History, Science, Preservation and Treatment of Cellulose Nitrate Still Film

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1 - Introduction

The early use of cellulose nitrate was not as a film base, but as an explosive. Nitration of cellulose was discovered in 1832, and by 1846 it was found that equal parts of both nitric and sulfuric acid were needed to form a stable cellulose nitration. Louis Menard (France) and John Parker Maynard (Boston) independently discovered collodion (cellulose acetate) around 1847. Fredrick Scott Archer <u>http://www.dunniway.com/archer/thechemist.html</u> is credited with inventing collodion photography with the Collodion Wet Plate negative in 1851. Commercial celluloid (cellulose nitrate solid plastic) was developed by John Wesley Hyatt in 1863. The first use of cellulose nitrate in photography was to create a light sensitive emulsion for the Collodion Wet Plate process in 1851. It wasn't until 1889, that the process for creating a self-supporting plastic film was made commercial.



Figure 1a & b: left, 1922 nitrate negative digitally captured in 2005 (16-bit at 4800 ppi), the envelop was stuck to the surface because the emulsion was softened by nitric acid deterioration of the gelatin. The condition shows the boundary between L4 and L5 state. On the right, shows the image after it has been manipulated in Photoshop to reveal information hidden by the paper envelope stuck to the soft gelatin.

Above is an example of an 85 year old nitrate negative that had softened emulsion (L4), which stuck to its envelope; the envelope paper is stuck to the emulsion layer. The image was partially repaired in Photoshop by selecting out the dark area created by the Kraft paper stuck to the emulsion, and manipulating the region (16-bit B&W) to yield enough visual information to reintegrate the image; some localized burning and dodging was required along the edges to help blend the transition.



Figure 2a & b: On the left, in the upper right quadrant shows ripples in the hardening collodion coating as it was being spread, and, the uneven coating found on the edge and in the corners of the collodion layer in this Ambrotype; taken from <u>http://www.collodion.com/bendingtree.htm</u>. On the right, is a recreation of unhardened gelatin plate with the "early" processing fault, emulsion was washed-off the corners during processing; image taken from <u>http://www.alternativephotography.com/process_dryplate.html</u>.

2 – History of Cellulose Nitrate in Photography

In **1851** Fredric Scott Archer published the Wet Collodion Glass Plate process. Cellulose nitrate polymer was used to create a silver bromide and silver lodide image emulsion that was panchromatic, fast and sharp, with an extended tonal range, on a dimensionally-stable glass plate. The collodion emulsion was pored on to a glass plate and rocked around to form an even coating. The edges show finger marks and ripples. The process endured for decades because of its outstanding technical properties.

The very rare albumen glass plate negative process was created about the same time: Niepceotype **1848**. It was also quite sharp, due to small silver particle size, but the dry albumen plate was very slow (< \approx 10x), and the surface was fragile. The equally rare, collodion-albumen dry plate variant is credited to Joseph Sidebotham in **1861**; it had far greater sensitivity with a tough surface when dry.

In **1860**, Richard Norris has been credited with developing the Collodion Dry Plate, which also enjoyed a very long life, through the 1930s.

The collodion medium was an emulsion of liquid cellulose nitrate plastic in solvents such as acetone or ether, with silver iodide/bromide, that was then sensitized with silver nitrate and exposed while still damp. Eventually the collodion process was adapted to the ambrotype and tintype (ferrotype), giving it a preeminent place in photography until about 1880-90 as one-of-kind images, but far longer as wet/dry glass plate negatives.

In **1871** Richard Maddox developed the process that would replace wet plates and provide the emulsion layer for the future -- the gelatin dry plate. Originally, gelatin plates were too soft when wet (see Fig. 2b) with lower sensitivity.

Charles Bennet made significant contributions to the gelatin technology when he developed (a) hardening of the soluble gelatin in **1873** and (b) in **1878**, showed that prolonged heating increased the sensitivity of the plate, yielding faster exposure times.



Figure 3a & b: On the left, is an 1906 Arnold Genthe image from the FAMSF collection, made on nitrate base amateur roll film right after the 1906 earthquake. On the right is an example of a 1900 gelatin dry plate taken from <<u>http://www.historiccamera.com/cgi-bin/librarium/pm.cgi?action=display&login=sitting</u>>.

In **1879**, Eastman developed an automatic coating machine. Later Eastman and Strong opened the Eastman Dry Plate Company, producing the first commercial plates in **1881**.

Gelatin plates were grainy and notably insensitive to the green (middle of visible spectrum), thus not panchromatic. It would be some time before a gelatin emulsion could respond equally to all colors, probably between 1910 and 1920.

2.1 - Nitrate Base Film in Motion Picture Film

One of the earliest creations of a self-supporting transparent strip of cellulose nitrate film, or a thin plate of cellulose nitrate plastic, was made in **1879** when John Carbutt of the Keystone Dry Plate Works sliced thin plates (35 mm wide) from a rigid celluloid block, and then coated them with a silver gelatin emulsion to make a Celluloid Dry plate.

The first "flexible" transparent polymer film was developed in **1885** when "Eastman American Film" cellulose nitrate film was introduced by the Eastman Dry Plate and Film Company. By **1889** the Eastman Corporation (Kodak) introduced the first commercial cellulose nitrate film as amateur roll film and MP film. Eastman Corp. subsumed the earlier company in 1889. Kodak was always a registered Eastman trade name.



Figure 4a & b: left, is an example of Edison 35 mm nitrate base motion picture film; right, is an example of a 1894 Edison viewer, Kinetoscope, images taken from http://www.sci.fi/~animato/filmhist/filmhist.html.

The availability of uniformly-coated roll film, that was far more sensitive than dry plate emulsions, led to the 1891/2 development of the motion picture camera by Edison. Above on the left, is a strip of 1889/90 Edison 35-mm MP (nitrate) film; on the right is an Edison 1894 Kinetoscope. The earlier Keystone nitrate film technology (1879) proved to be too rigid for use as a MP film, slowing development of motion picture technology.



Figure 5a & b: left, is an example of Lumière Brothers 35-mm acetate-base motion picture film; right, is a poster used to advertise the exhibition of moving pictures present in a theater, as opposes to the Edison peep-show seen in Fig 4; images pulled from http://www.xs4all.nl/~wichm/filmsize.html#variety.

