

SALT PRINT



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The Atlas of Analytical Signatures of Photographic Processes is intended for practicing photograph conservators and curators of collections who may need to identify more unusual photographs. The *Atlas* also aids individuals studying a photographer's darkroom techniques or changes in these techniques brought on by new or different photographic technologies or by the outside influence of other photographers. For a complete list of photographic processes available as part of the *Atlas* and for more information on the Getty Conservation Institute's research on the conservation of photographic materials, visit the GCI's website at getty.edu/conservation.

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Front cover: William Henry Fox Talbot, *The Open Door*, 1844. Salt paper print from a calotype negative, 14.9 × 16.8 cm. Photographed at Lacock Abbey. The J. Paul Getty Museum, Los Angeles.

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SALT PRINT

English: salt print

French: *le papier salé*

German: Salzpapier

HISTORICAL BACKGROUND

Thomas Wedgwood (British, 1771–1805) and Joseph Nicéphore Niépce (France, 1765–1833) developed the concept of the salt print process (Wedgwood before 1802, Niépce in 1816) but did not provide a solution for fixing or stabilizing their test images. No well-provenanced or authenticated images, and no test samples from their experiments, are known today. In 1832–34 Hercules Florence (French, 1804–1879), working in Brazil, developed the concept of silver- and gold-based photography and a primitive way of image fixing using a urine-based solution. His use of a camera is known in literature, but only copy samples are extant. In 1834–35 William Henry Fox Talbot (British, 1800–1877) developed an advanced concept of photography on paper and a method of stabilizing both photograms and camera images using a solution of sodium chloride. Following a suggestion by John Frederick William Herschel, Talbot later adopted Herschel's method of fixing photographic images using sodium thiosulfate (hypo).

Dates of publication: T. Wedgwood and H. Davy (1802); W. H. F. Talbot (1839 and later)

The development of silver-based photography has its roots in the observation and study of silver compounds when exposed to light and in the early development of photochemistry. Most authors agree that one of the most important contributions toward the development of photography was the work of the German physicist and professor Johann Heinrich Schulze, who, in 1727, observed and described the formation of geometric “images” on a glass bottle containing a sediment of calcium carbonate mixed with diluted nitric acid contaminated with a small concentration of silver. Through a series of experiments, he was able to show that the darkening of the light-exposed suspension was caused by a photochemical, not a thermal, effect. In later stages of his investigation, he covered the glass bottle with dark paper, out of which he carved stencils of letters. After exposure to sunlight and removal of the stencil, Schulze observed the first intentionally created “photogram” of white letters on a dark background.

Two other photochemists made important experiments and observations related to the future development of photography. In 1777 a Swedish chemist, Carl Wilhelm Scheele, described that an insoluble precipitate of silver chloride in water can be dissolved using a solution of ammonia. The Swiss scientist Jean Senebier conducted a series of experiments observing the darkening of

silver salt compounds under glasses of different colors. These crude but important photochemical experiments showed the different photochemical sensitivities of silver compounds when exposed to light of different wavelengths. Senebier's published measurements showed that to achieve similar levels of darkening of silver chloride-coated paper, the paper has to be exposed for 20 minutes under a red glass, 5½ minutes under a yellow glass, and within 29 seconds under a blue glass. Both sets of experiments were made with chemistry and photochemistry and performed by researchers who did not intend to use this procedure to produce images.

It was only toward the end of the eighteenth century that Thomas Wedgwood started his experiments with silver nitrate-coated paper and leather and produced the first photograms of leaves and other, similar objects. He was also the first to attempt to produce images using a camera obscura. As far as we know, none of his photograms survive today, and his seminal 1802 article, published together with the chemist Humphry Davy, describes his unsuccessful camera obscura experiments and his inability to find a workable procedure for fixing or stabilizing his photograms.

Joseph Nicéphore Niépce, in May of 1816, succeeded in producing the first successful camera obscura images (paper negatives); however, he also could not find a way to make his images stable. Based on his correspondence with his brother Claude, we know that in April of 1818 he gave up using silver muriate (silver chloride) in his experiments. None of these images exist today, but at least one of his 1816 images survived, still visible, until the late 1860s. Niépce later succeeded in finding a new light-sensitive material, bitumen, and he was able to produce the first fixed photographic and photomechanical images (1822–33), which are still in existence today.

The oldest photochemically produced images on paper that are still extant appear to be pharmaceutical labels produced by Hercules Florence. Not having available locally any mechanical printing facilities for the production of bottle labels for his pharmaceutical business, Florence scratched the design of his labels into dark varnish on flat glass and printed them on paper substrate sensitized with silver and/or gold chloride. He began his experiments in 1832, and his notebooks, which survive, show that he achieved good results in 1833–34. He also invented a method of fixing his copy images using a urine-based solution. His notebooks also describe his camera obscura experiments and contain a drawing of his camera and copy frames. None of his camera photographs have been located. Florence did not publish his experiments and procedures. His photographic work was, until the 1970s, virtually ignored by historians of photography.

William Henry Fox Talbot is usually considered to be the inventor of photography on paper. Regardless of previous experiments and attempts, Talbot produced a body of photographic work, ideas, writings, exhibitions, and patents that make him one of the most important and influential inventors and researchers in the history of photography.

