conducted and identification remains uncertain.

A) POLARIZATION

The Polarization Test can be performed with the simple viewer described below (Polarizing filters are also available at toy stores in many children's science kits). When viewed between cross-polarized filters, polyester and other highly birefringent materials exhibit red and green interference colors like those seen on soap bubbles. Cellulose nitrates and cellulose acetates do not show these interference colors.

To use the viewer, unfold the viewer and place a corner of the material in question over one polarizing filter. Close the viewer and hold the viewer up to a light source. Tilt viewer back-and-forth and side-to-side, as red and green interference colors will be most apparent in clear areas. If a material is badly deteriorated, examine it on a light table with one polarizing filter underneath and one on top of it.

Instructions for Making a Viewer

1. Tape together two pieces of mat board along their long edge.
2. At the left corner of each mat board, split an area slightly larger than the polarizing filter.
3. Cut a hole in each split area smaller than the polarizing filter.
4. Slip polarizing filters into each split board. Be sure to place the filters so that they are almost at cross-polars to one another. This will be at the point at which they block most of the light passing through them.
5. Apply double-sided tape to reattach the split boards and to hold the filters in place.

A visual guide to constructing a viewer is offered by the National Park Service: http://www.nps.gov/museum/coldstorage/pdf/2.3.1b.pdf.

B) DIPHENYLAMINE TEST

A solution of diphenylamine and sulfuric acid can be used to identify cellulose nitrate. This solution must be handled with caution as it contains *90% sulfuric acid*. In this solution cellulose nitrate turns a deep blue color. Cellulose acetate and polyester will not produce this color. However, cellulose nitrate is used in very small amounts in the manufacture of cellulose acetate and polyester products. This "subbing layer" does not appear to affect either the longevity or the safety of these materials, but may cause a very faint blue tinge to be seen in the support of the cellulose acetates and polyester.
Place the sample on a microscope slide and apply a drop of the prepared solution. After one minute, a cellulose nitrate sample will turn completely blue while the cellulose acetates and polyester will not. In some cases, a large cellulose nitrate sample may exhaust the solution and no blue color will form. Therefore, to confirm a negative test, apply two more drops and wait another minute to confirm that the sample is not cellulose nitrate.

NOTE: The solution is somewhat sensitive to light. Before testing unknowns, test the efficacy of the solution with a known sample of cellulose nitrate such as DUCO Cement or UHU All-Purpose Clear Adhesive.

Instructions for the preparation of this solution can be found in “The diphenylamine spot test for cellulose nitrate in museum objects." Canadian Conservation Institute Notes (17/2), http://www.cci-icc.gc.ca/publications/notes/17-2_e.pdf.

C) BURN TEST

Do not perform this test inside your building! Burning cellulose nitrate film cannot be extinguished. The burn test uses the flammable nature of cellulose nitrate for identification since both cellulose acetates and polyester are much less flammable. Cellulose nitrate burns quickly and has a characteristic yellow flame. Having known materials for comparison is particularly important for this test. Hold sample vertically with metal tongs. Be sure to ignite the strip from the top—only cellulose nitrate will burn downwards. For safety, have a large container of water nearby. Although the water will not extinguish the flame, it will keep it from spreading.

D) FLOAT TEST

Because trichloroethylene is both toxic and a carcinogen, this test should be conducted in a well-ventilated area. Wear rubber gloves, and act with extreme caution. The float test may be used to identify film base types due to their differing densities. The densest—cellulose nitrate—will sink, while cellulose acetate will rise to the top. Polyester should remain floating near the center of the solution. Results from this test may be difficult to interpret because deteriorated acetate film may sink to the bottom just as nitrate film would. Another complicating factor is that the specific gravities for cellulose nitrate and the cellulose acetates fall within a broad range, which may cause materials to behave differently. As with the other tests, having a known sample for comparison can be extremely helpful. Place the sample in a test tube of trichloroethylene. Shake test tube so sample is completely immersed. Then observe the location of the sample in the liquid. For more details, see the “Testing” section from Fischer & Robb. (1993).

Acetate Film Base

Beginning in the mid-1920s, highly flammable nitrate film was slowly replaced with cellulose acetate film base (cellulose diacetate, cellulose acetate propiarate, cellulose acetate butyrate and cellulose triacetate). It became known as "Safety" film. Despite this name, cellulose acetates do have stability problems. Like cellulose nitrate, the deterioration of cellulose acetate is autocatalytic: once deterioration has begun, the degradation products induce further deterioration. It affects the plastic support of acetate film, causing it to become acidic, to shrink, and to give off of acetic acid producing a vinegary odor.

