



672-- Man at steam pump in a N.Y. power-house
An Industrial design
By Lewis W. Hine- 1920



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A GUIDE to Fiber-Base Gelatin Silver Print Condition and Deterioration

BY GAWAIN WEAVER

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COVER: Lewis Hine, *Powerhouse Mechanic*, 1920 (Courtesy George Eastman House, Acc. No. 1978.0999.0018)

FRONTISPICE: (Page 3) Lewis Hine, [Steel worker on beam touching the tip of the Chrysler building], ca. 1931 (Courtesy George Eastman House, Acc. No. 1977.0165.0062)

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Introduction

The fiber-base gelatin silver print, or black-and-white print, as it is commonly called, was the form of virtually all twentieth-century fine art photography. In fact, until the color revolution of the 1970s, nearly every photograph—from snapshots to exhibition prints were fiber-base gelatin silver prints. These prints are present in large numbers not only in fine art collections, but in archives, historical societies, and family photograph collections. The ability to understand and evaluate the condition and deterioration of these prints are vital aspects of their appreciation and care.

The condition of a gelatin silver print can be described in many different ways. Prints are often said to be warm-toned and to have silver-mirroring or a patina. But what do we mean when we use these words? What kind of aging process, physical change, or deterioration are we really describing? What is their cause? What do they say about the history of a print? And, perhaps more importantly, what do they tell us about the future of a print? The purpose of this guide is to answer these questions, and to make the examination of a black-and-white print a more informative and rewarding activity. Understanding how a print deteriorates and the visual clues that indicate the various causes of deterioration can be very useful in the evaluation of a print's condition, authenticity, and material history.

This guide is designed for you if you care for gelatin silver prints as an archivist, collector, curator, or conservator. We begin with brief explanations about the physical nature of gelatin silver prints and a history of their processing and stability. But at the heart of this guide is the means to understand how and why deterioration manifests on a gelatin silver print. The section titled The Basics of Deterioration will be sufficient explanation for many readers, while those who desire a more detailed understanding may want to consult the Pathways found at the end of this guide.

What Color is Silver?

Silver is a precious metal with the white lustrous appearance that we see in silver jewelry or silverware (Figure 1). In photography, however, it appears quite differently. Instead of a large mass of polished metal, the silver that composes the image in a black-and-white print is present as very small particles, ranging around 0.5 micrometers in diameter. These particles are often filamentary—composed of long strands of silver tangled together, though they may become more rounded during processing (Figure 2). At this size, the particles of silver absorb light evenly across the visible spectrum, generally appearing as black or in shades of gray, depending how close together the silver particles are.



Left Top

Figure 1: Historic photograph of the Eastman Kodak Company's silver vault in Rochester, NY, where silver bullion used in making photographic film and papers is kept. In such bulk metallic form, silver has the white lustrous appearance with which we commonly associate it. (Courtesy George Eastman House)

Left Bottom

Figure 2: Filamentary silver from a Kodak Ektalure gelatin silver print as captured by transmission electron microscopy (imaged at 16,000x). Although there are many variations in shape and structure, gelatin silver prints typically contain this type of silver, which appears black or neutral gray. (©Government of Canada, reprinted with permission of the Canadian Conservation Institute)

As the particles get smaller, whether by design or decay, they lose their neutral tone. Warm-toned gelatin silver papers are manufactured with additives in the emulsion to restrain the growth of the silver halide crystals, resulting in smaller silver grains. And as prints decay, silver atoms can migrate away from the silver particles, gradually creating many smaller silver particles in place of the original filament. This causes a gradual warming of the image, as well as fading, since the smaller particles appear more yellow and sometimes cannot be seen at all.



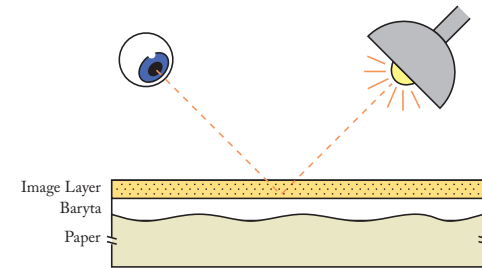
The color of silver also changes when it reacts with chemicals in its environment to form new compounds such as silver sulfide. This can occur intentionally during toning, or over time, as the silver image reacts with chemicals in the air, such as hydrogen sulfide. When this process occurs over time, the silver grains tend to disperse into smaller particles causing image fading. In contrast, toning causes an immediate reaction that better maintains the image particle size. The particles are made more robust by partially converting them to silver sulfide or by partially replacing the silver with a less reactive metal such as gold.

Given all these different factors—particle size, chemical changes, and toning—the causes of color in a print can be very difficult to explain. Scientific explanations for the colors seen in

prints are complex and cannot always account for the wide variety of colors found in them. But subtle differences in the way a print ages can give clues to its history and the reasons for its appearance today.

What Makes a Print Yellow?

Gelatin forms the matrix in which the silver image is suspended, and its clarity and transparency are an important part of the viewing process. In fact, it is doubly important, since light must travel through the gelatin layer twice before reaching your eye, multiplying the visual effect of any yellowing (Figure 3).



(Figure 3). Gelatin is naturally slightly yellow in color, though this is not noticeable on a gelatin silver print where the gelatin is highly refined, the coating is very thin, and dyes are often used in the baryta to offset the color of the gelatin (Figure 4).

However, yellowing can become visible as the gelatin ages. Chromophores—portions of a molecule that are responsible for color—can develop in gelatin as it interacts with its environment. A primary cause of such yellowing is contact with poor quality paper materials. These contain lignins and other components that have been shown to produce yellowing when in proximity to a photograph. This is one of the reasons why high-quality enclosures are recommended for the storage of photographs, particularly those that have passed the Photographic Activity Test.



Right top

Figure 3: The viewing of a reflection print, such as a gelatin silver print, requires that the light pass through the gelatin layer twice before reaching the eye. The same degree of yellowing will therefore be more visible in a gelatin silver print than in a negative or transparency. (Illustration by Peter Lazarski)

Right bottom

Figure 4: Grains of photographic gelatin in their dry state exhibit the natural yellow coloration of such purified gelatin, even though it initially appears perfectly clear in thin photographic layers.

The Nature of the Fiber-Base Gelatin Silver Print

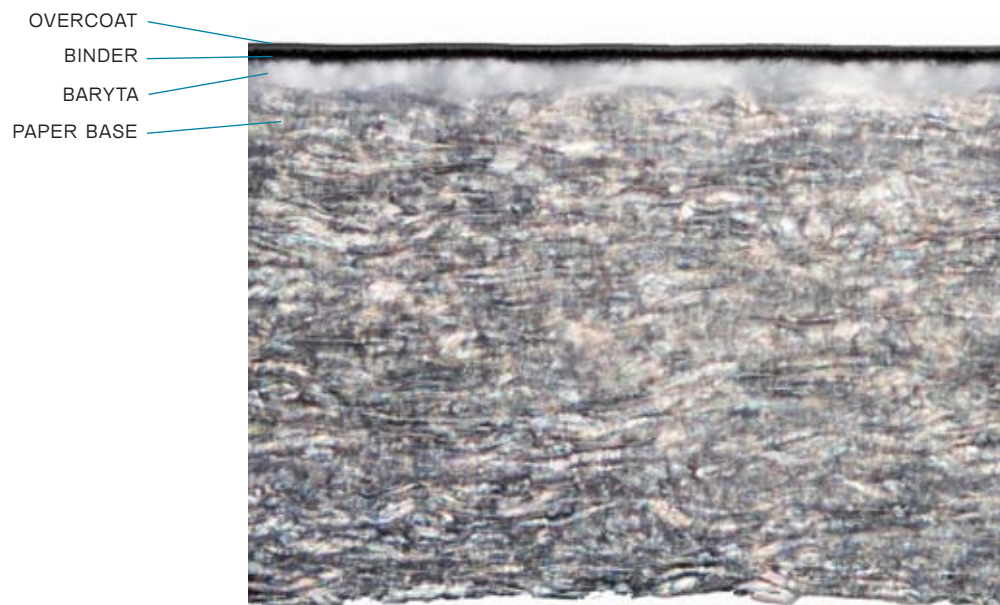


Figure 5: Cross-section of a fiber-base gelatin silver print showing its layered structure (Courtesy Image Permanence Institute)

A gelatin silver print is composed of four layers: paper base, baryta, gelatin binder, and a protective gelatin layer or overcoat.

The paper base or support serves as the substrate onto which the subsequent layers are attached. Paper is in many ways an ideal support: it is lightweight, flexible, and strong enough to withstand both wet processing and regular handling. The photographic paper base must be free of photoactive impurities such as iron and lignins. In order to obtain this purity, the paper was originally made from cotton rags, though after World War I there was a transition to purified wood pulp, which has been used ever since.

The second layer is the baryta, a white coating made primarily from gelatin and barium sulfate. Dyes were often added to modify color. The purpose of the baryta layer is to cover the paper fibers and form a smooth surface upon which to coat the gelatin.

Surfaces such as smooth, fine-grained, or silk can be created using a variety of textured felts and marking rollers in the making of the paper base, by variable calendaring of the paper base both before and after baryta coating, and by embossing the baryta-coated paper.

The third layer is the gelatin binder that holds the silver grains of the photographic image. Gelatin has many qualities that make it an ideal photographic binder. Among these are toughness and abrasion resistance when dry and its ability to swell in water and allow the penetration of processing solutions. Matting agents such as rice starch, corn starch, or silica can be added to the gelatin binder or the overcoat to modify gloss.

The fourth layer, called the overcoat, supercoat, or topcoat, is a very thin layer of hardened gelatin that is applied on top of the gelatin binder. It acts as a protective layer, providing superior abrasion resistance to the print surface.

HISTORY OF GELATIN SILVER PRINT MANUFACTURE

Now that we have an understanding of the structure of gelatin silver prints, we will briefly explore the history of their manufacture and processing. Gelatin silver prints were being made as early as 1874 on a commercial basis, but they were of poor quality, being a dry plate emulsion that was coated onto paper only as an afterthought. Coating machines for the production of continuous rolls of sensitized paper were in use by the mid-1880s, though widespread adoption of gelatin silver print materials did not occur until the 1890s. Early papers were made exclusively on rag paper, as wood pulp was not yet able to be purified sufficiently for photographic purposes. However, research at the Eastman Kodak Co. following World War I led to a full conversion to wood pulp for papermaking in 1929, and other manufacturers made the conversion around the same time. The early gelatin silver papers also had no baryta layer. It was not until the 1890s that baryta coating became a commercial operation, first in Germany, in 1894, and then at Kodak by 1900. Although the baryta layer is important in producing a smooth or glossy print, the baryta paper of the 1890s did not result in the luster or gloss print surface that became the standard for fine art photography in the twentieth century. Matting agents, light calendaring, and thin baryta layers produced low-gloss and textured surfaces. Higher gloss papers first became popular in the



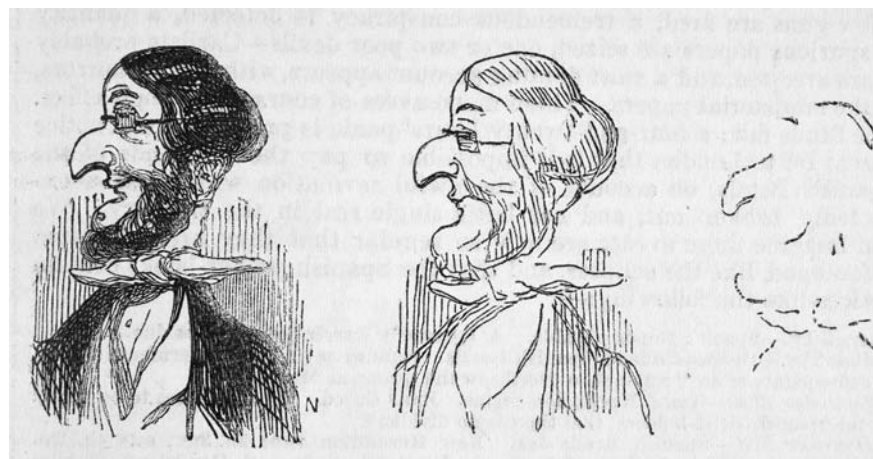
1920s and '30s as photography transitioned from pictorialism into modernism, photojournalism, and “straight” photography. In the 1930s, the number of available surfaces was at its peak. Since that time, certain print finishes have become more popular, others have been discontinued, but the fundamental aspects of gelatin silver prints have remained unchanged.

