

Restoration of Photographs by Neutron Activation

A remnant trace of image silver and relative freedom from halogens and other silver are required.

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Early in 1834 in England W. H. F. Talbot began experiments leading to his invention of the photographic negative and positive paper print (1), a technique that proved to be the forerunner of the most widely used system in modern photography. The Smithsonian Institution has a number of early Talbot photographs (2); although several retain their original brilliance, many show obvious signs of image degradation. In several instances the deterioration is complete. The risk of further loss of this valuable material led to an investigation of Talbot's techniques and the problem of restoration (3).

Earliest Experiments

Talbot's experiments centered around the light-sensitive properties of silver nitrate and silver chloride. His earliest tests showed a darkening reaction to sunlight on paper brushed with a solution of silver nitrate, a precipitate of silver chloride, or strong solutions of common salt (NaCl) followed by silver nitrate to form silver chloride in the paper. Although the response of these coatings was too slow, he observed that on the papers coated with the salt and silver nitrate solutions some border areas showed unusual sensitivity to light. Feeling that these areas had received less salt, Talbot modified his approach by coating with a weak salt solution which, after drying, was followed by a wash of silver nitrate. The result was a coating that turned black "uniformly and rapidly." This technique in the spring of 1834 yielded silhouettes of items—such as leaves and lace—placed in contact with the paper and exposed to sunlight (4).

Talbot found that if the salt concentration was increased beyond a certain point, the paper decreased in sensitivity. Thus, to make images "permanent," he used a strong solution of common salt as a final rinse. Image permanency, indeed, proved to be a major problem for Talbot. In addition to common salt, Talbot announced on 21 February 1839 that another of his image preservatives was a dilute solution of potassium iodide; this treatment resulted in a very pale yellow tint (5).

According to his own account on 31 January 1839, Talbot's earliest prints (around 1834) "became indistinct in process of time (the paper growing wholly dark) . . ." but some of his subsequent results lasted nearly 5 years without "deterioration." To prove this, he had exposed the pictures "for an hour to the full summer sun, and . . . the image . . . suffered nothing . . ." (4); as late as 1844 Talbot referred to this test as a proof of image permanency (1). Possibly as early as March 1839, Sir John Herschel (6, 7), pointed out that he, unlike Talbot, was unable to recommend the use of common salt as a preservative. Overall exposure to sunlight would not reveal the slower, long-range effects of chemical deterioration; it would only "print out" silver halide that had not been removed or was improperly inactivated.

Talbot's dilemma concerning image permanency was expressed in *The Pencil of Nature* (1), the first publication to be illustrated with photographs; referring to the use of potassium iodide he wrote,

. . . this process of fixation was a simple one, and it was sometimes very successful. The disadvantages to which it was liable did not manifest themselves until a later period; and arose from a new and unexpected cause namely, that when a picture is so treated, although it is perma-

nently secured against the *darkening* effect of the solar rays, yet it is exposed to a contrary or *whitening* effect from them; so that after the lapse of some days the dark parts of the picture begin to fade, and gradually the whole picture becomes obliterated, and is reduced to the appearance of a uniform pale-yellow sheet of paper. A good many pictures, no doubt, escape this fate, but as they all seem liable to it, the fixing process by iodine [*sic*] must be considered as not sufficiently certain to be retained in use as a photographic process, except when employed with several careful precautions which it would be too long to speak of in this place.

The use of common salt or potassium iodide alone as a preservative appears to have been discarded by the time of Talbot's 1843 patent (8).

In a paper presented in 1856 before a meeting of the Photographic Society of Scotland, Sir David Brewster reported that, although protected from light and damp, many of the Talbot pictures in his collection had almost completely faded (9).

Talbot's Progress

On 25 January 1839, before a meeting of the Royal Institution of Great Britain, Michael Faraday made the first public announcement of Talbot's photographic process; it was accompanied by a display of pictures (10). About 4 weeks later Talbot disclosed the following details of his "photogenic drawing" process (5):

1) Superfine writing paper is dipped in a weak solution of sodium chloride and wiped dry.

