

# PLATINOTYPE



Dusan C. Stulik | Art Kaplan



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The Getty Conservation Institute  
1200 Getty Center Drive, Suite 700  
Los Angeles, CA 90049-1684  
United States  
Telephone: 310 440-7325  
Fax: 310 440-7702  
Email: [gciweb@getty.edu](mailto:gciweb@getty.edu)  
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Front cover: Peter H. Emerson, *Gathering Water-Lilies*, 1880s. Platinotype print. © Royal Photographic Society/NMeM/Science & Society.

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# PLATINOTYPE

English: platinotype

French: *platinotype*

German: Platinotypie

## HISTORICAL BACKGROUND

The platinotype process was invented by William Willis (British, 1841–1923); patented by Willis in 1873. Johann Wolfgang Doebereiner was the first to describe the photochemical reduction of platinum salts (1826). He also discovered the photochemical reduction of ferric oxalate. In 1832 John Frederick William Herschel described the photosensitivity of a water solution of platinous (II) compounds when irradiated by UV radiation.

The first successful platinotype process was developed and patented by William Willis in 1873. In his first patent, titled “Improvements in Photo-chemical Printing,” Willis described an early version of the platinotype process but also suggested that salts of iridium and gold can be used in an analogous way. The chemistry of his first platinotype process also included the addition of silver or lead nitrates into the sensitizing solution. The addition of silver nitrate was omitted from Willis’s second patent, issued in 1878, in which Willis suggested the possibility of using palladium as an image-forming metal. In 1879 Willis founded the Platinotype Company in London, which was instrumental in the promotion of the platinotype process and the manufacture of a variety of platinotype supplies. The third Willis platinotype patent, from 1880, excluded the use of both silver and lead while increasing the amount of platinum compounds in the sensitizing solution.

The first commercial platinotype papers were offered for sale in 1880. These were the “hot developed” papers, followed in 1892 by “cold developed” papers. In 1887 Giuseppe Pizzighelli and Arthur von Hübl developed a POP variant of platinum paper.

The platinotype process was widely used by professional, art, and amateur photographers from about 1888 to the beginning of World War I. (An example print appears in fig. 1.) During that time a number of companies started to produce and market supplies for platinum printing. In 1911 the Platinotype Company marketed fifteen types of platinotype papers; Eastman Kodak and Gevaert each marketed eleven. These included the black and sepia variety of papers of different weight, thickness, surface characteristics, and texture. The price of platinum paper in the early 1890s was about the same as that of silver bromide enlarging paper. The cost of platinum metal started to rise by the turn of the twentieth century, just when the chemical industry had begun

**Figure 1** Peter H. Emerson, *Gathering Water-Lilies*, 1880s. Platinotype print. © Royal Photographic Society/NMeM/Science & Society.



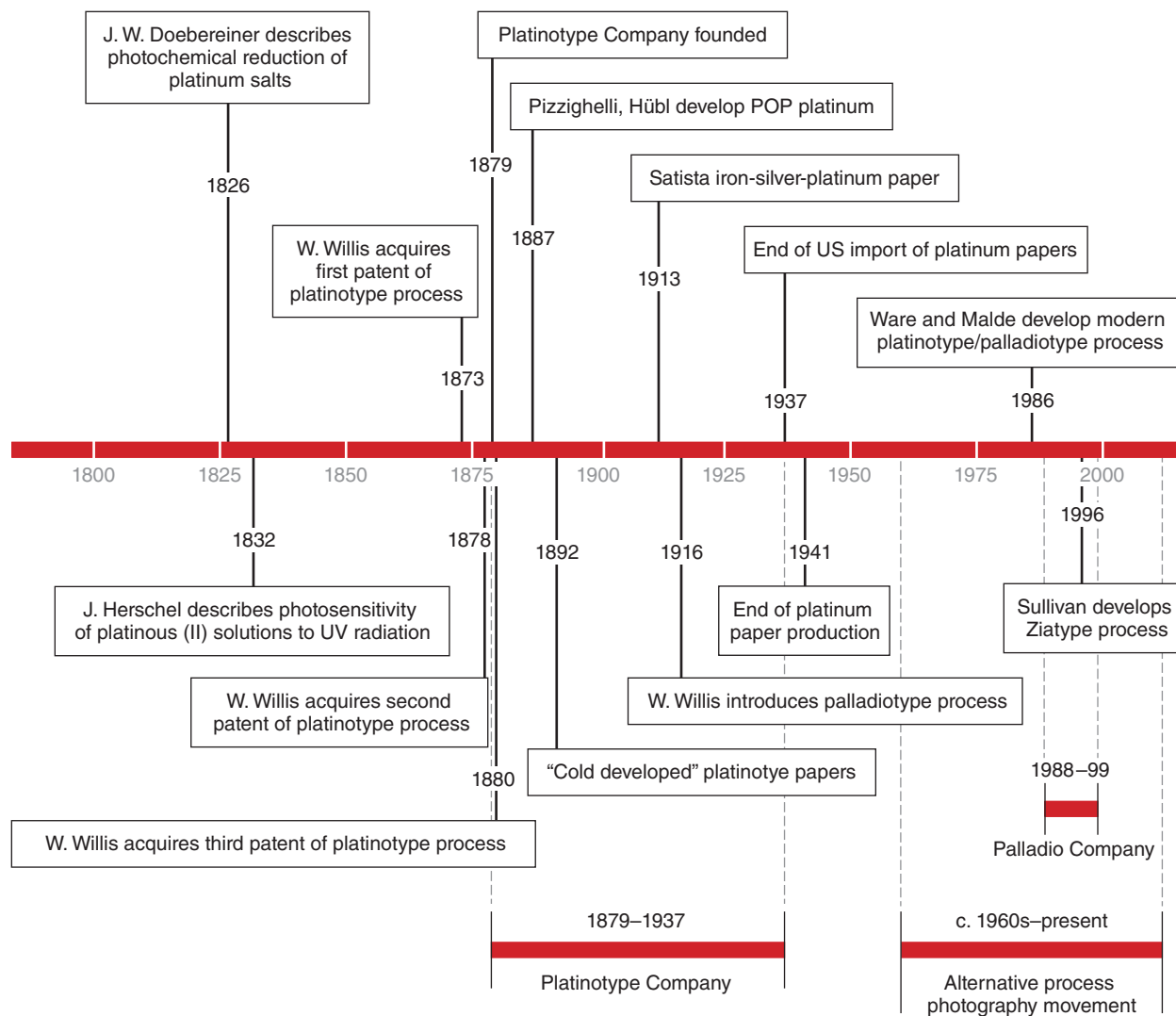
using it as a catalyst. Willis tried to economize the process and in 1913 introduced Satista iron-silver-platinum paper. During World War I the British government declared platinum a strategic metal and forbade its use in photography. In response, Willis introduced the palladiotype process in 1916. The period after the war was marked by the introduction of small-format photographic cameras that produced negatives too small to be used in contact printing. A wider use of enlarging processes focused more attention on silver gelatin photographic paper.

Production of commercial platinotype paper stopped in the United States in the 1930s and in Great Britain in 1941. The renaissance of alternative photographic processes, which started in the late 1960s, precipitated several attempts to reintroduce the commercial manufacture of platinum- and palladium-based photographic papers, but the production of these materials was short lived. Much more successful was the commercial production of chemicals and kits that gave photographers an opportunity to make their own platinotype or palladiotype papers. In 1986 Mike Ware and Pradip Malde developed and introduced a modern variety of Pizzighelli and Hübl's process from 1887. Ziatype, a new variant of the palladiotype process using a variety of double salts of palladium and other metals (lithium, cesium, etc.), was introduced in 1996 by Richard Sullivan in Santa Fe, New Mexico.

Figure 2 shows a historical timeline of the platinotype photographic process.

### Process Description

After 1879, when William Willis's Platinotype Company started supplying material for platinum printing, commercial platinum paper was usually sold packed with a drying compound in sealed metal tubes (fig. 3). Starting around 1940, commercial platinum paper was no longer available. In spite of several attempts to revive its manufacture (palladio paper of the 1980s, for example), the majority of modern platinotype prints were created on hand-coated platinum paper.



**Figure 2** Timeline of the platinotype photographic process.

**Figure 3** Three different kinds of commercial platinotype paper in their original metal tubes, shown with a capsule of calcium chloride desiccant that was used to extend the shelf life of platinotype paper.

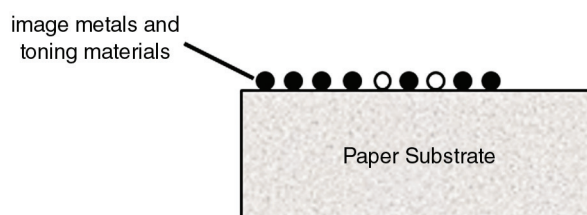


The platinotype process consists of several distinct steps:

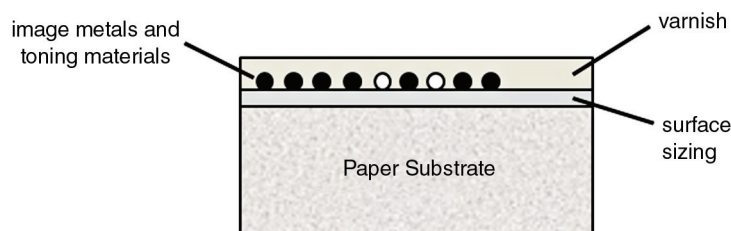
1. A selected paper for platinum printing is usually surface sized with starch or gelatin.
2. The dried sized paper is coated with a solution of ferric oxalate and potassium chloroplatinite and dried in the dark.
3. The dried sensitized platinotype paper is exposed under a negative using natural or artificial light sources containing UV radiation.
4. The light exposure produces a faint brownish image made from the photochemically generated ferrous oxalate.
5. The exposed platinum paper is fully developed in a solution of potassium oxalate or other platinotype developer. The platinotype image appears almost immediately.
6. The developed platinotype is “fixed” and cleared by dissolving and removing any unexposed ferric oxalate.
7. The well-fixed platinotype is washed in water and dried.

The contrast of platinotype photographs could be adjusted by adding a solution of potassium chlorate or dichromate salts. The tonality of platinotype prints could be controlled by processing (hot/cold developer, concentration of the developing solution) or by adding mercury salt to the developing solution. The addition of mercury chloride (Hübl has described the use of mercury citrate as well) usually pushed the tonality toward a brown or sepia color.

Figures 4a and 4b show schematic cross sections of a simple and a complex platinotype photograph.



**Figure 4a** A general cross section of a simple platinotype photograph.



**Figure 4b** A general cross section of a complex platinotype photograph.

## Main Application of the Platinotype Process

Platinum being the most chemically stable metal found in nature, the platinotype process was introduced in the late 1870s as a stable alternative to silver-based photographic processes. The process was used by photographers of the Pictorialist movement and by commercial photographers for high-end commercial portraiture.

## Noted Photographers Using the Platinotype Process

Manuel Alvarez Bravo  
Edward Sheriff Curtis  
Peter Henry Emerson  
Frederick Evans  
Laura Gilpin  
Gertrude Käsebier  
Robert Mapplethorpe  
Modern alternative process photographers  
Tina Modotti  
Irving Penn  
Pictorialists  
Edward Steichen  
Alfred Stieglitz  
Paul Strand  
Edward Weston  
Clarence White

## Possible Post-Processing Treatments of Platinotype Photographs

Toning  
Varnishing  
Intensification  
Tinting

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## Key Platinotype-Related Patents

- W. Willis, English Patent 2,011 (June 5, 1873)
- W. Willis, English Patent 2,800 (July 12, 1878)
- W. Willis, English Patent 1,117 (March 15, 1880)
- W. Willis, English Patent 1,681 (Feb. 2, 1887)

## IDENTIFICATION: PLATINOTYPES

### Visual Signatures

#### Visual Characteristics

The imaging material of platinotype images consists of finely distributed particles of platinum. The most important characteristic of an uncoated platinotype photograph is its deeply matte surface. Left unvarnished, platinotype images do not show any gloss even when observed at a low angle against a light source or when rotated in front of the eyes during visual examination. The tonality of untuned platinotype photographs can range from brown to rich black.

### CAUTION!

Many other photographic processes (palladiotype, kallitype, Van Dyke, etc.) may exhibit visual effects similar to those of platinotype photographs. Without chemical analysis, it is virtually impossible to correctly identify these photographic processes or process variants.

Some older platinotype images that were not completely cleared of the remaining ferric salts may exhibit a slight or more pronounced yellowing or reddish tonality of highlights (fig. 5).

In a number of cases, it was observed that papers and/or photographs that were stored for a long time in direct contact with a platinotype photograph may exhibit a clearly visible dark reddish-brown “image transfer” caused by the catalytic effect of platinum-metal particles (fig. 6). The image transfer can be imparted onto one or more layers of a platinotype presentation package, as seen in figure 7.

**Figure 5** A poorly washed and cleared platinotype photograph exhibiting a yellowing or reddish tonality. Residenzschloss, Dresden, Kupferstich-Kabinett collection.



**CAUTION!**

Platinum-toned silver-based photographs can also cause an image transfer. This phenomenon can be found rather often on the back side of many matte-collodion card photographs stored for some time stacked in a pile.

**Figure 6** “Image transfer” imprinted onto the back of a photograph through direct long-term contact with another platinotype photograph.



**Figure 7** An example of a multiple-page image transfer onto a glassine paper overlay (on right).



### Microscopic Characteristics

Important visual clues needed for the identification of the platinotype class of photographic images can be obtained when examining a photograph using a low-power stereomicroscope (figs. 8a–8c). Fibers of the paper substrate are clearly visible under a layer of platinum particles.

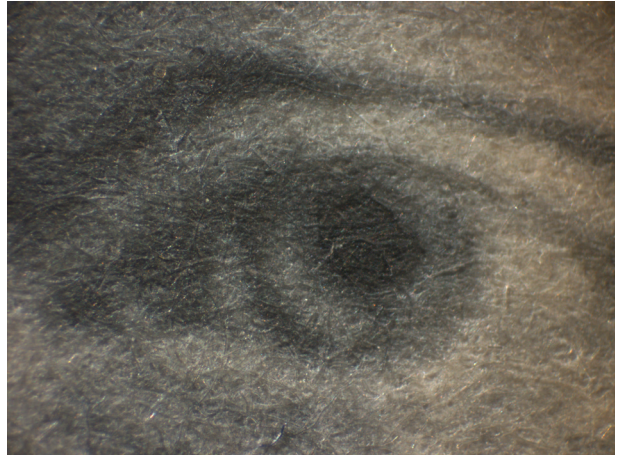
Some surface fibers appear to be slightly darker than the surrounding fibers. This feature is typical for all iron-based photographic processes. Individual platinum particles are of nanometer size and thus invisible when examined using visible-light microscopy with a diffraction-based resolution limit of about 2000 $\times$ . Observation of individual platinum particles requires the use of a transmission electron microscope (TEM) and the analysis and identification of the particles may need a scanning transmission electron microscope (STEM) in combination with an energy dispersive X-ray analyzer (EDX).