HISTORY OF PROCESSING AND IMAGE STABILITY

Processing has played a major role over the last 100 years in the stability of black-and-white prints, but concerns about the fading of silver-based photographs can be traced back to the beginnings of photography. In the 1840s, William Henry Fox Talbot's prints became so famous for their fading that a cartoon and poem published under the heading “Photographic Failures” appeared in the magazine *Punch* in 1846 (Figure 7). Image fading was often blamed on residual fixer (sodium thiosulfate or hypo) in the print—sometimes due to an intentional lack of washing that was done to achieve deep purple or brown tints. But this improved color came at the expense

of longevity, for the images soon faded to a pale yellow. In the early 1850s two-bath fixation was already in use by Blanquart-Evrard, in an attempt to ensure maximum permanence, in light of the poor reputation of Talbot's prints.

The problem of fading was severe enough that the Photographic Society of London set up a committee to address the issue in the spring of 1855. Later that year they published their first report, citing moisture in the presence of residual fixer and/or hydrogen sulfide as the basic reason for all fading. A majority of the committee were of the opinion that gold toning significantly improved image stability.



Hydrogen sulfide is a product of the combustion of coal gas and was pervasive in industrialized nineteenth-century London. Hydrogen sulfide and other pollutants that are harmful to photographic prints can be found everywhere in varying concentrations. Since it was not practical to remove such contaminants, attention was turned to the removal of fixer. Numerous methods and chemicals are recorded in the photographic literature over the next 100 years for the elimination of fixer, culminating in the 1940s when the Kodak Research Laboratories officially recommended the

Left

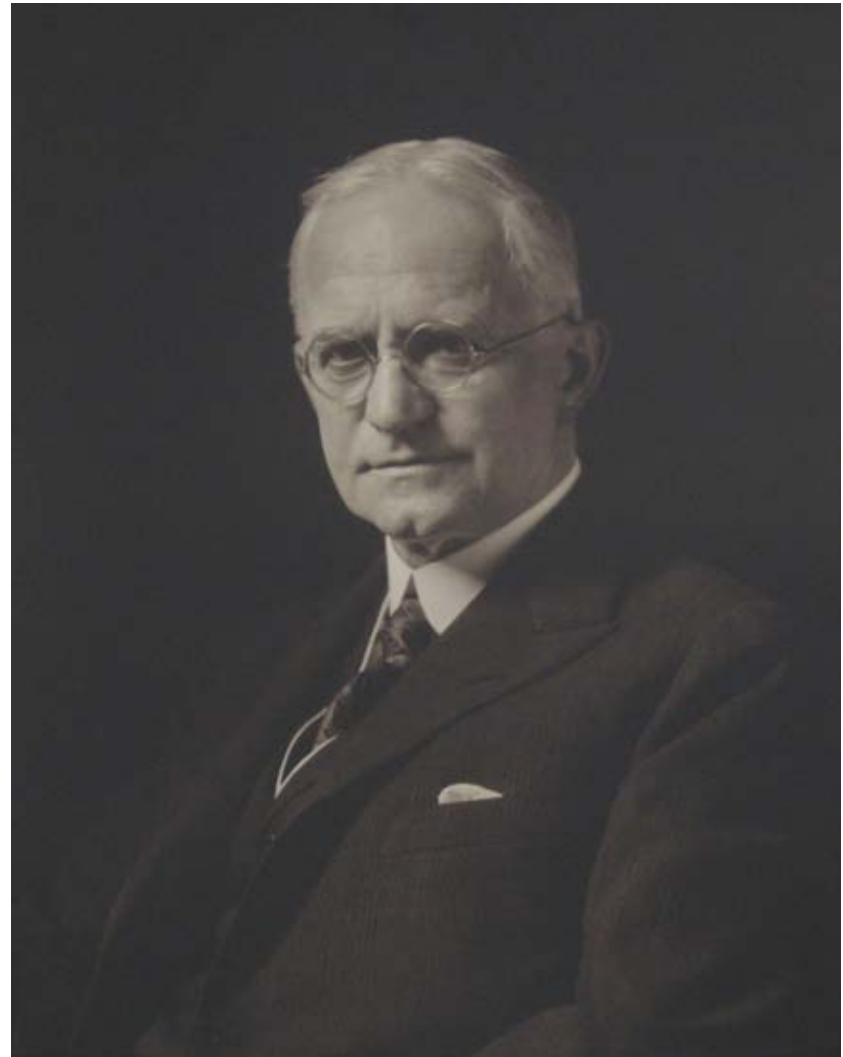
Figure 6: Eastman's Permanent Bromide Paper, ca. 1885. This very early example of gelatin silver developing out paper was available in only three types, A—Thin Smooth Surface, B—Heavy Smooth Surface, and C—Heavy Rough Surface. (Courtesy Mark Osterman)

Above

Figure 7: This drawing and the accompanying poem appeared under the title “Photographic Failures” in an 1846 *Punch* magazine. The poem compared a photograph to love, stating how the features of a portrait “Have vanished as affection flies—Alas!—where is it now?”

“complete elimination treatment” for all black-and-white photographic materials. This consisted of Kodak’s hypo eliminator solutions, which oxidized the remaining fixer into harmless sulfates. This extreme measure was based on the belief that even the minutest quantity of fixer remaining in the photograph would cause image fading. But in the 1960s, the Kodak Research Laboratories discovered something that no one had considered before—a small amount of fixer left in a print actually forms a protective coating of silver sulfide on the surface of the silver grains. In effect, residual fixer can act as a mildly protective toner and over-washing leaves the silver very vulnerable to deterioration. Since there was no way to know in practice exactly how much fixer was left in a print, the recommendation became simply to wash for the recommended times, but not to over wash.

Toning has always been considered important for image stability. Toning can act by replacing part of the silver image with a more noble metal such as gold or platinum, or alternatively it can act by forming a compound with silver that is more stable than silver alone, such as in selenium or sulfur toning. Gold and platinum toners were often used in the nineteenth century. By the beginning of the twentieth century, when many photographers had transitioned to gelatin silver prints, gold and platinum toners were still in use, along with newly-discovered selenium toner, and various sulfide toners. The sulfide toners were the most protective toners ever used. However, they generally yield a brown coloration which is disagreeable to many photographers. They were very popular in the form of sepia toner in the 1920s and ’30s, though they were used predominantly for portraiture. Selenium toner was perhaps the most widely used toner in twentieth-century fine art photography, and was first disclosed in a 1910 German patent. With selenium toning the photographer could make gelatin silver prints with a color anywhere from neutral or blue-black (i.e. no color change) to a purple-brown, an image color that many photographers found pleasing. Thus, photographers could benefit from the increased image stability of a toned print, without a disagreeable change in image color. Though not as effective as sulfide toners in protecting the image, selenium toning was a significant improvement over untoned prints. Its use was championed by Ansel Adams as early as 1950, in the first edition of *The Print*, and was a regular part of his working process throughout his career. The excellent condition of his prints today bear witness to both his meticulous working methods and the effectiveness of selenium toner when used properly and combined with good print care.



Above

Figure 8: This portrait of George Eastman is an excellent example of the protective qualities of sulfide toning. It has been displayed without glazing for many decades and does not exhibit even a hint of deterioration. (Courtesy George Eastman House)

Gelatin Silver Print Deterioration

EXAMINATION OF A PRINT TO JUDGE CONDITION AND DETERIORATION

Before we discuss the types of deterioration, we must first consider the act of examination, and some of the basic vocabulary that we use in describing the parts of an image. The importance of looking cannot be overemphasized in the understanding of print deterioration. Proper lighting will reveal aspects of a print that cannot otherwise be seen.



LIGHTING

Standard

First examine the print under strong lights and with no reflections in the surface of the print. These conditions will allow you to best observe the color and tonal range of the print. These are primary indicators of silver image condition and deterioration as outlined in the Image Decay section below (Figure 9).

Specular

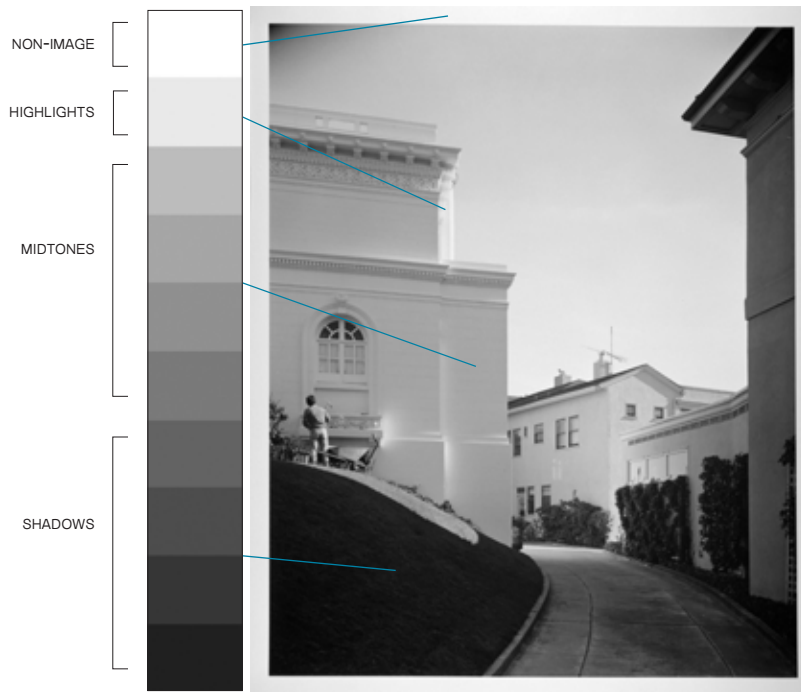
Now position yourself so that if the print were glossy, you would see a light reflected in its surface. This lighting position will emphasize surface texture and gloss, and any changes in them due to abrasion, ferrotyping, or mold growth, as outlined in the Gelatin Binder and Paper Decay section below (Figure 10).

Raking

Raking light is achieved by placing a single light source at a very low angle to the print surface, accentuating the surface texture and overall topography by throwing long shadows. Raking light will emphasize any unevenness in the surface caused by planar deformation or surface damage, as outlined in the Gelatin Binder and Paper Decay and Mechanical Damage sections below (Figure 11).

MAGNIFICATION

Although most significant information can be seen with the naked eye under good lighting, you may find a moderate degree of magnification useful in some circumstances. A 5x or 10x loupe will generally be sufficient, though some enjoy the extra power of a handheld 30x microscope. It takes some experience to understand what you are seeing at higher magnifications, so be careful about drawing conclusions when first using a magnifying device. A loupe can be useful in determining the presence or absence of a baryta layer. Details of retouching, and whether a mark is a scratch or an accretion, can often be revealed by magnification. However, for our purposes here, the trained and unaided eye is usually sufficient.



TONAL VALUES

The above gelatin silver print by Frank Gohlke exhibits a full range of values from bright white to deep black, providing a good example for the description of tonal values in a print in good condition.

Non-image areas are the lightest value possible in a print, where there is no silver image, and the brightness is determined solely by the whiteness of the support and the gelatin binder. White borders and light sources are often non-image areas.

Highlights range from white surfaces to very light skin or light gray objects.

Midtones range from snow in the shadows to gray stones and dark foliage.

Shadows range from dark materials with full texture and detail to the deepest black with no detail.

Above

Figure 12: Frank Gohlke, *Driveway, San Francisco, CA, 1979* (Courtesy George Eastman House, Acc. No. 1981.0949.0001; reproduced with the permission of Frank Gohlke)

SIDE BAR 3

Primary Factors in Image Stability

There are five factors that influence the long-term stability of the silver image: water, air pollutants, heat, processing and toning, and particle size (Figure 13).

Water in the form of atmospheric humidity swells the gelatin and allows for easier penetration of air pollutants. Water is also a necessary participant in the degradation of silver—it acts as the medium in which these reactions take place. Finally, migration of silver ions through the gelatin occurs more readily as relative humidity increases, and this migration is the foundation of silver image decay.

