Photographic Negatives

Nature and Evolution of Processes

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Advanced Residency Program in Photograph Conservation

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Photographic Negatives: Nature and Evolution of Processes, 2nd edition

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PREFACE

This booklet is a companion to the illustrated poster “Photographic Negatives—Nature and Evolution of Processes” published by the Mellon Advanced Residency Program in Photograph Conservation at the George Eastman House and the Image Permanence Institute. The booklet provides basic information plus a bibliography on the technology and long-term behavior of the types of negatives that are most likely to be found in photographic archives. It may be used in conjunction with the poster as a didactic tool to introduce general audiences to the structure of negative images and the changes in their component materials over time. The ultimate goal of both pieces is to assist caretakers in the identification of negative collections for the purpose of preserving them and promoting their use as sources of information and tools for investigation.

It is the intention of this publication to promote the appreciation of the photographic negative as a unique object deserving to be valued and preserved in its original format and material condition.

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INTRODUCTION

Photographic negatives are unique camera images used as masters for the production of multiple positive prints. Generated at the real scene, negative images are primary sources of visual information and represent half of the step towards the creation of the photographic print.

A black & white negative image is made up of fine silver particles (color negative images are made up of color dyes) embedded in a thin transparent layer called the *binder*. Together, the binder and the image substance form a single coat, which is often called the *emulsion*, on a transparent or translucent firm support (e.g., paper, glass, film, etc.). During *fixing* (i.e., transforming all of the silver halide crystals that were not exposed to light into a water-soluble compound that can be washed away), the negative image is stabilized and will not change upon further exposure to light and, if processed properly, will remain unchanged under ordinary environmental conditions. This allows for the printing of positive images (*positives*) from the negative over a long period of time.

COMMON TYPES of NEGATIVES and the DATES THEY WERE PRODUCED

Negative Type	Dates
Paper	1841– ca. 1865
Collodion on glass	1851 – ca. 1885
Gelatin dry plate	ca. 1878 – ca. 1925
Cellulose nitrate film	ca. 1889 – ca. 1950
Cellulose acetate film	ca. 1925 – today
Polyester film	1955 – today

The processes for producing negatives, as well as the supports on which they were created and the transparent medium (i.e., binder) that holds the light-sensitive salts that form the image after processing, have changed over the years. The table at the right lists the negatives most commonly found in photographic archives and the dates they were produced.

After exposure and processing, black & white negative images are formed by relatively large silver particles, which result from the exposure and *chemical development* of the silver-halide crystals (i.e., light-sensitive silver salts). In fact, because faster exposure times are preferred when capturing the real scene with a camera, negatives always have been produced with the aid of a chemical agent, called *developer*, which is introduced after the exposure. The developer magnifies the effect of the light upon the exposed crystals in the emulsion and produces a strong image from the otherwise invisible or "latent" image.

Color negative images are composed of chromogenic dyes (cyan, magenta, yellow) that form during development of the negative image around the exposed silver-halide crystals, which become filamentary silver particles after development. The filamentary silver particles are removed later during one of the color negative processing steps (called bleaching) leaving just the dyes.

In contrast to the creation of the negative image, early positive prints were obtained entirely through exposure to sunlight—without the aid of a chemical agent—until the turn of the 20th century when photographic papers for creating *developed-out* prints (which require the aid of a chemical agent) were commercialized.

Despite similarities in terms of image substance and processing methods, photographic negatives are made from different materials depending on their type of process and time period. Therefore, not all negatives are equal, nor do they behave the same over time. The lifespan of different types of negatives is determined by the least chemically stable of their components, which varies from one process to another. For example, negatives on glass supports may suffer from the symptoms and manifestations of glass decomposition, whereas negatives on plastic supports will show signs of degradation related to the inherent instability of the polymers employed in creating the plastic supports.

The conservation problems posed by negative collections are not just related to their material condition, but to other factors as well, such as the sheer quantity of negatives, accessibility to the collection and negative storage requirements

Nevertheless, understanding the chemical and physical properties of each type of negative, as well as the kind of processing they may have undergone, is the first step towards preservation.

PAPER NEGATIVES
1841 – ca. 1865

Background

The *calotype* was the first stable photographic system to produce a negative that could be used as a master for the creation of positive prints. (Talbot's "photogenic drawing" negatives, which preceded the calotype, were stabilized but not fixed.) Paper negatives created using the calotype process, and its later variations, were mostly made by British, Scottish and French photographers. The process debuted in 1841 and fell out of favor around 1865. Its heyday overlapped the introduction of the *collodion* on glass negatives, which produced much sharper prints.

Because the calotype process required longer exposure times, it was preferred for landscape and architecture photography while the wet collodion process on glass plates, which required shorter exposure times, was more suitable for studio portraits. Although better results were achieved by exposing freshly sensitized paper, the calotype process did not require carrying a portable darkroom into the field. Paper negatives could be prepared ahead of time with the light-sensitive salt (i.e., silver iodide), exposed wet or dry and developed at a later time. In addition, the lightweight paper supports were easier to carry and the paper could be rolled to make transporting them more efficient than the glass plate supports. These advantages of paper negatives made them popular choice for traveling photographers in particular.

Calotype negative (laterally reversed), top, with positive image below. Hill & Adamson (Scottish, active 1843-1848), [Two Newhaven Fisher-women], ca. 1845. 21.3 x 15.8 cm (8.375 x 6.25 in.). Gift of Georgia O'Keeffe, George Eastman House Collection.

Process

The calotype paper negative process incorporated all the basic steps of modern photography, including the development of an invisible latent image with a chemical agent, and the subsequent fixing of the image by eliminating the unexposed silver salts with sodium thiosulfate fixer (also known as *hypo*).

The original calotype procedure, patented by William Henry Fox Talbot in 1841, was a multistep process:

1. Iodize
2. Sensitize
3. Expose
4. Develop
5. Fix
6. Wash
7. Wax (optional)

Step 1: Iodize
Iodizing required preparing the surface of fine writing paper with light-sensitive silver iodide, an insoluble salt created by applying silver nitrate and potassium iodide in two separate coats. Brushing on a solution of silver nitrate in water and then immersing the paper support in a solution of potassium iodide in water[1] created the desired precipitate of silver iodide as well as a byproduct of potassium nitrate that was then rinsed off the paper. The iodized paper could be kept until needed for exposure.[2]

Step 2: Sensitize
Before exposure, the paper's surface was "sensitized" (i.e., made sensitive to light) by brushing on a solution prepared with:

- Silver nitrate
- Acetic acid (a chelating agent that acts as restrainer)
- Gallic acid (a reducing agent)

Step 3: Expose

Exposing the paper in the camera while it was still moist from sensitization allowed for faster exposure times than exposing it after the paper had dried. Exposure times typically varied from one to ten minutes.

Step 4: Develop

After exposure, the latent image was developed into a visible image by applying the same solution used for sensitization. Varying the ratios of silver nitrate/acetic acid and gallic acid in the developing solution affected developing times and image density. Any remaining developing solution was then rinsed off the paper.

Step 5: Fix

The negative was then fixed using sodium thiosulfate fixer (i.e., hypo) to remove the unexposed silver salts and prevent them from fogging the non-image areas.

Step 6: Wash

After fixing, the negative was washed thoroughly to remove the hypo residue. If this was not done, the sulfur present in the hypo adversely affected the image by causing rapid oxidation and fading.

Step 7: Wax (optional)

Waxing, usually with beeswax, made the paper support translucent and allowed shorter exposure times when printing the positives. Often negatives were waxed selectively on certain areas of the image (the darker zones) to make them more translucent, reduce the image contrast and obtain better positive prints.

Process Variations

Other formulas for creating paper negatives were similar to Talbot's calotype process in terms of the materials employed and the chemical principles on which they were based. These variations included:

- Applying silver iodide salt in a single coat (by dissolving this precipitate in a saturated solution of potassium iodide).
- Using potassium bromide in addition to the potassium iodide to form a light-sensitive compound of iodo-bromide of silver on the paper. Together, the silver iodide and silver bromide enhanced the negative's sensitivity.
- Floating or immersing the paper in the solutions instead applying them with a brush.
- Modifying the ratio of silver nitrate to gallic acid in both the sensitizing solution and the developer to the point of entirely eliminating one of them—the gallic acid from the sensitizer to prevent fogging/premature darkening of the paper (gallic acid was eliminated from the sensitizing solution since the early years of the process) and the silver nitrate from the developer to slow down the developing time and avoid staining.
- Forming the silver iodide right before exposure, by applying the sensitizing solution on top of a single coating of potassium iodide, was also a later simplification of Talbot's formula.