Observed at slightly higher magnification (25 $\times$ –200 $\times$ ), the microscopic image loses its typical matte character because of the inherent gloss of individual cotton fibers of the paper substrate. This gloss makes it difficult or impossible to identify the presence or absence of surface sizing. The black mass of platinum coats the individual cotton fibers without filling in or clogging the interfiber space of the paper (see fig. 8c). This effect is even more visible under the high magnification of a scanning electron microscope (SEM) (figs. 9a, 9b). The white particles in the SEM pictures are particles of metallic platinum. Even though some particles are submicron in size, they can measure up to 1 mm in diameter.



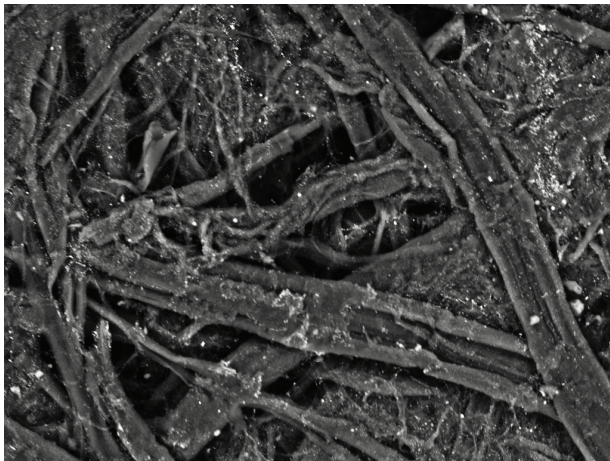
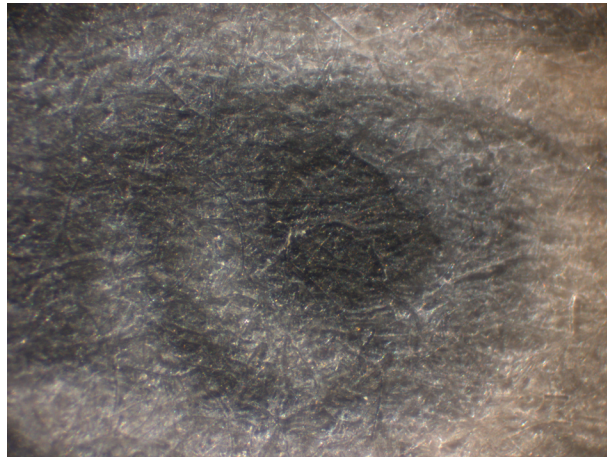


**Figure 8a** Detail of a platinotype photograph (6.3x magnification), showing clearly visible surface fibers.

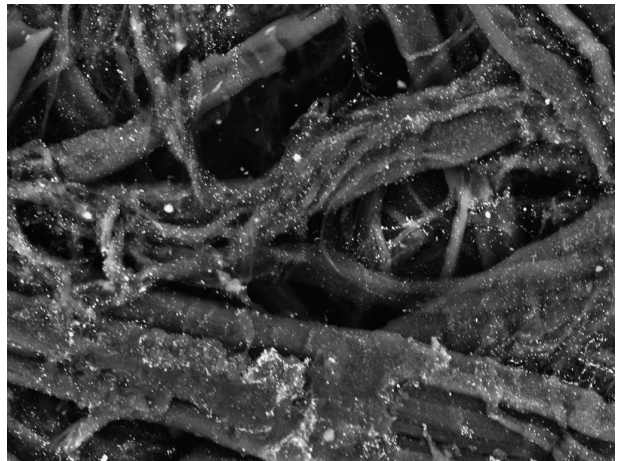


**Figure 8b** Detail of a platinotype photograph (25x magnification), showing clearly visible surface fibers.

**Figure 8c** Detail of a platinotype photograph (40x magnification), showing clearly visible surface fibers.



**Figure 9a** Detail showing the platinum-coated fibers of the platinotype photograph in fig. 8a (500x magnification), viewed on a SEM.



**Figure 9b** Detail showing the platinum-coated fibers of the platinotype photograph in fig. 8a (1000x magnification), viewed on a SEM.

## Analytical Signatures

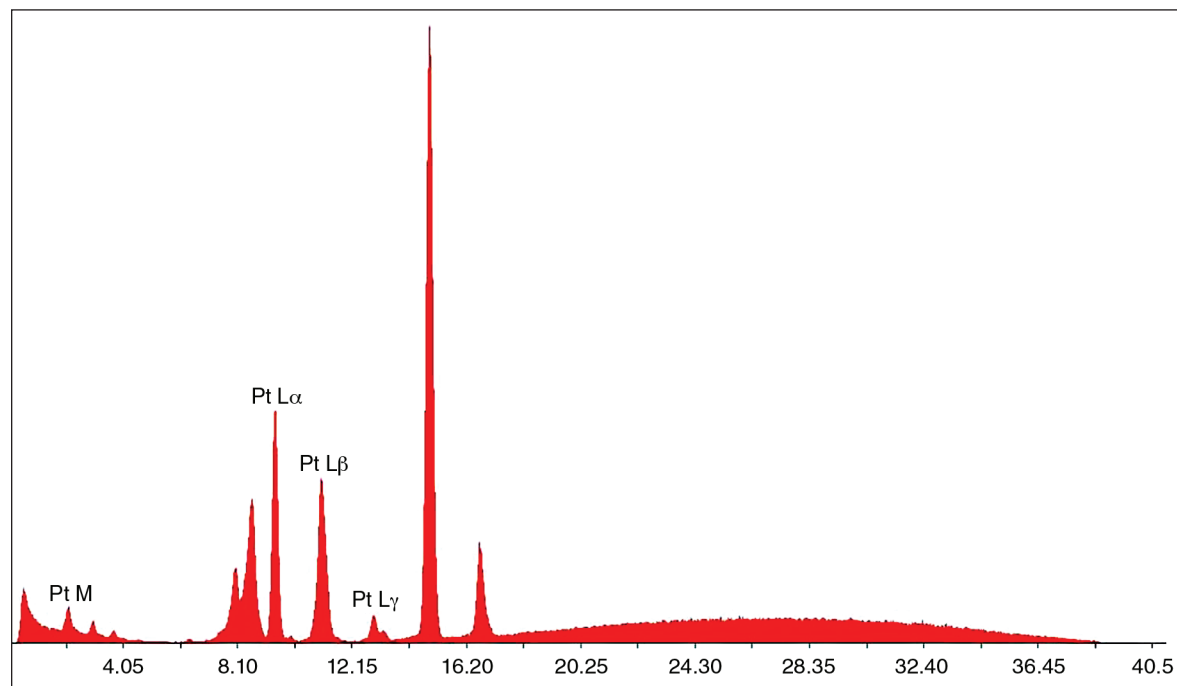
Microscopic investigation is usually successful in identifying a photograph based on its characteristics as a “platinotype-like photograph.” However, determining if the image is made using a platinotype, palladiotype, kallitype, or other process is beyond the capabilities of visual or microscopic investigation alone.

The most important analytical tool in differentiating between different platinotype-like photographic processes is XRF, which can detect most of the heavier (above sodium) chemical elements present in analyzed photographs with high sensitivity and a minimum number of spectral interferences. XRF analysis is also nondestructive and can be conducted without the need for physical contact with the analyzed photograph.

### XRF

XRF analysis of the platinotype photograph in figure 8a shows spectral peaks for platinum, the principal image element of the platinotype image. The XRF spectrum of a thin platinum film (99.6  $\mu\text{g}/\text{cm}^2$  of Pt) shows two characteristic spectral peaks (Pt  $L\alpha$  at 9.44 keV and Pt  $L\beta$  at 11.07 keV) of platinum with a typical spectral intensity ratio of approximately 5:4 (fig. 10).

The Pt K spectral peaks are at much higher energy and usually cannot be detected using portable or standard laboratory XRF spectrometers operating at an X-ray tube voltage of under 50 keV. Of other spectral peaks readily visible in the spectra of platinum-containing materials, the most important is the Pt- $M\alpha$  spectral peak at 2.05keV. This peak is located in a region rich with many potential spectral impurities ( $M\alpha$  of Au at 2.12 keV, Hg at 2.20 keV, and Re, our instrument



**Figure 10** XRF spectrum of a 99.6  $\mu\text{g}/\text{cm}^2$  thin film of platinum showing all major spectral peaks potentially visible in platinotype photographs.



anode of the  $M\alpha$ , at 1.84 keV, the  $L\alpha$  of Sr at 1.81 keV, the  $L\alpha$  of Zr at 2.04 keV, and the  $K\alpha$  of K at 2.14 keV). It should not be used as the primary spectral peak for the identification of the presence of platinum. The best way to identify platinum is to look for the Pt- $L\alpha$  peak, then for the clear presence of the lower-intensity Pt- $L\beta$  peak. The Pt-M peak is used only to confirm the presence of platinum.

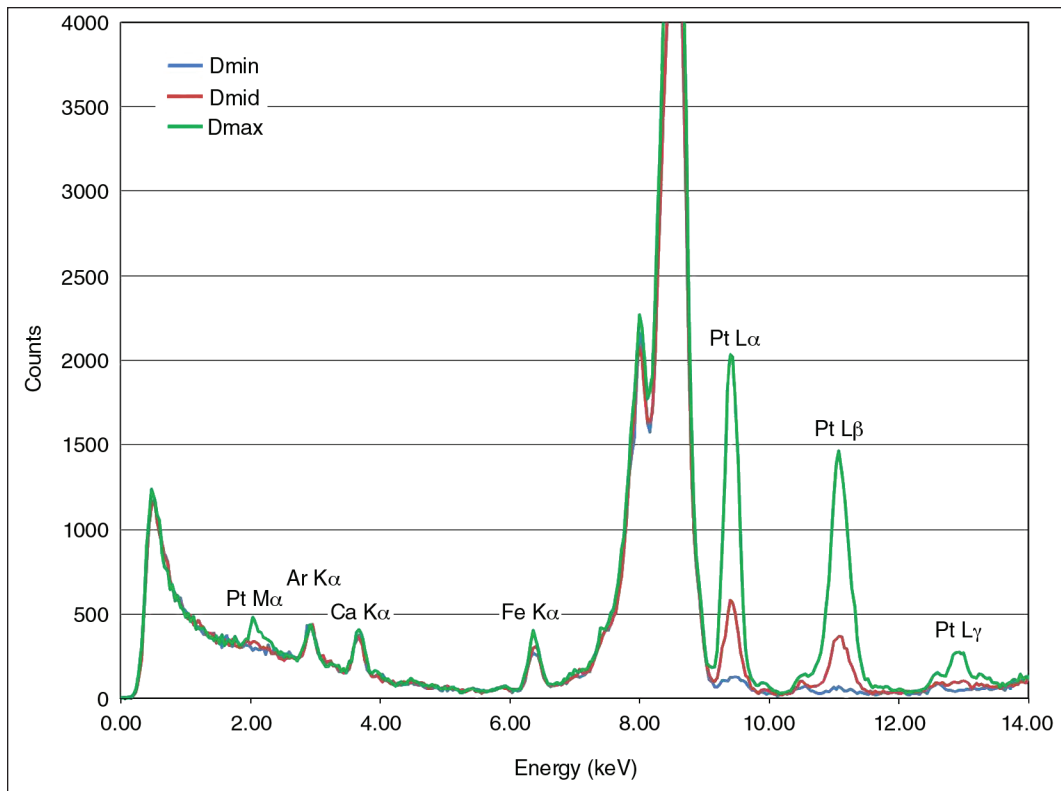
The platinum peaks of most platinotype images are usually accompanied by stronger or weaker spectral peaks for iron (Fe  $K\alpha$  at 6.40 keV and Fe  $K\beta$  at 7.06 keV). Many fixing/clearing procedures were developed and carried out in the past to dissolve unexposed ferric oxalate. However, our investigation shows that even after applying the best fixing and clearing procedures, enough iron is left in the platinotype photograph to allow for its detection using XRF (when the concentration of iron is very low, only the Fe- $K\alpha$  spectral peak may be clearly visible in the spectrum). The absence of silver (Ag  $K\alpha$  at 22.16 keV) in an analyzed photograph (fig. 11a) also indicates a non-silver-based photographic process.

An analysis of several areas of the image tonality has the advantage of differentiating between the presence of chemical elements (concentrations of platinum and iron that are different in the  $D_{max}$  and  $D_{min}$  regions) that are part of the image-forming process and elements (calcium) that are uniformly distributed throughout the paper substrate (fig. 11b). In some, namely older, platinotype images, low concentrations of palladium can also be detected (fig. 12).