See <u>http://www.sci.fi/~animato/filmhist/filmhist.html</u> and <u>http://www.ss4all.nl/~wichm/filmsize.html#variety</u> for a review of MP film formats and history. The Lumière brothers (France) created the first motion picture in-a-theater by 1895 using the 35-mm profession MP format made standard by Eastman and Edison (peepshow format) a few years earlier. Fig. 5a (left) is an example of Lumière Cinématographe 35 mm film with its two-sided, dual-round-sprockets per frame.

2.1 - Towards Roll and Sheet film for Still Photography

Cellulose nitrate roll film replaced paper-base negatives (1884) in roll film cameras in **1889**. Roll-film holders were developed for existing collodion wet and gelatin dry plate cameras. And there were numerous new amateur roll film cameras created for the new fast transparent film. By **1899**, Eastman had developed the continuous-wheel production of transparent film; before that, the film had to be cast on long tables. Cast film often has very small pimples and dimples on its base-side. Examples of amateur roll film cameras, below, were taken from URL http://historiccamera.com/reference.html.





Model: Kodak Improved No. 4 Folding Camera Production Dates: 1890 - 1897 Film: Glass Plates or Roll Film

Model: No. 4 Kodak Camera Production Dates: 1890 - 1897 Film: 250 Shot, Factory Loaded Roll Film

Figure 6a & b: Examples of amateur film cameras made, or distributed, by Eastman. There are many websites on this topic. All roll film cameras made before 1889 were designed and shipped with a roll of paper negative material.

Amateur roll film formats were the first nitrate base films, in the 1885-1895 period. They were used in amateur cameras, such as the Kodak World's Fair Souvenir A, B & C cameras (1891) with daylight loading, Kodak #4 Kodet (1894-5) and Folding Kodet, the Kodak #5 Folding (1890), above left) with Eastman Walker film holder and the Kodak #6 Folding cameras (1893); #4 Kodak Camera (1890-97, above right) came factory loaded with Kodak roll of film for creating 250, 4"x 5" images that were commonly contact printed as individual prints. Examples of early nitrate roll film are:

- a) roll film # 101 3.5"x 3.5" introduced 1895 and discontinued 1956
- roll film # 104 4.75"x 3.75" introduced 1897 and discontinued 1949 b)
- c) roll film # 109 4"x 5"-roll, introduced 1898 and discontinued 1924
 d) roll film # 116 2.5"x 4.25" introduced 1899 and discontinued 1984

At the time of creation, these films were designated by the name of camera in which they were used; the use of film "numbering" came later.

Eastman Company introduced Kodak NC film (non-curling films) for amateur cameras in 1903. Some roll formats had bigger negatives for creating larger prints, while still using the contact printing method common for the era. Non-curling films had a thin layer of gelatin on the back of the nitrate base, opposite the image emulsion; NC examples are:
a) roll film # 122 - 3.25"x 5.5" introduced 1903 and discontinued 1971
b) roll film # 123 - 4" x 5" introduced 1904 and discontinued 1949
c) roll film # 124 - 3.25"x4.25" introduced 1905 and discontinued 1961
d) roll film # 125 - 3.25"x 5.5" introduced 1905 and discontinued 1949

- e) roll film # 126 4.25"x 6.5" introduced 1906 and discontinued 1949

In 1902, film processing could be done in a machine by the user, rather than in a darkroom or sentaway to the manufacturer.

Non-curl roll film (NC) remained a standard roll film formulation through the 1920s. In 1930, Verichrome (panchromatic B&W) film was released on acetate base. It had greater latitude and tonal range, with finer grain than the NC nitrate based film it replaced; the film grain in some NC films is quite large (see Fig. 3a, 1906). Many amateur roll films (for stills) were not transitioned fully to acetate base until 1950. Some time in 1930s, professionals began experimenting with today's 35 mm (24 x 36 mm) format, as the German 35 mm range finder cameras became common. Professionals had been using roll film informally since the turn of the century (Fig. 3a), but many preferred glass plates in critical studio applications.

More data on roll film sizes with introduction and discontinuation dates can be found at http://www.nwmangum.com/Kodak/FilmHist.html and http://en.wikipedia.org/wiki/Film format for motion picture film. An excellent list of Kodak cameras with films used can be found at

http://www.kodak.com/global/en/consumer/products/techInfo/aa13/aa13.shtml in their Technical Publication AA-13. Images of cameras, manufacture data and detailed information on historic cameras can also be found at http://historiccamera.com/history links.html.

3 - Sheet Film for the Professional Photographer

The professional photographer generally used gelatin glass plates through the 1910s; they preferred its dimensional stability for professional applications. Eastman introduced Eastman Portrait Film, on nitrate base, in 1913. Eastman Portrait sheet film directly replaced dry plates for cameras using glass plates. Examples of professional camera equipment can be found in Fig. 7a-c; images of studio cameras were pulled from http://historiccamera.com/reference.html. By 1925 Kodak replaced the nitrate base film (Eastman Portrait) with Eastman Portrait Pan, a panchromatic film on acetate base. It is noted by a single square \Box notch, as opposed to the \lor notch in Eastman Portrait film.



frame, rack & pinion movement Film: Glass Plates

Mfg: Star-Reversible Back Camera, Mfg: Century Camera Company
Automatic latch, ground-glassMfg: Century Camera Company
Model: Grand Studio Outfit No. 1Mfg: Century Camera Company
Model: Grand Studio Outfit No. 8 Production Dates: 1900 - 1907 Film: Glass Plates

Production Dates: 1900 - 1909 Film: Glass Plates

Figure 7a, b & c: Cameras used by professional photographers: a) view camera on the left could be used either in field or in studio; b & c) the two on the right are glass plate cameras, similar cameras were used through the 1940s.

3.1 - Collodion Glass Plates were preferred by workers preparing material for photo-lithography in the printing industry; now called Prepress service bureaus. In the 1921 Mees' book [The Fundamentals of Photography, London, one of Kodak's early publications, explains that glass plates are preferred in some applications because of their broad light sensitivity (B&W film), speed and dimensional stability.