Air pollutants such as hydrogen sulfide or nitrogen dioxide in the atmosphere react with the silver image to cause fading and yellowing. Oxygen also plays an important role, allowing deterioration to occur in the presence of moisture and heat, without the need for more aggressive oxidizing gases.

Heat supplies more energy for deterioration reactions. Although the effect of heat is not as great as that of moisture, it has been shown experimentally that silver deterioration will occur more quickly at higher temperatures.

Processing and toning determine the composition and chemical environment of the image particles. Fixing and washing may leave the silver image particles either only slightly protected, vulnerable to deterioration, or highly prone to yellowing. Proper processing followed by sulfur toning is the most effective means to prevent deterioration, while selenium and gold toning also offer some protection.

Particle size plays an important role. Most developed-out black-and-white papers have silver particles ranging around 0.5 micrometers (1/160 the width of a human hair!). Slower speed papers, such as contact printing papers or printing out papers, have even smaller particles. Since most deterioration reactions occur on the surface of the silver particles, papers with smaller silver particles (with their greater surface area) are often more susceptible to decay.

You may have noticed that light has not been included here as a primary factor in image stability. Exposure to high levels of light for extended periods may cause embrittlement of the paper support, and the associated heat may speed image silver deterioration. However, compared to the damage that light inflicts on most color prints or on resin-coated gelatin silver prints, fiber-base gelatin silver prints are quite stable with respect to light exposure. Like all art on paper supports, prints on display should

be kept away from direct sunlight or high levels of indoor lighting. A limit of 300 lux is sometimes used as a guideline, though individuals and institutions may prefer to set stricter standards.

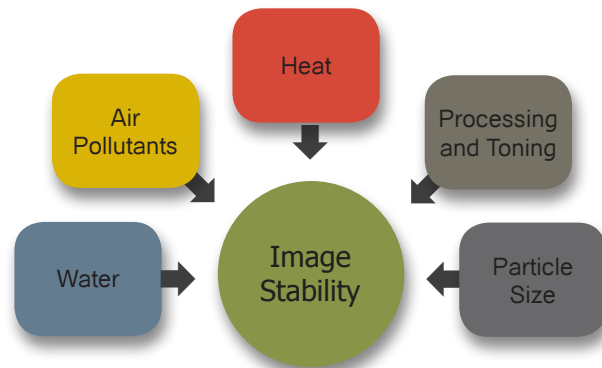


Figure 13: Primary Factors in Image Stability



THE BASICS OF DETERIORATION

Now that we understand the layered structure of the print, how to best examine it, and the primary factors in image stability, we are ready to approach the deterioration itself. Deterioration can be divided into several broad categories: image decay, gelatin binder and paper decay, and mechanical damage. We will examine these categories one at a time.

There are many details to learn about each form of deterioration, so if you would like to understand more about one of them, try reading the Pathway for that particular type of deterioration. Each Pathway is a form of deterioration with a unique appear-



ance, and their descriptions can be found at the end of the guide (pages 22–39). Sometimes deterioration can have more than one possible cause. You can use the deterioration charts (see pages 16–17) to locate the Pathway that you are curious about, or just use the references in the text to find the right one. Each Pathway (labelled P1–P16) is identified here in parentheses, e.g. (P3).

IMAGE DECAY

A black-and-white image would remain unchanged for a very long time if it were kept in a cool, moderately dry, and perfectly inert environment without exposure to any airborne pollutants. Sulfide toners can have a similar effect by converting the silver into the very stable compound silver sulfide. Selenium and gold toning provide some protection, but will not protect a print completely. In real life, there are no such perfect environments, and few prints are sulfur toned. For a typical gelatin silver print, image deterioration proceeds by exposure to pollutants in the presence of moisture and heat. The basic mechanism of silver image decay is the same in every case: the silver particles that form the typical black-and-white image (Figure 14) undergo changes in their shape and size, and may react with sulfur to form

silver sulfide. The change in particle size and the reaction with sulfur can produce dramatic changes in the color and density of the silver image (Figure 15).

Left

Figure 14: Lewis Hine, *Powerhouse Mechanic*, 1920. This is a good example of a gelatin silver print in excellent condition. It possesses a full tonal range with strong detail in the highlights and a nearly neutral image color. (Courtesy George Eastman House, Acc. No. 1978.0999.0013)

Above

Figure 15: Lewis Hine, *Powerhouse Mechanic*, 1920. This is a good example of a deteriorated gelatin silver print. The entire print has become yellowed, and the highlights have lost nearly all their detail. (Courtesy George Eastman House, Acc. No. 1978.0999.0018)

Nearly all image decay begins with a single step: the oxidation of the image silver into silver ions. The developed silver image is composed of particles of silver metal (see Figure 1). When silver from these particles are oxidized, they become silver ions (Ag^+). Unlike the silver metal (Ag^0), these silver ions are able to move within the gelatin. Thus, small dense image particles become larger clouds of even smaller particles. This oxidation and migration of silver atoms is the first step in image decay (Figure 16).

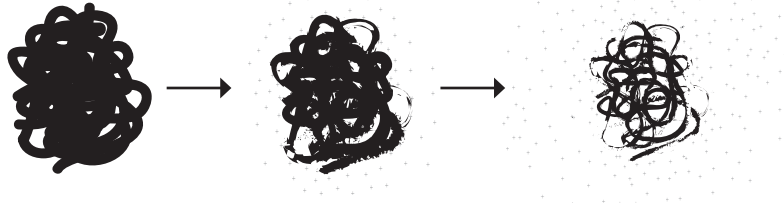


Figure 16: The breakdown of a silver image particle begins with the oxidation and migration of silver ions.

Once the silver has been oxidized to silver ions and has travelled away from the silver image particle it has three possible fates:

The first occurs when the migrating silver particles are quickly reduced to metallic silver. These new and smaller particles of silver appear yellow/orange (Figure 17). This yellow/orange discoloration typically occurs around the edges (Figure 20) and in the midtones and may be the result of exposure to fresh oil-based paint or varnish. See Sidebar 4 for a story of how this commonly occurs (P1).

The second result occurs in the shadows where there is a large amount of image silver. If the mobile silver ions reach the surface of the print, they form a metallic blue sheen known as silver-mirroring (Figure 18). This will occur only in the shadows, and either along the edges (P2) or across larger areas of the print (P3). Silver-mirroring along the edges is often caused by air pollutants, while more overall mirroring may be the result of contact with poor-quality storage materials.

The third and most common result is when the mobile silver ions disperse into very small particles of silver or react with a sulfur compound to form yellow/brown silver sulfide (Figure 17). Depending on the size and composition of the resulting silver or silver sulfide particles, the image may fade or shift to more yellow or brown tones. This may occur at the edges (P4), overall (P5), or in localized areas across the print (P6). Exposure to pollutants in the presence of moisture and heat is the most common cause. The deteriorated Lewis Hine print (Figure 15) is a classic example of this deterioration. The silver has broken down into smaller particles and some have likely reacted with sulfur to form silver sulfide. As a result, the highlights have faded, and the highlights and midtones have turned yellow/brown. In this case, even the shadows have been affected and display a warm brown tonality.

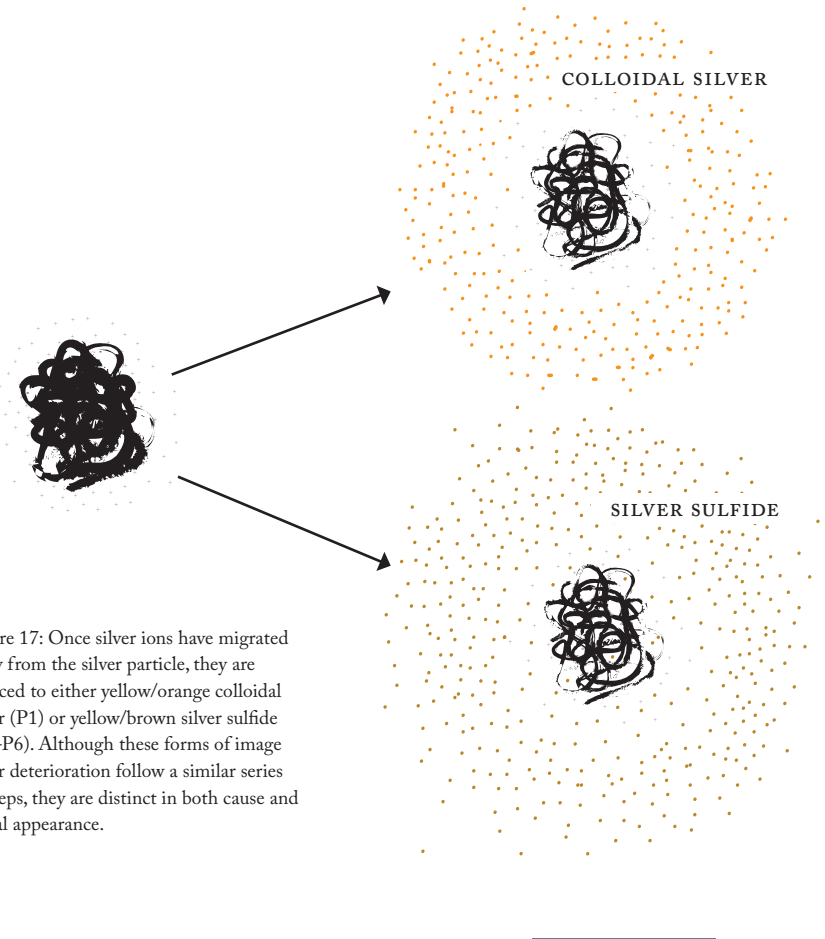


Figure 17: Once silver ions have migrated away from the silver particle, they are reduced to either yellow/orange colloidal silver (P1) or yellow/brown silver sulfide (P4–P6). Although these forms of image silver deterioration follow a similar series of steps, they are distinct in both cause and visual appearance.



Figure 18: Oxidation and migration of silver ions can also lead to silver-mirroring. This often occurs over extended periods of time, as the silver ions need time to migrate to the surface of the print and form a highly reflective layer of silver. This only occurs in the high density areas where the high concentration of image silver allows for a large number of silver ions to reach the surface (P2, P3).

Occasionally, faulty processing is the cause of this deterioration, and for this there is a telltale sign—the non-image areas, where there shouldn't be any silver at all, will have a yellow discoloration due to residual silver/fixer compounds (P7). But be careful in making this judgment! There is one other form of deterioration that can look deceptively similar. It is the yellowing of the gelatin binder that results from



contact with poor-quality storage materials (P7 and Sidebar 2). Also closely related to faulty processing are chemical stains and other localized image deterioration caused by contamination from chemicals or fingerprints (P8 and Figure 19).

That was a lot of information packed into a small space! The good news is that what you have just read is the most difficult part of gelatin silver print deterioration to grasp. To better understand the causes and why some deterioration occurs in one place and not in another, read the Pathway description for the deterioration that you are observing.

How do you make sense of it all when viewing a print? Try the following pointers.

PRINT VIEWING TIPS

1. Use proper lighting!
2. Determine the original tone of the print by looking at the shadow areas and darker midtones, which are most likely to have retained the original print tonality.
3. Now look at the midtones. Are they the same tonality as the shadows or have they become more yellow/brown?
4. And finally, look at the highlights, which are the most sensitive to change. Have they yellowed? Is full detail preserved in the highlights or have they begun to fade?
5. If there is fading or discoloration, is it occurring overall in the highlights and midtones, preferentially at the edges, or in random or localized areas across the print?
6. What about the non-image areas? If there is a clear border or specular highlight in the print, does it retain the original white or off-white color of the print, or has it yellowed? Such non-image area yellowing can be a result of poor processing or poor-quality storage materials. (The presence of silver-mirroring in addition to the overall yellowing suggests that storage materials are responsible, since mirroring is often prevented by poor processing.)

A parting note on gelatin silver print image decay: while it is useful to study the individual mechanisms of deterioration, it should be remembered that in real life, gelatin silver prints are a complex product of their manufacture, processing, and subsequent storage. Visible deterioration patterns will always be a complex combination of many factors, not all of which can be fully explained.

