Chapter II:

THE COMPONENT MATERIALS OF 19TH-CENTURY PRINTS AND THEIR FORMS OF DETERIORATION

The structures and component materials of 19th-century photographic prints are vulnerable to a variety of forms of deterioration. This chapter presents a general discussion of those structures and materials; the next chapter addresses the specific stability problems of individual processes. The extreme diversity of types of 19th-century prints should be apparent even from the brief history in the previous chapter. In the face of this diversity, a general knowledge of the component substances of prints, their behavior during long-term keeping, and especially of the problems caused by their laminate structures will help to establish appropriate handling procedures and environmental keeping conditions.

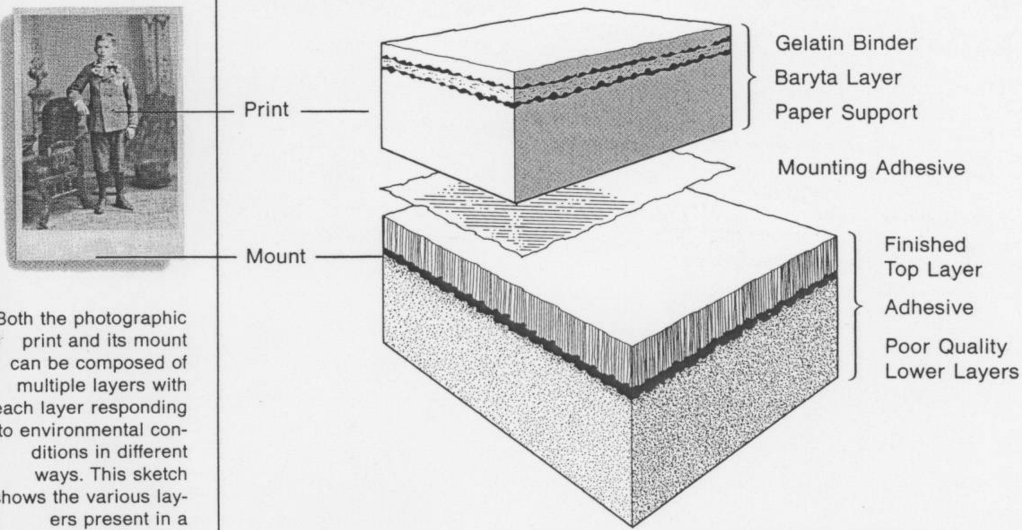
In assessing stability problems it is useful to consider photographic print materials in the light of a structural analysis in which the following "generic" components appear:

1. Final image material
2. Binder
3. Support
4. Secondary support
5. Surface treatments and adhesives

Not all 19th-century prints have all five of these components, but most do. In the discussion that follows, each component is defined and the properties of substances used in 19th-century prints are examined.

FINAL IMAGE MATERIALS

The image in every photograph is created by something that absorbs or scatters light. The substance which actually comprises the image in the finished, processed photograph is known as the *final image material.* In the case of prints, the final image material selectively absorbs light that would otherwise be reflected from the paper support. The final image material in most 19th-century prints is finely divided metallic silver, but a number of other substances can also be found.



Both the photographic print and its mount can be composed of multiple layers with each layer responding to environmental conditions in different ways. This sketch shows the various layers present in a mounted gelatin printing-out paper print.

In a real sense the final image material is the most important part of a print because it physically embodies the pictorial information. If nothing else were known about a photograph except the nature of its final image material, a general assessment of its relative permanence and many of its specific stability problems could still be made. For example, knowing that an image consists wholly or partially of metallic platinum would suggest that it would be quite resistant to fading, because platinum is a very stable chemical substance which does not easily oxidize or tarnish. On the other hand, knowing that part of the image in a print is applied watercolor might cause concern about light damage to its delicate pigments.

METALLIC SILVER

By far the most important final image material found in 19th-century photographs is *metallic silver.* All of the 19th-century print processes based on the light sensitivity of silver compounds formed images made of silver metal. The differences in appearance and variations in relative permanence among silver images depend on the *physical form* of the silver in the image deposit. An untoned salted paper print, for example, has a very reddish image color, while a contact-speed developing-out paper has a nearly neutral black image hue, even though both images consist only of metallic silver. Under adverse environmental conditions, the salted paper print will fade and lose highlight detail far more rapidly than the developed-out print.[15] The reasons for this have to do with the physical form of the silver image rather than any profound chemical differences. All silver images are made up of discrete particles so small that an electron microscope is needed to resolve them. The color and durability of silver images depend in a complex way on the exact size and shape of these particles, and on how closely they are packed together.[16]

Generally speaking, relatively small silver particles give warm image colors—yellows, reds and browns—while relatively large particles create black or nearly neutral images. Particle shape "fine-tunes" the effects of particle size. Highly elongated or irregular silver particles tend to make an image more neutral black than the same amount of silver in spherical particles. A third influence on image color is the closeness of the particles to each other. A compact group of particles interact with light as if they were a single, larger particle, and therefore produce a more neutral image. The nuances of image color among photographs with silver as the final image material stem from the interplay of these submicroscopic structural features.