Kodak released Kodalith film and plates http://www.kodak.com/US/en/corp/kodakHistory/1930 1959.shtml in 1931 for use in prepress applications. While 1935 is the first date noted for Kodalith on acetate base (Horvath, 1987), it has been assumed that the 1931-release was on nitrate base, as was the other commercial film, thick sheets of x-ray film. X-ray film was moved to acetate in 1933. Commercial films were all migrated to acetate base in 1939.

3.2 - Determining Nitrate Base -- all Unmarked Film Used Before 1950

Film should be considered to be on nitrate base if the film was made before about 1951, and not marked "Safety." There will be exceptions, but this rule of thumb will be accurate most of the time. Nitrate base use was phased-out beginning in 1909, and, Kodak terminated all nitrate base use by 1951. Other manufacturers probably phased-out nitrate base earlier, but they have not published their history; many are unfortunately victims of the move to digital technology with libraries long gone.

The 8, 9.5, 16, 22 and 28 mm amateur motion picture gages were all released on Safety base film. This was later set in law worldwide. The use of acetate base at Eastman began with the release of the amateur gauge motion picture film (22 mm) in 1909. The actual change-over began with the "Safety Film" announcement http://www.kodak.com/US/en/corp/kodakHistory/1878_1929.shtml at Eastman. For professional sheet film the release of Eastman's Portrait Pan Film in 1925 started the Safety base era in the format (Horvath, 1987, The Acetate Negative Survey Final Report)

The use of nitrate base in 35 mm still camera film ended in 1938. Eastman ended the use of nitrate base in commercial and professional sheet film in 1939. The use of nitrate base in thinner sheets (film packs) didn't end until 1949-50. Thin sheet film had two possible sources: (a) film-packs (2-1/4"x 3-1/4" or 4"x 5") were commonly used by press photographers because the next sheet of film could be brought into use very quickly, nitrate use ended in 1949; or from (b) single frames cut from rolls of amateur film, where nitrate use ended in 1950. Both thin sheets of film have no notches because they did not need to be loaded in a "film holder" with the emulsion side facing the lens.

Table 1: Critical Dates in the Development of Film and Nitrate Base

Brown = Cellulose Nitrate; Black = Cellulose Acetate & Other; Blue = Color Film; Green = Sound on Film 1826 Niépce invents the photographic image in France using bitumen on Pewter plate 1832 Hercules Florence created a process he called Photographie 1839 Daguerreotype invented first definable photographic format, one-of-a-kind image 1839 John Herschel developed the first glass negative 1850 Blanquart-Evrard develops albumen process; albumen dry glass plates are rare 1851 Archer publishes collodion wet plate process; fast, sharp and extended tonal range Collodion wet plates in common use, photographers must make their own plates, thru 1920-30 Harris develops collodion dry plate, 1/4-sensitivity, but purchase rather than make 1851 1960 Maddox develops gelatin dry plates; Eastman will popularize format later 1871 1879 John Carbutt develops & markets Celluloid sheet film at Keystone Dry Plate Works 1879 Eastman develops plate coating machine, still a few years from large scale manufacture 1880-1 Eastman and Strong (Buggy Whip Mfg. partner) form Eastman Dry Plate Co. 1883 Eastman markets roll film camera, but with paper-base negatives 1885 Kodak introduces Eastman American Film: limited release nitrate-base film First use of cellulose nitrate in roll and MP film; Eastman starts marketing roll film Edison Kinetoscope "peepshow" format - 35 mm MP film supplied by Eastman 1889 1891 1895 Lumiere brothers create the first 35 mm MP in-a-theater presentation format 1899 Eastman develops continuous-wheel formation of transparent nitrate film Eastman introduces NC (non-curling) roll film - coated with a thin anti-curl layer 1903 1903/4 Cellulose acetate plastic developed, in Germany or Switzerland 1906-8 Kinemacolor first commercial color MP process (UK) two-color additive process, filter wheel w/alt B&W frames; overtaken by Prizma Color 1913-17 (US) 1908 Cellulose Acetate "film base" developed by Eastman; manufacture begins in Australian factory Eastman releases **Eastman Safety positive** MP film Eastman public announcement of "Safety Film" after acetate vs. nitrate burn test 1909 1909 Acetate film base produced and sold by Dreyfus brothers (1904 developers; disputed claim) 1910 1910 Acetate film base produced by Dreyfus brothers in France 1910 Eastman's first use of cellulose acetate in film: Kodak 22 mm MP film 1910 Pathe' (Paris) markets first newsreel on acetate base, first time-based news media 1912 Pathé releases Pathéscope 28 mm professional MP format, only on acetate Safety base 1913 Prizma (I) developed by William Van Doren Kelley & Charles Raleigh 1913 Eastman Portrait sheet film introduced, transitioning from glass plate negatives Eastman introduces **Kodachrome** (1) subtractive color in MP formats **Technicolor** (I) two color additive (R & G filters in camera/projector) color MP process 1916 1916 1918 Prizma (II) Van Doren Kelley releases 2-color (R & B) subtractive process; lost suit to Technicolor 1919 Tri-Ergon (Engl, Vogt, & Massolle, German) developed sound process on film; Fox bought 1926 Eastman Portrait Film released; transition to nitrate sheet film for professionals; v notch at far right 1913 1925 Eastman introduces Pan Portrait film, the first sheet film on Safety base, with one square u notch 1928 Eastman Kodacolor 16 mm MP, 3-color (R, G & Blue-violet) additive lenticular (lens) technology 1929 Eastman Kodak produces integrated sound-on-film format, possibly Sonochrome Positive 1931 Kodak releases **Kodalith** sheet film (nitrate) for use in pre-press applications 1931 Verichrome (nitrate) panchromatic B&W replaced older roll films - finer grain, greater latitude 1933 Kodak ends nitrate base in x-ray film, one of the first uses of nitrate sheet film 1935 Kodak releases Kodachrome, color reversal film (positive) on 16 mm amateur film 1936 Kodak releases Kodachrome, color reversal film (positive) in 35 mm professional format 1938 Kodak ends nitrate base in 35 mm roll film for still-cameras 1939 Kodak ends nitrate base in portrait and commercial sheet film (normal thickness) 1941 Kodak introduces Kodacolor - color negative film; must be printed to be a positive 1942 Kodak ends nitrate in aerial high-res films: mapping, surveillance & military applications 1942 Innovative Verichrome film (fine grain) first produce on acetate base 1945-8 Cellulose Triacetate generally introduced into the film marketplace Kodak introduces Ektachrome color reversal film (positive upon developing) 1946 1948 Kodak uses triacetate base to replace nitrate base in 35 mm professional MP film, thru 1951 1949 Kodak ends nitrate base in the thinner sheet film used in film packs 1950 Kodak ends nitrate base for all remaining amateur roll films 1951 Kodak ends nitrate base in all remaining professional 35 mm MP film 1954 Kodak releases Tri-X (ASA 3-400) roll film, the first high-speed B&W emulsion

1955 Kodak develops Estar base for dimensional stability for film used in commercial printing processes

Not all manufactures marked or stamped their film. However, use of "Safety Film" was an important **marketing issue** used by all manufactures. The dangerous nature of nitrate base was well known from press accounts of theater fires.