An important variation of the calotype was the waxed paper process introduced by Gustave Le Gray in 1851. This process required waxing the paper before coating it with the light-sensitive chemistry. Once impregnated with the wax, the paper was then immersed in the iodizing bath, which contained a small amount of whey serum to improve the adhesion of the halides (iodide and bromide) to the waxed support.[3] Before exposure, the waxed paper prepared with the halides was immersed in the sensitizing solution.

Because the waxed papers were more resistant to the long immersion times required for processing the image, this process allowed the use of thinner and otherwise more fragile paper supports.

Le Gray's variation also allowed photographers to prepare sensitized paper supports ahead of time, expose them in multiple locations and then develop them at a later time.

Support

Examples of fine-wove papers used as negative supports[4] include:

- J. Whatman's "Turkey Mill"
- R. Turner's "Chafford Mills"
- Rives
- Saxe
- Canson Frères

Binder

With these types of negatives, the paper fibers themselves act as a binder to hold the silver particles that constitute the image on the surface of the negative.

Image

The image of a paper negative is formed by silver particles that result from the exposure of the sensitized surface and the *physical development* of the latent image with a *chemical reducing agent*. Physical development is a term used in photography to refer to development in the presence of excess silver ions, which build up the image density by bonding with the silver particles formed on the paper support through exposure and chemical development.

The color of the image of a paper negative can vary from neutral black or gray to brown, purple, and reddish-brown depending on a variety of factors:

- Type of paper support
- Type of sizing of the paper support
- Sensitizing solutions used
- Exposure
- Developing solutions used
- Presence of wax

Retouching

Paper negatives were often retouched to mask processing flaws, which were most observable in the sky of landscape negatives, or to enhance the negative with imagery. Retouching media included ink, pencil, watercolor and black pigment with a binding agent.

Positive Prints

Because the image is formed by silver particles embedded in the paper fibers of the support, prints from paper negatives are typically less sharp than prints from glass negatives, which began to be used in 1851.

Paper negatives were typically used to make positive prints on salted paper. After 1850 albumen paper (paper coated with a binder made of egg white) was also available for making prints. Albumen paper results in positive prints with more subtle details in the dark areas and a greater tonal range. With the introduction of albumen paper, salted paper then became known as "plain paper."

Albumen and salted papers were formulated to allow the creation of *contact prints*. Contact printing, as opposed to printing through enlargement, involves placing the negative directly in contact with the light-sensitive paper and exposing it to sunlight. This type of photographic paper is known as *printing-out paper*. In printing-out papers the image is formed completely through exposure to sunlight without the aid of any chemical agents (e.g., developer).

Stability/Deterioration

Despite the physical fragility of the paper supports and the ease with which they can be damaged by handling, paper negatives tend to be chemically stable due to the relatively large size of the negative's developed-out silver particles (as compared to the particles of printed-out papers) and the presence of wax.

Staining, if present, was often caused during the preparation of the paper or processing of the negative image. Crystallization of the wax and mold growth also have been detected in paper negatives.[5]

Storage

As with other photographic materials, paper negatives are best stored in a cool (10° to 18º C) and dry (30% to 40% relative humidity) environment.

Identification

A paper negative is recognized by the reversed tonal values of the image and its color, which may be gray, black, brown, reddish or purplish. The paper itself is thin and it is usually waxed either totally or partially. Paper negatives with less dense images are visible with transmitted and reflected light, while denser images are observable only with transmitted light.

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COLLODION GLASS PLATE NEGATIVES
1851 – ca. 1885

Background

The adoption of glass as a negative support in the mid-nineteenth century marked the beginning of a new era in negative technology characterized by sharper negatives and more detailed positive prints than those created through the paper negative processes.

The problem of getting the silver salts to bind (adhere) to a glass support was first solved by Abel Niepce de Saint Victor in 1848, with the introduction of the albumen on glass process. However, the glass support did not become dominant until 1851 when Frederick Scott Archer introduced the much faster collodion on glass formula, which used collodion as the image binder.

The collodion-on-glass negative process was also known as *wet plate*. This term derived from the necessity of exposing and processing the glass plate while it was still damp with the sensitizing chemistry to achieve optimum exposure speed. Because the poured plates had to stay wet throughout the entire process, collodion-on-glass negatives required a mobile darkroom that limited their ease of use outside of studio photography.

The wet plate process was practiced worldwide and negatives of this kind are found in most archives with 19th-century holdings; many of them are studio portraits.

Collodion on glass negative (laterally reversed), top, with positive image below. Mathew B. Brady (American, 1823-1918). ANNIE LEWIS, ca. 1868. 20.3 x 25.4 cm (8 x 10 in.). George Eastman House Collection.

Process

The collodion binder was made by modifying cellulose found in *cotton linters* with nitric acid, a process called *nitration*. The resulting nitrocellulose was dissolved in alcohol and ether to produce a viscous liquid called collodion.

Ten steps were necessary to create a negative image using the wet plate process:

1. Clean the glass
2. Iodize the collodion
3. Pour the collodion on the plate
4. Sensitize the collodion
5. Expose
6. Develop
7. Fix
8. Wash
9. Intensify (optional)
10. Protect

Step 1: Clean the glass
First the glass plate was cleaned with a mixture of alcohol and pumice or a mixture of nitric acid with a thin powder such as Tripoli, rouge or calcined lamp black. [6]

Step 2: Iodize the collodion
The wet plate process required iodizing the collodion to introduce halide by adding cadmium or potassium

iodide and bromide, depending on the formula.

Step 3: Pour the collodion on plate

The glass plate then was coated (usually by holding the plate at one corner) with the iodized collodion.

Step 4: Sensitize

Immediately after the collodion ceased to be free-flowing the plate was sensitized to form silver halide. This sensitizing step was accomplished by immersing the plate in an aqueous bath of silver nitrate. During the immersion, a fine deposit of light-sensitive silver iodide salt and silver bromide (if a bromide salt had been also added), was formed on and just under the surface of the thin collodion layer.

Step 5: Expose

The plate was exposed in the camera for 20 seconds to 3 minutes, depending on the lighting conditions and other factors like the temperature and relative humidity. This exposure to light resulted in the creation of a latent image.

Step 6: Develop

While the collodion binder was still moist, the latent image created during exposure was physically developed with a solution containing a reducing agent (i.e., developer) and free silver ions (i.e., silver nitrate). During the early years of the collodion era, the organic compound derived from phenol called pyrogallic acid was used (in acid solution) as a developing agent.[7] By 1860 a solution of ferrous sulfate was the most common developer.

Step 7: Fix

Sodium thiosulfate (hypo) was the primary fixer for collodion negatives in the 1850s. The introduction of potassium cyanide as a fixer for ambrotypes gave the wet plate photographer a second fixing agent. Cyanide was a faster fixer than hypo but it was also very poisonous. Both cyanide and hypo continued to be used for negatives throughout the collodion era.[8]

The fixer removed the unexposed light-sensitive silver salts from the collodion layer. This step was performed while the collodion was still moist.

Step 8: Wash

After fixing, the negative was washed thoroughly to remove the silver thiosulfate or silver cyanide compounds formed during fixing.

Step 9: Intensify (optional)

After washing, if the negative was too “thin” or weak to be printed, the image was usually intensified with gallic acid and silver nitrate[9] to increase its opacity.

Step 10: Protect

Once dry, the image was varnished with gum sandarac or shellac.[10] This coating provided physical protection to the thin, fragile collodion layer and prevented the silver image from oxidizing.

Process Variations

Important modifications to the collodion on glass process included:

- Dry or preserved collodion formulas
- Collodion emulsions

Dry or preserved collodion formulas

Dry or preserved methods (also referred to as collodion dry plate processes) included the application of a hygroscopic overcoat (a coating that absorbs moisture from the air to prevent drying), such as honey or beer. Albumen or gelatin was also added to the sensitized plate in order to keep the collodion layer permeable.[11] Removing the free silver nitrate before applying this coat, and using a large proportion of bromide as a restrainer, prevented the plates from fogging before use.[12]

Collodion emulsions

Collodion emulsions contained suspensions of the light-sensitive salts (silver iodide and silver bromide) so that the precipitation of these salts through the iodizing and sensitizing steps was no longer necessary.