Forms of Silver in 19th-Century Prints

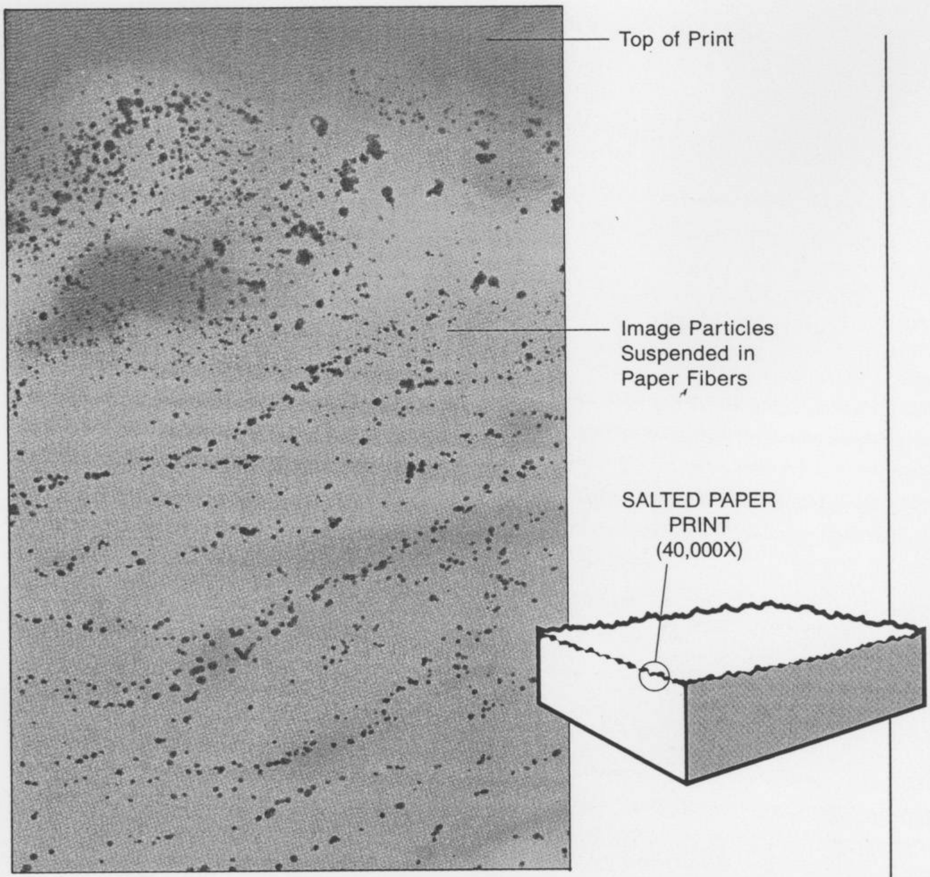
The microstructure of silver images, so crucial to their color and relative resistance to deterioration, originates during the initial formation of the image. There are three basic structural forms in which silver images occur: photolytic silver, physically developed silver, and filamentary silver.

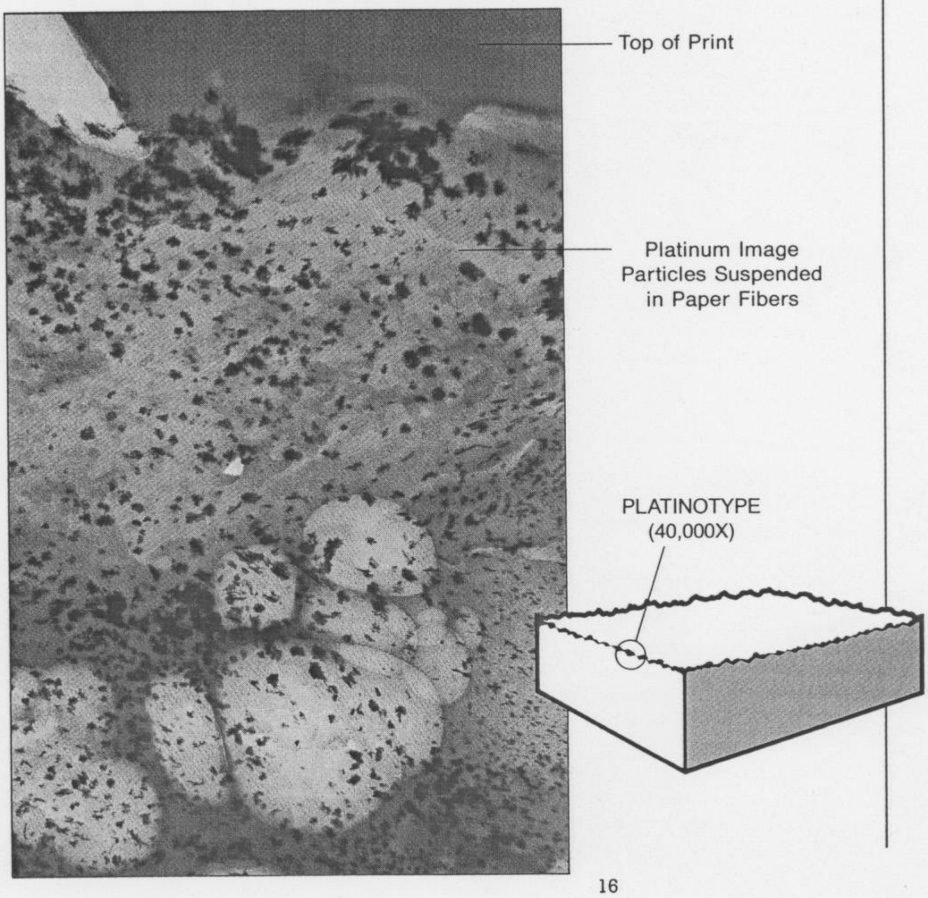
In all of the printing-out processes—salted paper prints, albumen prints, and gelatin and collodion printing-out papers—the image deposit is composed of *photolytic silver.* "Photolytic" literally means "separated by light." Of the three structural types of silver images, photolytic silver has the smallest particle size and produces red or brown image colors. Photolytic silver particles are roughly spherical. The images they produce have smaller and fewer particles in highlight areas than in shadow areas because the particle size is directly proportional to the amount of light received during exposure.

In a silver image formed by the use of a developing solution after a brief exposure to light, the physical form of the silver particles is determined by the nature of the developer.[17] However, development always creates larger particles than occur in photolytic silver. Developed-out images have near-neutral image colors, with individual particles which are often slightly larger in highlight than in shadow areas. The higher density of the shadow areas is caused by more, not larger, particles.

Certain developers produce round particles of a size up to several hundred times larger than photolytic silver particles. Such image deposits are known as *physically developed silver* and can be found in calotype negatives and in the wet collodion family of processes, including ambrotypes and tintypes. The developing solutions which produce physically developed silver were mostly used from 1840 to 1880, when few prints were done by development processes. Physically developed silver is therefore somewhat rare in 19th-century prints.

More common is *filamentary silver,* the form which occurs in the developing-out papers popular from the end of the 19th century to the present.





The individual image particles of the various 19th-century photographic print processes are so small that transmission electron microscopy is necessary to see them. These cross-sectional views depict a small area (usually near the uppermost surface) of each type of print.

