Preserving Your Collection of Film-Based Photographic Negatives

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TABLE OF CONTENTS

ABSTRACT

The problem presented in the title of this paper can be addressed simply by two words: cold storage. Recent research indicates that all cellulose-based film, whether it's a cellulose nitrate negative from the 1890's or a cellulose triacetate color transparency from the 1990's, share very similar deterioration mechanisms that are temperature and humidity dependent. On balance, relative humidity has been shown to be a less serious concern at low temperatures. What this means for a collections manager is that long-term preservation of a collection of film-based negatives is as affordable as a frost-free freezer.

HISTORY OF FILM-BASED PHOTOGRAPHIC NEGATIVES

Eastman Kodak pioneered the first practical use of flexible, transparent film in 1889. This nitrate-based film had a strong tendency to curl and was extremely flammable. In 1903, this film was refined, incorporating a thicker nitrate film base and a gelatin coating on both sides. The additional gelatin reduced curl and slowed the rate of decomposition of the film base, thereby somewhat reducing flammability. The danger posed by quantities of nitrate film was recognized following several disastrous fires. In particular, a fire in

1909 at the Fergusin Film Exchange Building in Pittsburgh prompted the National Board of Fire Underwriters to draw up regulations regarding the handling and storage of nitrate film. Similar regulations, in one form or another, are still in effect in local and state ordinances. Despite the known hazards, nitrate sheet film remained in widespread use until the mid-1930's, though use of nitrate roll and motion picture film persisted until the early 1950's.

The introduction of safety film in 1923 addressed the flammability issue by replacing cellulose nitrate film with cellulose acetate. By 1937, cellulose acetate film bases were, in turn, replaced with cellulose diacetate. The new films were significant improvements (ignition temperature for safety film is in the region of 800o to 1000o F as compared with 300o F for nitrate film in good condition). Diacetate films, however, were not without problems. Shrinkage of the film base, discoloration, and progressive embrittlement prompted the gradual replacement of diacetate with cellulose triacetate beginning in 1947. Cellulose triacetate remains in use today, though within the past few years, stability problems have come to light with it as well. Prior to the discovery of these problems, triacetate films had been considered suitable for archival records.

For the most permanent photographic records, films incorporating a polyester (polyethylene terephthalate) base are currently recommended. Though these films were introduced in 1955, manufacturing/engineering difficulties and the mistaken conviction that triacetate solved the problem of impermanence slowed their widespread use.

DETERIORATION OF FILM-BASED NEGATIVES

Recent research indicates that all cellulosic plastic materials have essentially the same deterioration mechanisms. In other words, nitrate, diacetate, and triacetate materials will deteriorate in much the same way and at essentially the same rate (Reilly, 1993). This research also indicates that the rate of deterioration is highly temperature and humidity dependant. Therefore, the age and type of film base of a particular negative has little bearing on its condition or future potential for deterioration.

The chemical reactions driving the deterioration mechanisms of nitrate and acetate negatives are autocatalytic. This means products of chemical degradation accumulate and catalyze further deterioration. Once deterioration starts, the rate of chemical activity continually gains momentum. To prevent the build up of the gaseous by-products of chemical deterioration, negatives should be removed from sealed "air-tight" containers such as metal film canisters or plastic bags (note: this recommendation is contingent upon a stable, moderate, storage environment). A well-ventilated storage facility is also important in inhibiting the concentration of these chemical by-products.

Deterioration of Nitrate

As cellulose nitrate deteriorates it produces nitric acid, nitric oxide, and nitrogen dioxide. These products are destructive to other film-based negatives, and especially to photographic prints. Other artifacts, metals for instance, will be harmed by proximity to deteriorated nitrate material.

Cummings has outlined the phases of nitrate deterioration (Cummings et.al., 1950) as:

1. Amber discoloration of film base. Noticeable fading of the image.
2. The film base becomes brittle. The negative becomes sticky, tending to adhere to paper enclosures or other negatives.
3. The film base is extremely brittle, exhibiting noticeable bubbles and emitting a noxious odor.
4. The film base softens and readily adheres to paper enclosures and other negatives. A strong noxious odor is evident.
5. The film disintegrates into a brown, acrid powder.