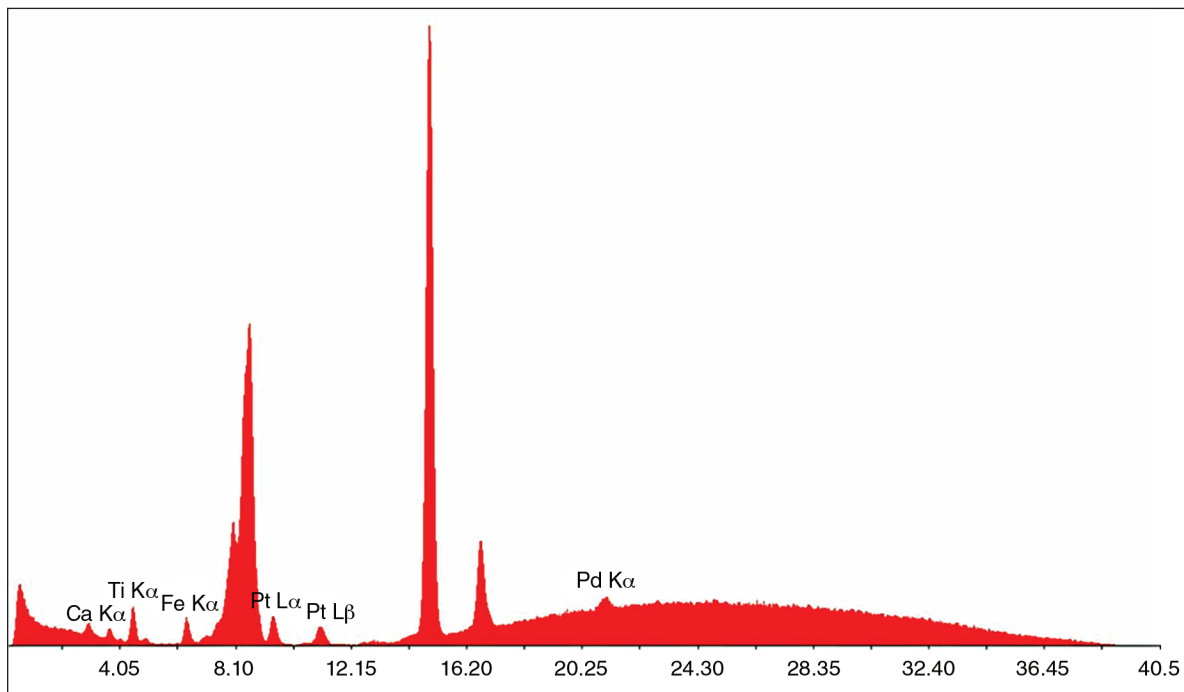
Finding a low concentration of palladium does not necessarily indicate the deliberate addition of palladium compounds to the sensitizing solution when preparing platinotype paper. Most platinotype photographs made before World War I are simple platinotypes. Only after 1917 did photographers start to use palladium metal—and, later, platinum-palladium mixtures—when coating their own paper.

**Figure 11a** Early 20th-century platinotype photograph by an anonymous artist.





**Figure 11b** XRF spectra recorded for Dmax, Dmid, and Dmin areas of the platinotype photograph in fig. 11a.



**Figure 12** XRF spectrum of an early platinotype photograph containing a low concentration of palladium.

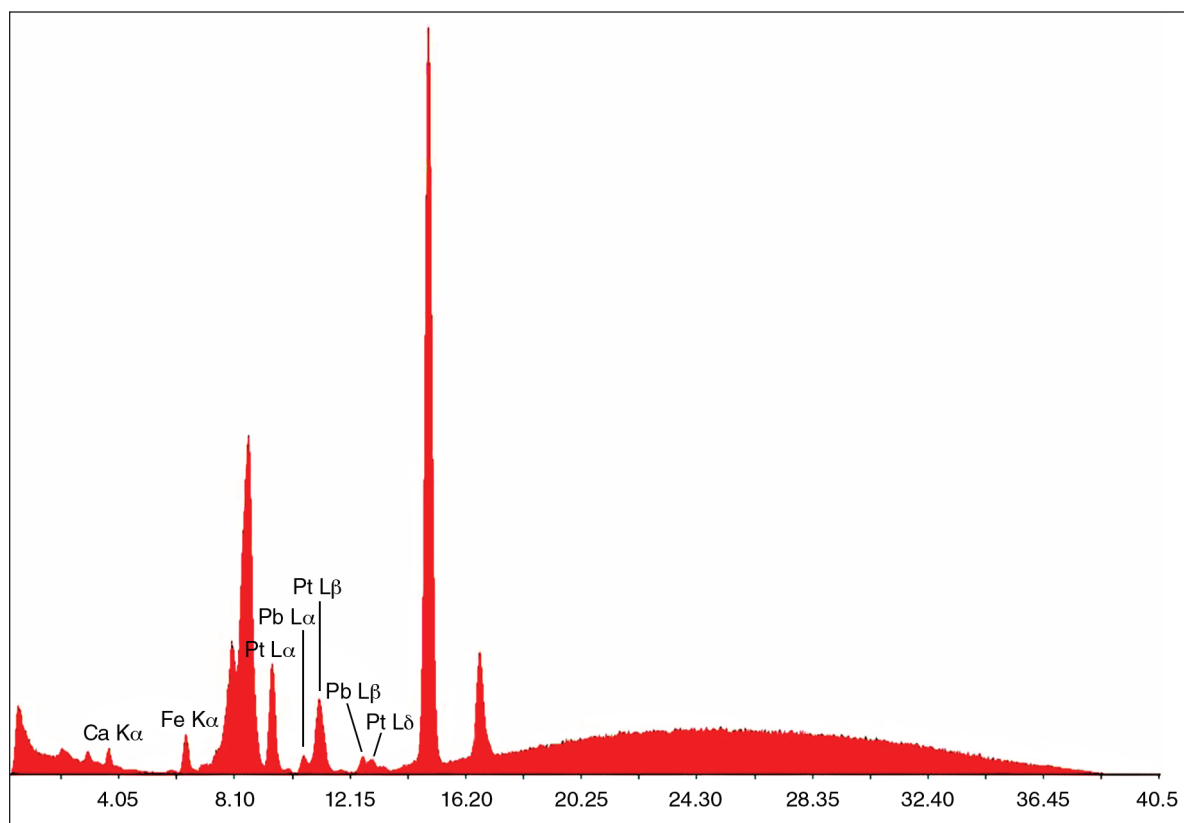
Early platinotype formulas used the addition of lead oxalate to facilitate good uniform development of the platinotype image (fig. 13). The lead oxalate was also recommended by Pizzighelli and Hübl for their POP variant of the platinotype process. Lead was introduced by Willis in 1873 as part of the platinotype process but was later eliminated. Several later platinotype formulas used the addition of lead oxalate to facilitate a more uniform reduction of platinum salts during development.

Some early platinotype photographers added a small amount of potassium dichromate to the sensitizing solution to increase the contrast of platinotype photographs made using low-contrast (“flat”) photographic negatives. Even a small concentration of chromium can be detected using an XRF spectrometer (fig. 14).

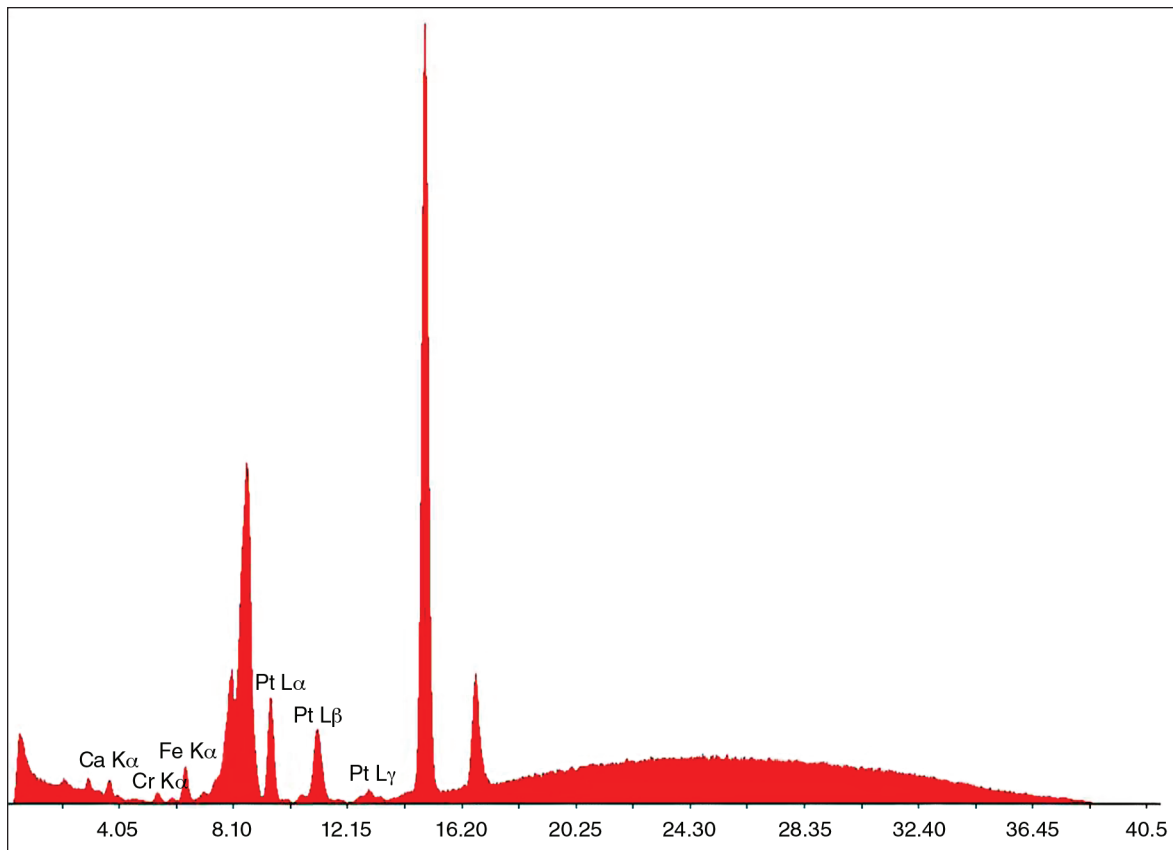
### CAUTION!

Some mounting boards and paper substrates also contain small amounts of lead. When a platinotype photograph is permanently attached to a mounting board, it is important to analyze both the board outside of the image and the photograph mounted on the board, then conduct a background subtraction (board signal) while interpreting the analytical results.

An alternative way to increase the contrast of platinotype images is through the addition of a small amount of potassium chlorate (KClO) to the sensitizing solution. The chlorate treatment cannot be detected analytically due to its high level of solubility, but the treatment is responsible for a visually detectable “patchiness” in the platinum image.



**Figure 13** Detail of the XRF spectrum of an early platinotype photograph, showing the presence of lead.

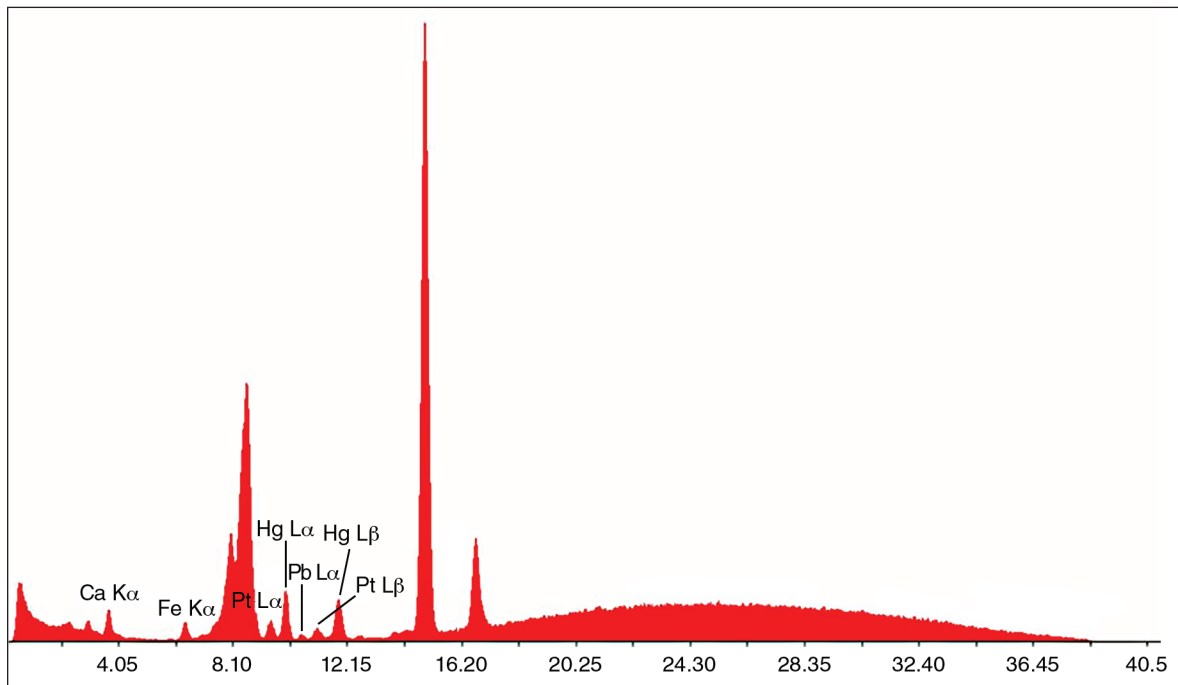


**Figure 14** XRF spectrum of a platinotype containing a small amount of chromium used to adjust the contrast of the final photograph.

The color and tonality of platinotype images can be changed slightly by adjusting the development conditions and the chemistry of the developing solution of an exposed platinotype paper. In general, “hot developed” platinum prints and “cold developed” platinum prints processed at higher temperatures of a developing bath yield brownish photographs. This is caused by a change in the particle size of developed platinum particles. The smaller particles appear browner than large particles, which absorb more light.

Some photographers did not like the dark-black tonality of platinotype photographs. In response, several manufacturing companies began producing an assortment of so-called sepia platinotype papers to answer the call for “warmer” or browner platinotype photographs. These papers included the addition of mercury chloride ( $\text{HgCl}_2$ ) to the sensitizing solution. A similar effect could be achieved by developing the platinotype photographs in a bath containing mercury chloride. The mercury chloride acts as a retardant for the development of platinum particles, reducing the particle size and making the final platinotype image appear browner. As such, the mercury treatment is more a physical effect than a toning effect. Mercury-containing platinotypes are often called “mercury-toned” platinotypes. Even though this description is not entirely correct, it has historical value and was widely used in the photographic literature. The presence of mercury in platinotypes can be readily detected using XRF analysis (figs. 15a, 15b).

**Figure 15a** Sepia  
platinotype photograph.



**Figure 15b** XRF spectrum of the print in 15a, indicating the presence of mercury.



In most cases, the concentration of mercury was much lower than the concentration of platinum, but our analysis of a large number of early platinotype photographs identified some platinotype images with a high concentration of mercury. Some commercial sepia platinotype papers (fig. 16) had mercury already incorporated into the sensitizing solution. Others relied on a modification of image tonality during the development phase based on the addition of mercury chloride to the developing solution.