2) A solution of silver nitrate, diluted "6 to 8 times with water," is spread on one side of the paper and dried with heat. This paper may then be used to produce silhouettes (print-out images) by placing objects on the surface and exposing it to sunlight.

3) The sensitivity is increased for exposure in a camera by repeating steps 1 and 2 until the paper reaches a point just short of becoming dark without exposure to light.

4) The image is rendered "permanent" with either a strong solution of sodium chloride or a weak solution of potassium iodide.

On 15 March 1839 Talbot described his silver bromide paper, which was made by washing paper alternately with solutions of silver nitrate and potassium bromide (11).

Talbot started experimenting with gallic acid as an "image accelerator" (first used by J. B. Reade) in April

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Fig. 1. Three early photographs, *a* and *b* by Talbot, before (*a-c*) and after (*A-C*) restoration by neutron activation. Photograph *a* shows two stains caused by masking tape.

1839 (12). In September 1840 Talbot recognized that it was a latent image that responded to development (13). Still troubled with fading photographs, Talbot in June 1841 recommended "restoring" them by redevelopment in a gallic acid-silver nitrate solution (14).

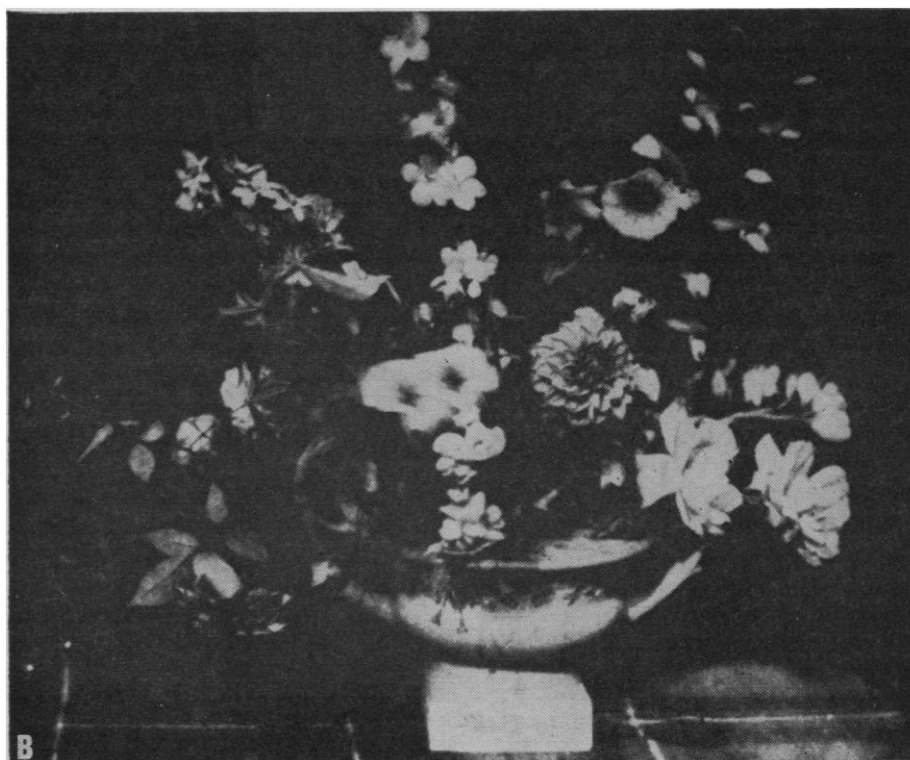
On 8 February 1841 Talbot patented his calotype paper process (15); this approach consists in coating paper with a solution of silver nitrate before a bath in potassium iodide. The paper is then dried and treated with an acidified gallic acid-silver nitrate solution. After exposure, the photograph is developed with the acidified gallionitrate of silver and the image is "permanitized" with a solution of potassium bromide or common salt.