Film exhibiting any of these conditions should be isolated from other negatives. Film in phases 1 or 2 is still useable, though copying is advisable. Most film in phases 3 through 5 is unusable. Moreover, it poses serious threats to health and safety and should be disposed of by qualified personnel.

Diacetate and Triacetate

The deterioration of cellulose acetate (diacetate and triacetate) films is characterized by the "vinegar syndrome." Very similar to the degradation of nitrates, acetates suffer from chemical decomposition resulting in the production of acids. Acetic acid, which is produced by deteriorating acetate negatives, is detectable by a characteristic vinegar odor. Also like nitrates, diacetates and triacetates become very brittle. The film base can develop bubbles and crystals. Diacetate and triacetate characteristically form deep, wavy grooves in the film base known as "channelling." This condition is the result of the film base shrinking in relation to the gelatin emulsion.

Like degraded nitrates, acetates that show signs of deterioration should be isolated and handled carefully to avoid health risks. Unlike nitrate film, however, deteriorated acetate film does not pose a serious fire hazard.

HAZARDS

Heath risks from deteriorated negatives

Deteriorated negatives, especially nitrates, can emit a noticeable and noxious odor. Such gasses can cause skin, eye, and respiratory irritations. Allergic sensitivity has also been noted, as has dizziness and lightheadedness. Handle deteriorated negatives in a well-ventilated area. Wear neoprene gloves, remove contact lenses, and limit exposure times. It is also advisable to wear goggles and a respirator with acid/organic vapor filter cartridges.

Fire hazard posed by nitrate negatives

The threat posed by degraded nitrate film to the security of a collection can not be understated. Spontaneous combustion of deteriorated nitrate film has been documented as low as 106o F. Once ignited, even nitrate film in good condition burns rapidly. Since it generates its own oxygen during combustion, nitrate film will burn even without the presence of air. Gas released during a nitrate fire can be lethal and is itself flammable. For these reasons, collections staff should never attempt to fight a nitrate fire.
Many federal, state, and local ordinances apply to the storage, transport, and disposal of nitrate film. In 1988, the National Fire Protection Association published Standard for Storage and Handling of Cellulose Nitrate Motion Picture Film (NFPA 40). The NFPA standard lists specific construction requirements for rooms housing quantities of nitrate material. Because nitrate film is classified as a hazardous material, the United States Department of Transportation regulates its shipping. Nitrate negatives in poor condition should be destroyed by a contractor specializing in the disposal of hazardous waste. Insurance policies should be examined to determine coverage in the event of a nitrate fire.

As previously mentioned, acetate film does not pose a serious fire hazard.

IDENTIFICATION OF FILM-BASED NEGATIVES

The positive identification of film-base type is no easy matter, though careful examination and testing can yield a great deal of information. Monica Fischer and Andrew Robb of the University of Delaware recently published a useful identification guide that provides dating information, deterioration characteristics, and other forms of analysis. The guide recommends that identification begin by looking for edge printing along the side of the film. Often nitrates are identified as such, while acetate-based films are identified as "safety film." Manufacturers' names also can reveal clues useful in identification. The next step is factoring in the date of the negative (if known). This information alone may be enough to identify the film.

If not, the guide provides a chart assessing deterioration characteristics such as those mentioned above. For example, an acetic acid (vinegar) smell is indicative of acetate films, while amber discoloration is characteristic of nitrate films. As further assistance in identifying the film base, the chart explains a series of destructive and non-destructive tests. The tests are relatively simple to perform, though results at times are difficult to interpret. Bear in mind that no guide will conclusively solve each identification problem presented by a large collection of negatives.

STORAGE TECHNIQUES, MATERIALS, AND ENVIRONMENT

General Recommendations

All negative enclosures should pass the photographic activity test as prescribed by American National Standards Institute (ANSI) Standard IT 9.2-1991. Before placing negatives in enclosures, dust them with a wide, soft brush. The negative enclosures can be labelled with a permanent, archival ink meeting ANSI Standard IT 9.2-1991. As a further precaution, the labeled side of the enclosure should be placed away from the emulsion side of the negative. Negatives in good condition should be handled only with lint-free cotton gloves (handling deteriorated negatives requires neoprene gloves, goggles and a respirator as mentioned above).