Despite the advantages of collodion emulsions and the collodion dry plate process, these methods were not used frequently by studio photographers due to the long exposure times they required. However, they were advantageous when creating:

- Non-camera images like *lantern slides*
- Enlargements and other graphic arts applications

Even after the introduction of the gelatin dry plate, the collodion process continued being used for these purposes due to the extreme sharpness of the images it produced.[13]

Support

The glass used for collodion plates was handmade and varied in composition. Glass was selected based on physical characteristics such as transparency, colorlessness, and lack of flaws or bubbles.[14]

Subbing

Subbing, a coating used to enhance the adhesion of the collodion binder to the glass, was applied occasionally when after-treatments were anticipated. Therefore, a very dilute coating of albumen may be found on some wet plate negatives between the glass and the binder.

Binder

The binder, a very thin and fragile layer of collodion, is vulnerable to scratches or other physical damage that can lead to image loss since the silver particles are on top and vary near the surface of this layer. For this reason, a varnish overcoat was essential for protecting wet plate negative images.

Image

The collodion process produced extremely sharp and detailed negative images. Typical collodion negatives may appear as positives when viewed against a dark background. They often have a dull, milky-tan or brownish-gray color by reflected light.

Wet plate images are made up of silver particles deposited on the surface and suspended immediately below the surface of the collodion binder.

The image color was determined by processing.[15] The image characteristics of different developing agents and fixing solutions are summarized in the table at the right.

THE EFFECT of PROCESSING on WET PLATE IMAGES

Processing Step	Solution	Effect
Development	Pyrogallic acid Ferrous sulfate	Darker, more burnt-umber in color Lighter, less burnt-umber in color
Fixing	Hypo Cyanide	Darker image color (brownish gray) Lighter image color (milky-tan)

Intensification or redevelopment can also affect wet plate images by making them darker and more neutral in color.

Retouching

Studio portraits created from wet plate negatives were routinely retouched with graphite, especially on the face of the figure. Areas to be retouched needed to be prepared by abrading the varnish overcoat to give the surface enough “tooth” to hold the graphite. Red or yellow oxide pigments with a binder, or paper, were used for masking large blank areas of the subject like the sky. These opaque materials were applied to either side of the glass support.

Positive Prints

Collodion negatives were mostly used for printing positive images by contact on albumen paper. Because they are printed by contact, the size of the positive is the same as the size of the negative. The high contrast of collodion negative images balances the typically low contrast quality of printing-out papers like albumen paper and results in properly contrasted positive images.

Stability/Deterioration

Collodion negatives are relatively stable. The following factors can turn them less stable and therefore more difficult to preserve:

- Original glass composition (excess alkali)
- Lack of a varnish overcoat
- Improper cleaning of the glass support (before pouring the collodion on the plate)
- Improper storage of the negatives

In general, the chemical composition of the glass is the most important factor relating the preservation of collodion plates. Some glass employed during the collodion era had a high proportion of sodium or potassium oxide[16,17] and was subject to chemical decay. This type of deterioration, called *alkali leaching* or "weeping glass", causes softening of the binder and varnish and the loss of adherence of the collodion to the glass.

The presence of a varnish overcoat is also essential for wet plate negative preservation; unvarnished collodion negatives are extremely fragile, easily abraded and oxidized. *Silver mirroring*—a blue-purplish metallic deposit on the surface of the binder—is a common sign of image oxidation.

Occasionally, collodion glass plates exhibit "emulsion frilling" (the binder peeling away from the glass), which occurred early in the history of this type of negative due to improper cleaning of the glass support before coating it with the collodion.[18]

Storage

When an unstable glass plate is stored under high relative humidity conditions, the surface of the glass develops a highly alkaline hydrated layer that adversely affects the silver image, the binder, and the varnish. These glass corrosion deposits appear as moist droplets in conditions of high relative humidity and form crystals when stored at low relative humidity.[19]

Collodion glass plates need to be stored at a cool to moderate temperature (below 18°C) and at 30% to 40% relative humidity. A relative humidity of less than 40% is critical to protect them from the effects of glass corrosion such as alkali leaching.[20] However, storage of chemically unstable glass at low relative humidity (below 30%) is not recommended because may it cause dehydration of the glass surface.[21]

Identification

To identify wet plate negatives place the negative against a dark background and the image will appear as a positive.

In addition, since these negatives were entirely handmade (unlike the machine-made gelatin dry plate negatives to follow), they also are identified by manufacturing irregularities such as:

- Rough-cut edges of the glass support
- Thickness of the glass (machine-made glass is usually thinner)
- The glass may not be perfectly square
- Uneven surface of the glass support
- Uneven surface of the varnish overcoat
- Uneven edges of collodion binder and varnish layers
- Uncoated corner (where the plate had been held during coating)

As the industrial era began glass became more standardized, more stable, less expensive, and more readily available.

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Gelatin on glass negative (laterally reversed), top, with positive image below. Lewis W. Hine (American, 1874-1940). SPINNER GIRL, ca. 1908. 12.7 x 17.8 cm (5 x 7 in.). Gift of the Photo League, New York: ex-collection Lewis Wickes Hine, George Eastman House Collection.

GELATIN DRY PLATE NEGATIVES
ca. 1878 – ca. 1925

Background

The replacement of collodion with gelatin binder was a major and far-reaching technical innovation in the history of photography. Gelatin changed all aspects of photographic technology and quickly became the dominant medium after the introduction of the dry plate process.

Gelatin, a protein product, is manufactured by the partial hydrolysis of collagen found in connective tissues and skin of animals. This protein provides a viscous medium to suspend the light-sensitive silver salts and form an emulsion with them.

Gelatin binder made possible the following:

- Photographic emulsions
- Exposure times of < 1 second
- Ready-to-use light-sensitive plates

Because the photographic emulsion already contained the light-sensitive silver salts suspended in it, the preparation of these salts from two separate solutions right before the exposure was no longer necessary. The emulsion also, owing to the photochemical properties of gelatin (in combination with the silver salts), made possible the commercialization of light-sensitive plates that allowed exposure times of less than one second. Sold ready-to-use, these glass plates required little photographic skills. Their long shelf life and the possibility of developing the image much later owing to the hygroscopic characteristics (drawing moisture from the air) of gelatin freed photographers from the need to carry a portable darkroom into the field.

Gelatin dry plates started being replaced as early as 1890, and they were almost completely replaced by the lighter nitrate film negatives by the end of the 1920s. However, they continued to be used for spectroscopic and astronomical applications throughout the 20th century because these applications require a perfectly flat, dimensionally stable, and transparent support.

Early gelatin glass plates

The first publication on the use of gelatin/silver bromide emulsion was by Richard Leach Maddox in 1871. Essentially, the emulsion was prepared by forming a precipitate of silver bromide in a warm solution of gelatin. This white precipitate needed to be sufficiently fine to remain in suspension in the liquid in which it was produced. It was then said to be in a state of emulsion. Throughout the 1870s other practitioners introduced improvements to Maddox's emulsion until a practical formula was created.

In 1873 John M. Burgess was already selling bromide emulsion to prepare dry plates but still with some inconsistencies in terms of the results it could produce. Richard Kennett achieved better results by washing the gelatin emulsion after the precipitation of the light-sensitive silver bromide to remove soluble byproducts like potassium nitrate,[22] which tended to spoil the plates. By 1874 Kennett was marketing both the ready-prepared plates and the dried emulsion, which he called "pellicle," to be dissolved in warm water and poured on the glass support by the photographer.[23] However only in 1878, when Charles Bennett discovered the effect of ripening the emulsion in terms of increased light-sensitivity,[24] did gelatin dry plates become popular and widely employed by professional and amateur photographers. Ripening promoted the reorganization and growth of the silver halide micro-crystals through the dissolution of the smaller crystals and their deposition on the larger crystals.