Unsuccessful in his attempts to draw using his Camera Lucida during his Grand Tour stop at Lake Como, Italy, in 1833, Talbot pondered ways to record images using the photosensitivity of different chemical compounds. He began his first actual experiments upon his return to England in 1834. First he made photograms and later tried to record distant objects using small cameras obscura. Talbot's iconic photographic paper negative of the oriel window at his Lacock Abbey

estate was made in August of 1835. This is considered to be the earliest photographic image on a paper substrate that is still in existence.

An article dated January 6, 1839, related to the January 7 announcement of the daguerreotype process by François Arago in Paris, inspired Talbot anew. In quick succession he improved the sensitivity of his photographic process, developed and tested a negative-positive process using his original salt paper negative/salt paper positive process, photographed small objects using a solar microscope, developed two methods for stabilizing photographic images after light development, developed a procedure for making his photographic negatives translucent using a hot beeswax treatment, adopted Herschel's method of fixing photographs using a sodium thiosulfate solution, published several introductory texts on his experiments and details on his procedures and potential use of photography, and exhibited a number of his photographic images before members of the scientific and art communities.

In 1840 Talbot introduced another major advancement, the calotype (also known as Talbotype) negative process, based on chemical development of the latent photographic image. He patented the calotype process in 1841. A salt paper print made by Talbot in 1844 is shown in figure 1.

The salt print positive process was the main positive photographic process used for salt print negatives from 1835 to February 1841, when the calotype negative process was introduced. The salt print process was used almost exclusively for printing calotype negatives until about 1850, when Louis Blanquart-Evrard introduced his silver albumen process. The majority of early albumen negatives (after 1850) and wet collodion negatives (after 1851) were also printed using both salt print and albumen positive processes. Albumen became the most important photographic positive process of the nineteenth century after about 1855.

Figure 1 William Henry Fox Talbot, *The Open Door*, 1844. Salt paper print from a calotype negative, 14.9 × 16.8 cm. Photographed at Lacock Abbey. The J. Paul Getty Museum, Los Angeles.



A number of articles, photographic manuals, and books published various improvements and modifications on the salt print positive process that focused on different methods of sizing photographic paper or on using different sensitizing or fixing formulas. Some paper-manufacturing companies also started producing special “photographic paper” that provided good wet strength for wet processing and the absence of metal particles notorious for creating black spots in the final images. A number of paper mills experimented with the production of special photographic papers for both salt print and albumen positive processes, but only a few were able to meet the strict demands of these processes.

Only two important modifications greatly affected both the visual appearance of final images and their light-fading stability. In 1847 P. E. Mathieu proposed using gold toning to modify image tonality and stabilize the silver image. Gold toning was used more widely after 1850, when it was highly recommended by Gustave Le Gray, and further accelerated following publication of the results of the so-called Fading Committee of 1855.

The second major modification of the salt print process was introduced by Blanquart-Evrard. His method of chemical development of positive prints—similar to the development of calotype negatives, which used a gallic acid-based chemical developer—replaced the slow and unreliable sun development procedure. This made the mass production of photographic prints possible and more economical. From 1851 to 1855 Blanquart-Evrard operated a photographic printing establishment near Lille in France, where he was able to produce up to several hundred salt prints a day from a single negative. Chemically reduced silver particles are usually much larger than photochemically developed silver particles, and the resulting photographic images had dark-brown or black tonality. The larger silver particles were also more stable against both light and chemical-pollutant fading.

Both the salt print paper negative and calotype negative processes will be discussed in the Photographic Negatives section (forthcoming) when dealing with photographic negatives. The main reason why these negative processes are mentioned here is that there is confusion related to paper negatives and paper positives in the photographic literature, in exhibition catalogs, and on labels describing different paper-based photographic processes in exhibitions of nineteenth-century photography. Many exhibited positive prints are called calotypes or Talbotypes even though they are just salt prints produced using salt paper or calotype negatives.

Figure 2 shows a historical timeline of the salt print positive process.

Process Description

Good quality paper—preferably handmade or mold-made watercolor paper—is soaked in a salt solution (this can be sodium chloride but is often sodium citrate and ammonium chloride, usually around 4% by weight) and dried. In subdued light, it is brushed with a generous coating of a silver nitrate solution (around 12% by weight, sometimes containing a small amount of citric acid) and dried in darkness or very subdued light. The paper is then exposed under a negative using a UV light source (perhaps 10 minutes in bright sunlight) until the image is darker than