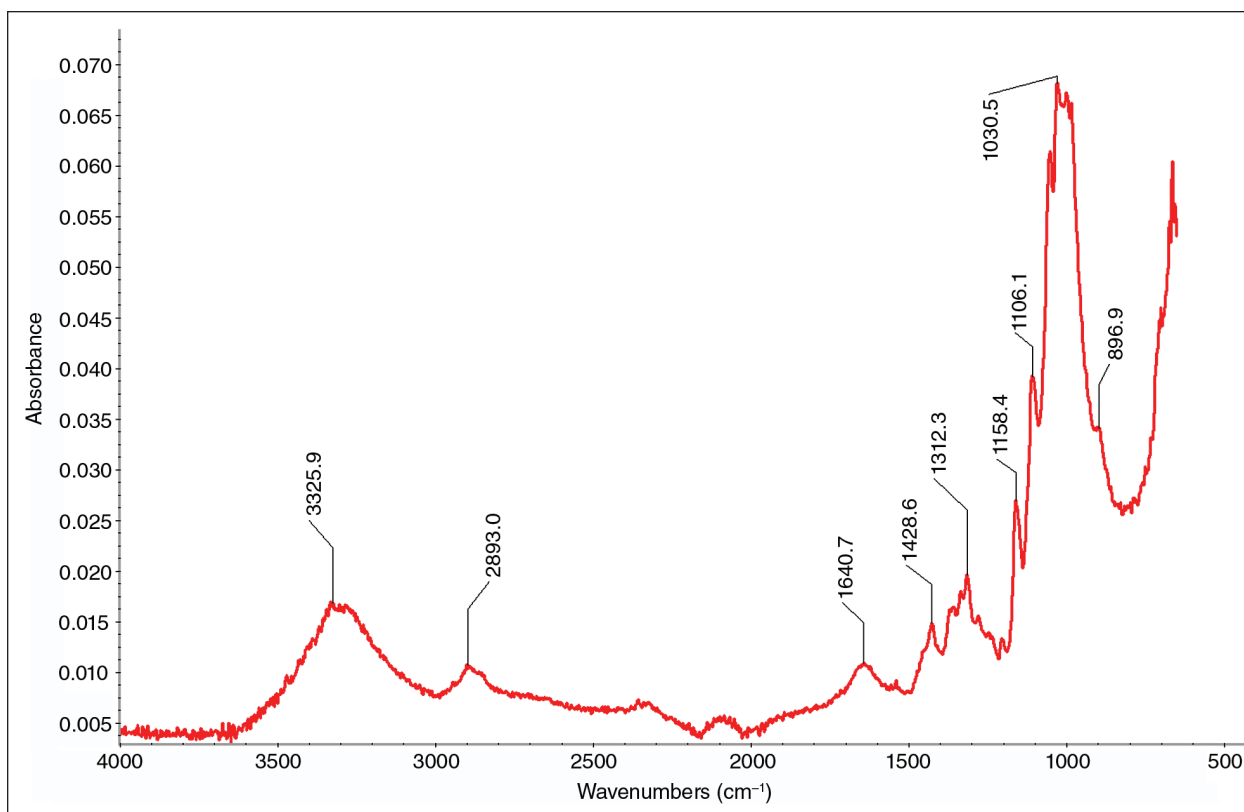
### FTIR

Infrared spectrometry is of minimal help when investigating platinotype-like photographic images. The platinotype image is composed mostly of platinum, which is inactive in the infrared region of the spectrum. Peak characteristics for the paper substrate (cellulose) are the main spectral peaks detectable in ATR-FTIR analysis of a platinotype photograph (fig. 17).

**Figure 16** Advertisement for sepia platinum paper, from *Instructions for Platinotype Printing* (Willis & Clements, ©1899).

18	
SENSITIZED PAPER	
<b>Heavy, Rough Black and Sepia (CC), Heavy, Smooth Black and Sepia (BB).</b>	
	Per doz.
3½ x 3½ .....	\$0 30
3¼ x 4¼ .....	30
4 x 5 .....	50
3⅞ x 5½ .....	55
4¼ x 5½ .....	60
4¼ x 6½ .....	70
5 x 7 .....	80
5 x 8 .....	95
5½ x 7¾ .....	1 25
6½ x 8½ .....	1 25
8 x 10 .....	1 85
10 x 12 .....	2 80
11 x 14 .....	3 75
14 x 17 .....	6 00
16 x 20 .....	7 00
20 x 26 .....	10 00
20 x 26 .....	per sheet, 85
Full size roll 20 in. wide, 26 ft. long, equalling 1 doz. sheets.....	10 00
The larger sizes should go by express.	
On receipt of 25 cts. we will forward, post paid, a small package of the Ready Sensitized Black Paper with Developer.	
Sample Sepia Paper and Developer 35 cts.	
Developer, 16 oz. (1 pint) . . . . .	15 cts.
Developer, for 50 oz. solution . . . . .	35 "
	Postage, 10 "
Developer, for 100 oz. solution . . . . .	60 "
	Postage, 20 "
Sepia Solution, 2 oz. . . . .	15 "
" " 4 oz. . . . .	25 "
" " 10 oz. . . . .	50 "





**Figure 17** Typical ATR-FTIR spectrum of a platinotype photograph.

The main spectral peaks visible in a typical ATR-FTIR spectrum of platinotype images are usually detected when analyzing pure cellulose (table 1).

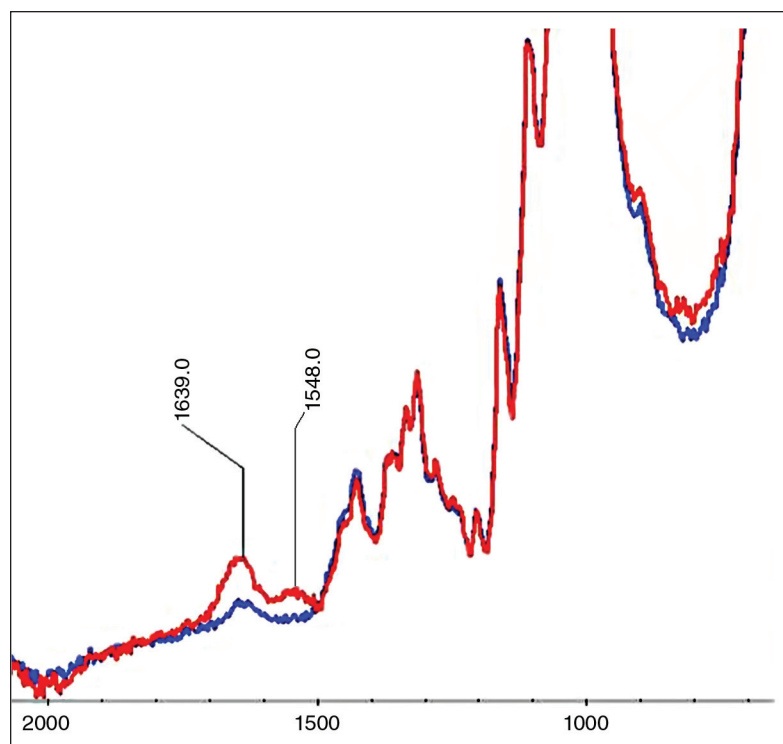
The amount of internal sizing material in most of the papers used for platinum printing is too low to be detected using nondestructive FTIR analysis. To prevent the penetration of the sensitizing solution deep into the body of the paper substrate, where it cannot be well exposed to UV light, some procedures call for surface sizing of the paper. A number of different sizing recipes that include the use of starch, agar-agar, gum arabic, or gelatin were described in the photographic literature. FTIR analysis of complex polymer carbohydrates (starches, agar-agar, gum arabic, etc.) is rather difficult, but in some cases gelatin-based sizing material can be detected (fig. 18).

Figure 18 shows that in a low-concentration gelatin typical for surface sizing, the Amide I peak ( $\sim 1640\text{ cm}^{-1}$ ) of protein (gelatin) is superposed on a peak of adsorbed water nearly always present in photographs. The other characteristic protein peak, Amide II ( $\sim 1548\text{ cm}^{-1}$ ), is very small. Other peaks, which are usually used to differentiate between gelatin and albumen, are not detectable at all. The interpretation of the FTIR spectra of surface-sized photographs is difficult and should be approached with caution.

**Table 1** Interpretation of the main ATR-FTIR spectral peaks of a typical platinotype photograph.

Peak Location (approximate)	Identification
3330 $\text{cm}^{-1}$	OH – free
2900 $\text{cm}^{-1}$	C – H, $\text{CH}_2$ , $\text{CH}_3$ stretching
2850 $\text{cm}^{-1}$	C – H, $\text{CH}_2$ , $\text{CH}_3$ stretching
1635 $\text{cm}^{-1}$	adsorbed water
1420 $\text{cm}^{-1}$	C – H
1315 $\text{cm}^{-1}$	C – H
1200 $\text{cm}^{-1}$	C – OH; C – CH
1155 $\text{cm}^{-1}$	ring breathing
1105 $\text{cm}^{-1}$	C – O – C glycosidic
1050 $\text{cm}^{-1}$	C – OH ( $2^\circ$ alcohol)
1025 $\text{cm}^{-1}$	C – OH ( $1^\circ$ alcohol)
895 $\text{cm}^{-1}$	C – O – C in plane

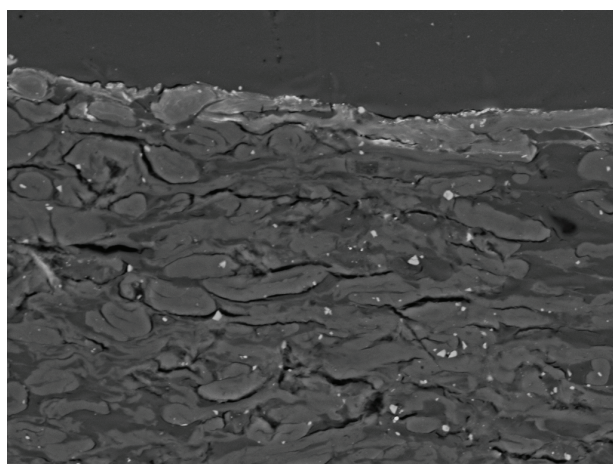
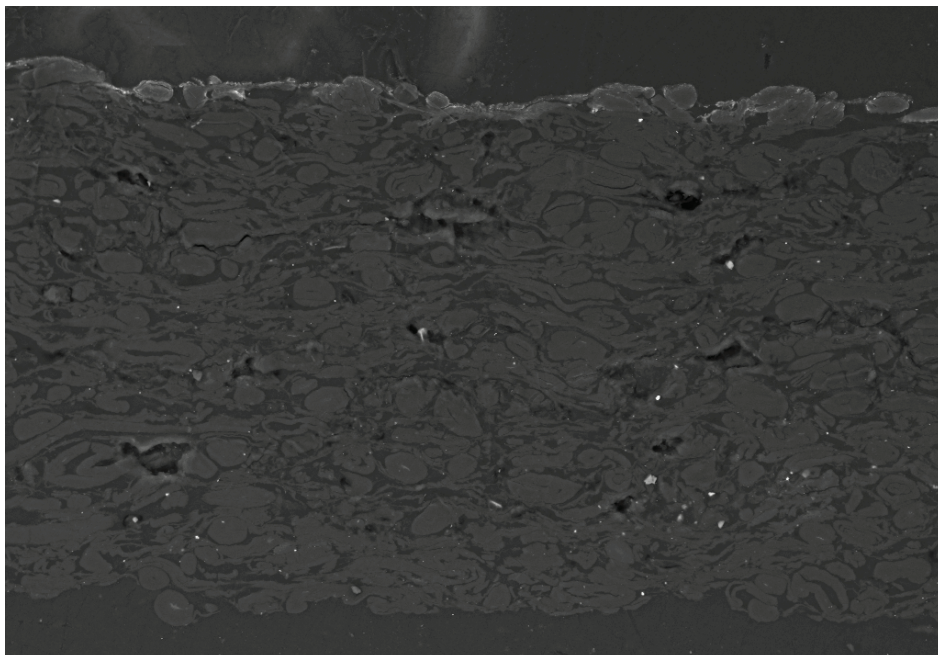
**Figure 18** Detail of the ATR-FTIR spectrum of a platinotype paper surface sized with gelatin (red), along with the spectrum of the same paper without any surface sizing (blue).



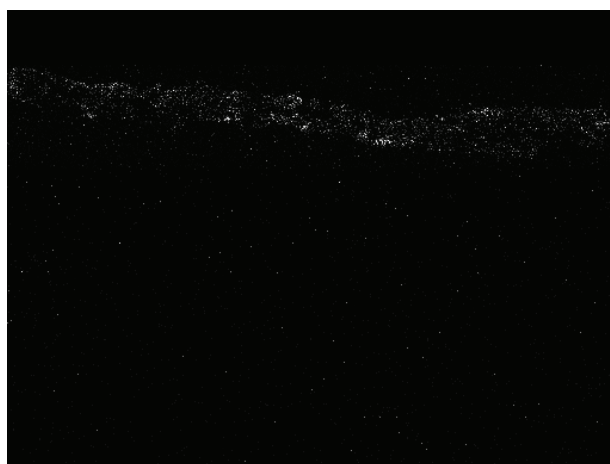
## Cross Sections

The preparation of cross sections of photographs requires physical sampling, which can be justified when dealing with study collection samples (this investigation). XRF analysis samples the entirety of the multilayered structure of a photographic image and often does not provide information on its stratigraphy. A study of cross sections from photographs under an optical or electron microscope provides in-depth insight into the layered structure of a photograph. When studied analytically (ESEM-EDX), some information on the distribution of different chemical elements within a photograph can be obtained as well (figs. 19, 20a, 20b).

**Figure 19** ESEM backscatter electron image of a cross section of a platinotype photograph.



**Figure 20a** ESEM backscatter electron image of the cross section in fig. 19 (500x magnification).



**Figure 20b** X-ray map showing the distribution of platinum in the cross section in fig. 19. Average thickness of Pt distribution is ~15 microns in the sample.

## Post-Process-Treated Platinotype Photographs

### Toned Platinotypes

In his book *Platinotype Printing*, published in 1897, A. Horsey Hinton wrote: “Though various methods have been suggested for modifying the colour of the platinotype print, it may be fair said that platinotypes, like carbon, is at its best when left alone.”

Regardless of Hinton’s statement, several toning procedures were developed by platinotype printers in response to a need to change or modify the tonality of fully developed platinotype images. Additional application of toning was used when the normal selection of black or sepia platinotype paper or modification of processing chemistry (temperature of development, addition of mercury chloride to the developing bath) did not produce the desired effects.

Historically the most commonly desired change of tonality for platinotype prints was to impart a brown color to the black-and-gray platinotype image. The two most important procedures for producing reddish-brown toning of already fully processed black platinotype images were uranium toning and the so-called Packham’s process.