For professional sheet film, the presence of a \lor notch on the far right denotes nitrate base in pre-1950 Eastman and Kodak sheet films, by itself, or in a group of notches. Thin sheet film had no notches; loaded in a holder, it only fit in a camera one way.

A single square \Box notch began to be used in 1925 for Eastman Pan Portrait Film, the first Eastman sheet film on safety base. Many other manufactures also used the square notch for acetate base film including Defender, Agfa and Ansco (USA-Agfa, because of WWII). Sometimes the Defender also used a half-circle. Hammer sheet film used the half-circle \bigcirc exclusively.

4 - Nitrate Film Chemistry and Deterioration

Nitrate film degrades because of its chemistry. The polymer is made by substituting a strong acid onto an anhydro-glucose polymer chain. Nitrate film is cellulose nitrate polymer cast into a wide sheet that is then coated with a light sensitive silver-gelatin emulsion. The final film width is always "slit down" from the wider, manufactured roll.

The Julie Reilly article, *Celluloid Objects: Their Chemistry and Preservation*, in JAIC, 1991, <u>http://aic.stanford.edu/jaic/artictoles/jaic30-02-003_indx.html</u> has a good overview of cellulose nitrate as a rigid structural polymer used in 3D cultural artifacts. It has only minor application to nitrate film base, but does cover its chemistry.

4.1 - Celluloid for 3D Artifacts

In 1856 Alexander Parkes developed bulk cellulose nitrate for forming three-dimensional solids, eventually called Celluloid. Parkes' notes described the solid as a "hard, horny, elastic, waterproof substance." It took unit 1870 for the patent to be finalized (Parkes won), and trademarked, as Celluloid, by Isaiah Hyatt. The Hyatt brothers marketed Celluloid as a replacement for Ivory (billiard balls, etc.). The use of camphor in processing, and as a plasticizer, was detailed by both Parkes and the Hyatt Bros., complicating the patent litigation.

4.2 - Stages of Nitrate Film Deterioration

The following is a list of nitrate film base deterioration states, with the related description of film condition:

Table 2: State of Deterioration of Nitrate based Film

- State Description
- L1 No Deterioration
- L2 Yellow, Silvering-Out with Slight Curl
- L3 Nitrate Smell and Film Distorted
- L4 Amber Colored Base, Imaging Fading and Some Slight Sticky Feel
- L5 Film Welds to Adjacent Film or to its Envelope, Permanently
- L6 Brown (Cellulose) Powder Present and Gelatin Liquefied

The states are not incremental; rather the deterioration process produces damage that has more than one state in a single piece of film. The worst state is the condition noted when describing the film. The familiar IPI, A-D Strips, used for Vinegar Syndrome evaluation, cannot be used for nitrate base film because the acid is much stronger; an acid indicating dye for nitrate base has not been found.

The start of the nitrate deterioration process produces **yellowing** of the base, and the movement of silver ions from the image to the surface causes **silvering-out**. Level 2 is yellowing and silvering-out due to small amounts of free nitric acid in the plastic base.

Level 3 shows **planer distortion**, but not a smooth curl. The continued progressive evolution of nitrate species, causing the noticeable nitric acid smell, tends to cause smaller cockles, or concave and convex planer distortions, due to loss-of-mass and damage to the gelatin. Nitrate film shows less pronounced curl than acetate film. Onset of planer distortion in nitrate film is later in the process, than that seen in acetate film.

In the L4 state, image silver is being **bleached** (made lighter) by the high acidity. At the same time, the lighter image is sitting on a film base that is getting darker; turning brown or deep orange, see Fig. 8b below. The low tonal range on dark base makes retrieving a good reproduction of the image during duplication difficult, and more time consuming. In addition, there is also the problem of the distorted shape of L4 film. The cockled planner distortion is more difficult to deal with than just

flattening curled film, as with acetate base film. The distortions can generally be dealt with by wet mounting in a thick layer of mild hydrocarbon solvent on large platen flatbed scanner.

8



Figure 8a & b: The 5"x 7" nitrate negative on the left (dating from 1920) is at Level 5 (L5); the emulsion is thoroughly welded to the glassine envelope because it was softened by the nitric acid degradation by-product; this image is long past salvaging. The nitrate negative on the right was created in 1922; it is L4 state. At an earlier time, it was used to create Figs 1a & 1b. The Kraft paper patch of the envelope in the center was removed using an alcohol-based solvent, which lead to the crack in the lower right corner.

In the L5 state (Fig. 8a), sheets of nitrate film or paper envelopes are **irreversibly stuck together**. The strong nitric acid damages the gelatin emulsion layer, not just the plastic base. The emulsion often feels tacky in the L4 stage (Fig. 8b), but L5 is defined by irreversibly welding of film and/or paper envelopes. The film is unusable because the image is bleached and the protein emulsion is highly degraded; see Fig. 8a.

In the final stage of nitrate deterioration, L6, the degrading cellulose turns into **brown cellulose powder** (se Fig. 10a), in the presence of the **liquefied gelatin**. The image is generally lost from the middle of stage L4, unless special procedures are used to salvage the image as seen in Figs. 1a & 1b starting with Fig. 8a.

4.3 - Nitrate Deterioration Process

The first part of the nitrate deterioration is call the **initiation phase**. It is relatively slow and proceeds at a rate depending on the surrounding environment and the condition of the polymer.