Microscopy by T. Van Dam, Research Laboratories, Eastman Kodak Company

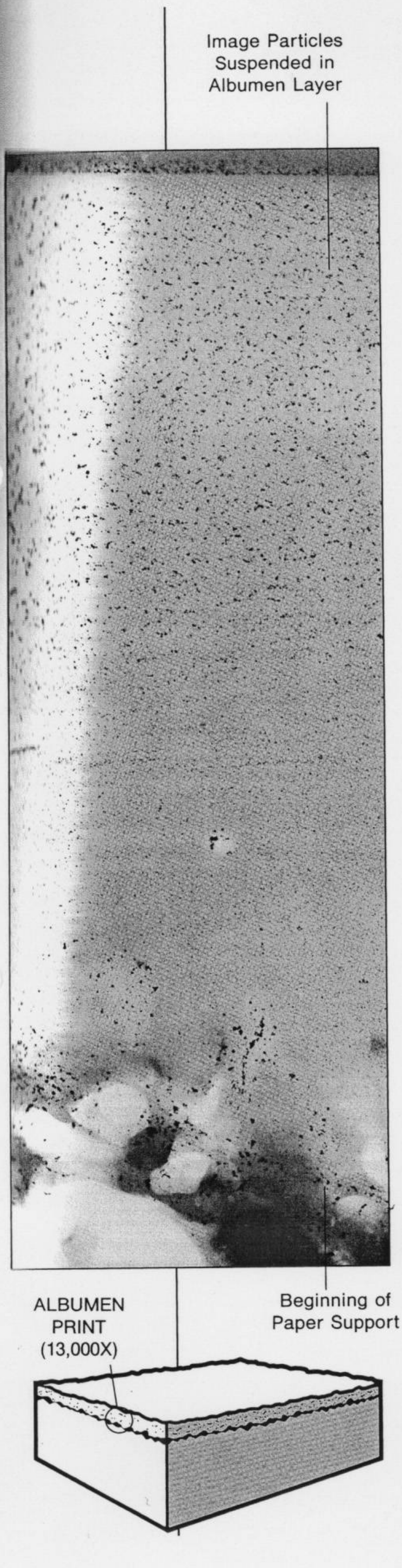
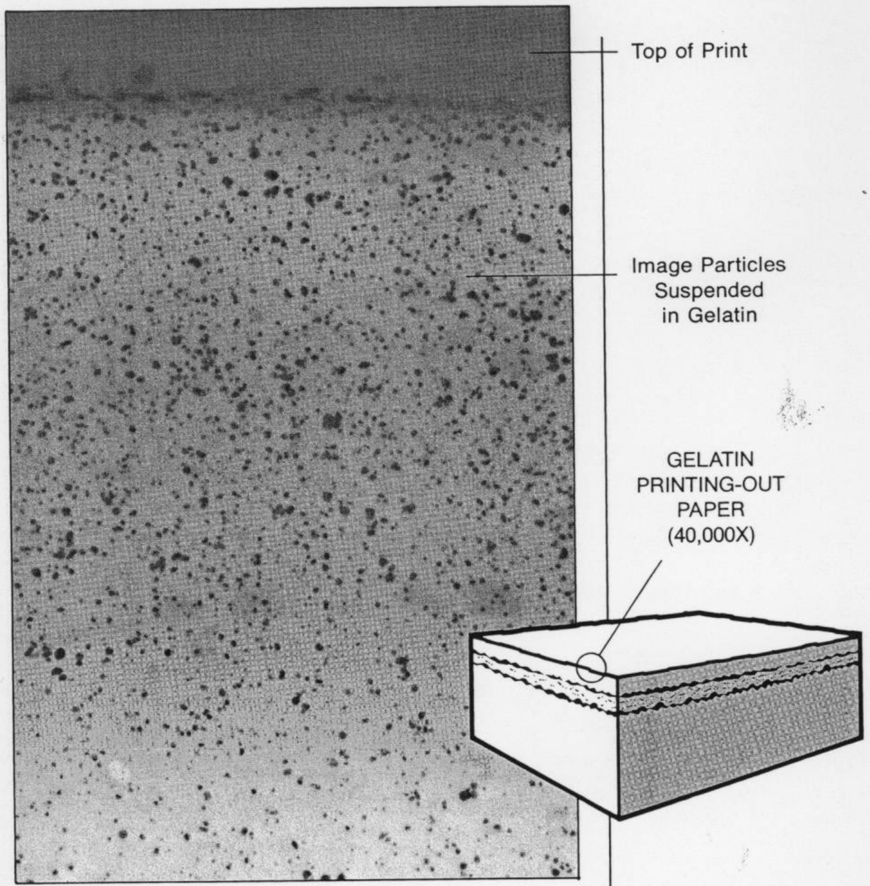
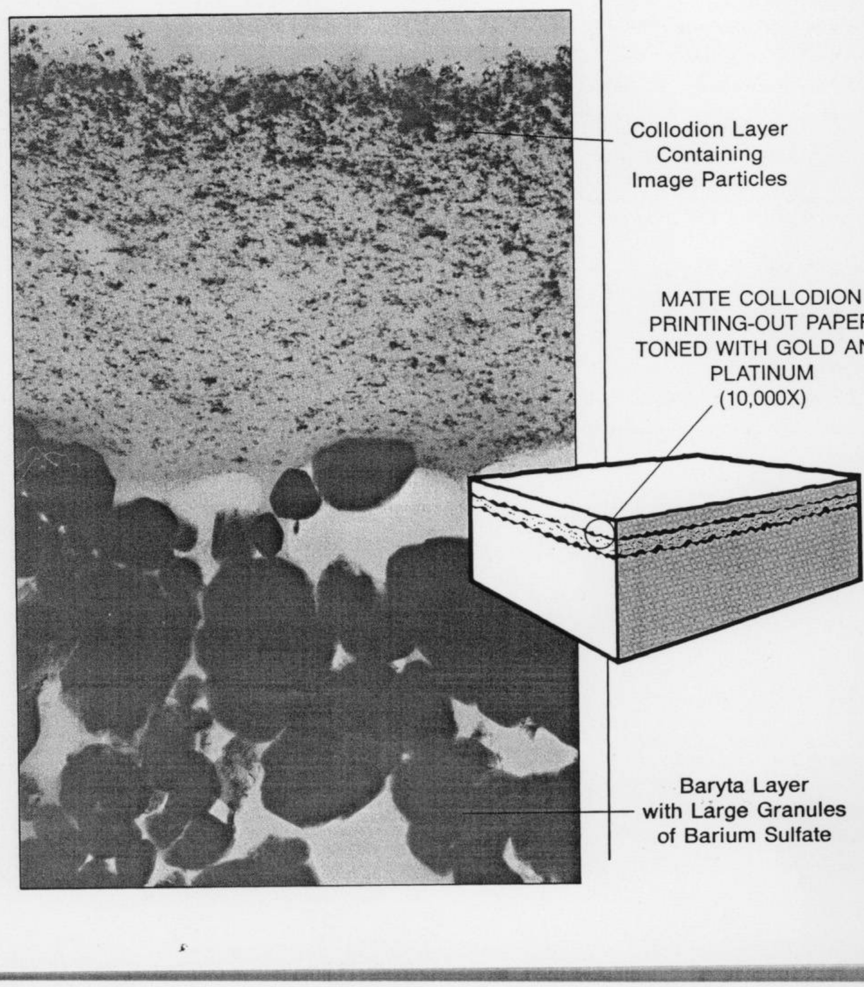