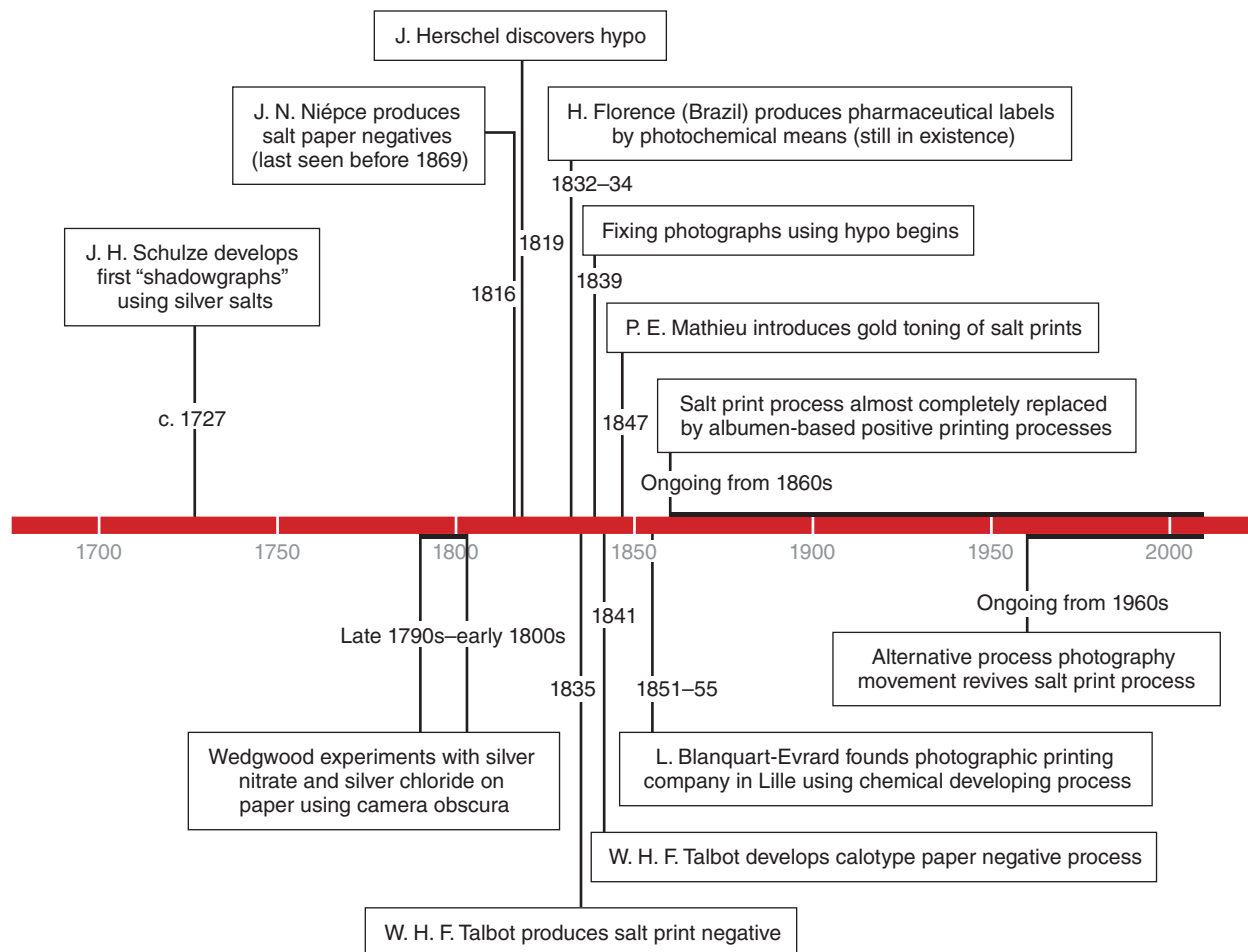
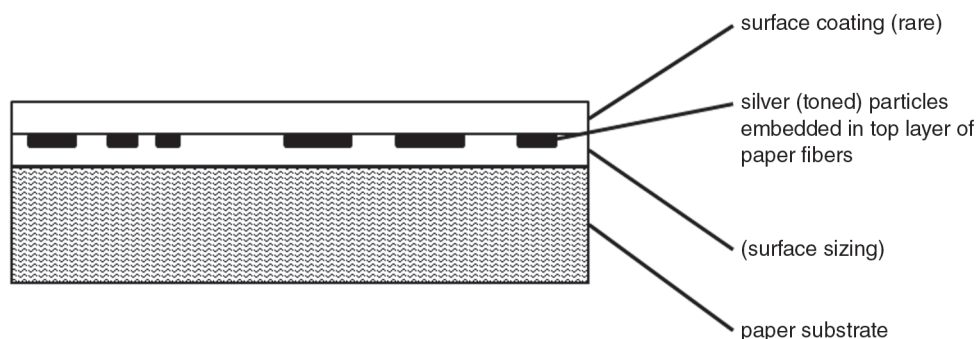


Figure 2 Timeline of the salt print positive process.

required. The paper is then washed in several rinses of water to remove excess silver nitrate, toned if desired (usually in gold toner), fixed in 5% sodium thiosulphate or dilute print fixer, and washed for an hour in water.

Figure 3 shows a schematic cross section of a typical salt print photograph.

Figure 3 Schematic cross section of a typical salt print photograph.



Main Application of the Salt Print Process

The salt print positive photographic process was virtually the only process used to create positive photographs from salt print negatives and calotype negatives after 1841. The process was also the main positive printing medium for early albumen negatives and wet collodion negatives. The salt print process was almost completely replaced by the silver albumen process by the middle of the 1850s, though it was still used by some photographers in proofing their negatives. After the 1960s and the birth of the alternative process photography movement, the salt print process was used on a very limited basis.

Noted Photographers Using the Salt Print Process

David Octavius Hill and Robert Adamson

Gustave Le Gray

William Henry Fox Talbot

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IDENTIFICATION: SALT PRINTS

Visual Signatures

The identification of salt print photographs may be challenging and difficult. A number of photographic processes yield a look and feel similar to that of salt prints. During the early period of silver albumen print photography, photographers tried to avoid creating glossy albumen photographs by diluting the albumen bath used in the preparation of albumen paper. Photographs created using diluted albumen have a semi-glossy or almost matte characteristic and are difficult to distinguish from salt print photographs printed on a highly sized paper substrate. (For further discussion, see Albumen section.)

Visual Characteristics

Most salt print photographs have a characteristic matte appearance. An uncoated salt print has a “sunken-in” appearance in the body of the paper substrate. Most salt prints were made using “quality writing paper,” and the differences between papers are noticeable when handling unmounted images. Viewed on a light table, many unmounted salt print photographs are semitranslucent, allowing for the detection of a paper watermark (fig. 4).