### Uranium Toning

Hinton described the uranium-toning procedure based on the toning of a platinotype photograph in a toner made by mixing a solution of uranium nitrate and acetic acid together with solutions of potassium ferricyanide and ammonium sulfocyanide. The platinotype photograph is toned until it achieves the desired deep-brown or red-brown tonality (fig. 21). The uranium-toning process can be reversed by washing the print in a dilute solution of ammonia.



**Figure 21** Platinotype photograph toned using uranium to achieve deep-brown or red-brown tonality.



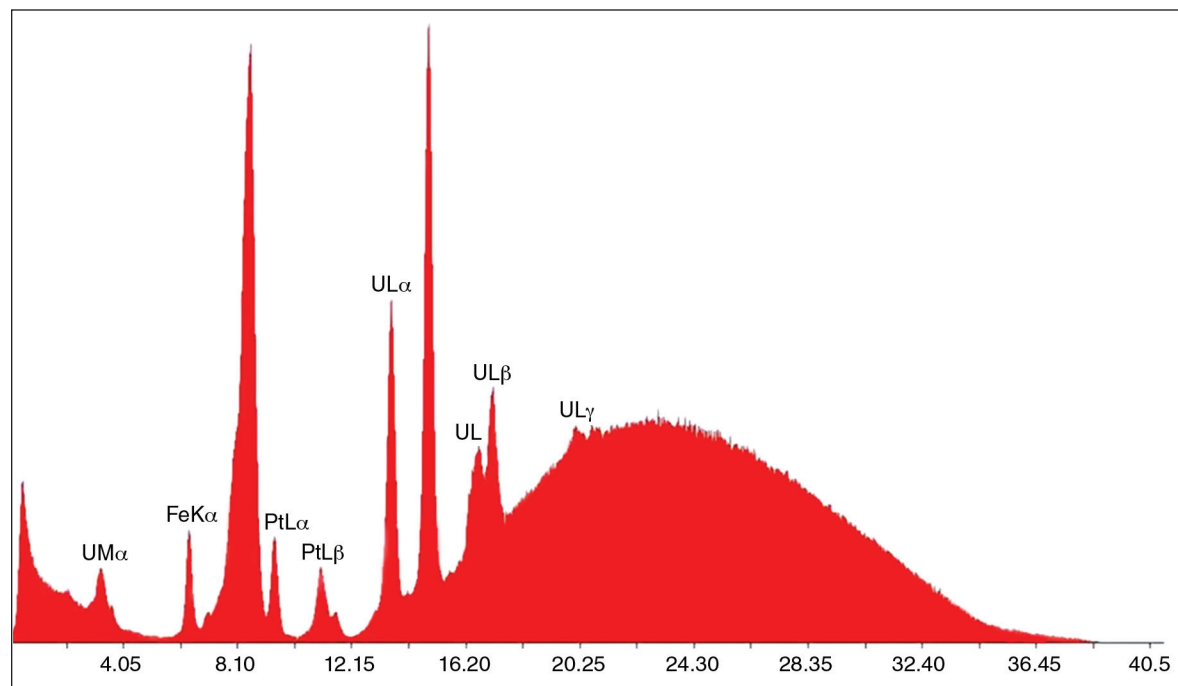
The presence of uranium is easy to detect based on the uranium U L $\alpha$  (13.61 keV) and L $\beta$  (17.22 keV) spectral peaks in the XRF spectrum (fig. 22). Uranium-toned photographs are only slightly radioactive. The radioactivity of uranium-toned platinotype photographs can be detected using very sensitive radiation probes. The amount of radioactivity is too low to cause any damage to photographic images or to be considered a health hazard when handling or when on display.

The presence of the uranium complex of the hexacyanoferric anion (uranium toning) is easily detectable based on the presence of a very prominent C $\equiv$ N vibration at 2062 cm $^{-1}$  (fig. 23). This peak occurs in a region of the IR spectrum relatively free of any spectral interferences.

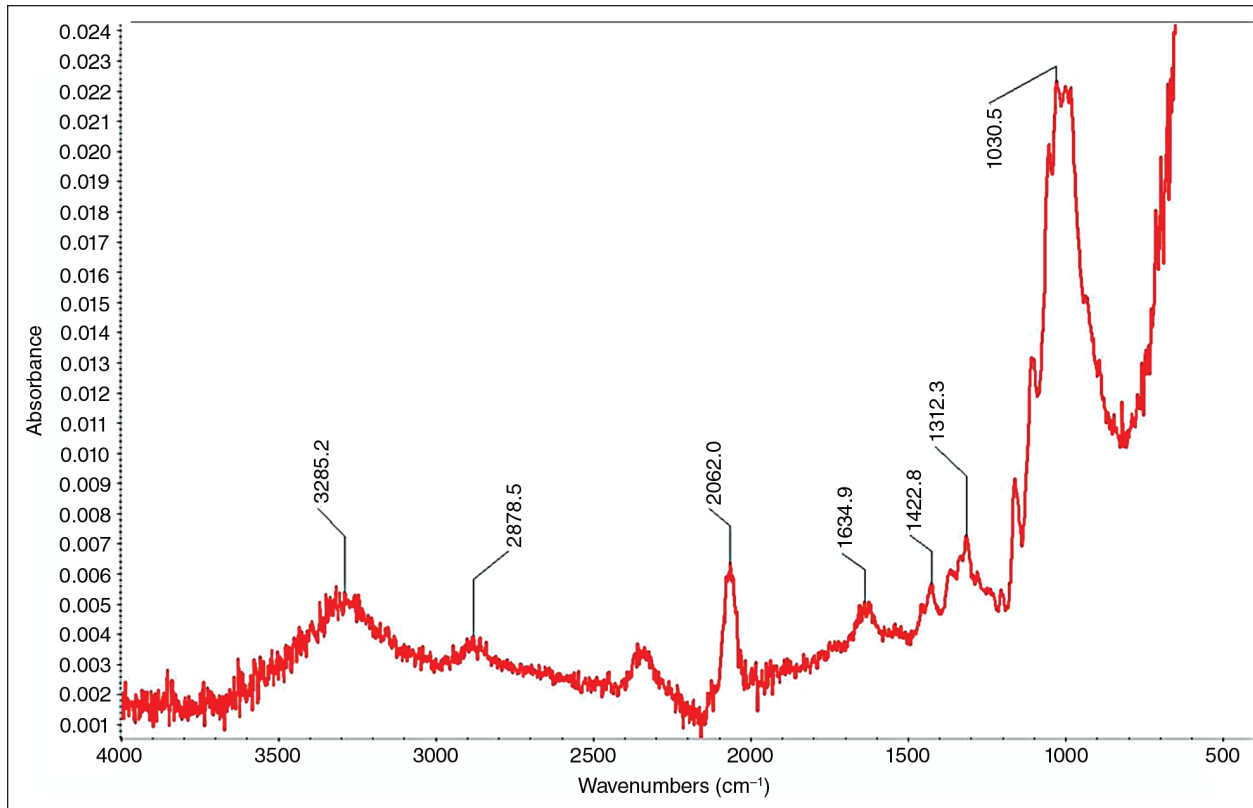
### Packham's Process

James Packham patented his catechu-based toning process in 1894 (Brit. Pat. 24,963, Oct. 27, 1894). A catechu-toned platinotype is shown in figure 24a along with its FTIR spectrum (fig. 24b). The platinotype photograph is toned in a hot water solution of catechu until the image achieves the desired brown tonality. Slightly stained highlights can be cleared by treatment in a weak solution of potassium dichromate followed by subsequent washing in water. It appears that Packham's process was used as a safer alternative to the mercury-based toning process. The final tonality of the toned platinotype is based on the presence of organic dye, and it is reasonable to expect that the toning effect is not going to be as permanent as treatment with mercury chloride solution.

The warm-red tone of platinotype images can also be achieved by development in a solution modified by the addition of copper chloride, mercury chloride, or lead acetate. Thus far we have not had a chance to analyze a red-toned platinotype image, but we expect that some copper



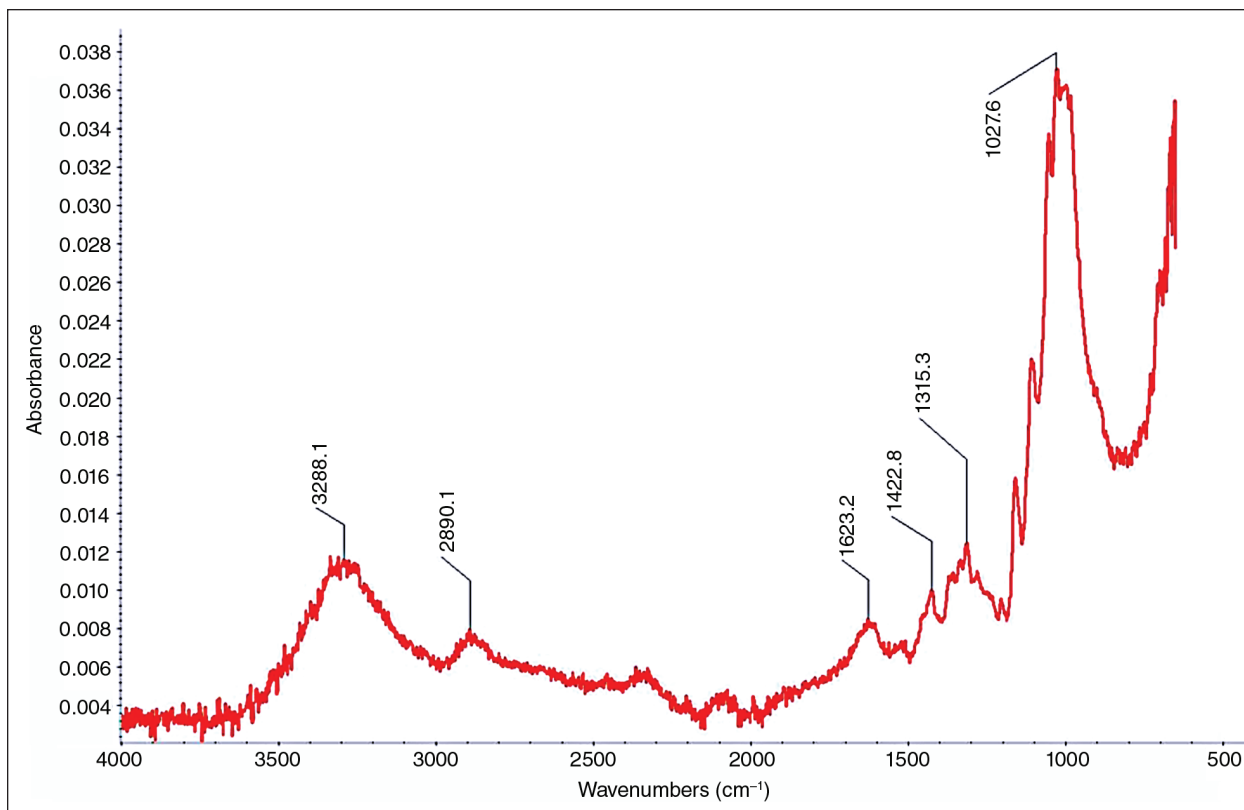
**Figure 22** XRF spectrum of a uranium-toned platinotype photograph.



**Figure 23** ATR-FTIR spectrum of a uranium-toned platinotype photograph.



**Figure 24a** Catechu-toned platinotype made using Packham's process.



**Figure 24b** ATR-FTIR spectrum of the platinumotype in fig. 24a.

would be incorporated into the image during the toning treatment and that spectral peaks of copper (Cu K $\alpha$  at 8.05 keV and Cu K $\beta$  at 8.90 keV) would be visible in the XRF spectrum of such a red platinumotype photograph.

#### **Dolland's Process**

The usual tonality of platinumotype images is black or blue-black, and there was a less likely need to impart a colder or blacker tint through after-process treatment. The most important cold-toning procedure for processed platinumotype photographs was Dolland's gold-toning process.

A. W. Dolland's gold-toning and image-intensifying process was first used in about 1894, when it was described in the photographic literature. A presoaked platinumotype photograph was placed on a flat horizontal surface. After removal of excess water using blotting paper, the surface of the platinumotype was covered with a very thin layer of glycerin and the image was brush-toned using a solution of gold chloride. Once the desired tonality and intensity of the image was reached, the toned platinumotype was treated in a solution of an alkaline developer to complete the reduction of gold chloride. The toning process was finished by thorough washing and drying of the toned platinumotype (figs. 25a, 25b).

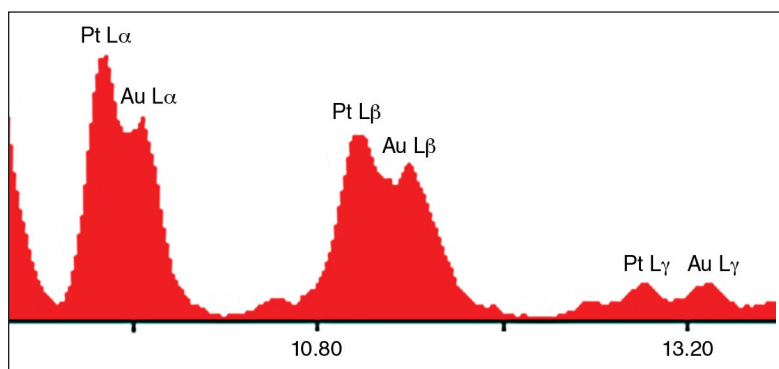
A simplified gold-toning process that omitted the developer-treatment step was also used. The results of such toning were usually satisfactory. Any residual gold chloride left in the fibers of the toned platinumotype was reduced photochemically when exposed to light, imparting a pink or

purple tint to the image. The visual identification of a pink or purple tint usually suggests the use of gold toning (see fig. 25a).

**CAUTION!**

Both gold and platinum are easy to detect using XRF spectrometry when photographs contain only one of these elements. Spectral peaks of gold and platinum (Au L $\alpha$  at 9.71 keV, Pt L $\alpha$  at 9.44 keV and Au L $\beta$  at 11.44 keV, Pt L $\beta$  at 11.07 keV) have a strong tendency to overlap (see fig. 25b). To clearly identify the presence of both elements, an XRF spectrometer must be used with a spectral resolution better than about 160 eV.

**Figure 25a** Paul Strand, *Garden Iris, Maine*, 1928. Gold-toned platinum print, 24.3 × 19.2 cm. Photograph showing a typical pink tint. The J. Paul Getty Museum, Los Angeles.