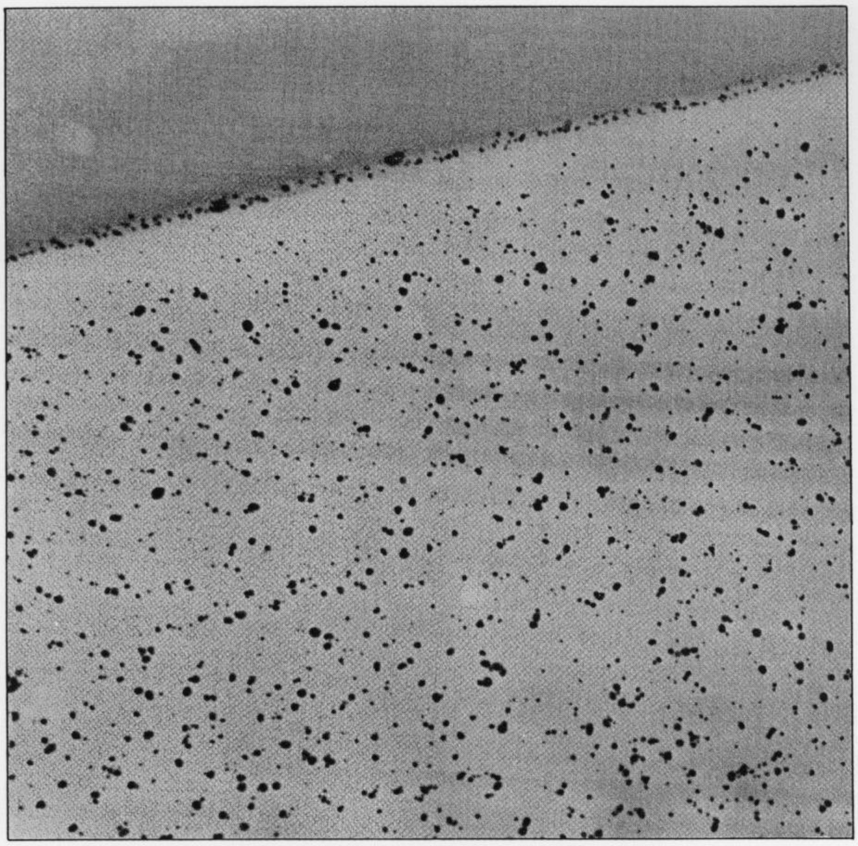
Image Particles Suspended in Albumen Layer
Beginning of Paper Support
ALBUMEN PRINT (13,000X)


Top of Print
Image Particles Suspended in Gelatin
GELATIN PRINTING-OUT PAPER (40,000X)


Collodion Layer Containing Image Particles
MATTE COLLODION PRINTING-OUT PAPER TONED WITH GOLD AND PLATINUM (10,000X)
Baryta Layer with Large Granules of Barium Sulfate

The image structure of a 19th-century albumen print consists of small, nearly round particles of silver, as shown in this cross-section transmission electron micrograph at 40,000X. Compare the size and shape of the albumen print particles with those of the contemporary black-and-white print shown below.

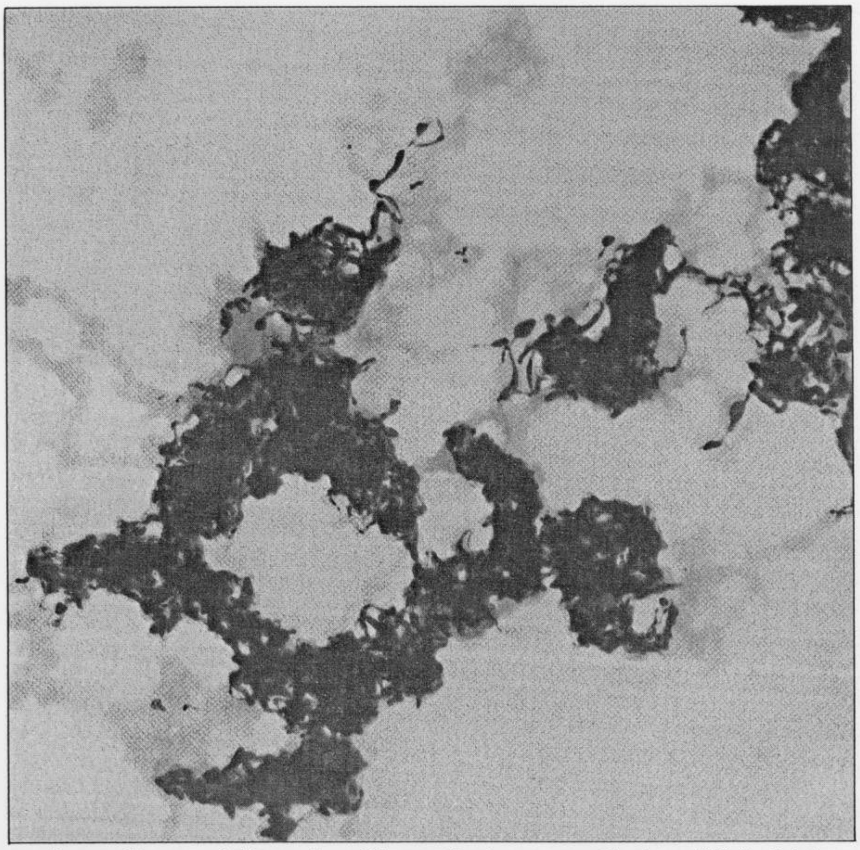
Microscopy by T. Van Dam, Research Laboratories, Eastman Kodak Company



Small Round Silver Particles—Albumen Print

The image structure of a modern gelatin developing-out print is comprised of isolated clumps of filamentary silver, as shown in this electron micrograph at 40,000X. The size and filamentary character of the silver clumps vary according to the emulsion-making technique and the developer used. Gelatin developing-out papers in the 19th century probably had a more filamentary structure than this modern paper because of the developer solutions in use at that time.