Seriously deteriorated negatives of any type should be isolated from those in good condition. Each negative should be placed into an individual paper envelope. If the envelope incorporates a glue seam, the gelatin emulsion on the negative should be placed away from the seam. Both the paper and the adhesive used for the envelopes should meet ANSI Standard IT 9.2-1991. Avoid the use of envelopes that incorporate a thumb-cut. Buffered paper enclosures are recommended for nitrate negatives. Though buffered papers generally have not been recommended for storage of acetate negatives, their use actually may be beneficial since the buffering material may help slow acid hydrolysis reactions (Nishimura, 1993). In any case, storage at a low temperature and a constant relative humidity below 50% would probably mitigate the effects (if any) of buffering agents.

Negatives should fit snugly, but not tightly, into boxes. The boxes should have reinforced seams, be acid-free with a high alpha-cellulose content, and meet ANSI Standard IT 9.2-1991. The boxes should have tight fitting, "clam-shell" type lids. Negatives of different formats (sizes) should not be mixed in the same box. Negatives should be boxed separately by film type.

Sheet film is ideally stacked flat in a drop-front box. However, sheets that exhibit severe planar deformations and brittleness should not be stacked but stored vertically in an appropriately designed box. Relevant information on original negative boxes (which are often constructed of highly acidic wood-pulp paperboard) can be photocopied onto acid-free, buffered paper. The boxes can then be retained separately from the negatives or disposed of, depending on curatorial prerogative.

Since there is clear evidence that tightly rolled film, especially nitrate, deteriorates at a quicker rate than sheet film, long rolls can be cut between exposures at reasonable intervals. The strips can then be slipped into polypropylene or polyethylene negative preservers. The preservers should then be placed flat into an appropriate drop-front box meeting ANSI Standard IT 9.2-1991.

Storage environment

Proper storage environment is critically important. Recent work at Rochester's Image Permanence Institute makes explicit the relationship between storage temperature/relative humidity and long-term stability. The results, published in the *IPI Storage Guide for Acetate Film*, predict the life span of fresh and already degraded films under different combinations of relative humidity and temperature. For instance, in a collection maintained at 70o F and 40% relative humidity, the *Guide* indicates fresh triacetate film will remain in good condition for only 50 years. To illustrate the effect of lower temperature, the *Guide* predicts that at 30o F and the same 40% relative humidity, fresh triacetate film will last for 1000 years. The *Guide* is a very practical tool for a collections manager, since the cost of an improved storage environment can be directly compared to quantitative benefits measured in years of additional preservation. As indicated by the *Guide*, cold storage is the only viable option to increase stability of material that already shows signs of deterioration and for keeping new material in good condition.

If cold storage is not an option over the short term, the storage facility should be well ventilated to prevent the build up of acidic gasses that drive the auto catalytic degradation reactions of cellulosic films. As much as possible, the environment should be stable, cool, and dry. Significant fluctuations of temperature and relative humidity should be avoided.

Cold storage

It is clear that film-based negatives are more stable if kept at or below the freezing point of water. In fact, cold storage is predicted to extend the life of diacetate and triacetate negatives in good condition by a factors of ten or more.

Sophisticated cold storage vaults precisely control both temperature and relative humidity. Such vaults tend to be set at moderate relative humidity (around 40%) with temperatures anywhere from near freezing to 40o F. The control of relative humidity in a cold storage vault is no easy matter and often requires complex engineering and upkeep. Often such vaults will be associated with staging rooms where film removed from the vault is slowly brought up to ambient environmental conditions. This gradual acclimation is thought to reduce stress on the film as it dimensionally adjusts to the new environmental conditions.
The cost of state of the art cold storage can be daunting. But while such systems are certainly ideal, a collection of film negatives may not survive the planning and fund raising process necessary to build the perfect cold storage vault.