The second part of the process is called the **autocatalytic phase**. The evolving nitrate groups [-NO₃⁻] that break loose from the cellulose-glucose backbone, create an environment that is acidic and exothermic. The presence of free strong acid further encourages deterioration of the cellulose polymer, which is highly acid-sensitive. In addition, the process gives off its own heat-of-reaction (exothermic). This heat acts as a ready source of localized chemical energy, encouraging further local cellulose deterioration and migration of the silver image to the surface.

The initiation phase is about 20-30% of the full cellulose deterioration process (artifact lifetime) taking about 20-40 years (of a sample with a "60-year" failure period). The rate of deterioration depends on (a) initial polymer purity and (b) the temperature and humidity of storage conditions. The autocatalytic phase is about 70-80% of the deterioration process, and takes a relatively short, 10-25 years, to reach an unusable state.

The products of nitrate film deterioration (nitric oxide, nitrogen dioxide, nitric acid and other gasses) will yellow and degrade the cellulose polymer, while also, softening the gelatin and oxidizing (bleaching) the silver image. As by-products evolve, they are often contained and concentrated by their storage enclosures causing more acid and heat to be evolved, which further speeds up the deterioration process.

In a quirk of fate, the presence of paper envelopes (even poor quality paper) slows the degradation process by absorbing some of the deterioration by-products, similar to a sacrificial anode in a corrosion process. Some paper is better than none.

4.4 - Life of Nitrate Film – "50-500 Years" (Quote from IPI in 2007)

It was assumed until very recently that nitrate-base films would have a life of 20 to 60 years. IPI spokesmen, at the PMG 2007 Winter Meeting, (GEH in Rochester, NY) recently announced that the life of cellulose nitrate film will range from 50 to 500 years, rather than their previous series of informal predictions that nitrate film would have a 20 to 60 year lifetime.

The earlier prediction had prompted many professionals to identify and destroy nitrate film. In addition, nitrate sheet film in paper envelops is not explosive, and does not give off explosive or flammable vapors. The evolving vapor, at its worst, is dilute nitric acid with a smell that is a mixture of degrading gelatin (animal skin, sinew and bones) and nitric acid; putrid rather than the vinegar smell.

It has been noted by numerous workers, in collection survey, after survey that much of the nitrate film found (60 to 115 years old) is still in L2 to L3 condition, such has the 100 year old roll film negative in Fig. 3a. Level 2 and L3 deterioration shows only yellowing, silvering-out (image silver migrated to the surface) with some minor planer distortion.

Table 3: Examples of Nitrate Film Base at Various Ages Showing Different states of Deterioration

100 years old	Level 2
70 years old	Level 2
70 years old	Level 3
85 years old	Level 4
80-87 years old	Level 5
	100 years old 70 years old 70 years old 85 years old 80-87 years old

Experience has shown that the average life of an "early-failure" nitrate film species was about 45-60 years. This has been found to be about 10-30% of collections held in storage. Only small portions (5-10%) of nitrate collections on the west coast, after early-failure specimens were found and isolated, are degraded to the L4-L5 state (brown, distorted and sticky). This film is now unusable, or it has been destroyed.

Most of the west coast collections (80-115 years old nitrate film) show, on average, only yellowing and minor silvering-out (L2-2.5). Most of the film is still quite usable and can be digitally capture quite easily; see Figs. 9c, below. Isolated examples damaged nitrate film images can be digitally restored, see Figs. 1a &b and Figs. 9a & b.

Nitrate film that degraded early probably had a portion of the original nitric and sulfuric acid (reactant and catalyst) left behind from manufacture. Polymer rinsing and washing is a critical manufacturing step that can be shortened to reduce production cost. The other cause of early failure is poor storage conditions, such as high heat and humidity. An example of common storage damage can be seen in Fig 9a; the 4"x 5" envelop lead to sever localized silvering-out and bleaching, on the much larger 8"x 10" negative.



Figure 9a, b & c: The left and center are before and after surrogates of an MGM image of Stan Laurel on nitrate base from the late 1930s. The left shows the image before digital restoration, which removed image damage caused by a 4"x 5" envelope that sat on a larger negative for decades. The center is after digital restoration, using 16- bits from the 3600 ppi original capture. On the right shows a very high quality nitrate base negative from the same 1930s MGM source that needed almost no digital restoration.

4.6 - Comparison to Acetate Base Film Deterioration

The side chain species evolving from cellulose acetate film base is a weak acid. Generally, it does not degrade the cellulose polymer chain as fast, or as much, as the stronger nitric acid evolving from nitrate film. In addition, the acetate groups are thought to be more volatile, not staying around to degrade the cellulose as severely, when housed in normal museum and archives storage environments.

Acetate deterioration is (a) slower (b) causes little deterioration of the gelatin emulsion and (c) does less damage to surrounding materials. The stronger acid, from the nitrate film base, breaks down the gelatin emulsion into smaller and smaller protein-polymer chains, eventually liquefying the gelatin into a sticky sludge.

In acetate film, the almost undamaged gelatin pellicle can be separated from the film base, and then copied quite easily. Even if the base is yellowed, bubbled, channeled and highly contorted out of plane, the base can be dissolved using a solvent (acetone or MEK, methyl ethyl ketone, or a mixture), leaving the intact silver-gelatin image emulsion layer behind.

4.7 - Final Issue with Nitrate Base - Internal Oxygen

As if the deterioration of cellulose base and gelatin by strong nitric acid wasn't enough, nitrate base contains chemically bonded oxygen [-NO₃-]. Even if stored in a vacuum, with oxygen scavengers or molecular sieves, nitrate film base will continue to degrade.

Should nitrate film be involved in a fire, the burning nitrate film cannot be successfully smothered with fire-fighting foam; it will continue to burn. [Note: the burning film can be cooled with massive amounts of water, below the energy level needed for a fire.]

4.8 - Molecular Sieve Use

Molecular sieves tend to absorb atmospheric oxygen and water vapor rather than selecting just "nitrate species" off-gassing from the film; they are of little help. IPI feels the effects of molecular sieves cannot be separated from the normal variations seen in the deterioration process.

4.9 - Could a Fire Occur in Nitrate Sheet Film?