Research Laboratories, Eastman Kodak Company



Large Clumps of Filamentary Silver—Contemporary Black-and-White Print

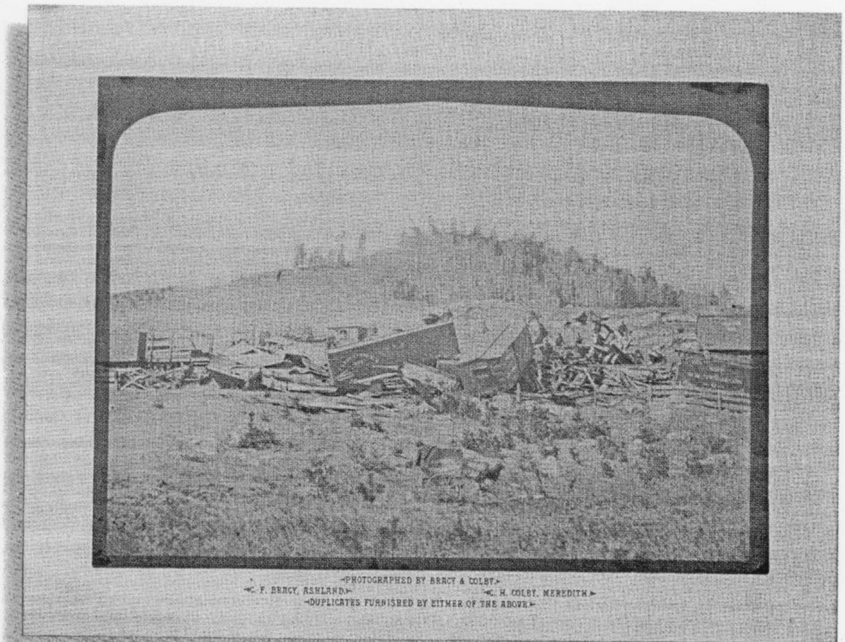
Along with the new bromide, chloride and chloro-bromide papers came new developing agents which deposited silver in the form of slender, twisted strands—hence the term "filamentary." A typical "particle" of filamentary silver consists of a bundle of intertwined filaments that are huge in comparison with the small spheres of photolytic silver. The large size and irregular, disordered structure of the filament bundles are ideal for absorbing light. They produce a neutral black image color.

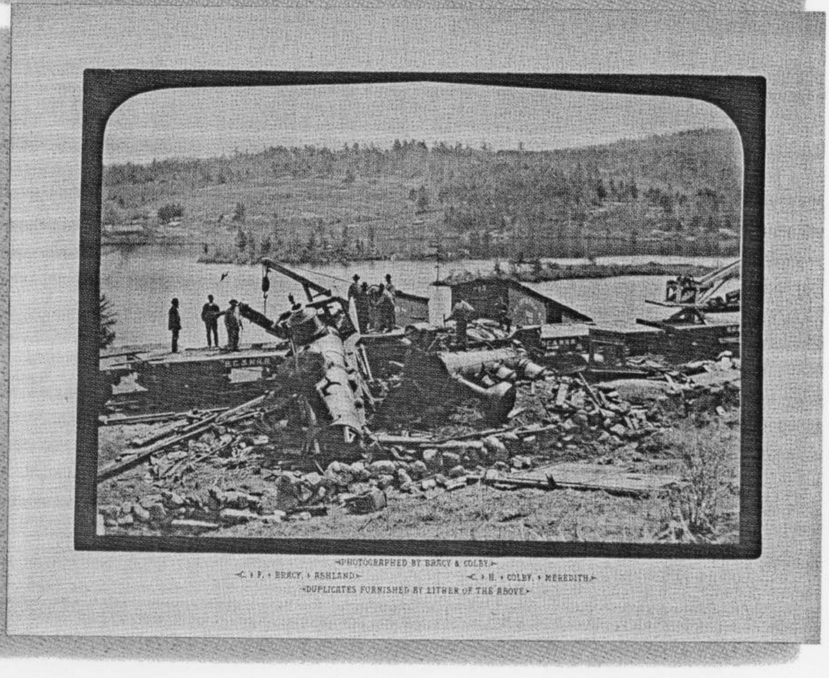
DETERIORATION MECHANISMS FOR SILVER IMAGES

The two basic mechanisms by which silver images deteriorate are sulfiding and oxidative-reductive deterioration. One need not be a chemist to understand these mechanisms and take appropriate measures to retard or prevent them.

Sulfiding Deterioration of Silver Images

Silver has a strong tendency to react irreversibly with sulfur to form the





These two albumen prints have both suffered from the effects of oxidative image deterioration caused by humid air and poor quality mount boards. The additional highlight yellowing, fading, and change in image color seen in the print on top are due to inadequate washing when the print was originally processed.

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very stable substance silver sulfide. The general type of deterioration resulting from this reaction is called *sulfiding*. The tarnish on silver household objects is the result of the formation of a thin film of silver sulfide due to small amounts of sulfiding gases in the atmosphere. Daguerreotype plates tarnish similarly. Sulfiding on paper prints can be due to either atmospheric sources of sulfur or, more commonly, sources within the print itself. Hydrogen sulfide and other sulfiding gases in the atmosphere do not usually occur in high enough concentrations to damage severely photographic prints. They act only as a contributing factor in the more significant damage done by oxidative-reductive deterioration. In some localized regions, however, the concentration of sulfiding gases may be high enough to cause serious damage.

A more extensive set of preservation problems arises from a source of sulfur intrinsic to prints—residual processing chemicals. Sodium thiosulfate, the compound used to fix silver images, is a sulfur compound which over time (though quite rapidly in the presence of moisture) breaks down and releases reactive sulfur to attack the silver image. All of the thiosulfate used in fixing must be removed by thorough washing in water if sulfiding deterioration is to be avoided. Thiosulfate is tenaciously retained by paper fibers and baryta coatings, so that prints with relatively thick paper supports or baryta layers (such as gelatin and collodion printing-out papers, and all of the gelatin developing-out papers) have more problems due to retained thiosulfate than albumen prints do. The thin paper support and lack of a baryta layer in albumen prints allow for effective washing in a relatively short time.[18]

The observable symptoms of sulfiding deterioration due to atmospheric sources of sulfur or retained thiosulfate differ somewhat for photolytic silver and filamentary silver. In filamentary silver images, the highlights are attacked first, turning yellow, fading and losing detail until the entire image is affected. The non-image areas for the most part remain white. Such deterioration can be rapid if large amounts of thiosulfate are present. It should be noted that the symptoms of sulfiding for filamentary images quite closely resemble those of oxidative-reductive deterioration (see p. 21), so that it is not possible to visually diagnose the cause as sulfiding.