Talbot's patent of June 1843, for improved calotype paper, set forth the procedure for removing the yellowish tint of calotypes by bathing them in a near-boiling solution of hypo (sodium thiosulfate) (8). "By this means, the picture is rendered more permanent and the transparency of Calotype pictures may be increased, by causing melted wax to penetrate into the pores of the paper. . . ." In the same patent Talbot also proposed an "io-gallic" paper (iodized paper treated with gallic acid, dried, and stored); for use it was sensitized with a silver nitrate solution.



The prints for *The Pencil of Nature* (1) were produced by coating paper first with sodium chloride and then with an "ammonio-nitrate of silver" solution containing some nitric acid (16). Although Talbot had been aware of the advantages of using hypo at least as early as 1 February 1839, having been informed of its usefulness by Sir John

Herschel (17), he probably did not officially incorporate it into his own technique until about the time of his calotype patent, 1 June 1843. Even then, he did not propose the use of hypo as a fixative, but as an agent for removing the yellowish tint of the potassium iodide that he employed as the image "permanentizer" (8).



Talbot sought to preserve his photographic images by using sodium chloride, sodium bromide, and potassium iodide as "stabilizers." These compounds render unused silver halides impotent by converting them into soluble or insoluble salts or complexes that are less sensitive to light than the original form. We now know that in time these salts or complexes may darken (print out or decompose). Effectiveness of the stabilizer is decreased if the excess is removed by washing, but this problem is not necessarily solved by permitting an excess to remain, because the excess itself may attack the image silver.

The need to wash a photograph thoroughly before placing it in hypo to prevent sulfurization (to a yellowish sulfur compound) was recognized by Herschel possibly as early as 14 March 1839 (6, 7). This intermediate wash, which was used after development and before final chemical treatment, is the predecessor of the modern stop bath.

Fixers dissolve the unused silver halides by forming soluble silver complexes that are removed during fixing and washing. Sodium chloride could have been used by Talbot as a fixer if the concentrations and volumes of solution had been adequate to dissolve the silver chloride, but it would not have been effective for silver bromide and silver iodide. A concentrated solution of potassium iodide, on the other hand, would have readily dissolved any of the three halides, but the dilute solutions used by Talbot were sufficient only to convert the silver chloride to silver iodide (18). Washing must eliminate any residual fixer that may eventually attack the image silver; there is no substitute for good fixing and washing.



Contamination

Paper fibers tend to retain hypo, and prolonged washing in replenished water is necessary to remove this chemical. Traces of hypo can yellow a photographic image by sulfiding. If exhausted hypo containing an excess of silver complexes is used, it is almost impossible to wash them completely from the paper fibers; in time the clear areas become yellowish as a result of reaction with the atmosphere to form a sulfide.

Residual chemicals and contaminants in the paper base, and adjacent storage materials, may contribute to image degradation. In addition to the "permanentizers" already discussed, residual gallic acid (18) or atmospheric contaminants such as oxides of nitrogen and sulfur or hydrogen sulfide may damage the image and the base. Halides remaining after inadequate washing may, in the presence of an oxidizer such as air, react with the image silver

to form silver halides and so degrade the photograph (18).

The rate at which a photograph deteriorates depends not only upon the concentration of the contaminants, but also upon storage conditions—exposure to sunlight, temperature, relative humidity, bacterial action, rate of air circulation, and replacement of fresh air around each picture.

Sir John Herschel

Talbot withheld his wholehearted endorsement of hypo even though he was informed of its value as a photographic fixative at least as early as 1 February 1839. His reluctance may be attributable to the fact that the use of hypo for photography was not his own. Although in a letter dated 1 March 1839 (19) Talbot strongly recommended hypo (appropriately crediting Herschel for the discovery), he appeared to negate its importance by pointing out the vir-



tues of his own discovery of the use of potassium iodide as a preservative.