**Figure 25b** Detail of the XRF spectrum of fig. 25a, showing overlap of the gold-platinum spectral peaks. The J. Paul Getty Museum, Los Angeles.



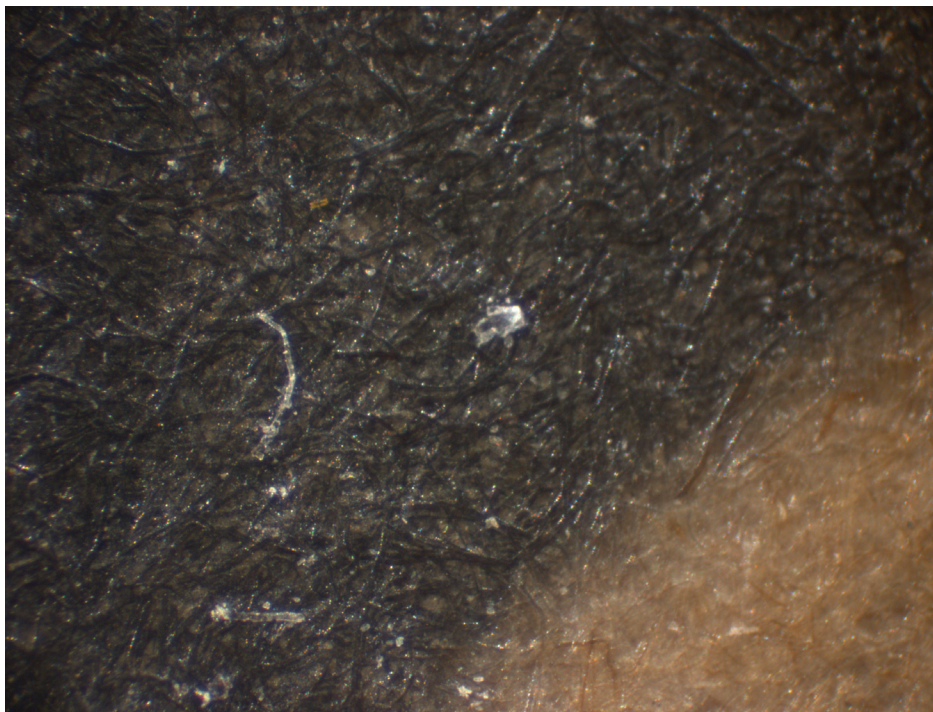
### Varnished Platinotype Photographs

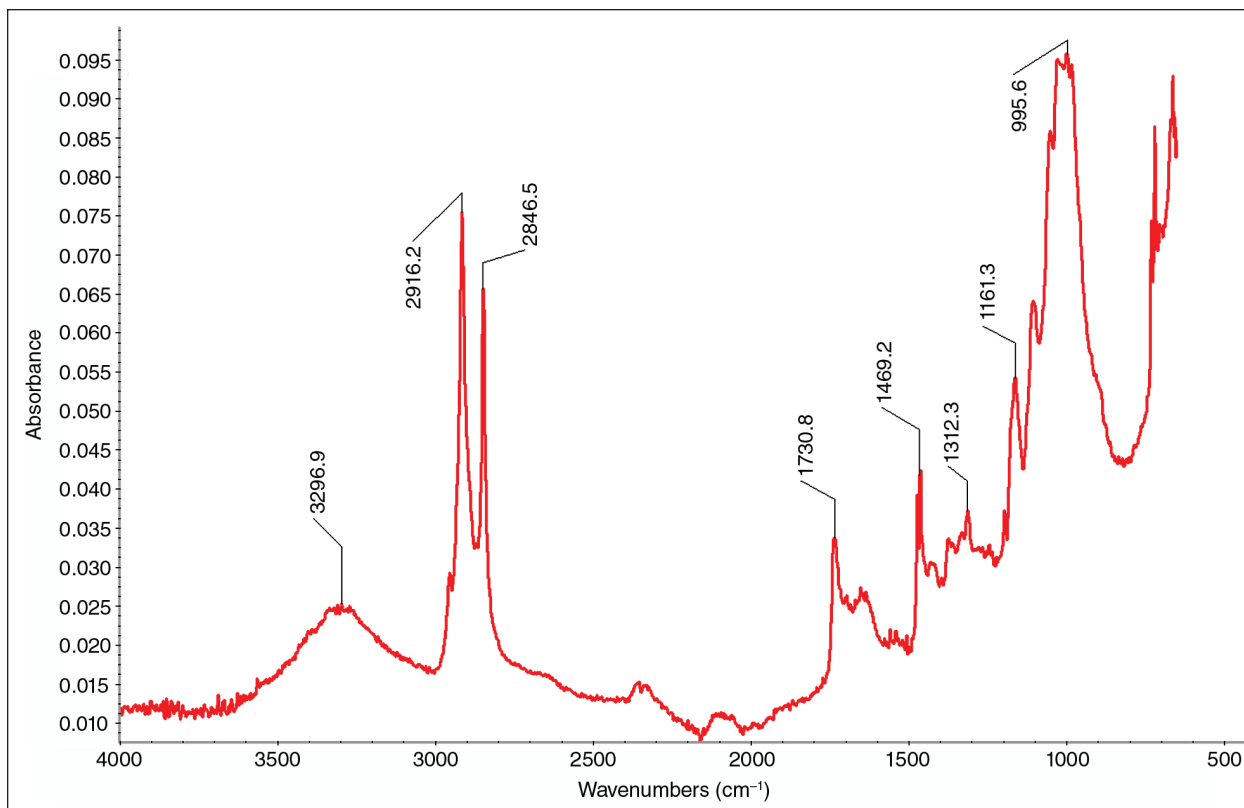
One of the most appealing characteristics of platinotype images is their deep matte surface. Most coated or varnished platinotypes were created in the 1930s. The application of a surface coating brings a slight sheen to platinum images. Visually, coatings on older platinum photographs can be recognized by a slight yellowing of the image highlights. The presence of organic coatings is sometimes visible under a low-power microscope (fig. 26). John A. Tennant, writing in *Photo-Miniature*, described the use of Jarman's collodion-based varnish, Holding's wax and turpentine varnish, and Warren's water megilp varnish formulations. Other, less traditional beeswax or mineral-based wax formulations are described in the photographic literature.

The most common material used for the varnishing of platinotypes was paraffin or beeswax. Figure 27 shows the ATR-FTIR spectrum of a beeswax-coated platinotype photograph. The most characteristic spectral peaks clearly indicating the presence of beeswax are strong C-H bonds ( $2916$  and  $2846\text{ cm}^{-1}$ ) together with the presence of a weaker but clearly visible ester bond ( $1730\text{ cm}^{-1}$ ).

Paul Strand was known to use stand linseed oil-based varnish for coating some of his platinum prints. Figure 28 shows the ATR-FTIR spectrum of a stand linseed oil-varnished platinotype.

**Figure 26** Photomicrograph of a varnish-treated platinotype (40× magnification).





**Figure 27** ATR-FTIR spectrum of a beeswax-coated platinotype.

## Intensification and Reduction of Platinotype Photographs

### Intensification with Platinum

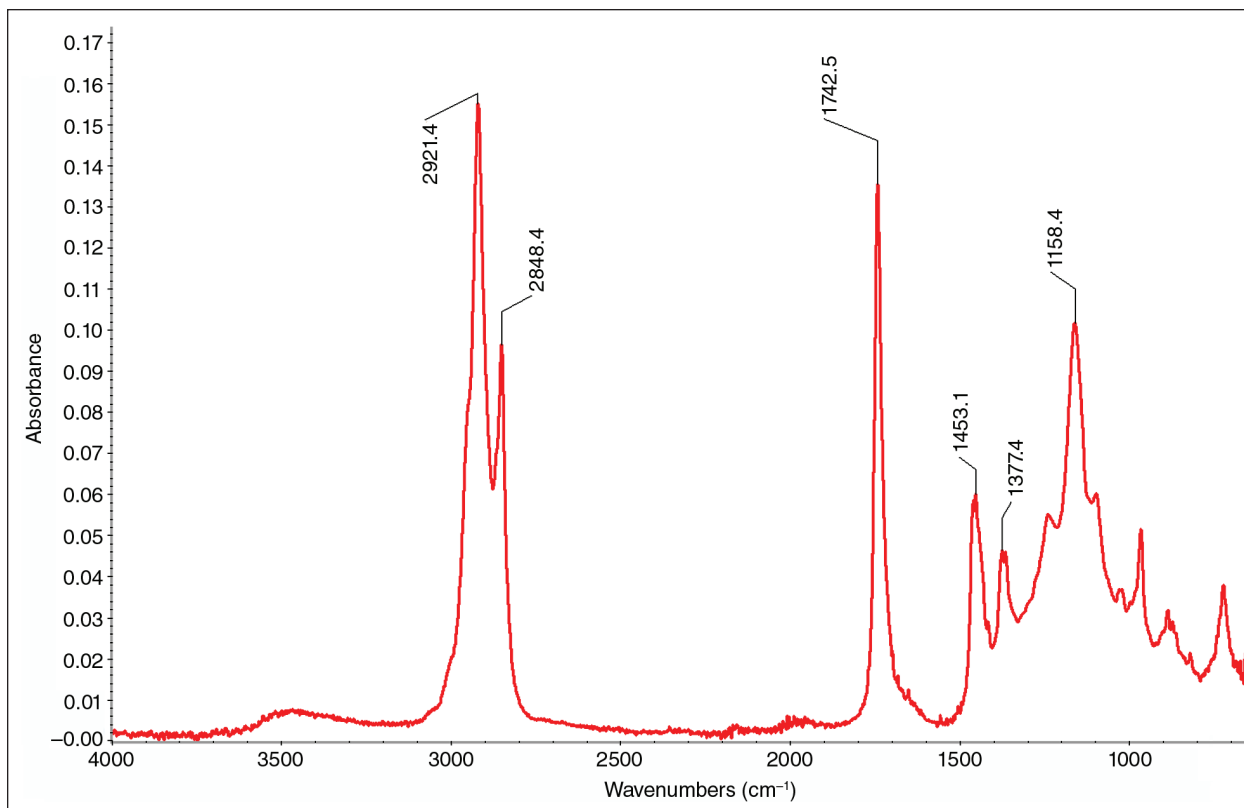
Underexposed platinotype photographs can be saved or partially corrected using different intensification procedures. The most common and widely used procedure was developed and introduced in 1895 by Hübl. It calls for the treatment of an underexposed platinotype image in a mixed solution of sodium formate and platinum perchloride. Being platinum based, this type of intensification treatment cannot be detected microscopically or analytically.

### Intensification with Silver

The intensification of platinotype photographs can also be achieved using a more economical but theoretically less permanent treatment involving a mixture of pyrogallic acid, citric acid, and silver nitrate. After reaching the desired level of intensification, the platinotype is washed, fixed using sodium thiosulfate, and washed again before final drying. Hinton addressed this in *Platinotype Printing*.

### **CAUTION!**

Silver-intensified platinum prints may have an analytical signature similar (the presence of iron, silver, and platinum) to that of Satista paper photographs, which is described below.



**Figure 28** ATR-FTIR spectrum of a stand linseed oil-varnished platinotype.

### Image Reduction

To reduce overexposed platinotype photographs, some photographic literature recommends treatment in a saturated solution of calcium chloride. The reduction process is stopped by treatment in a 5% solution of sodium sulphite, followed by a water wash. This procedure may cause paper deterioration, and the literature recommends this treatment only in extreme cases. This type of image reduction treatment also cannot be identified microscopically or analytically.

### Tinted Platinotypes

During the early twentieth century, a number of commercial photographers used platinotype photographs as the substrate in the production of tinted photographs (fig. 29) directed toward the home decoration market. This photographic movement was not of major importance in the history of mainstream photography, but it is possible that these photographers were the largest consumers of platinotype material in America between about 1900 and 1916.

Hundreds of thousands of tinted platinotype photographs were produced by several important photographers (including Wallace Nutting, David Davidson, Fred Thompson, and Charles Sawyer) and more than two hundred secondary and local photographers. Tinted photographs were offered to the public via trade catalogs, a number of department stores, and an army of traveling salespeople.



**Figure 29** Tinted platinotype photograph of an apple orchard.

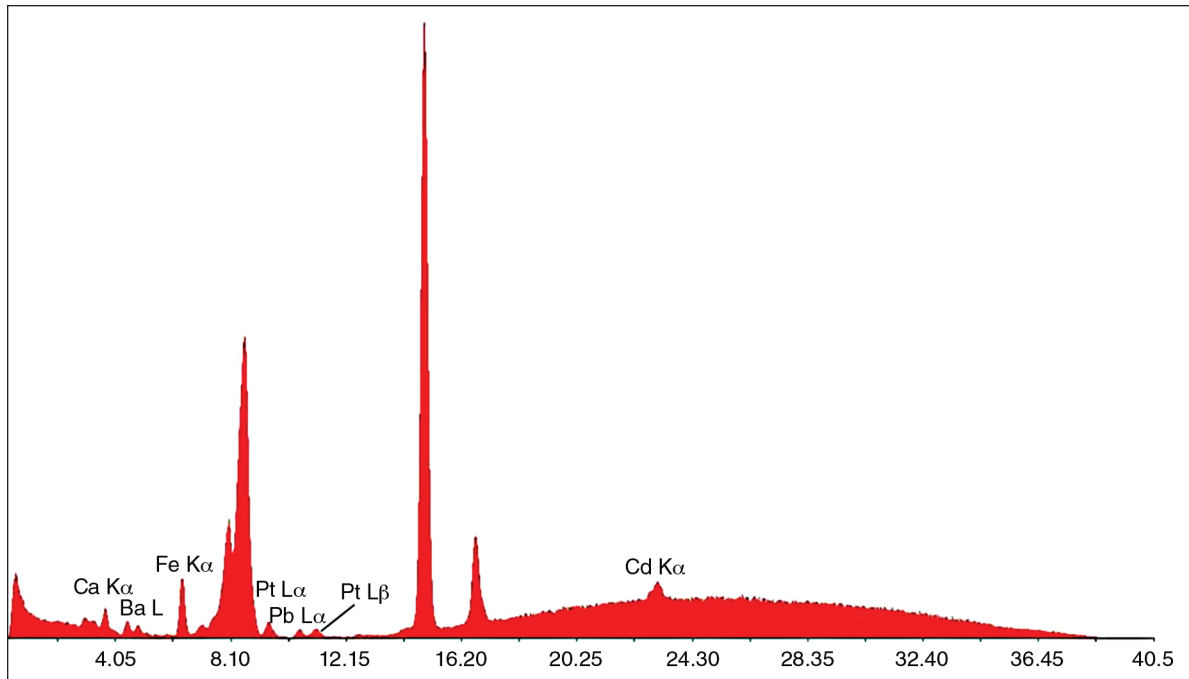
Most of the tinted photographs produced prior to 1915–16 were platinotype based. When the Kodak Company stopped its production of platinotype material in 1916 and platinum became a strategic material during World War I, many of these photographers transitioned to silver gelatin photographs.