Technical improvements in gelatin emulsion led to the introduction of the first commercially successful plates by Wratten & Wainright in London in 1878. In the United States, dry plates started being manufactured in 1879 by the Keystone Dry Plate Works, owned by John Carbutt.[25] In addition, in 1880 George Eastman founded the Eastman Dry Plate Company and also began producing dry plates.

The large-scale manufacture and commercialization of machine-coated gelatin glass plates took place during the 1880s and led to the development of the modern photographic industry.

Process

During the 1890s, improvements in gelatin glass plate technology made possible the creation of orthochromatic emulsions with extended sensitivity into the green and yellow wavelengths of the spectrum. The adsorption of cyanine dyes to the surface of the silver halide crystals provided them with light-sensitivity to these and other wavelengths[26] (other than red) and, by 1906, panchromatic plates (sensitive to the full visible spectrum) were already available.

The negative process consisted of the following steps:

1. Pour the plate
2. Expose
3. Develop
4. Fix
5. Wash
6. Intensify (optional)
7. Varnish (optional)

Step 1: Pour the plate

The glass plate was poured by hand between 1873 and 1878. Later pouring was done industrially by machine. The gelatin emulsion was warmed to liquify it so that it could be poured evenly onto glass that had been placed on a cool, level surface. It sometimes ran off the edges of the plate. Drying was a lengthy process during which the plate could not be touched.

Step 2: Expose

The gelatin emulsion glass plate allowed for exposure times in the camera of a second or less.

Step 3: Develop

At the beginning of the dry plate era, the latent image was developed into a visible image using inorganic developing agents (e.g., metallic salts like ferrous oxalate). In later years an organic compound derived from phenol (pyrogallic acid) was used in an alkaline solution as a developer. Hydroquinone was discovered in 1880 by Abney and became widely used. Other phenol derivatives were used as developing agents for dry plate negatives, among them:

- Pyrocatechin (hydroquinone isomer)
- "Hydramine"
- Para-aminophenol
- Metol[27]

Step 4: Fix

After development, the gelatin binder was hardened with a potassium or chrome alum solution and fixed with sodium thiosulfate.

Step 5: Wash

The plates needed to be washed thoroughly to eliminate the silver thiosulfate complexes formed during the fixing of the image.

Step 6: Intensify (optional)

A mistakenly underexposed plate made intensification necessary on occasion. To intensify the silver image (i.e., make it more dense or more opaque), mercuric-ammonium chloride, mercuric iodide, or cuprous bromide were used.[28] Other intensifiers that were used included silver or chromium ions.

Step 7: Varnish

Although varnish recipes exist in amateur and professional photography manuals, they were used only occasionally. Professional photographers sometimes varnished their negatives to protect them from the environment and prevent contamination with salts (e.g., silver, gold or platinum) present in the printing papers.[29] Protective varnishes listed in manuals include:

- Shellac[30]
- Copal
- Gum sandarac
- Zapon (celluloid)

The earlier the gelatin plate, the more likely it would have been varnished. Plates produced after 1890 were rarely varnished.[31]

Support

By the time the gelatin dry plate was introduced, photographers had gained some knowledge of the manufacturing process of the glass as it related to the surface, color clarity and durability. High quality glass made in Belgium, France, and the United States met the needs of photographic plates.[32] The glass was cleaned with acidic and basic solutions and polished with talc.

Subbing

To receive the binder and to avoid the formation of emulsion blisters the glass support was either:

- Coated with a subbing (substratum), a thin layer of gelatin hardened with a chrome alum solution.[33,34] Dilute albumen, India rubber[35] or soluble glass (sodium or potassium silicate)[36] also was used on occasion.
- Chemically etched. Chemical etching improved the bond of the emulsion to the glass.

Binder

The emulsion was composed of gelatin (the binder) and silver salts, which after exposure formed the silver particles/image substance.

Image

The image of a gelatin dry plate is formed by relatively large silver particles (as compared to those of the calotype and collodion negatives) that were created from the exposure and chemical development of the plate. The ribbon-like (filamentary) silver particles produced great opacity and a neutral-black image color.

Although rare in most collections, physically developed gelatin glass plates may be found on occasion. The image of these plates is usually gray or tan in hue.[37]

Retouching

When negative retouching was needed, a special medium was applied to the surface of the binder to create enough "tooth" to hold the pencil strokes. There were two kinds of retouching media: dope, which was thick, and varnish, which was thin. Etching or shaving the emulsion by means of a sharp blade was a common procedure to remove unwanted image density. Yellow or red filters, made with paper or paint, were sometimes applied to the back or the front of the glass plates to mask certain areas of the image.

RETOUCHING MEDIA

Medium	Components	Application
Dope	Balsam fir or gum dammar in turpentine	Locally with cotton ball
Varnish	Gum mastic in ether	Flowing the entire plate[38]

Positive Prints

Professional photographers used gelatin glass plates to make positive prints by contact on several types of papers, usually:

- Silver/gelatin printing-out papers
- Silver/gelatin developing-out papers
- Collodion printing-out paper
- Velox or gaslight paper (slow developing-out paper used by amateurs that could be printed by exposure to gaslight)
- Platinum paper, in which the image is formed by platinum particles, as opposed to silver particles

Stability/Deterioration

The long-term behavior of gelatin glass plates is related to:

- Stability of component materials
- Method of fabrication
- Chemical processing
- Storage environment

Glass stability

Some gelatin glass plates are also prone to glass decomposition. Early dry plates are more likely to suffer the effects of glass deterioration because they could have been made with chemically unstable soda and soda-lime glass (containing excess sodium or potassium oxides). These types of glass plates are likely to dehydrate at low relative humidity and to leech out hydrated alkali ions at high relative humidity.[39]

The formation of a highly alkaline hydrated layer (with the appearance of moist droplets) at the surfaces of the glass may contribute to the deterioration of all components of a glass plate negative. In the 1920s, the addition of aluminum oxide to glass formulations (alumino silicate) allowed the production of a more chemically stable glass support.[40]

Binder stability
High relative humidity promotes the growth of mold in the gelatin layer, which leads to the solubilization of the binder and eventually the destruction of the image.

Image stability
Silver image deterioration (i.e., oxidation) is common in gelatin glass plates. Oxidation of the silver particles causes fading, discoloration, and mirroring—a bluish-silver sheen on the surface of the binder resulting from exposure to high relative humidity.[41] Plates that were protected by a varnish overcoat rarely show signs of image oxidation.[42]

Structural stability
Failing of adhesion between the glass support and the binder layer may occur. Lifting or flaking of the emulsion from the glass is not uncommon in gelatin dry plate despite the presence of a substratum or the etching of the glass support. Factors that contribute to the deterioration and lifting of the emulsion layer include:

- Chemical and physical characteristics of the component materials
- Physical characteristics of the binder (e.g., propensity to shrink, degree of hardening, etc.)
- Storage environment humidity:[43]
  - Low relative humidity (exacerbates lifting and flaking due to shrinkage of the gelatin layer)
  - High relative humidity (causes softening of the gelatin binder and its adherence to any surface in contact with it, e.g., another glass plate, a storage envelope, etc., and the proliferation of mold)
  - Drastic changes in relative humidity (cause rapid shrinkage and exacerbate lifting and flaking of the gelatin layer)

Storage

Regardless the composition of their glass support, gelatin glass plates should be stored at a cool to moderate temperature (below 18°C) and at 30% to 40% relative humidity.[44]

Identification

Gelatin dry plates are very common. Most negative images show a gray or black image color. Rarely, one will find a physically developed negative image that will be gray or tan in hue.

Gelatin glass plates are recognized by their machine-made characteristics, such as:

- Even coating of the gelatin layer across the entire surface of the glass.
- Relatively thin, smooth support of standard thickness.
- Most glass supports were 2 to 3 mm thick (thinner than handmade glass).
- Standard sizes,[45] e.g.:
  - Lantern size (English)—3¼ x 3¼ inches
  - Lantern size (American)—3¼ x 4 inches
  - Quarter size plate—3¼ x 4¼ inches
  - Half plate (American), stereo plate, or cabinet plate—4¼ x 6½ inches
  - Half plate (English)—4¾ x 6½ inches
  - Whole plate—6½ x 8½ inches
  - Other common sizes—4 x 5, 5 x 7, 5 x 8, 8 x 10, 10 x 12 inches

Although most gelatin glass plates were machine-coated, during the 1870s they were still coated by hand.[46] Therefore, hand-coated plates occasionally may be found in photographic archives.