Herschel disclosed his fixing technique in March 1839 (6) and announced the details in February 1840 (7). He was well aware of the importance of a thorough final water wash: "... the hyposulphite of soda and silver being liable to spontaneous decomposition, accompanied with separation of silver in the state of sulphuret, it is necessary to be very careful in washing away the very last traces of this salt, especially if it be intended to use the photograph for re-transfers [making prints], in which case a deposition of sulphuret within its pores is fatal, since it renders the paper unequally opaque."

To ensure elimination of hypo, Herschel recommended that "it must be washed off with repeated and copious affusions of water, aided by a soft sponge, with a dabbing motion, turning the picture often, until the liquid comes off without the slightest sweetness" (7). His use of taste introduced a host of subjective variables. Taste adaption plays a large role: for example, after preliminary sweet tastes a greater amount of sweetener is required to impart a sweet sensation; and adaptation increases with solution concentration (20). Taste sensitivity can vary from subject to subject, so that a taste of sweetness discerned by one person may be completely undetected by another. Taste sensation can be affected by everything from temperature to personal stamina.

Although I have not yet conducted tests to determine whether tasting can detect residual hypo at the level necessary to ensure optimum keeping qualities, it is fairly safe to say that adoption of taste as an indicator of chemical elimination would be acceptance of a highly variable standard.

Herschel also recognized that the ingredients used in manufacturing different paper stocks varied and, in turn, affected sensitizing coatings. Before the Royal Society on 20 February 1840 he described his experiments with different papers and various sensitizing coatings (7).

In 1841 Robert Hunt noted that the more-sensitive papers tended to discolor rapidly in darkness and attributed this tendency to the organic constituents of the paper sizing and to the sulfur and sulfates used in the sizing and bleaching processes (21). He noted that paper should have a uniform texture in order to stabilize variations in the rates of absorption of solutions. Papers with

minute fibers or black or brown specks should not be used. Hunt recommended use of a thin, close-textured paper without pinholes or watermark. He found that organic sizing enhanced light sensitivity and that papers bearing the same description, but from different manufacturers, produced different results for a given sensitizing coating. He concluded that the paper should be chemically pure, and gave instructions on how to remove "metallic and earthy matters."

Restoration by Neutron Activation

The problem of restoration of photographic images can be approached in several conventional ways. One may deposit additional silver or other metals on the image silver by adding to the silver image colored compounds that are "seen" as opaque by the color-blind printing paper, or convert image silver into a more-opaque compound of silver. Also a faded, discolored, or stained image often can be corrected by photocopying, with the use of appropriate filters to minimize or eliminate the undesirable coloration. The images of the Talbot pictures with which we are concerned were considered too faint to be restored by photocopying. Alternative chemical treatment, if unsuccessful, might have jeopardized what remained of the images, rendering them useless for additional experimentation.

Talbot constantly varied his early experimental approaches, but no concise record of this work exists; thus the chemical characteristics of each example must be considered questionable. Although chemical analysis could provide some answers, such an approach might fail to reveal all of the constituents. To avoid error in working out these problems it was necessary to devise some nondestructive method of restoration; neutron activation suggested itself.

By irradiation of a photograph with neutrons, some of the image silver is rendered radioactive. Silver is present in the form of two stable isotopes: silver-107 and -109. Neutron irradiation converts portions of them to silver-108 and -110, respectively. Silver-108 decays (half-life, 2.3 minutes) (22) by emitting very-high-energy beta rays (1.57 Mev) and very-low-energy gamma rays.

Intensified copies of an original photograph were obtained by autoradiog-

raphy, the degree of intensification being controlled by balancing the initial level of activation and the duration of autoradiographic contact. It was essential to the success of this method that residual image silver (or silver complexes corresponding to the image) be present, however minute the quantity. Even if the image were no longer visible, as long as the paper base retained some image silver (or silver complexes corresponding to the image)—even only microscopic amounts—one could obtain the desired result. The presence of nonimage silver or silver halide meant that they too were made radioactive by the irradiation and then served only to mask the beta-ray emission from the image that was being recorded on the x-ray film. This approach could not succeed with pictures for which Talbot had used stabilization techniques instead of dissolving out the used silver salts, or which had been inadequately fixed.