#### **Production of Tinted/Painted Platinotype Photographs**

The production of tinted platinotypes started with straight photography by a photographer or the photographer's assistants. Some photographers implemented several formats of photographic negatives directly in the field or produced reduced or enlarged selected negatives in the darkroom. Successful images were identified, assigned a tentative title, and entered into a studio logbook. Tinted platinotype photographs were made available in many size variations for each given subject, from as small as 1 × 2 inches to as large as 30 × 50 inches. Larger sizes were printed using a single negative, but smaller-size negatives were multiplied on large glass plates. Sometimes more than a dozen identical photographs were exposed and processed on one sheet of platinotype paper.

The next step in the production of tinted platinotypes was the creation of a “model/master” picture and preparation of detailed coloring instructions that were usually attached to the model photograph to be archived for later use. In smaller studios, the photographer was also a colorist. Larger studios employed in-house or contract colorists who worked on large sets of identical photographs, applying one color after another (a workflow based on the coloring of one photograph by several workers was seldom used). Fully tinted platinotypes were usually board mounted with a photograph title and photographer signature written under the photograph. In larger studios, the photographer's signature was produced by a colorist based on an approved





**Figure 30** XRF spectrum of the green grass area of the tinted platinotype photograph in fig. 29.

design and style. The photograph's registration number corresponding to the studio logbook was usually written in pencil on the back of the photograph or matte board. Studio-framed photographs often carried a paper label of the photographer or studio.

The paints most widely used for tinting and painting were Windsor & Newton watercolor paints imported from England (Michael and Susan Ivankovic, *Early Twentieth Century Hand-Painted Photography*, Schroeder Publishing, 2005; Michael Ivankovic, *Early 20th Century American Prints*, Schroeder Publishing, 1998).

Both inorganic and organic pigments were used. Figure 30 shows the XRF spectrum of the green grass color field of the photograph in figure 29.

The XRF spectrum of the green paint clearly shows the presence of cadmium pigment. There is no green cadmium-based pigment in watercolor paint, so the presence of the cadmium indicates the use of mixed paint: possibly cadmium yellow mixed with indigo blue.

## IMPORTANT VARIANTS OF THE PLATINOTYPE PROCESS

Palladiotype

Platinum-palladium prints

Glycerin-developed platinotype

Satista iron-silver-platinum paper

Ziatype

## PALLADIOTYPE, PLATINUM-PALLADIUM PRINTS

The palladiotype process was invented by William Willis (British, 1841–1923) in 1916.

No patent was ever issued for the palladiotype process. The process was used from about 1916 to 1930; it has been used by alternative process photographers from the 1960s to the present.

The demand for platinum metal grew rapidly during the first decade of the twentieth century due to its application in the chemical industry as a catalyst in the manufacture of nitric acid for the synthesis of many industrial and military explosives. The price of platinum between the turn of the century and 1916 increased several times, and during World War I Great Britain declared platinum to be a strategic metal and forbade its use in photography. William Willis and his Platinotype Company introduced the palladiotype process in 1916 and substituted palladium-based photographic products for the much more expensive or restricted platinum alternatives.

Economic reasons were responsible for the much broader application of palladium or platinum-palladium photographic processes with the revival of alternative photographic processes in the 1960s and 1970s. The last few decades of the twentieth century also saw an attempt to reintroduce commercial platinum or platinum-palladium photographic papers. The US-based Palladio Company started to produce palladium-based paper commercially in 1988 but ended production by the late 1990s.

### Process Description

The palladiotype process is almost identical to the platinotype process. The sensitizing solution is usually prepared by mixing ferric oxalate, palladium chloride, and sodium chloride. Contrast control can be achieved through the addition of hydrogen peroxide or potassium dichromate. In comparison with the platinotype process, the addition of mercury (II) chloride to the sensitizing solution does not have a great effect on final tonality. Most palladium photographers claim that the palladium-based processes are more reliable than the straight platinum process.

Figure 31 shows schematic cross sections for a palladium and a platinum-palladium photograph. More complex cross sections that incorporate surface sizing or a post-processing varnish layer, as described above for platinotype photographs, can also be but are rarely found.

### Main Application of the Platinotype Process

The palladiotype process was a cheaper variety of the platinotype process. The palladiotype process was used when a photographer wanted to achieve a deep-brown or warmer-black tonality in the final print.

### Noted Photographers Using the Platinotype Process

Manuel Alvarez Bravo

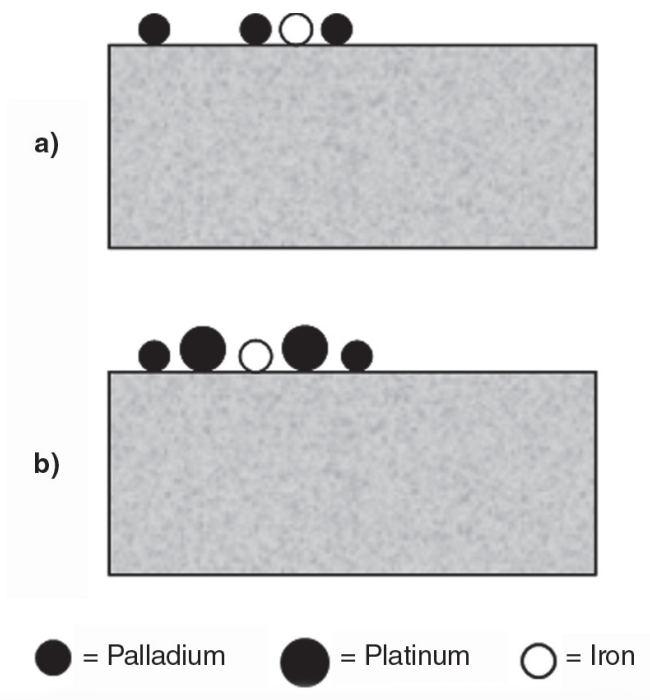
Modern alternative process photographers

Edward Steichen

Alfred Stieglitz

Edward Weston

**Figure 31** Schematic cross sections of (a) a typical palladium photograph and (b) a typical platinum-palladium photograph.



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- “Palladiotype.” 1917. *British Journal of Photography* 64: 60, 334.
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- Anderson, P. L. 1938. “Hand-Sensitized Palladium Paper.” *American Photography* 32(7): 457.
- Anderson, P. L. 1940. “Palladium vs. Silver for Photographic Prints.” *Photo Technique* 2(8): 58.
- Nadeau, L. 1994. *Encyclopedia of Printing, Photographic and Photomechanical Processes*. Vols. 1 and 2. Fredericton, New Brunswick, Canada: Atelier Luis Nadeau, 355–56.
- Cartier-Bresson, A. 2008. *Le Vocabulaire Technique de la Photographie*. Paris: Marval, 200.

## IDENTIFICATION: PALLADIOTYPES

In general, palladiotype photographs have a brownish tint that ranges from pure deep brown to a slightly warm black, but relying on the tint of the photograph for identification may be misleading. Both platinotypes and palladiotypes can be processed to produce a full scale of tonalities from light brown to black.

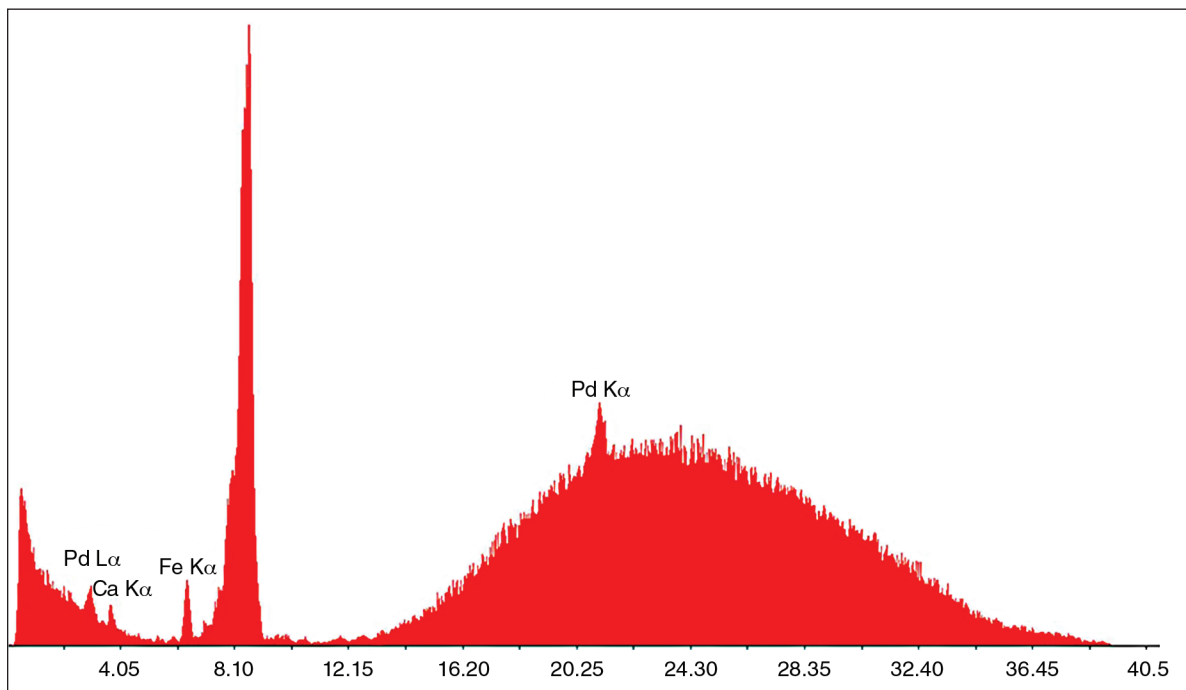
When inspected visually, palladiotypes can be easily misidentified as platinotypes or platinum-palladium photographs. Some salt prints, kallitypes, Van Dyke prints, and toned cyanotypes may also be misidentified as palladiotypes. XRF analysis usually solves all problems related to the identification of palladiotype images. Varnished palladiotypes can also be misidentified as varnished salt prints or gelatin- or collodion-based prints. ATR-FTIR analysis in combination with XRF analysis is usually able to solve these identification issues.

## Analytical Signatures

### XRF

Examples of palladium-based photographs, together with their XRF spectra (figs. 32, 33, 34a, and 34b), show the power of XRF analysis in providing detailed information about various photographic processes that are very difficult or impossible to identify visually or microscopically.

**Figure 32** Edward Weston, *Pajaritos (Little Birds)*, 1924. Palladium print, 19.1 × 21.1 cm. The J. Paul Getty Museum, Los Angeles. © 1981 Arizona Board of Regents.

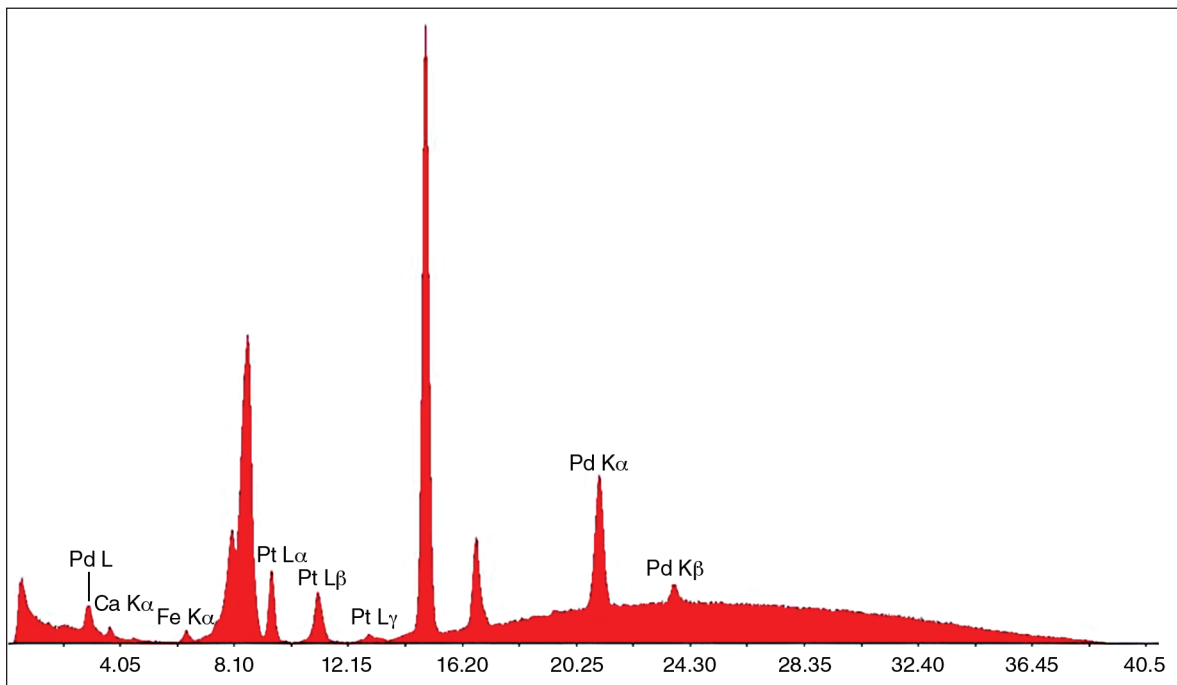


**Figure 33** XRF spectrum of the palladiotype in fig. 32.





**Figure 34a** Modern Pd/Pt photograph, 2003. Private collection.



**Figure 34b** XRF spectrum of the Pd/Pt photograph in fig. 34a.

The characteristic spectral peak of palladium is the Pd K $\alpha$  at 21.18 keV. When an analyzed photograph contains a relatively high concentration of palladium, the second spectral peak for palladium (Pd K $\beta$  at 23.82 keV) may also be visible and can confirm the presence of palladium. In most palladiotype photographs, palladium spectral peaks are accompanied by iron spectral peaks (Fe K $\alpha$  at 6.40 keV) from traces of iron still left in the photograph after clearing using complexing agents. In the case of Pt/Pd photographs, the intensities of the platinum and palladium peaks may vary for different photographs based on the proportions of each element introduced into the sensitizing solution. Spectral peaks of calcium almost always contained in the paper substrate also show up in the XRF spectra of palladium-based photographs.