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CELLULOSE NITRATE FILM NEGATIVES
ca. 1889 – ca. 1950

Background

The fragility and weight of the glass support of the gelatin dry plate led to a quest for a flexible and lighter support. Since 1854, Alexander Parkes had suggested using a flexible support made of several layers of plain collodion, but his idea never found an application.[47] Instead, celluloid (cellulose nitrate combined with a plasticizer such as camphor) became the first successful flexible and transparent photographic support. The general adoption of cellulose nitrate film for still photography began in the early 20th century and the use of glass negatives rapidly decreased.

Roll films were now possible due to plastic film's lightness and flexibility, and, coupled with affordable photography equipment, they led to rapid popularization of amateur photography.

Gelatin on nitrocellulose sheet film negative (laterally reversed), top, with positive image below. Nickolas Muray (American, 1892-1965). NICKOLAS MURAY FENCING WITH SANTELLI, 1928. 20.3 x 25.4 cm (8 x 10 in.). Gift of Mrs. Nickolas Muray. George Eastman House Collection.

Celluloid

The cellulose nitrate and plasticizer combination, or celluloid, was the first of a long line of what we refer to today as "plastics." It was first created by C. Schönbein in 1846 and was used after 1869 for the production of faux ivory objects.[48] The name "celluloid" was trademarked in 1873 by John Wesley Hyatt of the Celluloid Manufacturing Company in New Jersey, which produced it to make billiard balls, combs, shirt collar stays, faux tortoiseshell items, and many other items. In addition, the company produced celluloid in large blocks for cutting into sheets.

John Carbutt became the first to produce plastic film negatives using these sheets by applying a gelatin emulsion coating.[49] In 1887, he presented his plastic film negatives to the Photographic Society of Philadelphia and the Franklin Institute.[50] The negatives were only suitable for sheet film, however, since they were limited in length (due to the size of the blocks they were cut from), thickness (1/100 inch), and flexibility.

Roll film

In early 1889 Goodwin submitted a patent application (which he received much later in 1898) for a formula to create a celluloid plastic that could be cast into thin sheets of suitable length for rolling.[51] Goodwin joined forces with E. & H. T. Anthony & Co. and began producing "Climax Negative Films." An advertisement for the film touted it as the latest development:

> Anthony's *Climax Negative Films* are made upon a substance of recent discovery, which is admirably adapted to the manufacture of perfect negative film, combining transparency, strength and toughness of composition, which renders them capable of being made so thin as almost to eliminate the question of weight and bulk in carrying. They are made with a fine mat surface, which reduces halation, and are perfectly impervious to water.

By August of 1889 Eastman Kodak Company already was selling gelatin emulsion roll film on a cellulose nitrate flexible support. Soon after, celluloid became the only commercially important film support.

The new roll films, which were available in 3¼ x 4¼ inch, 9 x 12 cm and 4 x 5 inch formats, and were sold in spools of 24 and 48 exposures,[52] prompted the proliferation of small, hand-held cameras (which Eastman Kodak Company also sold) and the expansion of amateur photography.

The year 1895 marked the advent of Eastman Kodak Company's day-loading roll film, which used a flanged spool and opaque paper to cover the back of the film thereby protecting against exposure to daylight[53] and further fueled the amateur photography industry.

In 1912 Eastman Kodak Company started selling cellulose nitrate sheet films in the same formats (e.g., 4x5 inch, 5x7 inch, 8x10 inch) as glass plates[54] as well as plastic film pack negatives.

In 1900, Goodwin and the Anthony & Scovill Company (formerly E. & H. T. Anthony & Co.) filed a patent infringement lawsuit against Eastman Kodak Company. Goodwin soon passed away and fourteen years later, in 1914, Eastman Kodak Company lost the suit and had to pay restitution to the company, which by that time had become Ansco.

The 135mm or "miniature" roll film became popular after 1928 and was produced later by several companies including Eastman Kodak Company, Ansco, Dupont, Agfa, etc.

Although it is difficult to find information on when different nitrate film types were discontinued due to their inherent flammability, information on those manufactured by Eastman Kodak Company is more readily available.

EASTMAN KODAK COMPANY NITRATE FILM TYPES & DATES of DISCONTINUATION	
X-ray films	1933
135mm film	1938
Kodak professional portrait & commercial sheet film	1939
Aerial film	1942
Film packs	1949
Film rolls (616, 620, 828, etc.)	1950
Motion picture film	1951

Eastman Kodak Company last manufactured nitrate film in 1951. The dates nitrate film was discontinued by other companies are not recorded.

Process

Cellulose from cotton linters, the short fibers that adhere to the hull of the cotton seed after ginning (removal of the long fibers to be used in making cloth), is the basis for manufacturing celluloid. Cellulose is modified with nitric acid in a process called nitration to create nitrocellulose solid. This solid is dissolved in a solvent such as acetone and a plasticizer like camphor is added to create a thermoplastic material, which is cast into thin, flexible sheets or films.[55]

From this point forward negative image processing consisted of the following steps, which were essentially the same as those employed during the late dry plate era:

1. Expose
2. Develop
3. Fix
4. Wash
5. Intensify (optional)
6. Varnish (optional and very rare)

The chemicals used in the image processing have largely remained the same until the present day.

Support

Cellulose nitrate was used to create sheet, roll, and motion picture film as well as film packs. Common formats and sizes are listed in the table at the right.

COMMON FORMATS and SIZES	
Portrait and commercial sheet film	4 x 5, 5 x 7, 8 x 10, 11 x 14 inches
Sheet or 120 roll film	6 x 9 centimeters
Film packs	Same format as commercial sheet film
135mm roll film	35 millimeter strip
Amateur roll films (e.g., 820, 620, 616, etc.)	Various size strips
Professional motion picture film	35 millimeter strip

Subbing

The subbing used in cellulose nitrate film was a solution of diluted nitrocellulose, which improved the adhesion of the binder to the film support.

Binder

Like gelatin glass plates, the binder used for cellulose nitrate was gelatin that formed an emulsion with the silver salts. After exposure, these salts turned into silver particles that made up the image.

Anti-curl layer

After 1903, a layer of gelatin started being applied on the back of the plastic support to compensate for the tension exerted by the binder layer and provide dimensional stability to the negative. This bottom gelatin anti-curl layer contained anti-halation (anti-halo) dyes to prevent the exposure of the silver salts from light bouncing off the back of the support. The anti-halo dye was removed during image processing.

Image

Nitrate negative images are neutral black in hue unless they have already started to deteriorate. Negatives that have begun to deteriorate turn brown and then yellow.

Nitrate negatives were rarely varnished; however, manuals of the day recommended the following:[56]

- An aqueous solution of shellac containing borax and glycerin
- Dammar varnish

Retouching

Retouching was sometimes done on larger sheet film formats, but not on 35mm or 120 roll films due to their small image size.

Gum dammar was used as retouching medium for imparting the necessary "tooth" onto which pencil was applied.[57] Blocking out part of the image was done with red or yellow dyes like *Neo-coccin* or *Vanguard yellow*, which filtered some of the light passing through the negative.[58]

Positive Prints

Early nitrate negatives were contact printed on silver/gelatin printing-out papers and collodion printing-out papers. Later, they were printed by contact or enlargement on developing-out silver/gelatin photographic papers

Stability/Deterioration

Cellulose nitrate is very flammable and capable of sustaining combustion even in the absence of oxygen and underwater. Nitrate film was the cause of many fires and resulted in innumerable losses of archival records.

Nitrate film is also chemically unstable; the film support gradually turns yellow, brittle and sticky. It off-gases harmful corrosive products (e.g., nitrogen oxides that form nitric acid in the presence of moisture) with an acrid smell that cause fading of the silver image, decomposition of the gelatin binder[59] and, eventually, the destruction of both components along with the plastic support.

Nitrate film decay is irreversible and autocatalytic. Deterioration is generally categorized in six progressive stages, as shown in the table at the right.

Most negatives will retain legible photographic information into the third stage of decomposition. These negatives can still be duplicated if handled carefully.