Relatively inexpensive cold storage is available through the acquisition of a large commercial freezer. The freezer should defrost automatically (a cycle of three times a day is acceptable). Recent research indicates that precise control of relative humidity is, on balance, not of primary concern at such low temperatures (McCormick-Goodhart, 1993). Therefore, humidity controls within the freezer, if considered cost-prohibitive, can be omitted.

The cold storage "vault" can be equipped with a temperature read-out and a failure alarm. Once the volume of material entering the freezer has been determined, scientific materials vendors or representatives from the food service industry (among others) can be consulted for cost-effective options.

For cold storage, boxes containing negatives (packed in conformance with recommendations described above) should be put into heavy "zip-lock" polypropylene bags. The bags should be sealed and placed in the cold storage vault. Upon removal from

cold storage, the bags must remain sealed until the negatives come up to room temperature (8 to 12 hours should be sufficient). Avoid conditions of particularly high or low relative humidity when returning or removing items from cold storage.
Sealing negatives in a frost-free freezer contradicts the stated recommendation of maintaining a well ventilated storage facility. Nonetheless, for material in good condition, the benefits of cold storage far outweigh the drawbacks of sealing in whatever gasses evolve as a result of deterioration. Removal of seriously deteriorated negatives prior to placing the collection into cold storage is of utmost importance. Once in cold storage, the collection should be regularly monitored at reasonable intervals. Signs of active deterioration should be investigated carefully and negatives discovered to be in poor condition should be removed.

As previously mentioned, nitrate negatives should be stored separately from acetate negatives. But because identification of film-bases for a large collection can often be difficult, time consuming, and inconclusive, for those with limited resources, the cold storage of nitrate and acetate in the same vault is acceptable if all the material is in good condition (Nishimura, 1993). Conscientious monitoring of the collection is essential in this situation.

BASIC GUIDELINES FOR THE DUPLICATION OF HISTORIC NEGATIVES

Negatives that show advanced signs of deterioration, especially hazardous nitrate negatives, are often candidates for disposal. If possible, these negatives should be duplicated prior to their destruction. For large collections of negatives, a camera duplication system is the most economical (as opposed to contact printing). For efficiency, the camera should incorporate a long roll film-back. If possible, reduction of image size should not exceed 50%. Interpositives and duplicate negatives should be made onto a polyester-based film. Prints can be made from non-developer incorporated resin coated paper.
Duplicated negatives on roll film should be cut into individual frames. Duplicated material should be stored in individual, non-buffered enclosures and placed into boxes that meet ANSI Standard IT 9.2-1991. A storage environment of 35% relative humidity and 65^{o} F is considered adequate for duplicated materials.

The duplication of historic negatives is a highly technical field. Duplication vendors must meet rigorous standards that are explicitly spelled out in a binding contract, especially if historic negatives are to be destroyed following duplication. Tests for residual fix and proper contrast need to be conducted. Inspection of duplicated material requires visual and densitometric evaluations performed by both the vendor and the collection staff. Before embarking on a duplication program, seek advice from consultants who specialize in these processes and who can knowledgeably address such issues as duplication options, setting up quality assurance procedures, and the vendor contract.

CONCLUSIONS

Environmental controls are essential for the preservation of film-based negatives. It is clear that typical ambient conditions (that is, approximately 40% RH and 70o F) are not adequate for the preservation of nitrate and acetate material. Of particular importance is the fact that once deterioration of a collection of negatives begins, it gains momentum rapidly, leading to the swift destruction of artifacts and increased health and safety risks. The most economical way to preserve a collection in good condition is cold storage using frost-free freezer systems. Though negative duplication is a viable option, it is no substitute for proper collections care. The Image Permanence Institute predicts a coming "tidal wave" of film degradation, which is likely to overwhelm existing duplication resources. The only way to avert this tidal wave is to make environmental control the top priority for film-based negative collections.

Note: to order the *IPI Storage Guide for Acetate Film*, contact the Rochester Institute of Technology, Image Permanence Institute, 70 Lomb Memorial Drive, Rochester, NY, 14623-5604, (716) 475-5199.

To order Guidelines for Care & Identification of Film-Base Photographic Materials, contact the Art Conservation Program, Winterthur Museum/University of Delaware, 303 Old College, Newark, DE, 19716, (302) 831-2479.

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