There are two types of nitrate film, motion picture film (MP) and sheets of nitrate still film in paper envelopes; they have different properties based on their nitrate concentration.



Figure 10a & b: On the left is a reel of highly degraded nitrate motion picture film, L6 state. On the right is the interior of one of the AFI (JFK) film vaults from the 1975 nitrate motion picture film fire.

4.10 - Nitrate Motion Picture Film

In bulk, concentrated nitrate film (reels of motion picture film) held in a sealed can or sealed room, can be explosive. Nitrate movie film storage rooms often have blow-out ports with no fire suppression. Small (10-12' x 10-12') double-walled cinder-block rooms are generally used for movie film storage to limit the extent of fire damage.

In case of a fire, the blow-out port will vent the inevitable explosion so only that portion of the collection involved will be lost. Several small rooms are used to store a large collection of MP film. Fire suppression sprinklers and misters, foam-producing nozzles, pre-charged CO₂ and Freon-substitute dump systems have all been shown to be ineffective for cellulose nitrate MP fires, and thus, fire suppression is not designed into MP storage areas.

History, Science, Preservation & Treatment of Cellulose Nitrate Still Film <u>tivitale@ix.netcom.com</u> 11

Lowering the temperature of nitrate film decreases its energy level, decreasing the probability of a fire. Refrigeration both decreases the rate of deterioration, and the possibility of a fire. Failure of certain specific components in some humidity-controlled vaults can produced elevated internal temperatures; this can initiate a fire. Therefore, active vault designs are generally not used for MP film vaults.

4.11 - Nitrate Sheet Film in Paper Envelops

Nitrate sheet film in paper envelops has never started a fire, however, nitrate still film has been involved in fires caused by another source. The nitrate still film was not the source of the fire and was easily extinguished.



Nitrate sheet film in envelopes has never burst into flame or become explosive because the paper envelopes dilute the reactants.

Sheet film freezers and vaults do not need blow-out panels or explosion-proof motors or circuits. There are no flammable gases generated by degrading nitrate film.

The secondary rooms, holding nitrate still film vaults or freezers, do not need sprinklers. If a fire should start, only the direct application of multiple water streams from high pressure fire hoses are capable of cooling nitrate fires; small amount just produce acid an fog. The

rooms surrounding, the room holding the vault or freezer, can be sprinkled to prevent spread of a possible fire to other storage systems.

5 - Combustion of Nitrate Film

Combusting nitrate film (film on fire) has a heat output that is higher than wood, alcohol, coal or gasoline. Nitrate motion picture film is not considered an explosive unless it's contained. The combustion products are nitric oxide, nitrogen di- and trioxide, carbon monoxide, carbon dioxide, hydrogen, methane and possibly cyanide. It has generally been assumed that nitrate fires cannot be put out with water. Water and burning nitrate film will create an acidic fog that can cause substantial secondary damage (nitric acid fog) to unprotected artifacts and building materials.

5.1 - 2006 Washington State Archive Fire

Recently, there was a new development in the understanding of how to fight nitrate film fires. In a 2006 Washington State archive fire, a mixture of nitrate movie and still film was held in a humidity-controlled cold vault where the refrigeration failed. Eventually the nitrate MP film started a fire. The movie film fire also consumed some of the near by nitrate still film being stored in individual paper envelopes. The fire was put out with a massive amount of water, without creating an extensive nitric acid fog. The technique appeared to cool the burning nitrate movie film, below the ignition point, putting out the fire. This is the only way known to extinguish a nitrate fire. The only other way, has been to let fuel exhaust itself, hence the blow-out vents in small vaults.

5.2 - NFPA 40 -- Nitrate Film Fire Standard

Nitrate motion picture film ignition temperature is commonly considered to be about 300°F, based on NFPA 40 (1997). In laboratory experiments, nitrate roll film will combust when held at 325°F for 80 seconds; in 10 second when exposed to 400°F and in 3 seconds at 500°F; all in the absence of atmospheric oxygen. Rolls of decomposing nitrate movie film will catch fire when held at 106°F (attic conditions in summer) for 17 days in a sealed can.

Nitrate Fire Facts

- If a fire should develop in a space that contains nitrate film, the nitrate film will burn no matter the type of fire suppression. [Except for the Washington State archive fire experience referred to above.]
- Nitrate film has oxygen in its chemical structure so it can burn in a vacuum or if smother with fire-fighting foam.
- Nitrate fires will develop nitric acid clouds if sprinklers (especially water-mist type systems) are used to put out a fire containing nitrate film.
- No nitrate still film-in-envelops has been known to start a fire; however, there could be a

fire from another source in the room such as reels of nitrate motion picture film.

- Nitrate film in freezers is much safer than nitrate film in cabinets at room conditions because the "energy for initiation" has been lowered by the conditions within the freezer.
- Cold storage of all nitrate movie film is an absolute must.
- Nitrate by-product off-gassing is not a combustible gas, such as a solvent vapor, thus spark protection is not required; normal commercial freezers can be used.
- Reformatting the remaining nitrate still film to digital sub-masters is considered essential.

6 - Acquiring Nitrate Film

Do not shy away from acquiring nitrate base film from other agencies or retiring local photographers. Nitrate sheet film has never been known to spontaneously combusted, if stored in paper envelopes. Proper storage for any nitrate film is cold storage. Nitrate sheet film is commonly held in heavily buffered (CaCO₃) acid-free paper envelopes or 4-flap folders, one film sheet to an envelope or folder. The use of paper interleaving (envelopes) insures that the film will never spontaneously combust.

It is common for nitrate film to be copied (digital or film) and saved in cold storage. A less desirable option is to copy and destroy. Destruction of original material (the master) is not part of a preservation procedure, unless it is in stage L5 & L6. The wholesale destruction of nitrate still film by local Fire Marshals is due to their ignorance. If the custodians of a local collection are considering a "copy and destroy" option, contemplate holding their collection in your cold storage to obtain use of their images.