DETERIORATION STAGES of NITRATE FILM NEGATIVES

Stage	Description	Image Legibility
1	No deterioration	Legible image
2	Film support turns yellow and the image shows signs of silver mirroring	Legible image
3	Film becomes sticky and gives off a strong odor of nitric acid	Legible image
4	Film becomes amber in color and the image begins to fade	Partially legible image
5	Film is soft and can adhere to adjacent negatives or enclosures	No legible image
6	Film turns into a brown acid powder	No legible image

Negatives in the fourth, fifth and sixth stages of decomposition have no legible image.[60]

Storage

The permanence of nitrate negatives depends on the temperature and relative humidity in which they are stored. Cold (-15° to 4° C) and dry (30% to 40% relative humidity) environments are the only means of preserving nitrate originals over long periods of time.

Identification

Nitrate negatives are extremely common and numerous in most photographic archives. They may be identified through edge printing, curling (roll films prior to 1903), notch codes and destructive tests.

Edge printing

Films produced between the 1930s and the 1950s were often edge printed with the word "NITRATE" to differentiate the film support from the new acetate film. After 1930, safety film made of cellulose acetate started being used and needed to be distinguished from its highly flammable predecessor. Therefore, the word "SAFETY" was edge printed on these films. However, edge printing was not done by all manufacturers, nor was it done on all roll film formats.

Curling

Early cellulose nitrate amateur roll films were not edge marked, but can be identified by their tendency to curl into very tight scrolls. Later, the nitrate support was coated with gelatin on the reverse side to prevent such curling. These gelatin anti-curl layers started being used in 1903.

Notch codes

Nitrate sheet films may have different notch codes on the upper right edge (emulsion facing up), which were made for the purpose of identifying the film type or emulsion side in the dark. A "V" notch code (first from the edge) can identify Kodak sheet film prior to 1949 as nitrate. Film pack negatives do not have notch codes.[61]

Destructive tests

Several destructive tests have been used to identify cellulose nitrate negatives. These are listed in the table at the right.

Only those with professional training should perform destructive tests.

Differentiating between nitrate and acetate films was more important in the past when the standards for the storage of each type of film were different. Today's recommendations dictate that both should be stored in cold storage.

DESTRUCTIVE TESTS for NEGATIVE IDENTIFICATION

Test Name	Description
Diphenylamine	Used mainly by conservators, the diphenylamine test produces an intense blue color when the diphenylamine[62] reacts with a small sample of cellulose nitrate.
Flotation	The flotation test requires placing a small sample of the negative in a test tube of trichloroethylene solvent.[63] Samples of cellulose nitrate will tend to sink to the bottom of the test tube as opposed to cellulose acetate, which will stay near the top.
Burn	The burn test requires burning a small clipping of the negative. A negative made of cellulose nitrate will produce a bright yellow flame that will consume the sample quickly. *Note: Do not perform this test near other negatives because of the risk of fire.*

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Gelatin on diacetate film negative (laterally reversed), top, with positive image below. Lewis W. Hine (American, 1874-1940). ICARUS ATOP EMPIRE STATE BUILDING, 1931. 12.7 x 10.2 cm (4 x 5 in.). Gift of the Photo League, New York: ex-collection Lewis Wickes Hine, George Eastman House Collection.

CELLULOSE ACETATE FILM NEGATIVES
ca. 1925 – today

Background

Cellulose acetate film, also known as *safety film*, was developed as a substitute for the flammable cellulose nitrate film as early as 1897; however, the new material had no practical value at that time due to the difficulties in finding low cost and readily obtainable solvents to cast the film.[64]

During the period between 1925 and 1950, research on film supports centered on the development of a cellulose acetate that would replace cellulose nitrate but also duplicate its good mechanical qualities and its resistance to moisture.

Acetate is a generic term for the following:

- Cellulose diacetate
- Mixed esters of cellulose acetate
    - Butyrate
    - Propionate
- Cellulose triacetate

Diacetate

The first cellulose diacetate was produced commercially by Bayer & Co.[65] under the name *Cellit*. Cellit was used as a film support beginning in 1912 and allowed the introduction of the Kodak 16mm motion picture film for home movies in 1923.

Gelatin on 35mm cellulose acetate color film strip negative (laterally reversed), top, with positive image below. Denis Defibaugh (American, 1951-) July 4th Rodeo, Red Lodge, Montana, 1999. Collection of photographer.

Between 1935 and 1955 Agfa/Ansco and Dupont produced diacetate film supports that were used for sheet and roll film. In general, all diacetate films were inferior to nitrate films, most notably, because of their tendency towards high shrinkage.

Mixed esters

As a response to the physical instability of diacetate, Eastman Kodak Company started producing better film supports that were based on mixed esters of cellulose such as acetate butyrate and acetate propionate. These film supports were used for sheet, X-ray, aerial map and amateur roll film, but these were still inferior to nitrate film for use by the motion picture industry.[66]

Triacetate

During the 1950s triacetate started being manufactured on a large scale due to the availability and lower cost of methylene chloride, the solvent necessary to cast it. Cellulose triacetate support is still being used today for most roll films.

TYPES of ACETATE[67] PRODUCED AFTER 1925

Acetate Type	Dates	Film Type	Manufacturers
Diacetate	ca. 1923 – ca. 1955	Roll, sheet	Agfa, Ansco, Dupont, Defender, Kodak
Acetate propionate	1927 – ca. 1949	Roll	Kodak
Acetate butyrate	1936 – today	Sheet, X-ray, aerial maps[68]	Kodak
Triacetate	ca. 1950 – today	Roll	Almost every film manufacturer

Color

The first color negative film was

introduced by Kodak in 1942 under the name *Kodacolor*. A year later Agfa introduced a similar film called *Agfacolor*. Color photography is referred to as a silver-based sensitive system even though after processing there is no silver left in the film. Cyan, magenta and yellow dyes are formed during the development of the negatives in three distinct layers in the emulsion.

Process

During the first decade of the 20th century, by partially hydrolyzing cellulose triacetate, an acetone-soluble polymer called diacetate was obtained.

Like nitrate film, acetate is obtained from the cellulose fibers of cotton linters. During the process of acetylation (treating cellulose with acetic anhydride and a catalyst), acetyl groups are grafted onto the cellulose molecules. A plasticizer such as triphenyl phosphate or dimethoxyethyl phthalate is added to the cellulose acetate polymer. A thin layer of cellulose nitrate functioned as subbing for the gelatin emulsion. A gelatin anti-curl layer is always present on the base side of the film to counteract the tension exerted by the gelatin emulsion and provide dimensional stability.

For the most part, the steps used in negative image processing remained the same as those for cellulose nitrate, but an additional step referred to as toning was recommended to increase the chemical stability of the silver image. In practice this step was and is rarely performed. The cellulose acetate negative image processing steps include:

1. Expose
2. Develop: Hydroquinone and Metol continued to be used as developers. Other developing agents were also introduced.
3. Fix: Ammonium thiosulfate (i.e., *rapid fix*) started being used as a fixer in addition to sodium thiosulfate.
4. Wash
5. Intensify (optional)
6. Tone (optional and very rare): Toning involves changing the structure of the silver particles by the addition of a more noble metal (i.e., oxidation-resistant) such as gold or the formation of a more stable silver compound (e.g., silver sulfide).
7. Varnish (optional and extremely rare): Acetate black & white negatives could have been varnished, for protection, with an aqueous solution of shellac (containing borax and glycerin) or with dammar varnish.[69]

Support

Prior to the 1970s cellulose acetate was used to create sheet film, roll film, and motion picture film. In the 1970s polyester started replacing cellulose acetate for most sheet film applications. The table at the right shows common formats and sizes.

COMMON FORMATS and SIZES	
Portrait and commercial sheet film	4 x 5, 5 x 7, 8 x 10, 11 x 14 inches
135mm roll film	35 millimeter strip
120 medium format roll film	2.5 inch strip
Professional motion picture film	35 millimeter strip

Subbing

Diluted cellulose nitrate is used as the subbing to improve the adhesion between the binder and the cellulose acetate support.

Binder

As with cellulose nitrate, the binder for cellulose acetate is gelatin. This gelatin emulsifies the silver salts that, after exposure and processing, form the silver particles (silver image).