For photolytic silver images, the consequences of sulfiding are more distinctive and have several stages. The highlights are attacked first, becoming yellow and fading. The middletone and shadow areas become more neutral in hue before fading to a yellow or yellow-green color[19]. The intermediate blackening of the image is caused by a partial conversion of the photolytic silver image particles to silver sulfide. This actually enlarges them, and the larger, partially sulfided particles have new absorption characteristics and appear more neutral.

A photolytic silver image undergoing oxidative-reductive deterioration becomes progressively redder or yellower, with no intermediate blackening stage. This makes the visual identification of sulfiding deterioration in printing-out papers more certain than is possible with developing-out papers.

The second kind of sulfiding deterioration, due to improper original processing of silver prints, is caused by the use of exhausted fixing baths. The fixing action of thiosulfates depends on the fact that they form a series of complexes with silver ions. The nature of these complexes is determined by how much thiosulfate is available, and an excess is needed for the most freely soluble complex to be formed. Without enough thiosulfate, as in an exhausted fixing bath, the less soluble complexes predominate and remain in the print despite all attempts to remove them by washing in water. This has consequences for image stability quite different from those caused by residual thiosulfate alone. Most importantly, the non-image areas of prints fixed in exhausted fixer gradually become stained with a yellowish-brown deposit of silver sulfide, the ultimate product of the decomposition of silver thiosulfates. The presence of silver thiosulfate in image areas also leads to the formation of silver sulfide composed of silver from both the image itself and the thiosulfate. The net result is yellowing and fading; but because of the additional silver sulfide formation, somewhat more highlight density and detail are preserved than would be if the image were attacked by thiosulfate

Silver mirroring is a common symptom of oxidative-reductive deterioration in silver images. It appears as a bluish metallic sheen in dark areas and is most readily visible when a light source is reflected off the print surface at a low angle (right).

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alone. For all types of silver images, the staining effect of residual silver thiosulfate is obvious; but blackening and staining are good indications of retained silver thiosulfates in photolytic (printed-out) silver images.[20]

Oxidative-Reductive Deterioration of Silver Images

The most important deterioration mechanism for silver images is *oxidative-reductive deterioration*,[21] which occurs when silver is attacked by any of a wide variety of oxidants that convert metallic silver atoms to the highly reactive, highly mobile, colorless species known as *silver ions.* Unlike sulfiding deterioration, which can be observed as tarnish on silver spoons and other silver objects, oxidation only becomes a serious problem when silver is in the form of very small particles, as it is in photographs. This is because oxidation occurs at the surface of silver, and the small particles of photographic images have enormously more surface area relative to their total mass than do larger silver objects. The smaller the individual particles of a photographic image, the more rapidly they will be affected by oxidative-reductive deterioration. This is the primary reason why filamentary silver images have good inherent resistance to fading, and photolytic silver images do not. The fading of silver images which has plagued photography from its earliest days is mostly a consequence of oxidative-reductive deterioration.

The term "oxidative-reductive deterioration" is used rather than "oxidation" because this form of deterioration is a continuing cycle of chemical changes involving oxidation of silver to silver ions, migration away from the original particle site, and *reduction* back to metallic, elemental silver.[22] Oxidation damages the image because silver ions and whatever silver compounds may form are colorless and unable to contribute to the image by absorbing light. The reduction step of the cycle, the speed and extent of which depend on a number of factors, is sometimes beneficial because it returns the silver to the metallic state in which it can again absorb light and contribute to the image. But the metallic silver formed during reduction is deposited in a new location and in a different physical form than that of the original image. The net result of oxidative-reductive deterioration is a decrease in the total amount of silver in the metallic state and, more importantly, a physical redistribution and rearrangement of the image silver. Because the physical form of the silver determines its color and density, oxidative-reductive deterioration causes fading and shifts in image hue.

Oxidative-reductive deterioration involves a complex and difficult set of chemical reactions. Many oxidants can cause deterioration, and they need only be present in minute quantities to be effective. Oxidant gases are generated by industrial pollution, automobiles, and a host of other processes and materials, including heavy electrical machinery, oil-base paints, and poor quality cardboard.[23] One needs to be aware of the potential sources of oxidants, but it is impossible to detect their presence or deal with them as individual chemical species. To cope with oxidative-reductive deterioration—the most serious long-term threat to the survival of silver images—a method is needed to retard oxidation, regardless of the specific oxidant involved.

Fortunately, the rate of oxidative-reductive deterioration can be retarded by controlling relative humidity (RH). Moisture plays a central role in the oxidation of silver images. Under dry conditions little or no oxidation takes place; under very moist conditions the rate of oxidation is maximized. In terms of the silver image alone, the best storage conditions for photographs would be arid. However, some moisture is needed to prevent paper, albumen, and gelatin from becoming too brittle. The optimum relative humidity for a photographic collection should therefore be between 30 and 40%. (**Caution:** These conditions may not be best for leather or other types of objects. See Chapter VI.) Temperature influences the rate of oxidative-reductive deterioration—nearly all chemical reactions are faster at higher temperatures—but the decisive factor is relative humidity. Sustained high relative humidity is devastating to silver images, as shown by the generally poor condition of photographs stored in tropical regions.

Effects of Oxidative-Reductive Deterioration

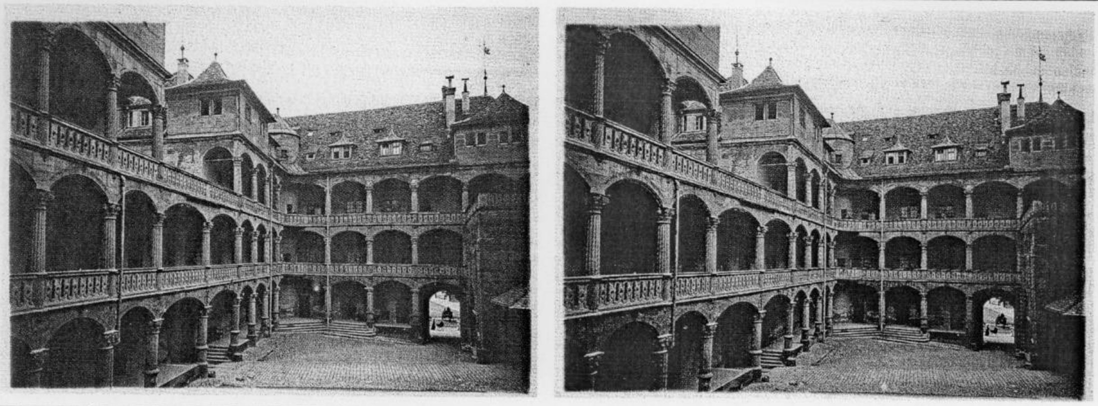
The visual effects of oxidative-reductive deterioration vary depending on the type of silver image affected. For printed-out (photolytic silver) images, the outstanding changes include rapid loss of highlight detail, overall fading, and a change of image color toward warmer (redder and yellower) hues.[20] The highlights of photolytic silver images have smaller and fewer particles than the shadows, making their lighter image tones particularly vulnerable to oxidative attack. The loss of the lighter tones robs photographic prints of their three-dimensionality by removing, for example, the delicate shadings found in faces and in the folds of light clothing. The loss of highlight detail occurs in all silver images, but is especially acute in photolytic silver images, whose generally small particle size also makes them fade faster in middletones and shadow areas. In addition, the photolytic particle size is within a range in which minor changes in size will alter image hue.