A useful tool in helping determine the amount of acid vapor present, and gain an overview of the condition of acid vapors in an entire collection are "A-D Strips" (acid-detecting strips) from the Image Permanence Institute at the Rochester Institute of Technology in Rochester, NY. They are acid-base indicator papers, which turn from blue to green to yellow in the presence of acid, and measure the extent of the acetate base support deterioration.

As with nitrate negatives, deteriorated acetate negatives are easy to identify, but in good condition, they are almost undistinguishable from other types of plastic films. There are four ways to identify acetate film base negatives.

1. Edge printing

Some cellulose acetate film base materials have the word "Safety" printed in the border. Edge printing may also include the name of the manufacturer, manufacturing code data, and notch codes. "The Acetate Negative Survey Final Report" by D. G. Horvath (http://louisville.edu/library/ekstrom/special/files/Acetates) is an invaluable resource for identifying cellulose acetates using this information.

Again, note that acetate negatives may have been copied at some point and the edge printing from the original will appear on the copy. Therefore, just because you see the words *acetate* or *safety* does not guarantee your item is acetate. See the section on testing to be sure.

2. Dating information

Type of Cellulose	***Sheet Film***	***Roll Film***
Cellulose diacetate	1925–1950	1920s–1935
Cellulose acetate propionate	1930–1945	1920–1945
Cellulose acetate butynate	1935–present	—
Cellulose triacetate	1945–present	1945–present

3. Acetate film base deterioration

When acetate base film is stored in a poor environment at high heat and humidity—or exposed to acidic vapors from nearby degrading film—it undergoes chemical reactions within the plastic support to form acetic acid. This acid causes the support to become acidic, brittle, and shrink. In turn, the acid spreads into the gelatin emulsion or into the air creating a harsh, acidic odor. It is a slow form of chemical deterioration known as "Vinegar Syndrome." It places acetate film at risk, and then deterioration may place otherwise stable photographic materials at risk as well.

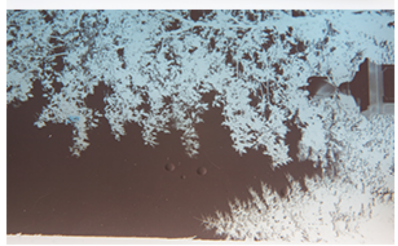
Deterioration is generally catalogued in six progressive stages:

Level 1
No deterioration.

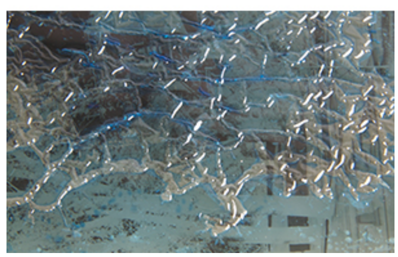
Level 2
The negatives begin to curl and they can turn red or blue.

Level 3 (not shown)
The onset of acetic acid (vinegar smell); also shrinkage and brittleness.

Level 4
Warping can begin.



Level 5
The formation of bubbles and crystals in the film.



Level 6
The formation of channeling in the film.

4. Testing

See nitrate testing section.

CARE

Environment

The deterioration of both cellulose nitrate and cellulose acetate negatives is highly dependent on temperature and relative humidity. Ideally, to minimize decomposition, negatives should be stored in a freezer. At freezing temperatures, the natural decomposition of cellulose nitrate and acetate is slowed down. While the cold storage of small numbers of negatives is sometimes feasible, the cost and inconvenience of freezing a large collection can be prohibitive. However, cold storage is predicted to extend the life of acetate negatives by a factor of ten or more. For more information, see Reilly (1997).

A good resource on cold storage is the National Park Service online interactive training program *Cold Storage: A Long-Term Preservation Strategy for Film-Based Photographic Materials* available at http://www.nps.gov/museum/coldstorage/NPSColdStorage.swf.

In general, a large commercial freezer (which should defrost automatically) is a relatively inexpensive cold storage unit. A combination of chemically stable boxes placed in polypropylene bags and then sealed with humidity control cards is a design that works well in preserving photographic materials in cold storage. This allows the stored items to warm at room temperature safely (8–12 hours should be sufficient) and can be easily accessed. The Safe Care® Archive Freezer Kits are available at Hollinger Metal Edge, Inc. (http://www.hollingermetaledge.com).