Watermarks are important for both provenancing and authentication of early salt print photographs. Any existing watermark should be well documented and added to the registrar database of photographs. A number of publications record historical watermark design changes, watermarks used by paper mills in various regions, and watermarks used by individual paper mills. An example of a watermark is shown in figure 5.

Many salt print photographs (1835–50) were not gold toned, and the tonality of the image may range from light brown to reddish brown. Some experts claim it is possible to determine if the salt print positive was printed using a paper negative or a glass collodion negative. Prints from a paper negative would be less sharp because of the light-scattering effect of the individual paper fibers from the negative. This works rather well if the paper negatives were not waxed to make



Figure 4 Six versions of Talbot's salt paper print *The Open Door* (fig. 1), displayed on a light table. Among them are several types of paper watermarks. Collection, National Media Museum (NMeM), Bradford, UK.

Figure 5 Detail of a Talbot salt print showing paper's watermark. (Image has been enhanced to bring out watermark.) Collection, National Media Museum (NMeM), Bradford, UK.



them more translucent, or if the waxing procedure was not performed efficiently. Well-waxed or varnish-saturated negatives usually do not provide fiber clues that would allow for a highly reliable determination of the type of negative (paper or glass collodion) used to create the print.

Microscopic Characteristics

Under an optical microscope, a salt print photograph shows the deposit of photochemically reduced silver particles on top of and between individual fibers of the paper substrate (figs. 6a–6c). Higher magnifications indicate the presence of sizing material coating the paper fiber surface and plugging in some areas between individual paper fibers. Silver particles are too small to be detected individually under an optical microscope. The glossiness of individual paper fibers is often difficult to distinguish from the glossiness of a surface-sizing medium. When reading optical micrographs, it is important not to overinterpret observed image features. FTIR analysis provides much more reliable information on the presence or absence of surface sizing.

Analytical Signatures

XRF

XRF analysis of unmounted salt print photographs should be relatively easy to interpret. Three versions of Talbot's photograph *The Open Door* were analyzed in our Talbot project study (see fig. 4). The recorded XRF spectra show the presence of different concentrations of silver, which is the imaging element of all of the images, and traces of calcium (Ca) and iron (Fe) from the paper substrate (figs. 7a–7c).

The most important finding from the analysis of a larger number of Talbot's photographs was the presence of cobalt and arsenic. We previously detected cobalt in salt print photographs in 1997 during our investigation of salt prints by David Octavius Hill and Robert Adamson (see the XRF spectrum in fig. 8). The presence of both elements is due to small particles of smalt (blue cobalt



Figure 6a Optical micrograph of a salt print photograph (10× magnification).



Figure 6b Optical micrograph of a salt print photograph (25× magnification).

Figure 6c Optical micrograph of a salt print photograph (40× magnification).

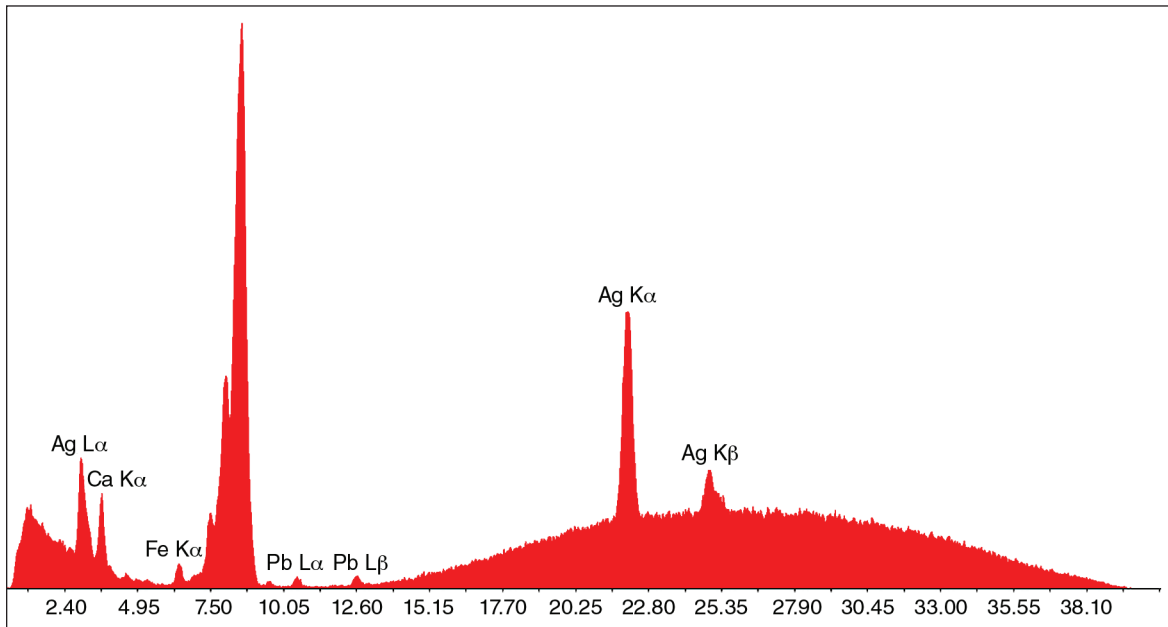


Figure 7a XRF spectrum of the first *Open Door* photograph.