The situation is better with filamentary silver images. The ultimate consequences of oxidative-reductive deterioration in such images will be fading, loss of highlight detail, and a change in image hue to yellowish-brown. The images, however, will take much longer to reach such a level of deterioration. Under adverse conditions, there is the same amount of chemical assault on filamentary images as on photolytic images, but filamentary images have more silver and are structurally much better equipped to resist attack. The filament bundles are larger than they need to be to create a black image color. As they deteriorate, individual filaments become shorter and break up into smaller pieces, but the bundle retains its capacity to absorb light. Eventually the filamentary character of the image silver is lost, a significant amount of the image silver migrates away from the bundle, and the remnants of the filaments impart a yellow-brown image color.[24]

In all types of silver images the reduction of migrating silver ions can also lead to changes in the appearance of the image. The formation of silver "mirrors," a bluish metallic sheen in shadow areas, is a result of the reduction of silver ions at the very uppermost surface of gelatin, collodion, or albumen[25] layers. Silver mirroring is a symptom of oxidative-reductive deterioration, and can be found in nearly every type of silver photograph with a separate binder layer. It occurs most frequently in glossy developing-out papers, but does not occur in binderless print materials such as salted paper prints.

TONING OF SILVER IMAGES

Nineteenth-century photographic printing made much greater use of precious metal toning—the treatment of the silver image with gold, platinum, or a combination of the two—than does modern printing. Except for some early examples, all of the



Gold toning alters the image color of silver printing-out papers. An untoned print is brick-red, while the color of a toned print (right) is usually purplish-brown. (Examples on gelatin printing-out paper prepared by Dr. Fritz Wentzel).

IMP/GEH

printing-out papers used during the 19th century were toned, usually with gold.

A toned silver image undergoes two significant transformations: a change in its composition to a silver-gold or silver-platinum alloy, and a physical change in the size and shape of the image particles. Printing-out papers were toned to improve their appearance by altering their color and to improve their image stability. During toning, some of the silver atoms are replaced with atoms of gold or platinum. The gold does not form a "skin" on the surface of the silver particle, but actually becomes distributed within the crystalline structure of the silver. In the process, the particles become somewhat smaller and are distorted from their original shape.[15]

Gold-silver and gold-platinum-silver alloys have different light absorption characteristics than pure silver and are far more resistant to oxidation. The change in image color which results from toning is a function of both the alteration of particle shape and its composition. Toning a neutral black, filamentary silver image with gold or platinum protects it from oxidation but does not alter its color. Photolytic silver, however, is dramatically altered in color when toning treatments affect its particle size and composition. The amount of color change and degree of protection against oxidation depend on how much silver has been replaced by the other metals. Gold toning of photolytic silver images tends to make them colder and more purple in image hue, transforming the warm red color of the pure silver image to brown, purple or even blue-black. Platinum toning, which was not extensively practiced until the 1890s, turns a photolytic silver image brown. Platinum toning was most often done in combination with gold toning, yielding nearly neutral tones.

Gold toning by itself protects photolytic silver images to some degree, but does not make them stable. Gold-toned printing-out papers are still less durable than untoned filamentary silver images. But the combination of gold and platinum toning makes photolytic silver more resistant to oxidative attack than untoned filamentary silver. Except for problems with surface abrasion, gold-and-platinum-toned matte collodion printing-out papers survive, for the most part, in excellent condition. Gold-and-platinum-toned prints are also more stable under sulfiding attack. Although they are resistant to sulfiding attack from retained thiosulfate, they become stained in non-image areas when silver thiosulfates are present.

Controlled sulfiding of silver images was also used as a toning treatment for both photolytic and filamentary images. Sulfur toning was widely used during the 1840s to alter the color of salted paper prints. It was claimed that all of the image colors possible with gold toning could be achieved through the controlled sulfiding of the image. Whether or not this was true, it soon became apparent that sulfur-toned salted paper prints were far less stable than their untoned counterparts. It was impossible to limit the sulfiding of photolytic silver images to the precise intermediate state at which a neutral image hue was achieved but no further sulfiding would occur. By 1855 the technique had been repudiated in photographic literature, and gold toning was standard.[26]

When filamentary silver images were produced at the end of the 19th century, sulfur toning enjoyed a revival—this time with better results. Filamentary silver images are more amenable to sulfur toning than photolytic images. They retain more density and detail with a pleasing brown or "sepia" color, when converted to silver sulfide. By slightly overexposing a print and completely converting the silver to silver sulfide, fully satisfactory and very stable prints can be made on most types of developing-out papers.[27]

the support. Although the particle size in platinotypes affects image color somewhat (brown, blue-black, and neutral black hues are possible), the image color will not change over time due to changes in particle size, shape, or composition.

Platinum is an excellent catalyst for many chemical reactions. Some reactions occur on the surface of platinum which would not otherwise occur, and in which the platinum itself does not take part or become affected. The catalytic activity of platinum causes the frequently observed phenomenon of "transfer images." This occurs when a paper or board in contact with a photograph becomes discolored with a brown or yellow stain, which is an exact, positive duplicate of the photographic image. A transfer image can be created by either a pure platinum image or a platinum-toned silver print, and is formed when the discoloration of the paper or board is catalyzed or "speeded up" by contact with the platinum. The transfer image consists of those parts of the paper or board which are in a more advanced state of deterioration than the areas not in contact with the platinum.