Left

Figure 19: Edward Weston, [Tina Modotti], ca. 1925. This small print exhibits fingerprint stains most likely caused by the print surface being touched with darkroom chemicals such as fixer. (Courtesy George Eastman House, Acc. No. 1974.0061.0141; ©1981 Center for Creative Photography, Arizona Board of Regents)

SIDEBAR 4

Heat, Humidity, Paint Fumes, and the Benefits of Toning

A well-processed and untoned gelatin silver print is a fragile object. Untoned silver particles have a great deal of surface area and are very eager to react. Discoloration that is simply the result of this fragility is often blamed on poor processing, but this is not usually the case.

In the late 1990s, a New York City photographer's work was exhibited in a non-climate controlled gallery during a particularly hot and humid summer. The prints were carefully processed but not toned. The photographer had never had any problems with her work before. During this show, however, yellow/orange discoloration appeared along the edges in the light midtones (Figure 20 and P1). The photographer consulted with the Image Permanence Institute in Rochester, NY, to understand the cause and develop a solution. Selenium toning was chosen for its ability to provide both protection to the silver image and retain the prints' tonal aesthetic. One of the untoned discolored prints was hung in the studio darkroom, and several years later, when the darkroom was being repainted, the painter failed to remove the print from the wall prior to painting as he had been instructed. The print was finally removed after several hours' exposure to fresh oil-based paint fumes, but it was too late. Within days, the yellow/orange edge discoloration had extended into the midtones across the entire photograph. What had begun by exposure to heat, humidity, and New York City air was dramatically increased by a more concentrated dose of atmospheric contaminants. Identical effects have been seen on prints by another photographer that were stored in crates soon after the interior of the crates were sealed with varnish. While toning will increase the resistance of silver to such attacks, a combination of toning and proper environment is necessary for complete protection.



Figure 20: Yellow/orange edge discoloration, as seen here in this detail from the right edge of a gelatin silver print, is caused by exposure to certain air pollutants, particularly peroxides. Untoned or lightly toned prints are more susceptible than well-toned prints to this form of deterioration.

GELATIN BINDER AND PAPER DECAY

The gelatin binder and the paper support are both organic materials, and are susceptible to change and deterioration by exposure to water or high relative humidity (RH). These can be the result of poor storage conditions or disasters such as flooding or fires where water is used to extinguish the flames.

When exposed to water or high RH, the gelatin layer expands and softens. In this swollen state, the gelatin is more vulnerable to mechanical damage. There is also a



danger of the gelatin detaching from the baryta layer, particularly at the edges (Figure 21). This is known as frilling at the edges, or blistering on the surface of the print. Frilling and blistering may occur during processing of the print as well, particularly during extended times in processing solutions or when processing baths are at higher than normal temperatures (P9). Exposure to water may also cause tide lines and other water-related stains both in the gelatin and in the paper, which may be very difficult to remove (Figure 22 and P10). A change in the surface gloss is very likely when a print is wetted, particularly if the print dries against another surface, such as a piece of glass. When this happens, the gelatin print conforms to the glass and assumes its high gloss surface. This is known as ferrotyping (P11).



Left

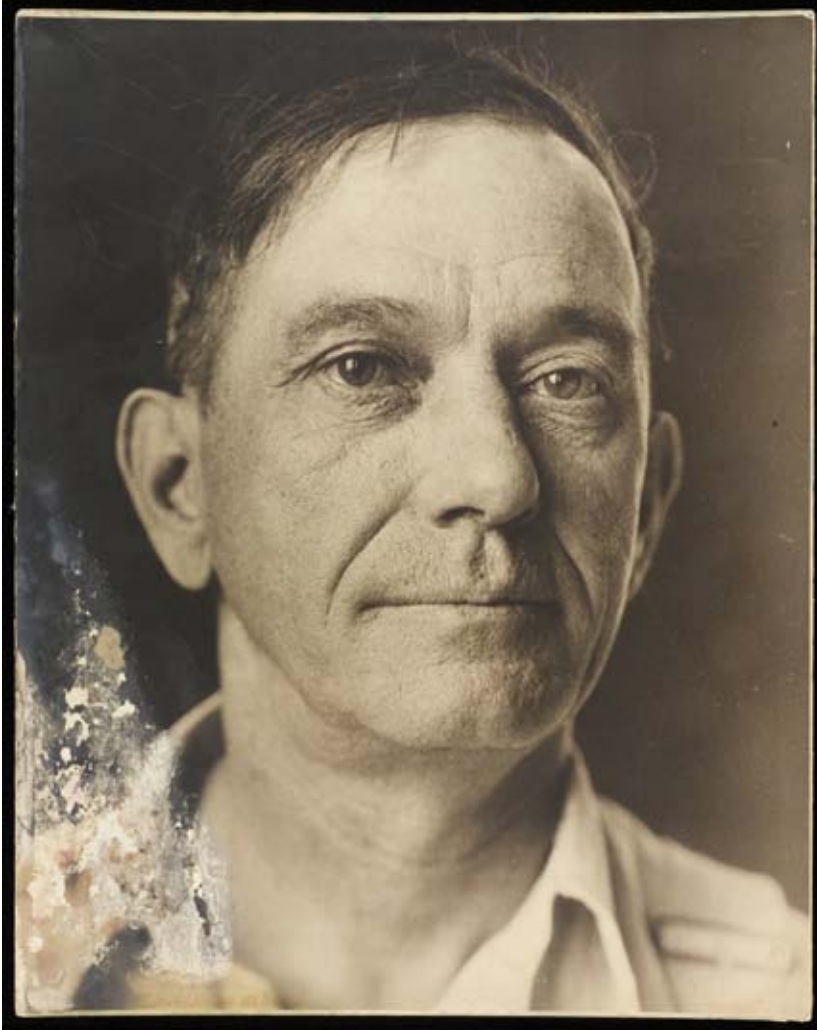
Figure 21 (and detail): Edward Weston, *Pepper*, 1930. The frilling of the emulsion along the bottom edge is the result of water exposure. It is emphasized in the detail by photography in raking light. (Courtesy George Eastman House, Acc. No. 1970.0162.0004)

Above

Figure 22: Edward Weston, *Rhyolite, Nevada, Ghost Town*, 1938. The brown staining is the result of exposure to water. In this case, it appears that the colored material was leached from nearby poor-quality boards. (Courtesy George Eastman House, Acc. No. 1974.0061.0080)

Images by Edward Weston ©1981 Center for Creative Photography, Arizona Board of Regents

If a print is damp for more than a day or two, it is also likely to grow mold (Figure 23), which can lead to staining of the paper and gelatin (P12). The mold also has a weakening effect on the gelatin, making it readily soluble in water. If prints that are mold-damaged are exposed to water, the gelatin layer may dissolve or lift from the support, causing complete loss of the image. This can also occur when early gelatin silver prints with unhardened gelatin layers are exposed to water.



Left

Figure 23: Lewis Hine, [Portrait of worker, Empire State Building], ca. 1931. This portrait of an Empire State Building worker has sustained significant mold damage in the lower left corner, resulting in the degradation and loss of gelatin binder. (Courtesy George Eastman House, Acc. No. 1977.0154.0066)

Water and Fire Disasters

SIDEBAR 5

On Memorial Day, 1978, nitrate films stored in the Eastman House's old incinerator went up in flames, quickly spreading to several adjacent buildings. One of these buildings, a previous barn, was being used for the temporary storage of a travelling exhibition. The framed exhibition photographs were packed in crates, and in the ensuing fire fight these crates were drenched in water. They were removed from the building as soon as it was safe, and unpacked immediately on the museum grounds, but not before the brown discoloration was leached from a nearby board, staining an Edward Weston print (Figure 22).

Of course, this is the least of what could have happened. Prolonged immersion in water, especially in the case of a print with an unhardened binder could have led to complete loss of the image, or at least significant frilling and blistering of the gelatin binder, and possible mold damage (Figure 23).



Figure 24: Fires often lead to water damage to photographic prints, such as in this fire on the grounds of George Eastman House, May 29, 1978. (Courtesy George Eastman House)

MECHANICAL DAMAGE

Mechanical damage includes all purely physical, non-chemical damage, including tears, creases, surface abrasions, dog ears, dents, and delamination. It is the most straightforward form of deterioration, but it does come in different forms, and it's useful to be clear about the terminology we use to describe it.

The edges of a print are uniquely exposed to certain forms of mechanical damage, such as binder folding-over and loss, delamination, and dog-eared corners. These damages occur when the edges of a print come into contact with another object. Perhaps the most common is folding-over of the gelatin binder along the edges. Small pieces of binder are lifted up and folded-over onto themselves or simply broken off. This is less noticeable when the print is overmatted or when the print has a white border. Delamination occurs when the paper support is split at the edge, while dog-eared corners are a combination of delamination, binder lifting, and some creasing that occurs at the corners.



The surface of the photograph is also quite vulnerable. For example, loss of binder by scraping may occur if a photograph is stored unprotected in a drawer that is too full (Figure 25 and detail). Other damage, such as minor surface abrasions, tears, and creases all fall into this category, and they can make a significant impact on the viewing of a print.

The causes and prevention of mechanical damage are readily understandable. Careful handling and a basic knowledge of good mounting and storage practices is all that is needed to prevent such damage.



Figure 25 (and detail): Edward Weston, *Dillard King, Monteagle, Tennessee*, 1941. The detail highlights mechanical damage to the print, with complete loss of image and exposure of paper fibers in the damaged area. (Courtesy George Eastman House, Acc. No. 1966.0070.0055; ©1981 Center for Creative Photography, Arizona Board of Regents)

DETERIORATION CHARTS

These charts are designed to help you to organize the varieties of gelatin silver print deterioration in a logical manner. The charts are color coded by the type of deterioration: yellow for *Image Decay*, blue for *Gelatin Binder and Paper Decay*, and gray for *Mechanical Damage*. When examining a print, try to match the deterioration on your print with a description on the left side of the chart, and with a location from the right side of the chart. Often, location is the key to differentiating between similar types of deterioration. The thumbnail images on the right are a quick reference for each *Visible deterioration* category. The text or the Pathways at the end of this guide should be consulted for more detailed information.

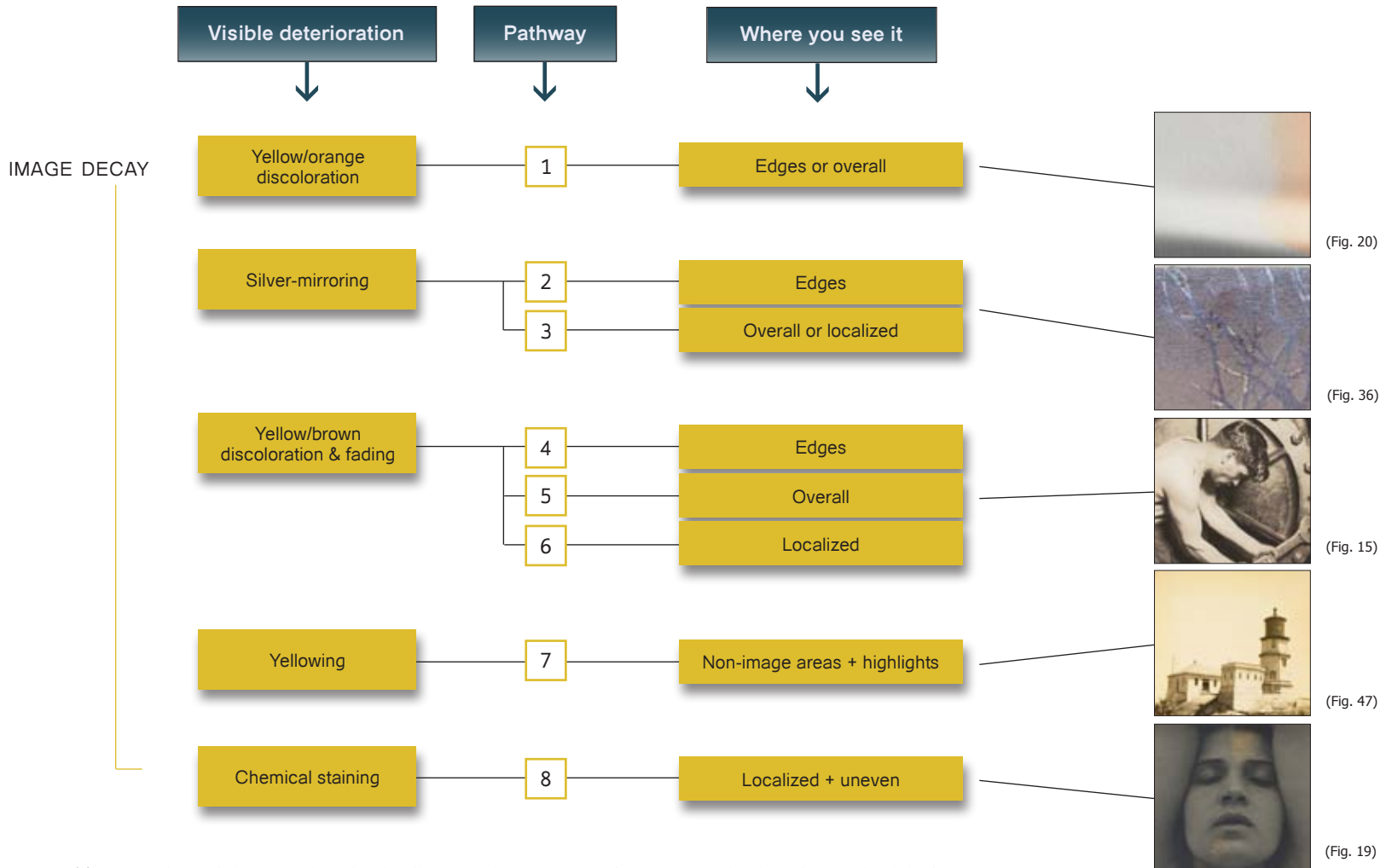


Figure 26: The primary forms of silver image decay found in fiber-base gelatin silver prints. See the associated Pathway for more detailed information.