The adoption of a "copy and destroy policy" often pushes acquiring cold storage out of the universe of options. Since outside funding is always several years away, a short-term solution of destroying the nitrate film is sometimes considered. If the relatively modest funds needed for simple cold storage in upright freezers is lost due to the adoption of a more expensive, copy and destroy strategy, the cold storage initiative is often lost permanently at the institution. Another source of loss is if cold storage projects, of reasonable scope, are pushed aside in favor of seeking larger amounts of grant funding for humidity-controlled vaults or reformatting, to either digital or Estar-base film (analog). In the intervening years, the institution can end up with unusable nitrate film, no cold storage and no digital sub-masters. A sub-master in this context is considered to be the "digital master," when made at a quality that is equal or beyond the bandwidth of the analog (film) original.

If nitrate-base film is immediately put into inexpensive cold storage, planning can go forward with less haste and more deliberation. Meanwhile, the degradation process is slowed to 150-5000 years (based on cold storage temperature), from 15-100 years at room conditions.

7 - Cold Storage of Nitrate Film

Cold storage is the only way to maintain nitrate film.

All nitrate film should be separated from other photographic materials.

7.1 - Storage of Nitrate Film

Buffered paper envelopes are desirable for all nitrate and acetate film. Four-flap folders are thought to be superior for the housing of degraded film, because less mechanical manipulation will be necessary to make it available for viewing. Digital image capture will make handling unnecessary.

Nitrate motion picture film should be separated from the nitrate still film, and sequestered into a dedicated freezer. Low temperature freezers would be best for reels of nitrate motion picture film.

Table 3: Effects of Cold Storage on Nitrate Base Film

70°F at 50% yields	1 time improvement of lifetime
70°F at 30% yields	1.7 times improvement of lifetime
40°F at 30% yields	18 times improvement of lifetime
-4°F at 30% yields	580 times improvement of lifetime
-15°F at 40% yields	11650 times improvement of lifetime
-25°F at 40% yields	13500 times improvement of lifetime

In-depth reports on the deterioration and cold storage of nitrate base film have not been done, as they have been for acetate and color film. Therefore, data on generic organic materials is used to describe their performance in cold storage.

7.2 - A Local Solution -- \$180K Active Humidity-Controlled Walk-in Vault

A local museum has a small (10' x 10') nitrate sheet-film storage vault that cost them over \$150, upwards of \$200K to plan and build. The planning and design started over 15 years ago, when the active design of humidity-controlled vault was the only option. After construction and fire suppression

History, Science, Preservation & Treatment of Cellulose Nitrate Still Film tivitale@ix.netcom.com 13

issues were resolved, it began to be used recently. The vault is held at 40-45°F at 50% RH, an 18times improvement in longevity.

7.3 - Cold Storage in upright Freezers

Cold storage is the only effective way to slow the deterioration process because it eliminates a major portion of the heat energy which drives the deterioration process forward. Decreasing the energy available for chemical reactions slows the process. At -25°F and 35% RH, the deterioration rate is decreased 2500 times (uncorrected for age and TOS) compared to storage at room conditions. Assuming a normal time-out-of-storage (TOS) the actual preservation advantage is more on the order of 40-times improvement; an excellent preservation outcome.

A Sears' auto-defrost, 20 ft³ cu ft, upright freezer (\$800 delivered) can be used for storage at about 0°F. Appliance stores also a series of smaller chest-type manual-defrost freezers, ranging in size from 4 to 8 ft³ (large TV to the size of a desk) can be used for smaller collections, priced from \$180-350. The larger [20 ft³] upright will cost about \$50-100/yr (\$3.75/ft³) and the smaller will cost about \$35-60/yr (\$2.38/ ft³).

Table 8: Effects of Cold Storage on Acetate Base Film

Lifetime for	
New Film, Years	Storage Conditions
45	70°F at 50%RH
175	55°F at 40%RH
1900	30°F at 30%RH
1600	30°F at 30%RH + 5 days-out-of-storage per year
31,500	0°F at 30%RH
1900	0°F at 30%RH + 5 days-out-of-storage per year
110,000	-15°F at 30%RH
1900	-15°F at 30%RH + 5 days-out-of-storage per year

Stand alone freezers have similar operating cost to the active humidity-controlled vaults, due to the lack of economy of scale for the freezers. A passive vault would run at about a third, to a quarter, of the cost to operate upright freezers or active vaults.

Certain upright freezers (low temp freezers) are capable of -25°F, but the affordable units are the smaller under counter size holding 4-6 ft³, rather than the 20 ft³ of the normal 0°F upright <u>http://www.cooler-store.com/summit_upright_freezer_under_counter_1090_prd1.htm</u> and <u>http://www.cooler-store.com/summit_upright_freezer_low_temperature_1147_prd1.htm</u>. The cost to purchase is about \$1000, and \$100-125/yr to operate. Larger, 20-70 ft³, low temperature upright freezers (-25°F) can be purchased for \$4-12K. Installing a walk-in low temperature freezer makes better sense if portability is not an issue. Passive type walk-in freezers capable of -15 to m-25°F run about \$20-40K.

7.4 - Bags for Cold Storage

Average sized Ziploc bag will hold the following, with the inclusion of ample good quality matboard, blotters or quality cardboard as a moisture buffer

- 2-4 reels of film (500-1500 ft) per bag
- 50-200 sheets of 4 x 5 film in acid-free envelopes
- 25-100 sheets of 8 x 10 film in acid-free envelopes
- 200-400 slides in 10-20 slide protector pages
- 6-12 video cassettes per bag
- 4-8 boxes of microfilm per bag
- glass plates don't lend themselves to bag storage

See Gaylord Catalog (800-448-6160) and IMPAK Corp for ready-made bags and Metal Edge Inc. catalog (800-862-2228) for Freezer Kits.

Marvelseal 360 is a metalized polyethylene and polypropylene barrier film that is heat-sealable. It has a Nylon exterior that is slightly tougher than the Marvelseal 470. Escal bag material is a newer bagmaking product that is clear. I have not used Escal, but it is getting favorable reviews. It is 4 times the cost of Marvelseal, but it's clear so you can see labeling inside; search online for sources.

A professional bag sealer should be chosen because the width of the seal is about ½", rather than the 1/8"-seam found in refrigerator bag sealers. The Futura Portable heat sealer, Barrier model, can be

purchased for about \$65 from (a) Audion Packing Aids Corp, San Rafael (415-454-4868), (b) one of the online suppliers of bagging supplies such as IMPAC Corp. or http://www.sorbentsystems.com/footsealer.html; or (c) the conservation materials suppler selling the Marvelseal products.