Cellulose acetate film is composed of four layers:

1. Gelatin emulsion (top layer)
2. Subbing cellulose nitrate (subbing for gelatin emulsion)
3. Cellulose acetate film (support layer)
4. Gelatin (bottom anti-curl layer to provide dimensional stability)

The bottom gelatin anti-curl layer contained anti-halation (anti-halo) dyes to prevent the exposure of the silver salts from light bouncing off the support. This dye was removed or bleached out during the negative image processing but the compound remained in a "leuco" (i.e., invisible) state.

Image

Black & white cellulose acetate negatives have a neutral black image color. Color cellulose acetate negatives have an orange tint due to the masking couplers used for color correction.

Retouching

Retouching was even more rare in cellulose acetate negatives. However, it could have been done on larger sheet film formats, but not on 35mm or 120 roll film, due to the small image size.

Positive Prints

Most positive prints from cellulose acetate negatives are printed by enlargement.

Black & white cellulose acetate negatives are printed on silver/gelatin developing-out photographic papers. These can be divided into two categories:

- Fiber-base papers, so called to distinguish them from resin-coated papers
- RC (i.e., resin-coated) papers, which came into use during the 1960s

RC papers can be processed very fast because the paper support is coated on both sides with a polyethylene layer, which prevents the processing solutions from penetrating the paper itself. For the same reason, they do not curl or cockle during drying as fiber-base papers do.

Color negatives are always printed on RC papers, which are called *C print* (chromogenic color) papers.

Stability/Deterioration

Although the problem of flammability was eliminated with acetate film, it, like cellulose nitrate, is unstable and subject to deterioration in ordinary room conditions due to its chemical composition. Acetate's deterioration process, known as *vinegar syndrome*, is autocatalytic and moisture and temperature dependent. Nearly every collection has already experienced losses due to vinegar syndrome, and many more losses are expected in the future.[70] To protect film collections, survey tools such as acid detectors[71] have been developed.

Deterioration is generally categorized in six progressive stages[72] as shown in the table at the right.

Color

Chromogenic color dyes are not permanent. Therefore, color negatives may suffer from two inherent problems:

- Instability of the acetate support
- Fading of the dyes

In fact, early Kodacolor negatives are now unprintable.[75]

DETERIORATION STAGES of CELLULOSE ACETATE FILMS

Stage	Description	Image Legibility
1	No deterioration	Legible image
2	Negative gives off a vinegar (acetic acid) odor, starts to shrink and become brittle	Legible image
3	Negative begins to curl, may show blue or pink staining[i]	Legible image
4	Negative warps	Legible image
5	Liquid-filled bubbles and crystalline deposits form between the layers of the negative[ii]	Depending upon the extent, the image may or may not be legible
6	Channels form on both sides of the negative[iii]	Depending upon the extent, the image may or may not be legible

[i] In stage three, the regeneration of anti-halo dyes, originally present in the anti-curl layer but transformed into colorless leuco dyes during image processing, is prompted by the acetic acid released by the film support and the consequent pH decrease of the gelatin layer. Pink colors are found in some black & white Kodak films, while blue colors are found in some black & white Agfa and, Ansco films.[73]

[ii] In stage five, exudation of the plasticizer causes the liquid-filled bubbles and crystalline deposits that form on both surfaces of the film beneath the emulsion (i.e. binder) and the gelatin anti-curl layers.[74]

[iii] In stage six, as the film base shrinks, the bond between the gelatin emulsion and the base lets go in some areas causing the emulsion layer to buckle up in a way that is described as "channeling." The same channeling occurs on the other side of the film support as the gelatin anti-curl layer also buckles up due to shrinkage of the film support.

Storage

Although deterioration of cellulose acetate film is inevitable, it can be slowed with proper storage. The best storage conditions for both black & white and color cellulose acetate film are cold (-15° to 4° C) and dry (30% to 40% relative humidity) environments.[76] However, transferring negatives to a more stable support such as polyester is the best way to preserve the longevity of the images.

Identification

Cellulose acetate negatives may be identified by

- Edge printing
- Notch codes
- Destructive tests

Each is discussed in more detail below.

Edge printing

Cellulose acetate is usually edge printed with the word SAFETY. Depending on the place of manufacture, the symbol "°" may be added between the letters (e.g., "S°AFETY" for film manufactured by Kodak in the United States).

Notch codes

Film notch codes are cuts on the edge of the sheet films that can be used to identify the film type and locate the emulsion side in the dark. Cellulose acetate films produced by Kodak between 1925 and 1949 carried a U-shaped notch (first from the edge).[77]

Destructive tests

The flotation and burn tests mentioned in the section devoted to nitrate film also can be used to identify cellulose acetate. In the flotation test acetate clippings should remain close to the surface of the solvent in the test tube.[78] In the burn test, acetate may ignite, but very slowly in comparison to nitrate, and it will burn without a flame.

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POLYESTER FILM NEGATIVES
1955 – today

Background

Polyester film was first employed for negatives that required high dimensional stability (e.g., graphic arts photographic film[79]). During the 1960s and 1970s it gradually replaced acetate as a support for many types of sheet films. Estar and Cronar are brand names for polyester.

Polyester film base is inherently more chemically stable than either cellulose nitrate or cellulose acetate film bases because it is a completely synthetic polymer (as opposed to nitrate and acetate, which come from the natural polymer cellulose).

Polyester is a generic term for two types of film supports:

- Polyethylene terephthalate (PET), developed commercially after World War II
- Polyethylene naphthalene (PEN), introduced by Kodak in 1996 under the Advantix brand name

Process

PET is insoluble in all common solvents and, therefore, it is impractical to cast it from a solution. Instead it is cast from a melt in the same way as polystyrene. Once cooled, the amorphous sheet is biaxially oriented by stretching it at a suitable temperature in both the length and width directions. To provide thermal stability, the oriented sheet, while still mechanically restrained in the machine, is heated considerably above the stretching temperature. This causes a growth of crystallites in the polymer and has the overall effect of locking the polymer chains together so that the sheet is dimensionally stable up to much higher temperatures.[80]

PEN is obtained through the reaction of ethylene glycol with 2,6-naphthalene dicarboxylic acid. The chemical stability of this polymer is as high as that of PET.[81]


Gelatin on polyester sheet film negative (laterally reversed), top, with positive image below. Denis Defibaugh (American, 1951-). Van Loan Cottage, Bar Harbor, Maine, 2001. 10.16 x 12.7 cm (4 x 5 in.). Collection of photographer.

Support

PET has the highest strength, toughness, stiffness, and tear resistance of any commercial film base at normal temperatures, however, it is not as easy to splice as the cellulose ester film base because of its limited solubility.

Binder

The binder used in polyester negatives, as with other types, is made of gelatin.

Image

Black & white polyester negative images are neutral black in color, while color polyester negatives have an orange tint due to the masking dyes that are used for color correction.

Retouching

By this time, most consumers had their own cameras and visits to a photographer to sit for a portrait had become less common. Therefore, the skills needed by photographers to retouch negatives became less common, and most retouching from this point forward was done during the creation of the positive image.

Positive Prints

As with cellulose acetate negatives, black & white polyester negatives are printed on fiber based or RC silver/gelatin developing-out photographic papers and color negatives are printed on C print papers.


Gelatin on polyester color sheet film negative, top, with positive image below. Photographer unknown, ca. 1970. [Golfers]. 10.16 x 12.7 cm (4 x 5 in.). George Eastman House study collection.

Stability/Deterioration

Polyester film base is inherently more chemically stable than either cellulose nitrate or cellulose acetate. Because it is cast from the molten polymer it does not contain solvents or plasticizer, which might slowly diffuse away and cause shrinkage or other problems with age.

After 50 years of manufacturing, polyester film support has shown exceptional chemical stability and good physical performance.[82] Black & white films on polyester base, together with toning (stabilizing treatment of the silver image), can provide an extraordinarily long-lived pictorial record.[83]

Although polyester film support has shown exceptional chemical stability and good physical performance, the chromogenic dyes found in color negatives on polyester supports are not permanent and may fade rapidly at room temperature.

Storage

Black & white negatives on polyester support may be stored at a temperature of 18º C or lower and a relative humidity of 30% to 40%.

As with nitrate and acetate film, color negatives on polyester support require cold storage for their long-term preservation.

Identification

Like acetate, polyester film may include the edge printing “SAFETY.”

Because polyester film support is highly birefringent, it is easily identified by the interference patterns (rainbow colors) it produces when viewed between two crossed polarizing filters.