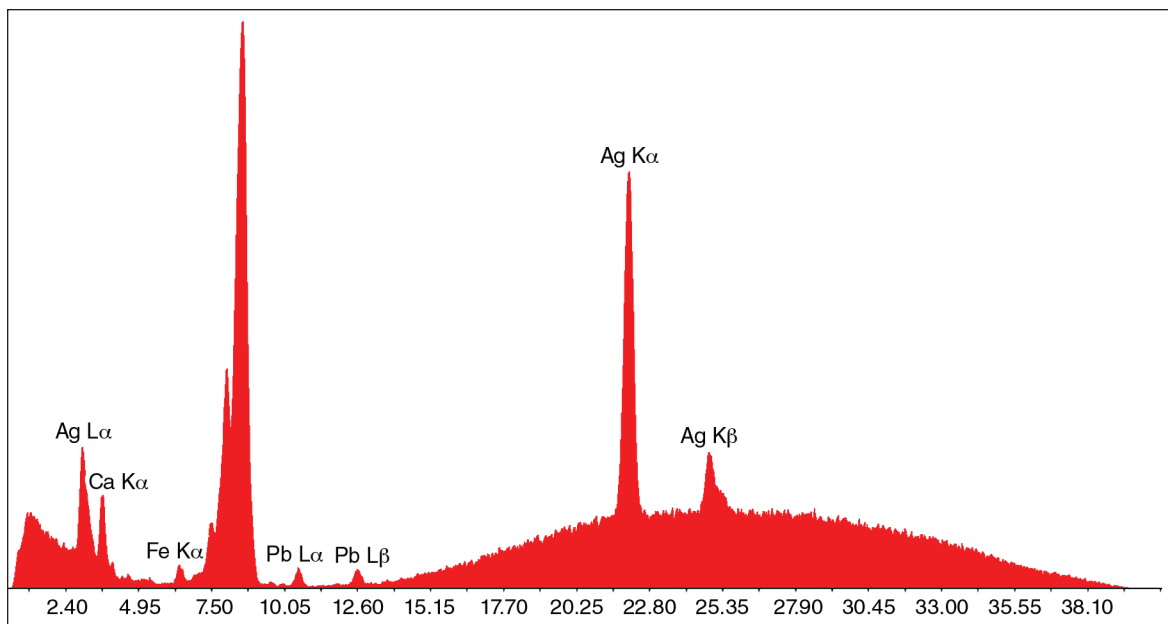


Figure 7a XRF spectrum of the second *Open Door* photograph.

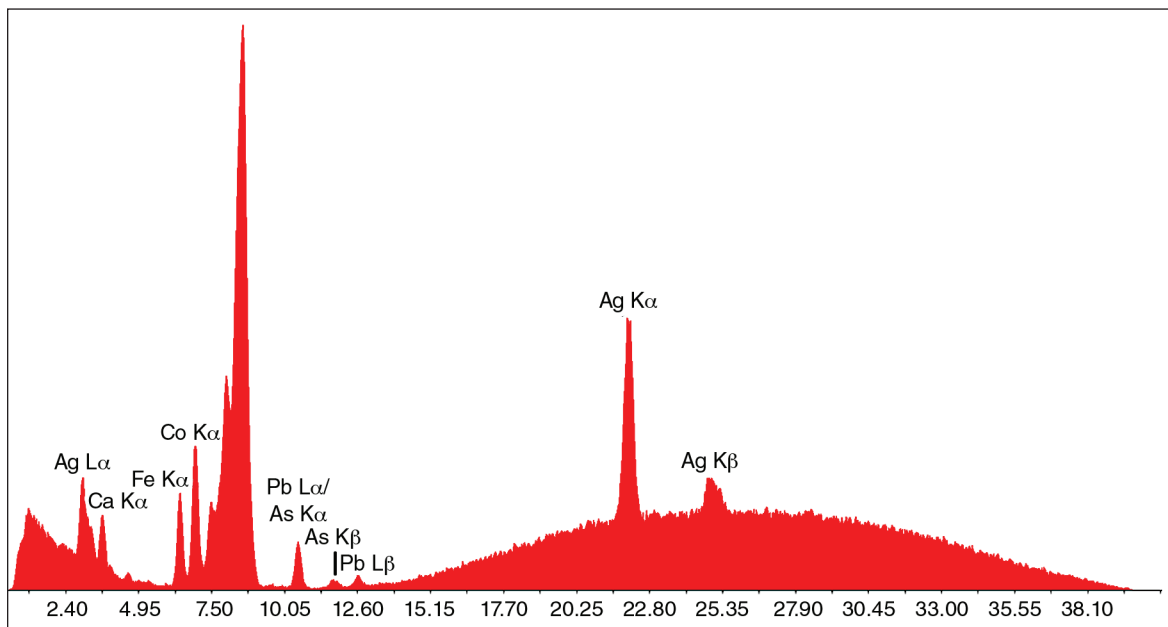


Figure 7c XRF spectrum of the third *Open Door* photograph.

glass) that manufacturers added to the paper fiber mass to help prevent yellowing of writing paper during natural aging. Being glass, smalt particles also contain small amounts of arsenic that were once added during smalt manufacturing to avoid foaming and the appearance of gas bubbles in the solid smalt mass.