Environmental factors which influence the degradation of paper, such as temperature, moisture and air pollution, also influence the rate of the catalytic transfer image phenomenon. Prints in storage should be interleaved or properly housed in sleeves or mats so as not to damage each oth-

This platinotype in its folder illustrates how prints containing platinum can cause the formation of a duplicate transfer image. While the paper cover was closed, its discoloration was catalyzed by the platinum metal, thereby producing the transfer image.

IMP/GEH

METALLIC PLATINUM

Although platinum-toned silver images were more numerous, true platinotypes, in which the final image material consists entirely of metallic platinum, were also made in large numbers during the 19th century. The platinotype's image is in the physical form of irregular, sometimes elongated masses of the same size or a little larger than photolytic silver image particles. The microstructure of the platinotype image is quite different from that of a photolytic silver image toned with platinum because the deposition of the platinum metal occurs under different conditions. The outstanding characteristic of platinum images is their resistance to both oxidative-reductive deterioration and sulfiding. Under normal environmental conditions, the platinum image can be regarded as permanent and unchanging. Preservation difficulties with platinotypes tend to stem from other print components, especially er in this way. The catalytic activity of platinum can also threaten the paper support of the print by contributing to its embrittlement or discoloration.

COMPLEX IRON SALTS

The final image material of cyanotypes is a mixture of two iron compounds, ferrous ferricyanide and ferric ferrocyanide, both of which are blue. These iron complexes are usually stable under normal environmental conditions, but are subject to photochemical deterioration and lose their color in the presence of alkalies. Exposure to light chemically changes cyanotype images to a colorless form. To some extent the change reverses itself in the dark and the blue color is restored, but the conservator must always seek to limit photochemical deterioration by carefully controlling the illumination of cyanotypes while in storage or on display. Cyanotype images subjected to alkaline conditions fade to a very pale brown and lose almost all detail and density.[28] Cyanotypes should therefore not be treated in alkaline solutions of any kind or be stored in alkaline-buffered paper enclosures.

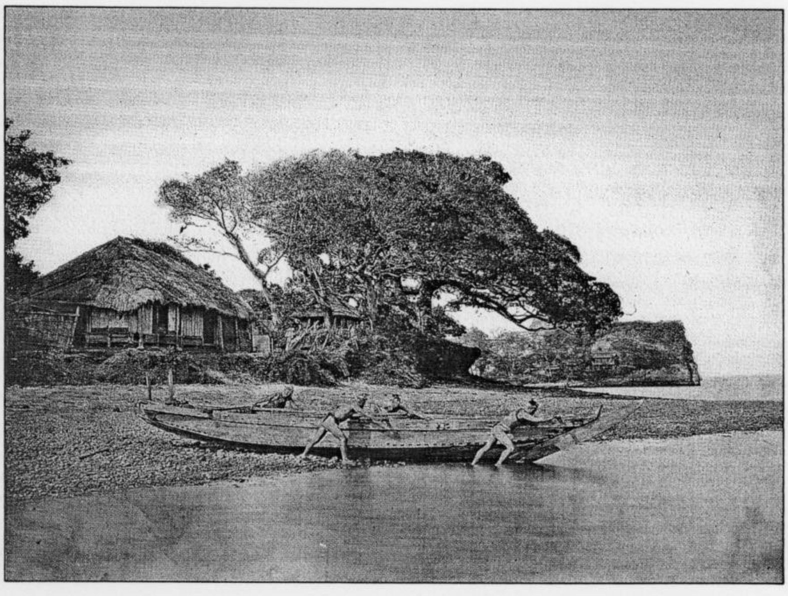
PIGMENTS AND DYES

As described in the first chapter, a number of 19th-century photographic print processes used pigments or dyes as the final image material. A *pigment* is a solid substance added to another substance to give it color. A *dye*, for the purposes of this discussion, is a synthetic, organic colorant typically added from a solution, and not as a solid. It is impossible to adequately discuss here all of the pigments and dyes used during the 19th century (there is an extensive range of literature on the subject), but a few generalizations can be helpful.

Pigments are typically oxides or salts of transition metals and have excellent stability compared to silver images. Nineteenth-century print processes which used pigments as the final image material included carbon prints, gum bichromate, and a number of related processes. The various pigments used in these prints show small differences in sensitivity to atmospheric pollutants and some differences in stability to light, but essentially all images in which pigment is dispersed in a binder like gelatin or gum arabic have good overall stability.[29]

Synthetic dyes as a group are far less inherently stable than pigments, particularly in response to light. Dyes were used in 19th-century photography in hand-colored prints and transparencies, in tinting albumen and baryta layers, and as an occasional substitute for inorganic pigments in the carbon process. The stability of synthetic dyes varies widely, but most are affected in the dark by temperature, moisture, and pollution.

Minimizing light damage should be the chief concern for images in which dyes or pigments have been used as applied color. Such coloring is com-



Many 19th-century photographic prints contain applied coloring, as in this Japanese albumen print enhanced with watercolors.

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Hand-coloring of albumen prints with watercolor and (after the mid-1860s) synthetic dyes took several forms. This is a so-called "tissue stereo" which is colored on the back side. By reflected light (top), no color is visible; but when illuminated with transmitted light (bottom), the lifelike coloring is apparent.

IMP/GEH

monly encountered in salted papers and albumen prints, but is less common in gelatin and collodion printing-out papers. Prior to the 1860s, the only colorants used were artist's watercolors. Synthetic dyes, often recognizable by their intensity of color, were used for hand coloring as soon as they became available.

Illumination levels and display times must be carefully controlled when exhibiting images which include either pigments or synthetic dyes as applied color. A watercolor pigment lightly applied to a photographic print does not have the same level of light stability that it has when present in much greater quantity in a gelatin or gum binder. The synthetic dyes extensively used to tint the albumen prior to the coating of albumen paper are so sensitive to light that only prints in albums or those never displayed have kept their full coloration.[30] The great dilution of tinting dyes in albumen paper contributed to their poor light stability. The coloration that dye gives an albumen print is a subtle but definite part of the image, and every effort should be made to identify tinted prints and protect them from light damage.

When an overall tint was desired in print materials with a baryta layer, the dye was added to the baryta/gelatin substratum rather than to the gelatin or collodion sensitized emulsion. The light stability of tinted baryta layers was much better than that of tinted albumen layers. Pigments, and to some extent dyes, also served as the final image material in 19th-century photomechanical (printing) processes.

BINDERS

The *binder* is the transparent layer in a photographic material in which the