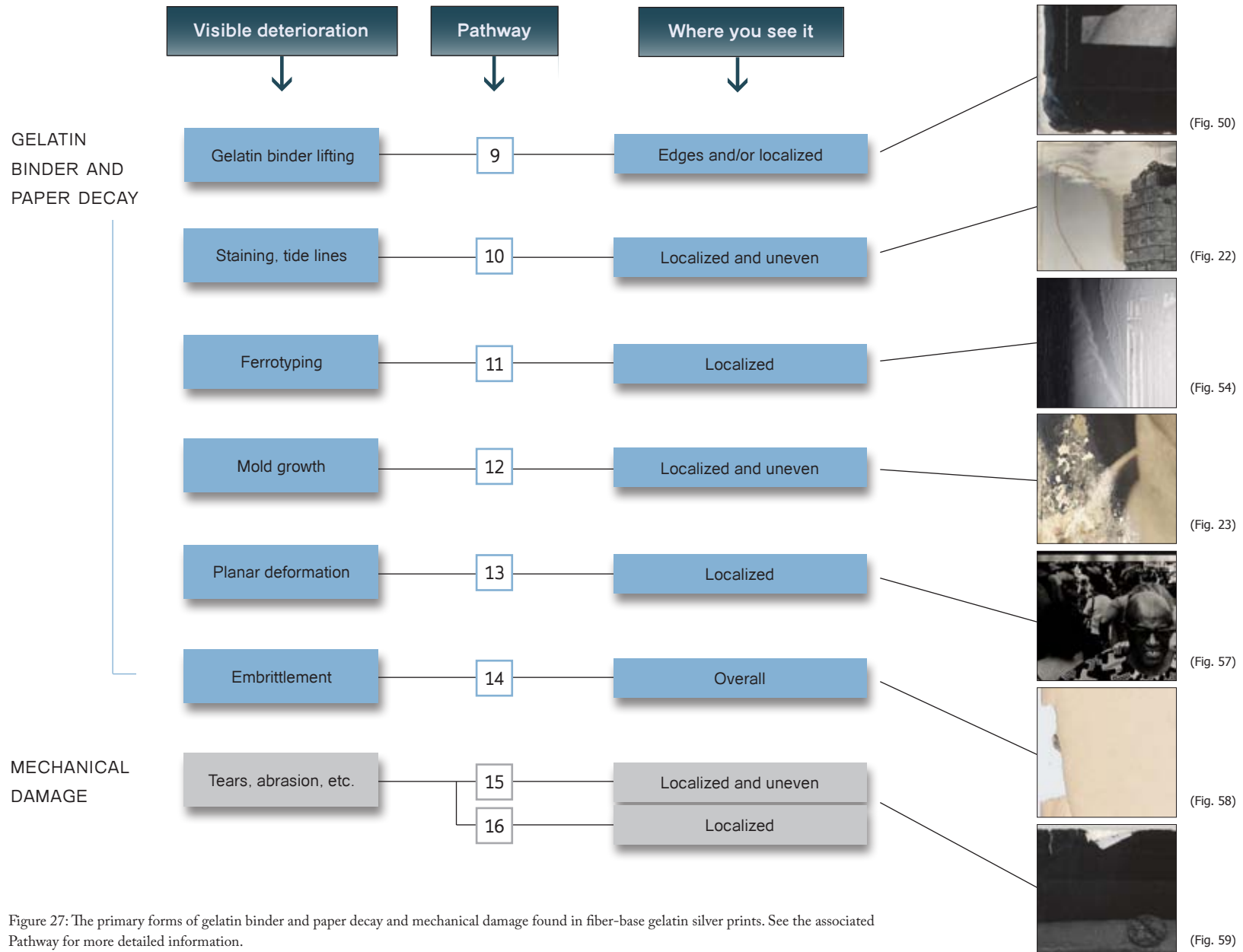


Figure 27: The primary forms of gelatin binder and paper decay and mechanical damage found in fiber-base gelatin silver prints. See the associated Pathway for more detailed information.



Figure 28: Yousuf Karsh, *Winston Churchill*, 1941 (© Yousuf Karsh)

Age, Deterioration, or Patina?

The visible signs of age are valued, just as a vintage print is preferred over a later print. While the aging of a print is certainly a form of decay, the line between deterioration and patina, within fine art photography, is drawn by aesthetics rather than science. The following comments are addressed primarily to fine art photography, though they have relevance to anyone interested in gelatin silver print condition and deterioration.

Some forms of aging may enhance a print in the eyes of the collector or connoisseur. They are signs of authenticity, and, as long as they do not disfigure the image, they are often valued. Silver-mirroring is a classic example. A print with moderate mirroring around the edges, or even heavy mirroring that complements the image, is enhanced by this form of deterioration. The removal of silver-mirroring has been known to be detrimental to a print's perceived value, as exemplified by the case of the Edward Weston print discussed in Sidebar 6.

A warm tone is another common example of deterioration that is often valued as patina. Warm-tone gelatin silver prints are an oft-used term in the fine art market today, which can refer to both toned prints and prints warmed by the oxidation of the image over time (P3). This photograph of Winston Churchill is a good example (Figure 28). It is slightly warm-toned, which, no matter how subtle or charming, is a result of deterioration. The corners are slightly dog-eared. There is some mirroring along the edges though it cannot be seen in the lighting used for taking this photograph. This warm-toned effect combined with subtle silver-mirroring along the edges creates the classic vintage print aesthetic and increases the print's value.

What if we take the warm-tone effect a little further? This 1930 photograph by Paul Woolf of the New York skyline has dramatically yellowed highlights and midtones (Figure 29). However, it suits the subject. The print and its yellowing together make a truly beautiful photographic object. The fact that it looks nothing like it did when



it was printed in the 1930s is irrelevant. Of course, the print is highly valued in the fine art market.

Forms of deterioration that do not enhance the appearance of a print also detract from its value. Yellow/orange discoloration is always unsightly. The color contrasts strongly with the usual neutral, blue-black, or brown-black appearance of a gelatin silver print. Severe levels of yellow/brown discoloration and fading are also detrimental to a print's value, as are chemical stains and other uneven forms of deterioration. Rather than blending with or enhancing the image, these forms of deterioration impose a dissonant pattern.

Even visually appealing signs of age are distinguished only by degree from the more advanced forms that are visually degrading. While

the signs of a vintage print can be pleasing in the present, it should be remembered that the continuation of that same process will result in objectionable changes in the print's appearance in the future. A proper storage environment and careful handling will help to ensure the stability of a print and its enjoyment by future generations.

Care should be taken in the interpretation of many forms of deterioration. Silver-mirroring, yellow/brown discoloration, and yellowing can, under some circumstances, be added or removed, possibly with the intention to deceive. As in any fine art field, the provenance of a print is an important aspect of its value. Questions about the

condition and material history of individual prints can be addressed by a qualified photograph conservator.

Left

Figure 29: Paul Woolf, *New York Skyline at Dusk*, 1936 (Courtesy Keith de Lellis Gallery)

The Value of Deterioration

Silver-mirroring can be a highly valued aspect of a print's condition. It is a signifier of age and authenticity and can be a beautiful addition to a print's aesthetic. The following story revolves around the removal of mirroring from a valuable print. There are many possible interpretations of the outcome.

On April 7, 1998, an early Edward Weston print depicting two shells was sold at auction at Sotheby's New York (Figure 30). A full page reproduction and extensive description in the auction catalog highlighted its importance. A unique feature of this print was the halo of mirroring that emanated from the edges, surrounding the shells, and seeming to assure the print's authenticity. It sold for \$101,500 (with premium)—a very strong price at the time.



Six years later, on April 23, 2004, the same print came up for sale at Phillips de Pury & Company. It was estimated at \$200,000–300,000, a very reasonable estimate based on the market at that time. In the meantime, however, the silver-mirroring had been removed from the print. In auction house terminology it was “bought in,” meaning that it failed to meet the minimum price or reserve set by the seller, and therefore went unsold. The removal of mirroring is a simple treatment from a technical point of view. The complexity lies in the decision to remove it. Silver-mirroring is a form of deterioration—of oxidation and migration of silver, to be specific. It is not, for the most part, an aspect of the artist's intentions—in fact, most photographers process their prints carefully in an attempt to avoid such deterioration in the future. And while mirroring can complement an image, it can also obscure it.

Did the removal of the mirroring cause a reduction in the perceived value of the print? Perhaps. The photographic art market is very complex, and it is impossible to say definitively why this print failed to sell the second time.

Cleaning and other conservation treatments can be done while leaving silver-mirroring fully intact. Treatments should be considered carefully with a qualified photograph conservator. An understanding of deterioration and its effect on value are important factors in reaching an informed decision.

Figure 30: Edward Weston, *Shells*, 1927 (Reproduced by permission of Sotheby's, Inc.; ©1981 Center for Creative Photography, Arizona Board of Regents)

When is Conservation Treatment Necessary?

Certain forms of deterioration, caused by water, high relative humidity, or mechanical damage are unstable and require treatment to prevent further deterioration. Binder lifting can, under some circumstances, be unstable. Loose flaps of binder are an obvious sign of instability. Bubbles in the binder may or may not be in need of stabilization. Prints with recent staining or tide lines should be referred to a photograph conservator as soon as possible. This type of damage can often be removed immediately after it occurs, but becomes progressively more difficult to treat as days and weeks pass. Mold growth indicates a serious deficiency in the photograph's storage environment. Affected photographs should be air dried as soon as possible to prevent further mold growth, and the photographs should be stored elsewhere until the environmental problem can be remedied. Although in the case of water damage resulting from a water or fire disaster a conservator should be involved in the recovery effort to minimize the resulting damage. Ferrotyping can also be avoided through proper storage environment. If a print is framed, be sure that it is not in contact with the glazing. Tears and other physical damage may place the photograph at greater risk if affected areas are fragile or otherwise vulnerable to continued damage.

Chemical decay usually cannot be reversed. Intensification and other forms of chemical treatment are very risky and, even at their best, do not return prints to their original state. The use of intensification on fine art prints to reverse the appearance of silver image degradation is considered unethical in many situations. Furthermore, experiments have shown that its use with gelatin silver prints is very dangerous and often results in damage to the gelatin binder. Other forms of chemical treatment may be able to reduce or eliminate yellow/orange discoloration and mirroring, though any form of chemical treatment carries certain risks and must be evaluated carefully. There may be some situations in which the type of print, its condition, age, and deterioration justify the risk of certain types of chemical treatment. Such decisions must be made on a case-by-case basis.