Before use of this technique on the irreplaceable originals, it was necessary to determine whether irradiation had undesirable effects on the image or the base; there also was the possibility of heat damage from the field of flux. For test purposes a modern gelatin-silver halide 20- by 25-centimeter print was irradiated for 7 minutes in an atomic pile (23); access to the field of flux was made through a tunnel by which a remotely controlled dolly transported specimens into a region of fairly low activity within the pile (about 10^9 neutrons $\text{cm}^{-2} \text{sec}^{-1}$). To prevent contamination the print was sealed in a polyethylene bag.

In order that this work be done as close as possible to the pile, x-ray film (Kodak KK) was enclosed in a light-tight black paper envelope. Upon emergence from the tunnel the print was removed from the bag and the image was placed in intimate contact with envelope-wrapped film. The irradiated print was always handled with tongs and extreme care was taken to minimize exposure of personnel to radiation.

Autoradiographic contact was maintained for 10 minutes and the film was processed for the recommended time. The autoradiograph showed a strong image, somewhat mottled, with inadequate contrast and definition, and with low maximum densities. The result was sufficiently encouraging to indicate that successful copies could be obtained by balancing the level of irradiation and durations of autoradiog-

graphic contact and development. The original print showed no sign of damage.

A higher flux was needed to increase the level of radioactivity for a stronger autoradiographic exposure; this tunnel region was therefore abandoned and a different portal was used to give access to a region of very high activity (5×10^{12} neutron cm^{-2} sec^{-1}).

To improve definition, the film envelope was eliminated to provide intimate contact between image and x-ray film under darkroom conditions. Access to the pile was effected through a pneumatic-tube system, the specimen being transported in a cylindrical-tube carrier (rabbit) that limited the print dimensions to a maximum of 15 centimeters. An overly dense image resulted. To reduce density the print was again irradiated for the shortest time, but autoradiographic contact was reduced to 3 minutes and a slower, finer-grain, higher-contrast film (Kodak M) was used; this approach was successful.

To avoid size restrictions imposed by use of the rabbit and to obtain the flux necessary for this work, a different portal with relatively high activity was used (3×10^9 neutron cm^{-2} sec^{-1}). The field of flux was reached by pushing the specimen carrier (boat) along the passageway with a long flexible pole. The results with other early Talbot prints confirmed the theory that, unless residual nonimage silver or silver halide had been removed reasonably well from the photograph by suitable fixing and washing, this technique was unsatisfactory.

A Talbot print, of ceramic pieces arranged on shelves (Fig. 1a), showed on the reverse side that masking tape had been in contact with the picture; with time the adhesive had "leached" through the paper and stained the image a dark brown, and carbon tetra-

chloride, benzene, and xylene failed to remove the stain. Irradiation for 20 seconds, autoradiography for 7 minutes, and normal development resulted in an intensified image and elimination of the two prominent stains.

Another badly stained and faded print (not attributed to Talbot), showing the portrait of a man (Fig. 1c) was irradiated (15 seconds) and autoradiographed (7 minutes) in the same manner. Some of the stains were subdued or eliminated, but an exception was one area in which they were recorded more prominently; evidently the original print had been retouched with a medium that responded readily to the neutron activation; moreover, numerous black spots resulted from foreign particles embedded in the base either during manufacture of the paper or during processing.

The last print to be irradiated was a small photograph by Talbot that had faded completely, the paper containing no visible image. After irradiation in the rabbit for 2 to 3 seconds, autoradiography for 5 minutes, and processing as for the two previous prints, an image of a standing man dramatically emerged.

Summary

Badly faded or stained photographs or radiographs, negative or positive, can be restored by use of neutron activation and autoradiography, provided that at least a trace of image silver is present and that the picture is relatively free of halogens and other silver.

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23. With the cooperation of E. V. Sayre, chemistry department, Brookhaven National Laboratory.
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