XRF analysis of early British salt print photographs showed the presence of cobalt. Microscopic investigation of the paper substrate revealed that cobalt is present in the form of tiny smalt

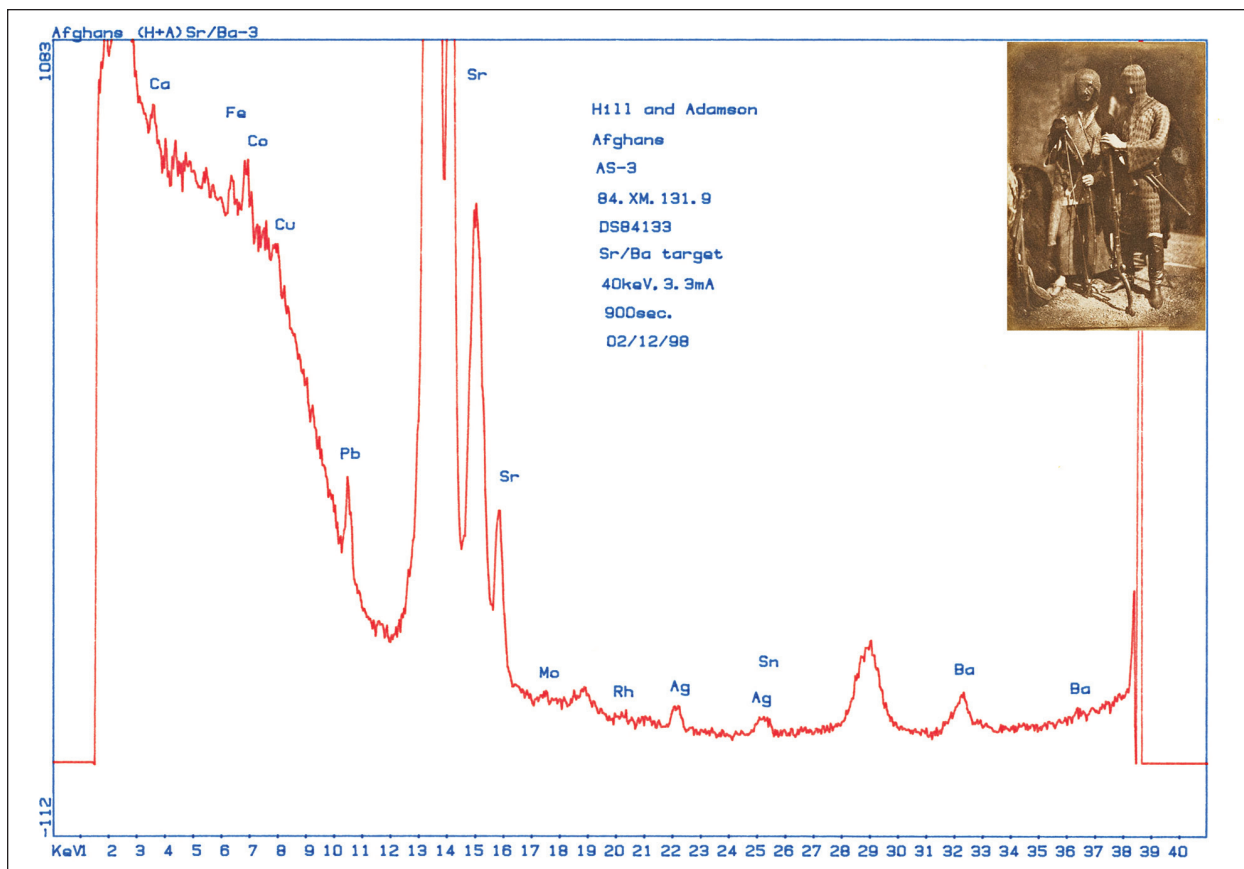


Figure 8 XRF spectrum of Hill and Adamson, *Lane and Peddie as Afghans*, 1843 (see inset). Salted paper print from a calotype negative. Spectrum obtained using a KeveX 45 laboratory instrument that indicated the presence of cobalt. Photograph, The J. Paul Getty Museum, Los Angeles.

particles embedded in the body of the paper substrate. Under low magnification these particles look like small specks of impurities, but under higher magnification and good illumination, the individual particles become bright blue (figs. 9a, 9b).

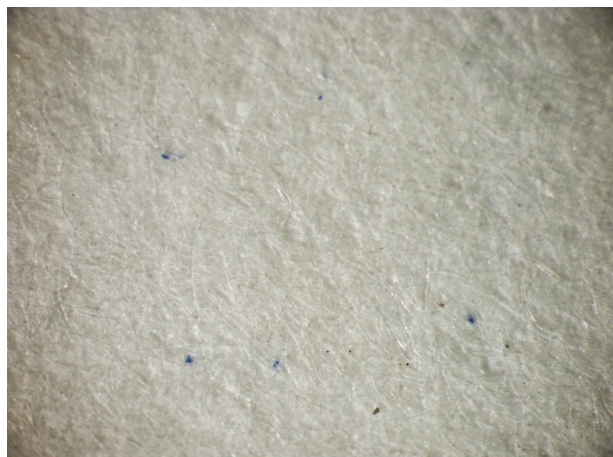


Figure 9a Micrograph showing individual small particles detected in Talbotype photographic paper (40x magnification).