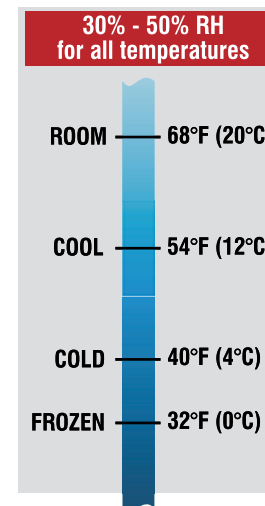
The best treatment for chemical decay is proper storage. Prints that were poorly processed will inevitably undergo a certain amount of yellowing, fading, or discoloration. There is no effective treatment that can be done to prevent this, except for toning, which should be done during the initial photographic processing if the print is intended to last for a long time. However, the vast majority of prints were not improperly fixed or washed, they are simply more or less susceptible to chemical decay as a result of the natural tendency of silver to oxidize (or tarnish) and thereby undergo various chemical changes. Although it is often impossible to predict which prints are most sensitive to fading and discoloration, we do know what causes this to occur most quickly: high temperatures, high relative humidity, and air pollutants.

Recommendations for the Storage of Gelatin Silver Prints

Proper storage conditions are the most effective method of ensuring the long-term preservation of gelatin silver prints. But what qualifies as proper storage conditions? In the most general terms, proper storage means cool and moderately dry conditions, and appropriate storage materials.

Since nearly every form of deterioration is dependent on heat and moisture, it is important to keep your photographs out of the attic or other rooms with extremes in temperature and relative humidity. Room temperature is acceptable, but cool or cold is preferred when it is practical, and when humidity can be controlled under those conditions. Freezing storage can be used, but it is not always practical for access, and in the case of gelatin silver prints does not provide a substantial enough advantage over cold storage to warrant the added expense (Figures 31 and 32). (Other types of photographs, such as color materials, or negatives and transparencies on cellulose acetate film base, strongly benefit from the use of frozen storage). Relative humidity should be kept moderately low, between 30 and 50%. High RH will accelerate chemical decay and even cause the growth of mold, while prints at lower RH will become brittle and more prone to cracking and other mechanical decay.

ROOM	Fair
COOL	Good
COLD	Very good
FROZEN	Very good



Poor-quality storage materials can also be harmful to gelatin silver prints. If possible, prints should be stored in photographically inert enclosure materials such as 100% cotton rag or 100% alpha cellulose fibers. If a storage material has passed the Photographic Activity Test (PAT), a very stringent testing method, you can be assured that it will not harm the silver image or cause staining of the gelatin.

Above left

Figure 31: Simplified storage recommendations for gelatin silver prints

Above right

Figure 32: The four temperature categories. Room, Cool, and Cold refer to “anchor-point” temperatures of 68F, 54F, and 40F, while FROZEN refers to all temperatures 32F and below.

(Courtesy Image Permanence Institute)

Looking Forward

Careful examination of gelatin silver prints and an understanding of how they deteriorate gives the print collector, connoisseur, conservator, or archivist another tool to gain insight into the photographer's working methods, the subsequent history and care of a print, and its requirements in future storage, handling, and display.

Everyone has a slightly different reason for looking. Some want to know when the print was made, others are interested in how it was made, or perhaps simply in better understanding its current condition. The collector might wish to discriminate between deterioration and original intent, while the conservator must understand more precisely the material or chemical nature of the deterioration in order to more safely and effectively carry out a conservation treatment. Archivists may be responsible for large collections, and preventing further deterioration is a fundamental aspect of their work. For them, a greater awareness of deterioration may illuminate the consequences of neglect, and help them set guidelines in the storage and handling of their collections.

For these and many other individuals interested in gelatin silver prints, condition and deterioration is often one of many avenues of inquiry, and its understanding deepens their appreciation and enjoyment of the black-and-white photographic art form.

However, an understanding of condition and deterioration is only one tool among several that are being developed within the conservation field to gain a deeper understanding of the gelatin silver print. The fiber-base gelatin silver print is remarkably complex and diverse. There is no single type of print, any more than there is a single type of automobile. From the paper support to the baryta layer, to the gelatin binder, every aspect of the gelatin silver print has been manufactured in different thicknesses, with different compositions, with raw materials from different geographic locations, applied with different machines, made with different additives, and with many and varied textures and surfaces. The resulting variety of photographic papers that fall under the umbrella of fiber-base gelatin silver print is staggering. This diversity allows for many different areas of investigation.

Recent areas of study include the appearance and fading of optical brightening agents, the identification of fibers from the paper support as a means of dating, and even the ratio of barium and strontium within the baryta layer! An area of research that has shown particular promise in recent years is surface. The nature of the print surface is influenced by a variety of manufacturing choices including the preparation of the paper, the thickness of the baryta, and the addition of various matting agents in the gelatin binder and topcoat. The surface can be studied analytically, but it can also be studied effectively with the unaided eye or with low-power magnification as an important aspect of the aesthetic history of black-and-white prints and the choices that photographers made in their own work.

The twentieth century is behind us and many people now view gelatin silver prints as an historic or alternative photographic process. We are in a period of rapid and profound transition, in which these prints are viewed differently than they were only a few years ago, when traditional silver-based photography was transitioning to digital photography. As one of the most significant visual records of the twentieth century, these artifacts are valued more and more every day. This ever-increasing value means something different to each collector, scholar, archivist, conservator, appraiser, student, or connoisseur, all of whom would do well to enhance their discriminative knowledge of the twentieth-century's gelatin silver print.

PATHWAYS: Deterioration in Detail

P1: YELLOW/ORANGE DISCOLORATION, EDGES OR OVERALL

Well-processed prints in good condition are readily susceptible to this form of silver image deterioration. Yellow/orange discoloration is caused by exposure to air pollutants that oxidize the silver metal to silver ions (in the presence of moisture and heat), and then reduce them back to metallic silver after a brief period of travel through the gelatin (see Figures 16 and 17). Peroxides are particularly effective at causing this discoloration, because they have the unique ability to act as both an oxidizing and reducing agent in relationship to silver. These silver ions travel through the gelatin and reform as numerous smaller silver particles, known as colloidal silver. The colloidal silver particle size



that results from exposure to peroxides causes the silver to appear yellow/orange in color.

Water is also a key participant in this deterioration mechanism. Higher relative humidities cause an increase in gelatin moisture content, which causes an increase in the ability of pollutants to enter the gelatin, and the ease with which silver ions migrate within the gelatin. In addition, water is the medium in which these oxidation/reduction reactions occur. This is why a moderately dry environment is so beneficial in the preservation of gelatin silver prints.

The dependence of the deterioration upon exposure to air pollutants results in the edges being affected first, while more intense or long-term exposure may cause overall discoloration (Figures 33 and 34). It has been shown in the case of silver-mirroring that enhanced deterioration along the edges is due to the relationship between a flat object such as a photographic print and the concentration gradients of the gases in the surrounding space, which leads to greater exposure of the edges to airborne contaminants. It is reasonable to assume that any deterioration resulting from exposure to air pollutants will follow similar edge patterns.

Left

Figure 33: This detail of a gelatin silver print exhibits yellow/orange discoloration in the light midtones across the entire print. This is the result of exposure to high concentrations of peroxides from fresh oil-based paint (see Sidebar 4).

Right

Figure 34: This detail of yellow/orange discoloration on a gelatin silver print shows the typical edge deterioration pattern resulting from exposure to air pollutants.

Whether it occurs along the edges or overall, yellow/orange discoloration is limited to the light midtones. Non-image areas do not have silver and will not be affected. Shadow areas are also not affected.

Yellow/orange discoloration is commonly caused by exposure to peroxides from fresh oil-based paint or varnish, though it has also been observed in warm and humid conditions when the print is exposed to unknown pollutants in urban air (see Sidebar 4). Prints that are displayed unframed or without glazing are more easily affected by this form of deterioration since they are more directly exposed to air pollutants.



P2: SILVER-MIRRORING, EDGES

Over time some air pollutants (in the presence of moisture and heat) can create a sustained migration of silver ions in all directions. When these silver ions reach the print surface, they form a reflective layer of silver, commonly referred to as mirroring or silver-mirroring. It is most easily seen when the print is examined in specular light, and it appears as a highly reflective sheen with a bluish cast. Mirroring only occurs in the shadow areas of the print where there is sufficient silver, which can be clearly seen in the print by Alfred Stieglitz, shown here in both standard lighting (Figure 35) and specular lighting (Figure 36).



Left
Figure 35: Alfred Stieglitz, *Lake George*, ca. 1930

Right
Figure 36: Alfred Stieglitz, *Lake George*, ca. 1930. The silver-mirroring is emphasized in this photograph by the use of specular lighting.

(Courtesy George Eastman House, Acc. No. 1974.0052.0033)



Above
Figure 37: Edward Weston, *Shells*, 1927. Shown here as reproduced in a Sotheby's auction catalog, this print exhibits the classic pattern of silver-mirroring along the edges. The story of the removal of the mirroring is told in Sidebar 6. (Reproduced by permission of Sotheby's, Inc.)

When silver-mirroring forms preferentially along the edges, it indicates that air pollutants play a role in the oxidation of the silver. The mirroring then moves slowly inward, creating a halo-like effect around the center of the image (Figure 37). Be aware that mirroring, though often a good indicator that a print is at least 20 or 30 years old, can also be removed from a print, as described in Sidebar 6, or even added.

Mirroring along the edges caused by air pollutants can be mimicked by a poor-quality window mat (P3). It has been observed that mirroring often does not occur on poorly processed prints. The sulfur from the residual fixer combines with the silver ions to form stable silver sulfide before the silver can travel all the way to the surface.

Silver-mirroring is closely related to yellow/brown discoloration and fading (P4–6). When the same oxidation and migration of silver that produces silver-mirroring in the shadows occurs in the midtones and highlights, the result is fading and or warming of the image, depending on the size, density, and composition of the resulting silver particles. This can be clearly seen, for example, in Figure 36.



Below
Figure 38: Edward Weston, *Shells*, 1927. Shown here as reproduced in the Phillips auction catalog, April 23/24 2004, the print no longer exhibited any silver-mirroring. (Reproduced by permission of Phillips de Pury & Company)

P3: SILVER-MIRRORING, OVERALL OR LOCALIZED



Figure 39: A gelatin silver print from Albert Mebes' 1913 *Der Bromsilber- und Gaslichtpapier-Druck*. Overall silver-mirroring has resulted from contact with the book's paper that contains unpurified wood pulp.

While fully purified wood pulp is harmless to photographs, and in fact has been used for photographic paper base since the 1920s, paper and boards made from wood pulp (from which the non-cellulose components have not been fully removed) can cause staining of the gelatin and image silver degradation. Such unpurified wood pulp contains lignins and other extractives, which may cause silver-mirroring when left in proximity to a gelatin silver print. Paper materials that often use this wood pulp include newsprint, grayboard, and cardboard.

Image silver degradation can occur locally or overall depending on the size and shape of the offending material and its contact with the print. If the poor-quality core of a matboard is exposed to the print only along the edges, it can result in edge mirroring, mimicking the effect of air pollutants, as discussed in Pathway 2. If overall contact occurs with a poor-quality paper then mirroring will appear overall in the shadows (Figure 39).

Gelatin staining caused by paper materials made with unpurified wood pulp is discussed in Pathway 7.

P4: YELLOW/BROWN DISCOLORATION AND FADING, EDGES

Yellow/brown discoloration and fading occurs along the edges of a print for two reasons: air pollutants or storage materials. Air pollutants will cause edge discoloration due to concentration gradients in the air surrounding the print, while a window mat may expose only the edge of the print to the deteriorating effects of a poor-quality matboard. This discoloration and fading is often limited to the highlights and midtones, while the shadows remain unaffected, or exhibit some silver-mirroring. Yellow/brown discoloration and fading can be clearly seen on the edges of Edward Weston's print, *St. Roche Cemetery* (Figure 40).



Yellow/brown discoloration and fading of the photographic image is the classic form of gelatin silver print deterioration. The mechanism is the oxidation of silver to silver ions and the migration of these silver ions through the gelatin (see Figures 16 and 17). The final disposition of these silver ions is what determines the visible result of deterioration. Some of the silver ions will remain as silver ions—they are invisible. Other silver ions nucleate new silver particles that are smaller than the original. Depending on their size, these will be invisible or yellowish in color. Still others may react with sulfur to form silver sulfide—a very stable compound. Silver sulfide can be invisible (very small particles), yellow (medium size particles), or brown (large particles) depending on both the size and the concentration of the particles. These varying fates of the silver ions explain why the effect of silver image degradation is unique for the different densities in an image. The light highlights of deteriorated prints are often faded because the small quantities of silver form very small particles of silver or silver sulfide. The darker highlights and midtones are yellow/brown because of the larger amount of silver available for particle formation, and the shadows are brown-black or even neutral. The shadows are the last to be affected, and for various reasons often retain their original color.