Add 2-3 sheets of good-quality buffered 4-ply matboard (or 3/16" of buffered blotters, 4-5 sheets) to each bag as a moisture sink. See the University Products (800-336-4847) catalog for cut-sizes of matboard. Materials should be labeled on the exterior of the storage bags. A label with actual contents is very helpful, but a unique number that is referenced in a nearby paper cataloged or online database is more efficient. The materials should be held in a controlled room that has a stable relative humidity, such as 40-45% for about 1-2 weeks before they are sealed into the storage bags. This will increase the life over the average 65% RH conditions found in the Bay Area.

7.5 - Warm-Up Process

When photographic materials are taken out of cold storage they must be allowed to warm to room temperature in a sealed bag before they are exposed to the unlimited water content of a room. Allow 6-12 hours for the "average" bag to adjust back to room condition before cutting seal (or opening the Ziploc bag), when held in a thermal barrier holder such as a Styrofoam cooler. Longer is required if there is a great deal of air, or film, in the bag.

Warming-up in a "cooler" prevents temperature gradients, because the thermal barrier prevents rapid warming of the bagged materials.

Shorter warm-up times can be use for tightly-conforming bags holding relatively small amounts of materials. The bag will need to sit on a rack in a well ventilated room. There will always be concern about warming too fast, but a 2-4 hour warm-up can be used in critical situations. The Styrofoam cooler method is recommended and preferred.

7.6 - Time Out of Storage

Time out of storage (TOS) will decrease the useful life of materials in cold storage. IPI distributes written materials to figure TOS for (1) Color Film and (2) Acetate Base film. Basically, 5-days TOS per year (for sub-zero storage conditions) lowers life by 90% -- 0.1 x years = years with TOS. If the useful life starts at 1000 years it becomes 100 years, when using sub-zero cold storage.

Time-out-of-storage (TOS) for 5 days suggests the following 6-steps:

- (1) Someone requests a slide on Monday
- (2) Taken out of the freezer for the 6-12 hour warm Monday evening
- (3) The user gets back to the slide Tuesday
- (4) They copy or use it on Wednesday
- (5) They give it back to the operator on Thursday
- (6) Sometime on Friday the operator reseals the package and gets it back into the freezer

All this assumes that the work area has consistent temperature and humidity, not requiring a preconditioning period.

7.7 - Storage Materials and Solutions

Devices for storage (low use-priority artifacts can be held in groups with interleaving):

- acid-free folders (Metal Edge)
 oversized folders made from acid-free/buffered paper (Permalife in Gaylord)
- oversized folders made from acid-free/buffered Tan Barrier Board (Gaylord)
- standard-sized large folders made from acid-free/buffered paper (Metal Edge)
- L-sealed Mylar folders of various sizes (Metal Edge)
- Mylar Document Protectors (Gaylord)
- Self-made Mylar folders made from Mylar (0.003-0.005" thick) on the roll
- Bulk in acid-free/buffered Archival Record Cartons (gray corrugated, Gaylord)
- Bulk in Standard Record Storage Boxes (Metal Edge, Tan, buffered)
- Within intellectual groups in Archival Document Cases (Tan, Lignin-free, Gaylord)

Foldered paper-base materials can be held in boxes such as

- Acid-free/buffered Archival Record Storage Cartons (gray corrugated, Gaylord)
- Archival Document Cases (Tan, Lignin-free, Gaylord)
- Drop Front Storage Boxes (Metal Edge, Tan)

Books, pamphlets and notebooks can be held in

Archival Document Cases of various sizes (tan, lignin-free, Gaylord) within Document Preservation

Binders (Gaylord)

- within Case Binders (Gaylord) using Glue-in attachment
- Individual Book Boxes (Metal Edge)
- Corrugated Book Storage Boxes (Metal Edge)

7.8 - Inner Housing – sleeves or interleaving

Inner housings protect the surface of a print or negative from damage when in a storage container. All historic images need surface protection such as sleeves, four-flap folders, page protectors (virgin polyethylene or poly propylene), or, single folders made from acid-free unbuffered paper, Permalife[™] paper(with low buffering level), acid-free glassine or polyester (Mylar).

Sleeves: All the existing glassine and clear sleeves (Kodak triacetate) should be replaced with acid free paper envelopes, polyester sleeves or 4-flap paper folders.

Interleaving: Original prints held in groups within a single folder should be interleaved with some sort of acid free material such as acid-free glassine, Permalife[™] paper or unbuffered acid-free tissue. Glassine is generally my choice because it has minimal texture, is easy to handle, is translucent and is now acid free (started about 20 years ago). Older glassine can be very acidic and should be eliminated from all collections. Buffered material are often not recommended for photographic materials, in a flood the extra alkalinity can soften gelatin.

9 - Other Resources

David Horvath *The Acetate Negative Survey* (1987) final report to the National Museum Act (funder) can be found at http://library.louisville.edu/library/ekstrom/special/AcetateNegativeSurvey.pdf

Collection of **Images of Kodak Edge Printing** through 1967 by Brian Prichard <u>http://www.brianpritchard.com/KODAK%20Edge%20Printing.htm</u>

Extensive information on **Film Date Codes** by Brian Prichard, including Kodak, Fuji, Agfa, Selo and Ilford <u>http://www.brianpritchard.com/Date%20Codes.htm</u>

Henry Wilhelm and Carol Bower *The Permanence and Care of Photographs* (1993) 758 pp <u>http://www.wilhelm-research.com/pdf/HW_Book_758_Pages_HiRes_v1a.pdf</u> also individual chapter downloads.

Tim Vitale Paper, Photographs & Electronic Media Conservator Digital Imaging & Facsimiles Film [Still] Migration to Digital Format Digital Imaging & Facsimiles Preservation Associates 1500 Park Avenue Suite 132 Vid Emeryville, CA 94608

510-594-8277 510-594-8799 fax <tjvitale@ix.netcom.com> <<u>http://briefcase.yahoo.com/tvitale@pacbell.net</u>> [Use of the URL above may require a "Yahoo! ID" to download files]

Albumen Photography Website (2001) <<u>http://albumen.stanford.edu</u>> VideoPreservation Website (2007) <<u>http://videopreservation.stanford.edu</u>>