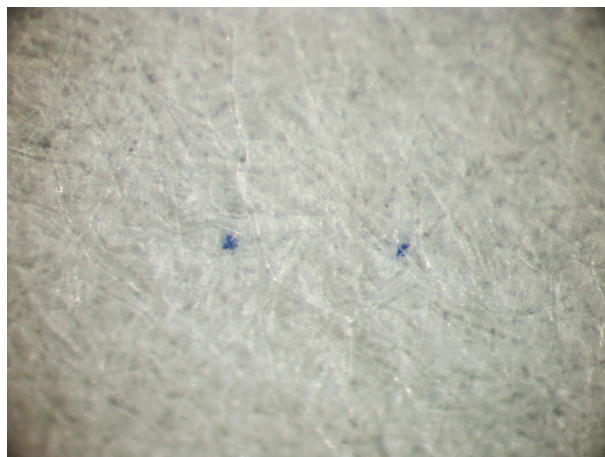


Figure 9b Micrograph showing individual small particles detected in Talbotype photographic paper (80x magnification).

Figure 10 Rolls of calotype-era Talbotype paper. Collection, National Media Museum (NMeM), Bradford, UK.



The number of small particles in a given area is low, but the high sensitivity of the XRF analysis allows for their analytical detection in most cases. Several rolls of different types of Talbotype photographic paper from the calotype era, courtesy of the National Media Museum (NMeM) collection, provided an opportunity to analyze and compare concentrations of cobalt in several paper substrates (fig. 10).

In our consultation with paper experts, we learned that small particles were added to paper fiber stock during the paper-making process to increase whiteness and combat yellowing during aging. Our XRF analysis has shown that the concentration of cobalt varied greatly among different types of paper, even in papers from the same mill. Several of Talbot's salt prints from the NMeM collection were printed on paper substrates with such a high concentration of small particles that the paper appeared almost light blue (fig. 11a, right). Its XRF spectrum is shown in figure 11b.

FTIR

ATR-FTIR analysis of salt print photographs is more complicated than the analysis of photographs coated with a high concentration of organic binder (albumen, collodion, or gelatin). The main organic component of salt prints is cellulose, an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand $\beta(1\rightarrow4)$ linked D-glucose units. Individual functional groups of cellulose exhibit a high level of spectral overlapping. Instead of several characteristic spectral peaks that could be used in identifying cellulose, the ATR-FTIR spectrum of cellulose is composed of a broad spectral envelope of overlapping peaks (fig. 12).

The presence of gelatin size can be detected by the presence of a relatively small-intensity Amide I spectral peak at $\sim 1640\text{ cm}^{-1}$ and also by the possible presence of the Amide II spectral

Figure 11a Two images of one of Talbot's bird photographs, one on typical paper (left) and one on bluish paper. Collection, National Media Museum (NMeM), Bradford, UK.

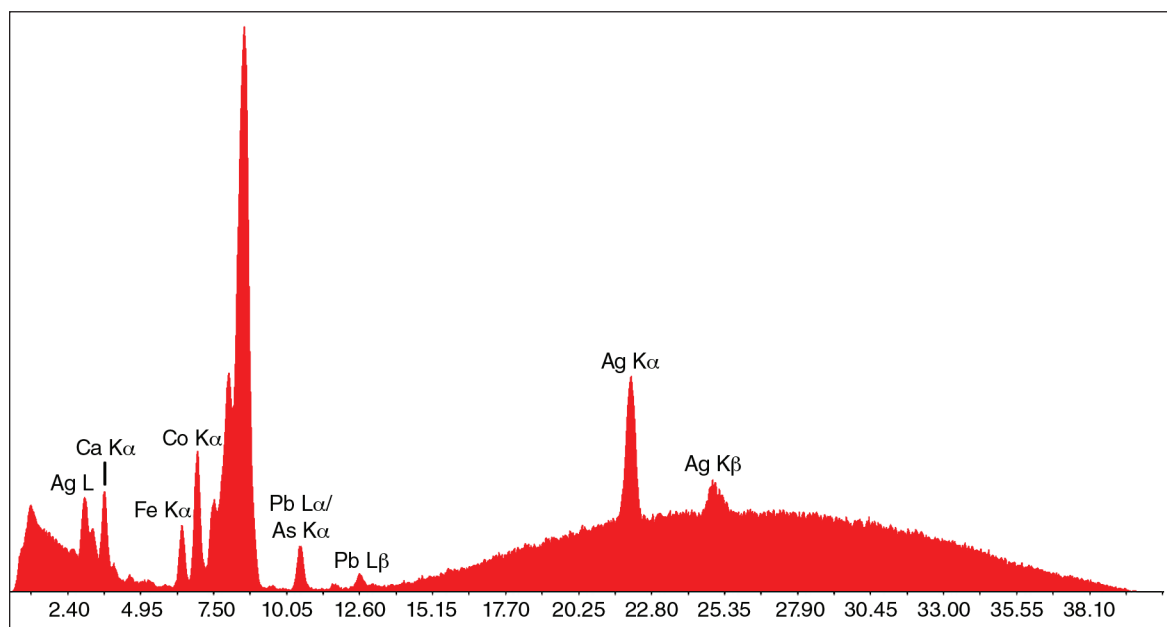


Figure 11b XRF spectrum of the photograph on right in fig. 11a, showing a high concentration of cobalt.

peak at $\sim 1530\text{ cm}^{-1}$. The presence of starch-based sizing material is much more complex. Both the starch and cellulose fibers are complex carbohydrates, and the ATR-FTIR spectrum does not allow for a simple way to deal with strong spectral overlaps of both components. If needed, microanalytical tests for the detection of starch can be used but would require physical sampling of the material.