A low cost set up for storage would provide a controlled environment with the constant temperature at 68° F (20° C), and relative humidity between 20% and 30%. Rapid changes in temperature and humidity will hasten deterioration. A dark and well-ventilated area around the negatives allows gases to dissipate.

STORAGE

Because they present a great potential hazard to other materials due to their flammability and the strong acid formed from gases that the negatives release, cellulose nitrate negatives should always be stored separately from other negatives in a collection.

Three layers of protection are recommended for the storage of film base photographic materials. Negatives should be placed in sleeves, the sleeves placed in a box or drawer, and these boxes or drawers on shelves or in a cabinet. Motion picture film and microfilm should be stored in unsealed containers in cabinets or on shelves. All enclosures should pass the Photograph Activity Test (PAT) as described in ISO Standard 18916:2007 (http://www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=31940).

Negatives should be stored in individual, seamless, high alpha cellulose content paper enclosures. These enclosures are recommended to allow for the dissipation of harmful gases. Acid-free paper will resist deterioration caused by the formation of acids. Enclosures that have been used to store negatives must never be reused. These enclosures retain acids from previous materials, and anything placed in them will be damaged. Disposal of used enclosures is recommended in order to avoid reuse.

James Reilly's invaluable "Image Permanence Institute's Storage Guide for Acetate Film" has information on this as well. It is a tool for evaluating and planning storage environments for acetate-based photographic film.

REFORMATTING/DIGITIZATION

Reformatting is an ongoing process. Negative collections should be inspected regularly for signs of deterioration. Any negatives that show signs of deterioration should be digitized as soon as possible. The more advanced the stage of deterioration, the sooner the negative should be reformatted to minimize the amount of image detail lost. Other factors that need to be considered are size and use of collection, space available for storage, and financial resources.

Nitrate and safety negatives that need to be handled but are in good condition should still generally be digitized. The digital image can then be used while the original remains in cold storage. This minimizes the potential of damage to, or loss of, the original negative.

A wide array of digital systems are available for capturing and storing photographic images. The access capabilities of these systems are impressive; however, if being used as a preservation method, the institution should have a good digital preservation policy in place before deciding that the only retained copy of a negative will be digital.

Digitized files require active management. Digital image collections should be created in standard file formats, such as TIFF, with sufficient image resolution to capture a high level of detail. Metadata describing the object and the technical specifications used in the creation of the digital object should accompany each file. Imaging photographic negatives requires expertise (or dependence on a company with that expertise) and data will have to be migrated over time as the hardware and software become obsolete.

A plan for redundant storage will help ensure long-term access to materials, but once files are placed on a storage device, they must be checked regularly to guard against device failure and data loss.

For more information on digitization for preservation, please see NEDCC Leaflet 5.10 *Digital Preservation.*

CONCLUSION

Any collection of photographic negatives presents a series of complex tasks and challenges, ranging from identification to storage to duplication. An informed approach to a collection should rest on a solid foundation of accurate identification of film base materials in a collection, a good understanding of the collection's present and future uses, and maintenance of proper storage and environment.

RESOURCES

Fischer, Monique, and Andrew Robb. "Guidelines for Care and Identification of Film Base Photographic Materials." *Topics in Photographic Preservation* 5 (1993): 117-122.

Reilly, James M. *IPI Storage Guide for Acetate Film*. Rochester, NY: Image Permanence Institute, 1993. https://www.imagepermanenceinstitute.org/webfm_send/299.

Reilly, James M., Peter Z. Adelstein, and Douglas W. Nishimura. *Preservation of Safety Film: Final Report to the Office of Preservation, National Endowment for the Humanities*. Rochester, NY: Image Permanence Institute, Rochester Institute of Technology, 1991.

Ritzenthaler, Mary Lynn, and Diane Vogt-O'Connor. *Photographs: Archival Care and Management*. Chicago: Society of American Archivists, 2006.

Valverde Valdés, María Fernanda. *Photographic Negatives: Nature and Evolution of Processes*. Rochester, NY: Advanced Residency Program in Photograph Conservation, 2005. https://www.imagepermanenceinstitute.org/webfm_send/302.

Wilhelm, Henry, and Carol Brower. *The Permanence and Care of Color Photographs: Traditional and Digital Color Prints, Color Negatives, Slides, and Motion Pictures*. Grinnell, Iowa: Preservation Publishing Company, 1993. http://wilhelm-research.com/book_toc.html.