It is interesting to observe the difference between the results of sulfiding when it occurs over time through the deterioration mechanisms discussed here and the sulfiding achieved by toning. When the formation of silver sulfide

is made to occur quickly, as in sulfide toning, the size of the silver particles is more nearly maintained and an overall brown coloration is achieved. In contrast to sulfide toning, when sulfiding occurs over time by exposure to air pollutants or poor-quality storage materials, the silver has had time to oxidize and travel through the gelatin. This leads to smaller particle size, and the resultant fading and yellowing.

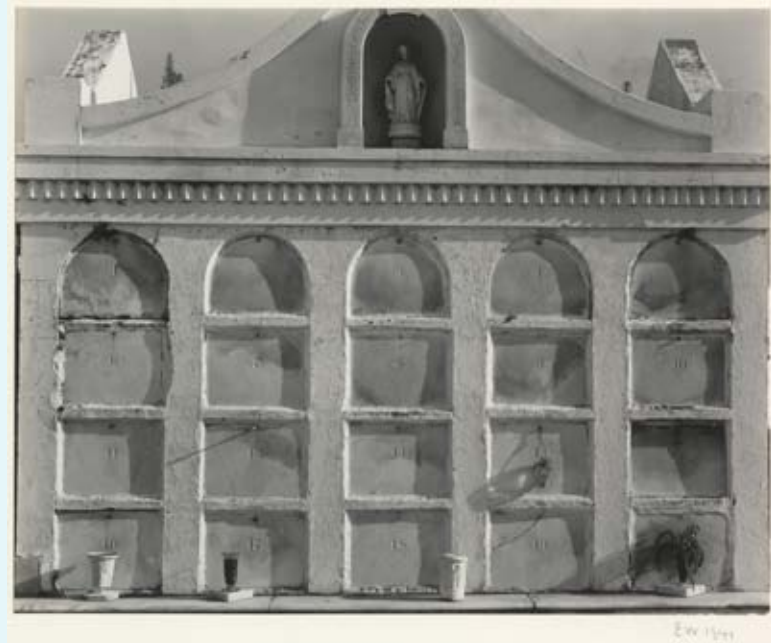


Figure 40 (and detail): **Edward Weston, *St. Roche Cemetery*, 1941. Yellow/brown discoloration and fading commonly occur at the edges of a photograph when deterioration is the result of exposure to air pollutants.**

(Courtesy George Eastman House, Acc No. 1966.0070.0008; ©1981 Center for Creative Photography, Arizona Board of Regents)

P5: YELLOW/BROWN DISCOLORATION, OVERALL



Yellow/brown discoloration and fading, as described in Pathway 4, may also occur over the entire image after prolonged exposure to air pollutants in the presence of water (i.e. high RH will accelerate deterioration). It can also be caused by contact with poor-quality storage materials or by faulty processing. However, these two causes may also create yellowing in the non-image areas (P7).

In its most subtle and charming form, this deterioration appears as the slightest warming of the neutral image, visible only in the highlights and midtones. This patina can be a seductive attribute of an aged print, but it must also be understood for what it is—a form of decay that can ultimately lead to loss of highlight details and overall yellow/brown discoloration of the image silver. As with edge discoloration, the shadows often retain their original tonality or gain only subtle warmth of color. Sometimes the shadows will exhibit silver-mirroring (P3) while the highlights and midtones fade and discolor.

It is often assumed that this form of deterioration is a result of poor processing. While this can be true in some cases, it is an oversimplification that does not do justice to the complexity of gelatin silver prints. Every factor in Figure 13 plays a role in the relative stability of a gelatin silver image over time. Processing is one of these factors, but even processing is not a simple question of good or bad. Processing yields prints with varying degrees of resistance to deterioration across a broad spectrum from nearly bulletproof when a print is sulfur toned, to very susceptible to decay, such as an improperly washed or fixed print. Beginning with this variable degree of protection, prints are then exposed to a broad spectrum of environmental conditions including differences in temperature, humidity, and air pollutants. When examining a print with overall yellow/brown discoloration, keep these factors in mind, and do not jump to the conclusion that simply because the print is discolored and faded, it must have been processed poorly. Poor processing is discussed in Pathway 6, and while there are some cases where poor processing is certainly the cause, in most cases it is not so cut and dry.

Left

Figure 41: This gelatin silver print of Winston Churchill by Yousuf Karsh shows very slight warming of the image. Karsh processed his prints very carefully, and it is not likely that this print was poorly processed. However, this print was not kept by a museum, and was subjected to unknown conditions, which may have included extremes of temperature, relative humidity, and light. Careful processing and perhaps toning have protected this print very well, even though the image silver has undergone some deterioration. (Image © Yousuf Karsh)

Center

Figure 42: Paul Woolf's gelatin silver print of the New York skyline is more strongly discolored than the Karsh print, but poor processing may not be the culprit. The non-image areas or whitest highlights are not yellowed, so poor fixing or washing may not be to blame. It was probably not toned, and may have been washed for too long, leaving the silver image vulnerable to oxidation and migration. The image is partially converted to silver sulfide and is thus likely to be quite stable and not prone to further deterioration. (Courtesy Keith de Lellis Gallery)

Right

Figure 43: This image of Lewis Hine's *Powerhouse Mechanic* may be our best candidate for poor processing. The highlights have dramatically faded, and even the deepest shadows exhibit a significant color shift. Although there is no white border to help identify yellowing of the non-image areas, there does seem to be yellowing of the non-image area highlights (specular highlights) within the print, such as the reflections in the steel above the mechanic's head. (Courtesy George Eastman House)

P6: YELLOW/BROWN DISCOLORATION AND FADING, LOCALIZED

Localized yellow/brown discoloration and fading is generally caused by storage materials or faulty processing. It is similar to overall discoloration (P5), except that poor processing is much more often the cause, and this is often very obvious. A common example is storage against a label that is adhered to the back of another print, leading to discoloration in the shape of the label. Another example is the partial overlapping of prints in the fixing or washing baths. This prevents complete fixing or washing in the overlapped area, leading to yellow/brown discoloration in the shape of the overlapped print. This yellow/brown discoloration is silver sulfide that forms when the residual fixer decomposes and reacts with the image silver. The residual fixer may also react with the residual silver from the fixing bath and result in yellow/brown discoloration even in areas with no image silver such as white borders or other non-image areas such as specular highlights.



Figure 44: Lewis Hine, *Preparing hot-house frames, truck garden, NY state, ca. 1920*. This print is an excellent example of poor processing that leads to image discoloration. It appears that another print was in partial contact with this print during fixing or washing, as evidenced by the right-angle shape of the discolored area. (Courtesy George Eastman House, Acc. No. 1978.1000.0004)

P7: YELLOWING OF NON-IMAGE AREAS AND HIGHLIGHTS



Above
Figure 45: Alfred Stieglitz,
Equivalent, 1929 (Courtesy
George Eastman House, Acc. No.
1974.0052.0023)

Right
Figure 46: Alfred Stieglitz,
Equivalent, 1931 (Courtesy
George Eastman House, Acc. No.
1974.0052.0013)



Yellowing of non-image areas can occur for two reasons: faulty processing and contact with poor-quality storage materials. Although the visible result can be similar, the two forms of yellowing are very different in nature.

Faulty processing results in silver-fixer compounds remaining in the print after processing. This can be the result of not enough time in the fixing bath, exhausted fixer, or not enough washing. The results are not immediately visible, but over time the fixer (sodium thiosulfate) breaks down and reacts with the silver to form small particles of yellow silver sulfide across the entire print. This weak yellow staining is generally only visible in the non-image areas and highlights, while in the midtones and shadows it is masked by the silver image. The residual fixer will decompose and react with the silver image, causing yellow/brown discoloration of the image in the highlights and midtones. If faulty processing is the cause of discoloration, silver-mirroring will likely not be seen, since the sulfur in the print reacts quickly with the silver ions, preventing their passage to the print surface (Figure 45).

These two *Equivalents* by Alfred Stieglitz were made during the same time period and likely processed using a similar technique. However, one has yellowed (Figure 45), while the other remains in excellent condition (Figure 46). The yellowing appears to be present in the highlights, indicating faulty processing, although the lack of clearly defined non-image areas makes it difficult to know for certain.

Poor-quality storage materials may also cause overall yellowing of the gelatin, which will be most visible in the non-image areas and highlights. Although it can have a similar appearance, it is not caused by yellow silver sulfide as described above. It is usually a very subtle yellowing and is a result of interactions between the gelatin binder and components of paper materials made from wood pulp from which lignins have not been fully removed (see Sidebar 2). The slight discoloration of the gelatin can impart to the print a certain aged, mellow quality that is often associated with older prints. In exceptional cases, the gelatin staining can be quite severe (Figure 47).



Figure 47: The gelatin silver prints on the first and last pages of this photograph album exhibit strong yellow staining of the gelatin as a result of their close proximity to the covers, which were made with lignins-containing board. Pictured here are the front cover (top), a page near the middle of the album that was not strongly affected by the covers (left), and the last page that was in contact with the back cover (right). (Courtesy Katharine Whitman)

P8: IMAGE DETERIORATION IN LOCALIZED AND IRREGULAR PATTERNS

Uneven processing or other chemical contamination can result in uneven localized image deterioration. Fingerprints with yellow/brown discoloration are sometimes seen. This can result from the handling of prints with fingers contaminated with developer or fixer solutions. Even clean hands can result in yellow discoloration as the salts present in sweat transfer to the photograph (Figure 48).

Another cause might be a mounting or other adhesive applied to the back of the print. Such adhesives may be hygroscopic and increase the localized water content in the photograph, thus enhancing deterioration. If the adhesive were a rubber cement, it could cause yellow staining as the adhesive aged or as sulfur-containing components of the adhesive reacted with the image silver.



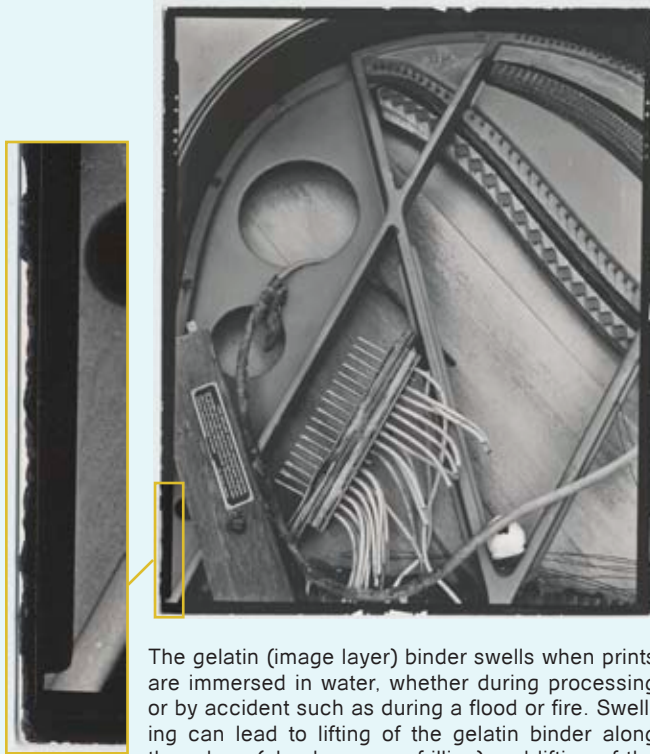
Figure 48: Edward Weston, [Tina Modotti], ca. 1925. This detail shows a silver sulfide stain caused by touching the print surface with fingers contaminated with processing chemicals such as fixer. (Courtesy George Eastman House, Acc. No. 1974.0061.0141; ©1981 Center for Creative Photography, Arizona Board of Regents)

The causes of other spots and uneven patterns of deterioration may remain a mystery when the details of a prints history are not known, although an understanding of Pathways 1–7 often enable one to form a reasonable hypothesis.