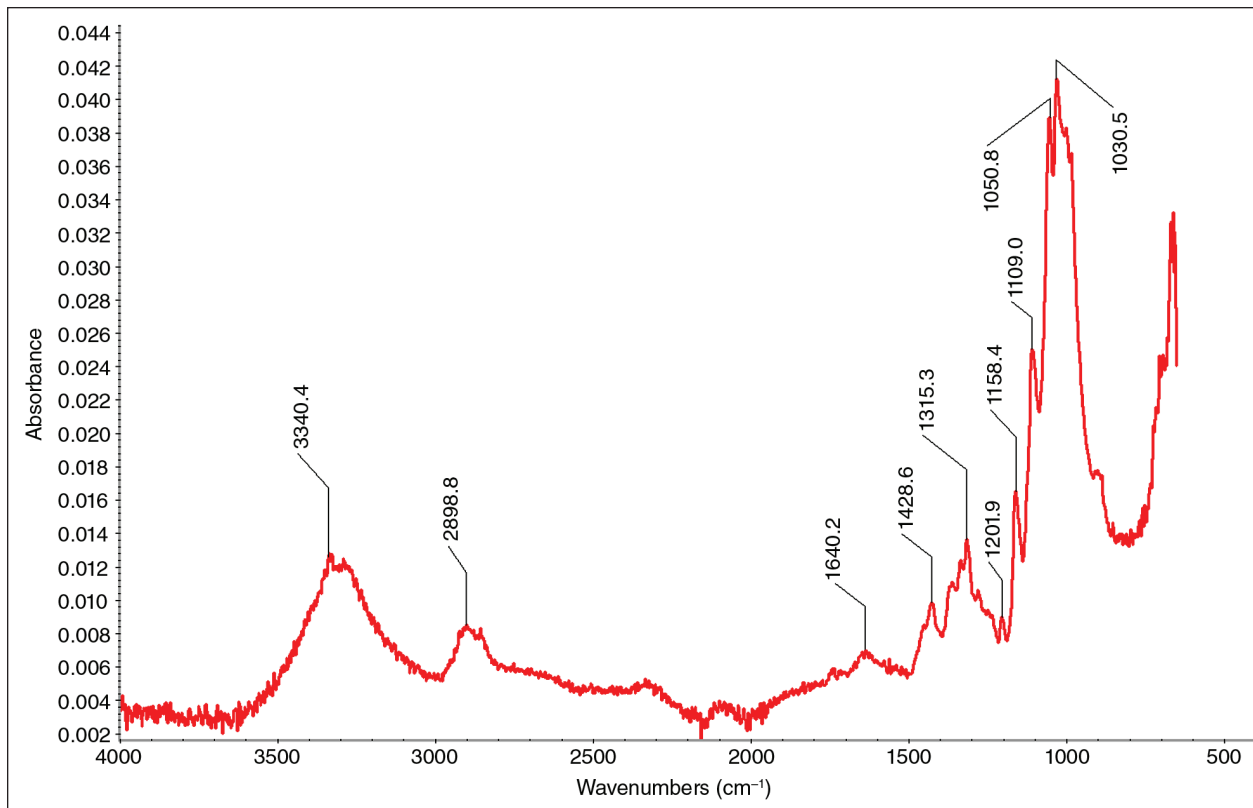


Figure 12 ATR-FTIR spectrum of pure cellulose, showing a broad spectral envelope of overlapping peaks.

Paper for salt print negatives and positives required a relatively high wet strength to withstand treatment in toning and fixing baths and multiple washings after processing. This was accomplished by internal sizing of the paper using different organic binders. The photographic literature describes the preference of English paper mills for using gelatin as the internal size and the use of starch-based internal sizing by French and other continental paper mills.

INTERPRETATION GUIDE

Table 1 Summary of the main microscopic and analytical signatures of salt print photographs and some processes commonly misidentified as salt prints. The information below is for typical versions of each process. Exceptions to each entry may exist but are rare.

Salt Prints															
Process	Surface Coating	Paper Fibers	Ag	Au	Pt	Fe	Hg	Ba	Other Inorganics	Cellulose	Albumen	Collodion	Gelatin	Other Organics	Tonality
Salted paper	(X) ^{***}	X!	X!	(X)	-	-	-	-	(Ti)*	X!	(X) ^{***}	-	(X) ^{**}	-	Brown-black
Albumen	(X)	X	X	(X)	(X)	-	-	-	(Ti)*	X	X	-	-	(coatings)	Brown-purple
Collodion	-	-	X	(X)	(X)	-	-	X	Sr	-	-	X	-	-	Brown-black
Gelatin	(X)	-	X	(X)	-	-	-	X	Sr	-	-	-	X	-	Range depending on toning
Platinothype	-	X	-	-	X	X	(X)	-	(Pd) [†] , (Ti)*	X	-	-	-	-	Brown-black
Palladiothype	-	X	-	-	(X) [†]	X	-	-	Pd, (Ti)*	X	-	-	-	-	Brown
Kallithype	-	X	X	-	-	X	-	-	(Ti)*	X	-	-	-	-	Brown
Tannin toned cyanotype	-	X	-	-	-	X	-	-	(Ti)*	X	-	-	-	CN	Brown

X Present Small concentration of protein (gelatin) can be detected in some papers internally sized with gelatin

- Absent Beeswax, albumen (albumen coated), gelatin coated (very rare)

() May be present Some modern prints on 20th- and 21st-century substrates containing TiO₂

! Key signature Modern platinothypes/palladiothypes can have a mixture of both Pt and Pd metals



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