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GLOSSARY

Albumen: Egg white.

Albumen paper: Paper with a coating made from an egg white base.

Ambrotypes: Collodion wet plate negative images that appear as positives due to the black background affixed to the back of the glass support.

Anti-curl: A gelatin layer applied to the back of plastic film supports to counteract the tension exerted by the gelatin binder.

Anti-halo layer: A dark layer at the back of a glass or plastic support that absorbs light during exposure to prevent it from bouncing back and creating a halo effect.

Binder: Thin, transparent layer containing the image substance.

Calotype: Paper negative process introduced by Henry Fox Talbot in 1841.

Celluloid: A plastic made of cellulose nitrate with a plasticizer such as camphor.

Cellulose ester: Plastic produced by modifying cellulose chains through a process called esterification.

Chemical development: The chemical reduction of silver-halide crystals into metallic silver particles called filamentary silver. It is different from physical development in that all the image-forming material is present in the binder and no silver is added by the developing solution. Every negative type except collodion and paper negatives were/are created using chemical development.

Chemical reducing agent: Element or compound with a strong tendency to give electrons in a redox (reduction oxidation) reaction and thereby becomes oxidized.

Cockling: Planar deformation or buckling.

Collodion: Cellulose nitrate lacquer, a viscous liquid made by dissolving nitrated cotton in alcohol and ether.

Cotton linters: Short fibers that stick to the hull of the cottonseed after the long fibers (used in making cloth) have been removed.

Developed-out image: An image that is created through exposure and chemical development.

Developer: Chemical reducing agent that magnifies the reaction started by the exposure of the silver-halide crystals to light and produces a strong image from the otherwise invisible or latent image.

Developed-out images: Negatives or positive prints produced through exposure and development of a latent image with a chemical agent.

Developing-out photographic papers: Papers on which a negative is exposed but the image remains latent until it is made visible by chemical development.

Dry plate: A glass plate negative containing a silver image on a gelatin binder.

Emulsion: A suspension of light-sensitive silver halide salts in a viscous medium (e.g., a gelatin solution) forming a coating on photographic plates, film, or paper.

Filamentary silver: Opaque silver particles that result from the exposure and chemical development of light-sensitive silver-halide crystals.

Fix: Transform all silver-halide crystals that were not exposed to light into a water-soluble compound, which can be later eliminated from the photographic material through a final wash

Image substance: Opaque material that is present in a quantity proportional to the image density and forms the visual information of the negative.

Lantern slide: A positive image on glass that is meant to be viewed with a projector (as opposed to being printed on paper).

Latent image: A change caused by light during the exposure of a light-sensitive silver halide crystal, which is then magnified by the developer and leads to the chemical reduction of the entire crystal.

Nitration: Introduction of nitro groups into the cellulose chain through an esterification process with nitrate and sulfuric acid.

Physical development: Development with a developing solution (i.e., chemical reducing agent) that contains excess silver ions, which add opacity to the image. Silver particles produced through physical development are slightly different in shape and size from those produced by chemical development. Collodion and paper negatives were produced using physical development.

Plasticizer: A compound made of molecules of smaller size than a polymer, which are added to the polymer during the manufacture of a plastic material to provide flexibility.

Polymer: A large molecule made of smaller units called monomers.

Positive prints: Images showing correct, not inverted, tonal values.

Print by contact: To print not through enlargement, but by placing the negative directly in contact with the light-sensitive paper and exposing it to light.

Printed-out positives: Images produced entirely through exposure to sunlight, or an ultraviolet-rich source, without the aid of a chemical reducing agent. These positives were contact printed and have a reddish or purplish-brown hue with subtle details in the dark areas.

Printing-out papers: Papers on which a negative is overlaid and exposed to sunlight until the image is fully visible.

Sensitizing: Formation of the light-sensitive silver halide crystals.

Silver mirroring: Chemical deterioration of the silver image that leads to the formation of bluish silver deposits on the surface of the binder.

Subbing layer: An extremely thin, transparent layer that adheres the binder to the negative support.

Support: Firm or flexible material, which is optimally transparent or translucent (e.g., paper, glass, cellulose nitrate, cellulose acetate, polyester), that acts as a base for the image-binder layer of the negative.

Velox/gaslight paper: Photographic paper used by amateurs. This slow developing-out paper could be printed by exposure to gaslight.

Wet plate: A glass plate containing a silver image in a collodion binder.

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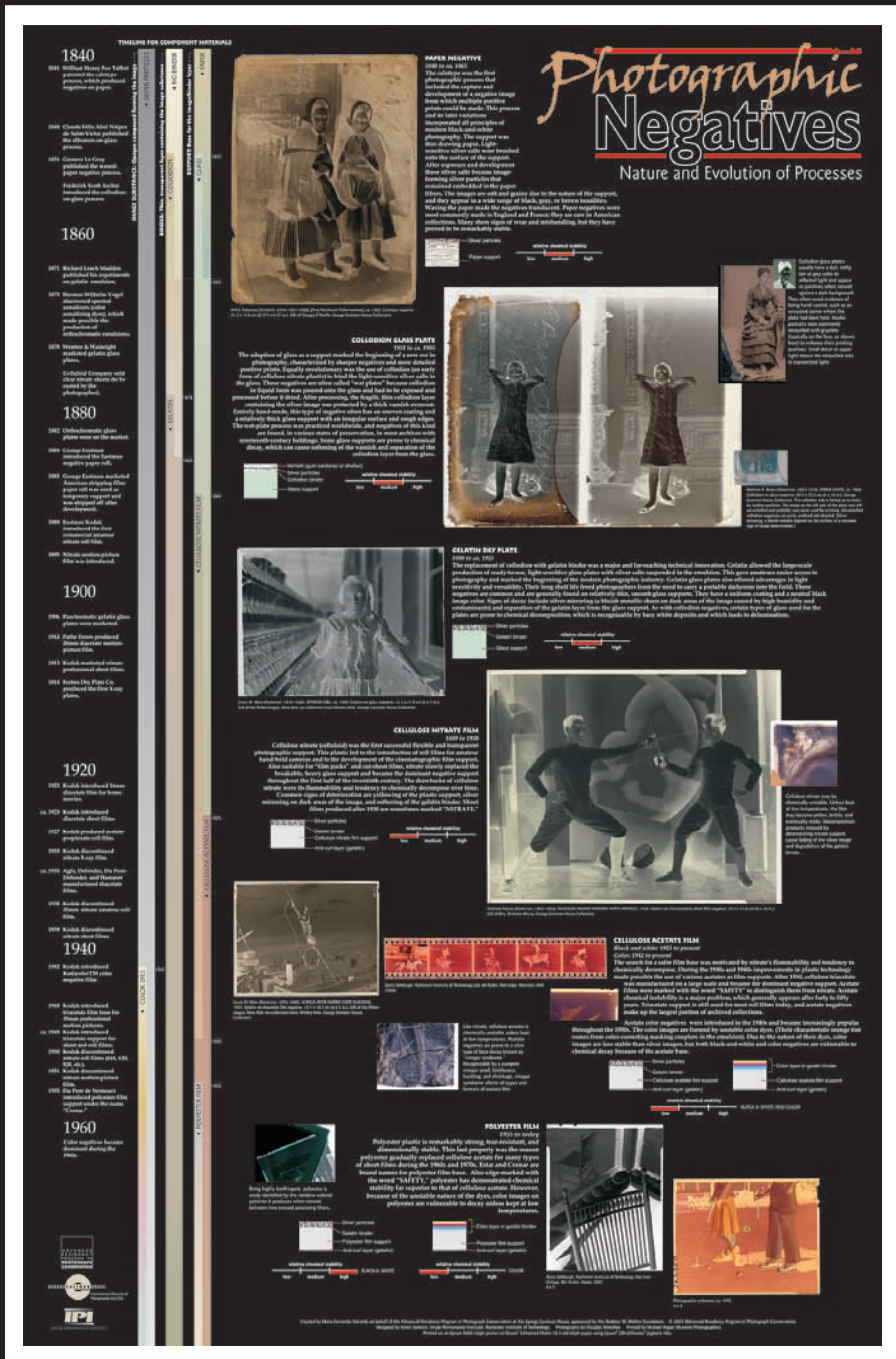

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