Figure 49: Lewis Hine, *From Sicily*, ca. 1905. Silver sulfide stains caused by what appears to be contamination by processing chemicals. (Courtesy George Eastman House, Acc. No. 1977.0177.0007)

P9: GELATIN BINDER LIFTING, EDGES OR LOCALIZED



The gelatin (image layer) binder swells when prints are immersed in water, whether during processing or by accident such as during a flood or fire. Swelling can lead to lifting of the gelatin binder along the edges (also known as frilling) and lifting of the gelatin binder across the print as small bubbles (also known as blistering). The potential for damage to the gelatin binder is dependent on factors such as the length of immersion, the temperature of the water, the pH of the water, the amount of agitation, and the sensitivity of the gelatin binder. The only one of these factors which is a function of the print itself is the sensitivity of the gelatin, which is dependent on the degree of hardening. The sensitivity of the gelatin to water damage can also be increased by mold (P12).

Chemical hardening of the gelatin binder occurs during manufacture of gelatin silver paper as well as during processing.

Figure 50: Edward Weston, *Meraux Plantation House, Louisiana* [piano close-up], 1941. Frilling of the gelatin binder can be seen at the lower right edge of this print. As the print does not appear to have been damaged in a fire or flood, the frilling is most likely a result of the original processing. (Courtesy George Eastman House, Acc. No. 1973.0248.0002; ©1981 Center for Creative Photography, Arizona Board of Regents)

Hardeners such as formaldehyde or chrome alum create links between the gelatin molecules. The effect is to decrease the swelling that occurs when the paper is immersed in water. Hardening is a balance—too much and the gelatin does not allow sufficient penetration of processing solutions—too little, and the gelatin binder swells excessively, and is more prone to mechanical damage during processing as well as frilling and blistering.

The secretive nature of early manufacturing obscures any detailed knowledge of hardening practices and when they began. However, conservation treatment experience indicates that early gelatin silver papers are often very sensitive to water. In addition, photographic literature of the late nineteenth and early twentieth century often implies that early gelatin silver prints, ca. 1885–1900, were not hardened during manufacture, or were only lightly hardened.

Frilling of the binder along the edges of the print can be a part of the original processing. This is seen particularly on prints that receive processing beyond the standard develop/stop/fix, such as bleaching and redevelopment, reducing, or toning (Figure 50).

Floods and fires may also lead to frilling or blistering (Figure 51).



Figure 51: Edward Weston, *Pepper*, 1930. This print appears to have been damaged in a disaster. Details show frilling along the edges and blistering near the center of the print (see also Figure 21). (Courtesy George Eastman House, Acc. No. 1970.0162.0004; ©1981 Center for Creative Photography, Arizona Board of Regents)

P10: STAINING AND TIDE LINES



When a gelatin silver print is immersed in water, stains may be caused by the transfer of colored substances from nearby materials. This could be brown organic matter from paper materials made from unpurified wood pulp, or the bleeding of ink stamps or writing from the back of the print. This most often occurs as a result of water damage from floods or the extinguishing of fires (see Figure 22 and Sidebar 5).

Prints that are signed or otherwise annotated in ink are in danger of not only staining, but of loss of markings that are important to the provenance or value of the print. For these reasons, a pencil rather than a pen should be used for the marking of prints or enclosures.

Figure 52: **Anonymous, [Portrait of a young man, front and back of print], ca. 1930.** This undated portrait has tide lines from water damage at some point in its past. Despite the obviously poor treatment that this photograph has received, the image is in remarkably good condition. This is attributable entirely to sulfur toning, which has converted the image to silver sulfide. (Collection of the author)



P11: FERROTYPING AND OTHER SURFACE CHANGES

Even brief exposure to water will cause some change in the surface qualities of a gelatin silver print. This may be a subtle change in many cases, while on some prints it will be quite noticeable. For example, a ferrotyped print, which was initially dried against a smooth metal surface to produce a high gloss, may lose its high gloss after wetting and air drying.

Ferrotyping is not only a technique used to produce a high gloss on fiber-base prints. It also refers to a form of print damage, when a print is exposed to water or a high relative humidity while in contact with a smooth surface. The gelatin swells and reforms in the shape of the surface it is contacting. A common example is when framed photographs are pressed against their protective glass and either accidentally exposed to water or exposed even briefly to a warm and humid environment. These types of surface changes are most easily observed in specular light, as can be seen in the images of an Edward Weston print in normal (Figure 53) and specular lighting (Figure 54).



Left

Figure 53: Edward Weston, *Belle Grove Plantation House, Louisiana* [open window], 1941.



Right

Figure 54: Edward Weston, *Belle Grove Plantation House, Louisiana* [open window], 1941. The ferrotyping damage is emphasized when specular illumination is used.

(Images Courtesy George Eastman House, Acc. No. 1966.0070.0040: ©1981 Center for Creative Photography, Arizona Board of Regents)

P12: MOLD GROWTH



The properties of gelatin as it interacts with water make it an ideal photographic binder, but as we have seen, it also makes it susceptible to damage by water. As a hygroscopic protein, gelatin is also an excellent medium for biological growth.

If prints remain damp or in conditions of 70% RH or higher for more than a day or two, there is a high risk of the onset of mold. These microbes secrete enzymes that breakdown the gelatin, allowing it to dissolve easily in water. Damp basements, water leaks in the storage area, floods, and the extinguishing of fires with water are all conditions that often lead to mold growth. If there are limited environmental controls, even high humidity weather conditions can be enough to place your photographic materials in danger.



Left
Figure 55: Lewis Hine, [Portrait of worker, Empire State Building], ca. 1931. Water-damaged photographs often exhibit severe mold damage and consequent staining and loss of emulsion.

Right
Figure 56: Lewis Hine, [Portrait of worker, Empire State Building], ca. 1931. Specular lighting highlights the loss of sheen resulting from the breakdown of the gelatin binder.

(Images Courtesy George Eastman House, Acc. No. 1977.0154.0066)



The growth of mold weakens the gelatin, but it will also likely create stains that will be very difficult to remove, since treatment in water becomes difficult once the gelatin has been weakened. The colors of mold vary, and black and red stains are commonly found on mold damaged photographs (Figure 55). Mold damage to the gelatin binder will always result in a loss of gloss in the print surface, most noticeable in specular lighting (Figure 56).

Mold may also grow on the paper support or mount, though it will not weaken the paper as rapidly as the gelatin binder. Staining and tide lines are often seen on the paper, though these may not be visible when viewing the print from the front.

P13: PLANAR DEFORMATION OR COCKLING

The two primary layers of a gelatin silver print, the paper and the gelatin binder, expand and contract at different rates in response to changes in relative humidity and temperature. To understand this better, first consider a sheet of uncoated photographic paper and a sheet of gelatin separately. The sheet of gelatin is uniform in its composition and will expand and contract uniformly along its width and length. In contrast, the sheet of uncoated photographic paper has a grain direction, meaning that the paper fibers are oriented preferentially in a single direction, called the machine direction. This is the direction of travel of the paper as it was being formed on a papermaking machine. An interesting property of paper fibers is that when they are wetted, their width increases more than their length. So a sheet of paper will expand more across its width (against the grain, or cross machine direction) than it will along its length (with the grain, or machine direction).

Now let us return to a gelatin silver print. When it is wetted, the paper and the gelatin both expand and become limp. As it dries the gelatin contracts equally in both directions. The paper and gelatin shrink about the same amount along the width of the paper (against the grain), but in the grain direction, the paper does not shrink nearly as much. The result is that as the gelatin dries and shrinks it pulls the paper up, causing a curling of the paper. Keep in mind that the grain direction is not necessarily related to the orientation or the size of the image or the paper.

The above description is the very simplest case and is the cause of print curl. However, what if the paper dried along the edges faster than at the center, or the gelatin dried before the paper, or the mounting prevented the print from expanding along the top edge? Any of these and many more situations like them, which influence the expansion or contraction of the paper or the gelatin, will cause planar deformation or cockling either locally or overall.

Figure 57: Leon Levinstein, *Residential Area, Morgantown, West Virginia, June 1935, 1935*. Planar deformation of this print is accentuated by photography in raking light, and includes cockling along the top edge of the print and a slight curling of the vertical edges, indicating a horizontal machine direction. (Courtesy George Eastman House, Acc. No. 2004.0852.0008; ©Howard Greenberg Gallery, NYC)



P14: *EMBRITTELEMENT OF THE PAPER SUPPORT*

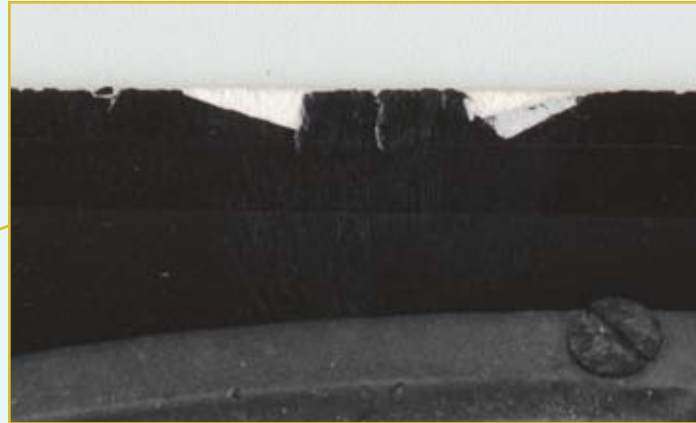


The flexibility of a photographic print is an important quality in its long-term physical stability. This flexibility enables it to withstand the rigors of handling with a minimum of damage. Flexibility can be lost over time as the paper is exposed to moisture, heat, and the degrading effects of poor-quality storage materials. These can lead to a shortening of the cellulose chains and a consequent embrittlement of the paper support. This loss of flexibility, combined with improper handling, may lead in turn to cracking of the photograph. Generally speaking, photograph supports are of very high quality, and it requires a very poor environment to cause this level of decay. However, older photographs, particularly those made before the 1930s, have more variability in their quality, and may be more prone to brittleness.

Figure 58: **Lewis Hine, [Slums, shantys, and people], ca. 1910. Embrittlement of the paper has led to significant losses along the edges of the print. (Courtesy George Eastman House, Acc. No. 1978.1025.0026)**

P15: TEARS, CREASES, ABRASION, ETC.: EDGES

Figure 59: Edward Weston, *Meraux Plantation House, Louisiana* [piano close-up], 1941. Delamination of the paper support and folding-over of the image layer and upper layer of the paper support are clearly evident in this detail of the top edge. (Courtesy George Eastman House, Acc. No. 1973.0248.0002; ©1981 Center for Creative Photography, Arizona Board of Regents)



Damage to a print as a result of handling and poorly designed storage is one of the most common forms of deterioration. Such damage generally occurs very quickly and proper handling and storage will prevent any further damage.

The edges and corners are particularly vulnerable to mechanical damage as they are most often in contact with hands, mounting corners, and other objects. The most common forms of damage include bending of the corners, delamination of the paper support, and separation of the gelatin binder from the baryta layer. Left untreated, this can lead to areas of complete loss of the image layer along the edges.

P16: TEARS, CREASES, ABRASION, ETC: LOCALIZED

While edges are often the first and most common place to find mechanical damage, the surface of the print can also be affected. Damage to the surface often has an influence on the viewing of the print. Scuffing, light scratches, and minor surface abrasions are quite common on older prints, and can be quite distracting depending on their severity. The image itself is not usually affected, since the topcoat protects the image layer. In addition, the silver is distributed throughout the image layer, such that small losses at the surface do not remove an appreciable quantity of silver image.

More severe forms of mechanical damage include creasing or tearing of the photograph, deep scratches, and complete loss of areas of the print—most often the corners.

Left

Figure 60: Lewis Hine, *Italian family looking for lost luggage*, 1905

Right

Figure 61: Lewis Hine, *Italian family looking for lost luggage*, 1905. This detail, taken with specular illumination, highlights surface cracking that resulted from flexing of the print. Cracks in the image layer are not common, as it requires significant stress to induce them. This may occur when the gelatin image layer of a print has become brittle and is then flexed. Such lack of flexibility may be the result of age-embrittlement or very dry conditions, such as below 20% relative humidity.

(Courtesy George Eastman House, Acc. No. 1977.0177.0134)



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