#### **FTIR**

Similar to platinotypes, FTIR analysis of palladiotypes shows only a spectrum of the paper substrate or paper-sizing material similar to that shown in figure 17. FTIR analysis of palladiotypes would be used only if the presence of a surface coating is suspected. The character of FTIR spectra of varnished or coated palladiotypes is similar to the spectra of coated platinotypes (see fig. 27).

## **GLYCERIN-DEVELOPED PLATINOTYPES**

The glycerin-developed platinotype process was invented by Alfred Maskell (1864–1931) in 1892.

#### **Process Description**

The addition of glycerin to the platinotype developer considerably retards the development of the platinotype image. One of the applications of this effect was to arrest the development of accidentally overexposed but undeveloped platinotypes. The other, more important application of glycerin development was for localized control, both in portraiture and in art photography to produce vignetting or painterly effects (figs. 35a, 35b).

Instead of immersing the light-exposed platinotype print in the developer, the development was performed with a brush. Using several mixtures of glycerin developer provided a high level of control over the process. Once developed to the desired level, the print was transferred to the clearing bath. Glycerin development also allowed the achievement of a double-tone effect in which parts of the image were treated with a straight developer and some local parts—such as the hands or face—with a developer containing mercury chloride.

#### **Noted Photographers Using the Glycerin-Developed Platinotype Process**

Alice Boughton  
Commercial portrait photographers  
Joseph Keiley  
Alfred Stieglitz

#### **Bibliography**

Steiglitz, A., and Keiley, J. T. 1900. "Improved Glycerine Process for the Development of Platinum Prints."  
*Camera Notes* 4: 221–26.



**Figure 35a** Glycerin-developed platinotype showing localized glycerin development.



**Figure 35b** Glycerin-developed platinotype showing brush development.

## IDENTIFICATION: GLYCERIN-DEVELOPED PLATINOTYPES

Glycerin-developed platinum photographs have a sketchy character, and it is obvious that some parts of the image (background or distracting details) were eliminated. Many glycerin-developed portraits also have a form of vignetting that is more asymmetrical than the vignetting achieved using standard tools. Old glycerin-developed platinotypes exhibit a darker halo in the area covered by glycerin. XRF analysis can provide information about which metals were used to create the “duotone” platinotype photographs.



## SATISTA PAPER PHOTOGRAPHS

The Satista process was invented by William Willis (Platinotype Company), patented 1913.

After developing and patenting a number of versions and modifications of the platinotype process, William Willis patented, in 1913, an iron-silver-platinum paper that was later made available commercially by his Platinotype Company in London under the name Satista paper. The development of Satista paper was based on Willis's discovery that the presence of platinum salts increases the efficacy of ferric oxalate reduction of silver halide salts. The fully processed image of Satista paper is made of both silver and platinum. Unlike kallitype photographs, which were usually of a brown tonality, Satista prints had the look of platinum or matte-collodion prints. Satista paper used less platinum and was cheaper than commercial platinum paper. The paper could be manipulated in weak light, and its processing was very similar to that of platinotype photographs. Satista paper was available commercially from about 1914 until the beginning of the 1930s.

### Process Description

Willis's patent of 1913 describes the basic chemistry of Satista paper, but the process description is rather difficult to decipher due to his attempt to include all possible chemical and process variants in order to make his patent as strong as possible against all potential users who endeavored to circumvent his patent rights. Our study of the patent, in combination with the analytical investigation of a number of Satista paper photographs, allowed us to formulate at least an outline of the process:

1. The paper substrate is coated with a gelatin-based emulsion of silver chloride or bromide. The emulsion should be free of any silver nitrate salts.
2. When dried, the coated paper is coated again with a solution of ferric oxalate containing potassium chloroplatinite.
3. The coated paper is dried in the dark.
4. The commercial or coated Satista paper is exposed in a contact frame under a negative.
5. The exposed paper is developed in a solution of potassium oxalate.
6. The developed Satista paper is cleared in a solution of potassium bisulphate and potassium oxalate.
7. After clearing, the Satista print is washed in several changes of water.
8. The washed print is fixed in a solution of sodium thiosulfate (hypo).
9. The fixed Satista print is washed in several changes of water and air dried.

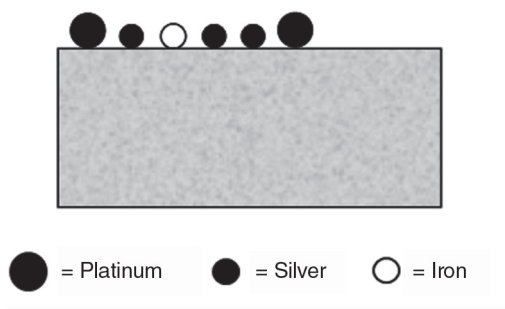
Figure 36 shows a schematic cross section of a typical Satista photograph.

### Main Application of the Satista Paper Process

The Satista paper process was intended not only to be more economical than platinum printing but also to produce visual effects and permanency similar to those of standard platinum prints.



**Figure 36** Schematic cross section of a typical Satista paper photograph.



## Noted Photographers Using the Satista Paper Process

Alfred Cohn  
Alfred Stieglitz  
Paul Strand

## Bibliography (by date)

“Satista Paper.” 1914. *British Journal of Photography* 61: 777.  
Nadeau, L. 1994. *Encyclopedia of Printing, Photographic and Photomechanical Processes*. Vols. 1 and 2. Fredericton, New Brunswick, Canada: Atelier Luis Nadeau, 422.

## Satista Paper–Related Patents

English Patent 20,022 (Sep. 4, 1913)  
French Patent 462,849 (Sep. 22, 1913)

# IDENTIFICATION: SATISTA PAPER PHOTOGRAPHS

## Visual Signatures

### Visual Characteristics

Satista paper photographs resemble lightly varnished platinum and palladium photographs. In some cases, localized fading of the silver image or silver mirroring in dark areas may indicate that the image is not a standard platinum photograph. The presence of more extensive retouching and a number of image flaws are also cited as visual signatures (Nadeau).

### Microscopic Characteristics

Under a microscope, Satista photographs show a particle structure slightly different than that of standard platinotypes. Owing to the presence of a gelatin emulsion layer, platinum and silver image particles do not follow individual paper fibers. An optical micrograph of a Satista photograph also shows the presence of more organic material than would be found in unsized or lightly sized platinum photographs.

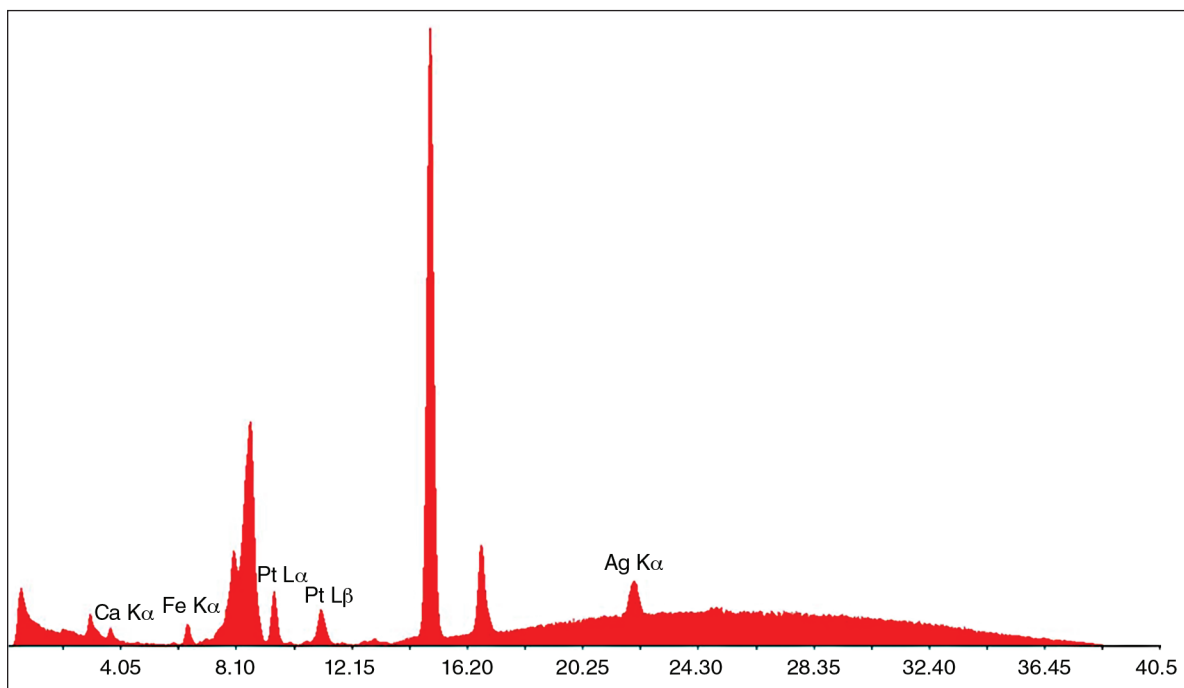
## Analytical Signatures

Visually, Satista paper photographs resemble varnished platinotypes or matte-collodion prints. The main difference is the presence of a baryta layer. To resolve whether the photograph is a platinotype or Satista paper requires the use of elemental analysis. The most difficult identification problem is deciding if the photograph is a silver-toned (intensified) platinum print or Satista paper. Quantitative XRF analysis is needed to resolve this.

### XRF

An untuned Satista paper photograph (fig. 37a) and its XRF analysis (fig. 37b) show the presence of iron, silver, and platinum.

**Figure 37a** Paul Strand, *Still Life with Pear and Bowls*, 1916. Untoned Satista paper photograph, 25.7 × 28.7 cm. The J. Paul Getty Museum, Los Angeles.



**Figure 37b** XRF spectrum of the untuned Satista paper photograph in fig. 37a.

## **FTIR**

The emulsion layer of Satista paper is usually very thin and difficult to identify using an ATR-FTIR spectrometer. To detect the gelatin binder typical for commercial Satista paper, the time of analysis should be increased so that enough data can be collected to detect the weak Amide I and Amide II peaks superposed on the background signal from the cellulose of the paper base.

## **IMPORTANT VARIANTS OF THE SATISTA PAPER PROCESS**

Satoid paper

Japine paper (glossy and semi-glossy variants of Satista paper containing a gelatin layer)

## **WARE-MALDE NEW PLATINOTYPE PROCESS**

The Ware-Malde process was invented by Mike Ware and Pradip Malde in 1986.

The POP variant of the platinotype process was developed in 1887 by Giuseppe Pizzighelli and commercial POP papers were later made available from several manufacturers. The paper required moisture to be present in the sensitized paper, which made it difficult to achieve consistent results. In 1986 Mike Ware, in collaboration with Pradip Malde, developed a new, more reliable variant of the Pizzighelli process.

The process is based on a modification of the chemistry of the sensitizing solution and on a more consistent humidification of the sensitized paper. The Ware-Malde process can be used with platinum, palladium, or different mixtures of both metals. Depending on the metal used and the control of humidification, the Ware-Malde process yields a broad range of print tonalities, from neutral black to sepia to Van Dyke brown.

### **Process Description**

The major modification of sensitizing chemistry, when compared with the old Pizzighelli process, is the use of ammonium chloroplatinite for Pizzighelli's potassium chloroplatinite. Using a series of humidity-controlling salts or salt solutions, reproducible control of humidification of the sensitized paper can be achieved (calcium chloride RH 32%; calcium nitrate RH 55%; ammonium nitrate RH 80%, etc.). In general, lower relative humidity of the sensitized paper produces warmer tonalities, while higher relative humidity produces cooler tonalities. The humidified paper is exposed to light in a contact frame. Usually a thin Mylar foil is inserted between the negative and the humidified paper to protect the negative, and the humidified paper is backed up with a thin sheet of plastic to slow the drying process. No development is needed because the image is printed out by light exposure. The Ware-Malde process calls for fixing, clearing, and washing of the print using ethylenediaminetetraacetic acid (EDTA), Kodak Hypo Clearing Agent, and water. Fully processed prints are usually heat dried.

### **Main Application of the Ware-Malde Process**

The Ware-Malde process represents one of several modern platinotype and palladiotype processes. The modified sensitizing chemistry and good control of humidification of the sensitized paper

prior to light exposure allow for consistent printing results and a well-controlled variation in print tonality.

### **Bibliography (by date)**

- Ware, M. J. 1986. "An Investigation of Platinum and Palladium Printing." *Journal of Photographic Science* 34: 13–25.
- Ware, M. J. 1986. "Platinum Reprinted." *British Journal of Photography* 133(42): 1190–94.
- Malde, P. 1994. "New Solutions for Platinum Printers." *View Camera Magazine* 7(5): 36–41.

## **IDENTIFICATION: WARE-MALDE PLATINOTYPES AND PALLADIOTYPES**

The photographs produced using the Ware-Malde process do not have any unique visual, microscopic, or analytical signatures that would allow differentiating them from similar photographs produced using developer-based platinum/palladium processes.

### **ZIATYPE**

Ziatype was invented by Richard Sullivan in 1996.

The Ziatype process is another modern variant of Pizzighelli's POP process using palladium-based chemistry. An example of a Ziatype print is shown in figure 38.

**Figure 38** Amy Holmes George, *Torso*, 2003. Ziatype print. © Amy Holmes George.





## Process Description

The Ziatype process uses a lithium palladium complex salt in combination with ferric ammonium oxalate to facilitate photochemical reduction of palladium and provide enough hygroscopic water to allow for POP image development. Tonality and contrast of Ziatype photographs are controlled chemically, unlike other Pizzighelli processes in which both tonality and contrast are controlled by humidity.

## Main Application of the Ziatype Process

The Ziatype process provides tighter control over processing chemistry and more consistent results than the standard palladiotype process. The process is used by a number of modern alternative process photographers.

## Bibliography

Weese, C. 1997. "Ziatype: A Brand New 19th Century Process." *Photo Techniques Magazine*, August/September: 19–28.

## IMPORTANT VARIANTS OF THE ZIATYPE PROCESS

Tonality modified Ziatype photographs using tungsten, cesium, and gold chemistry

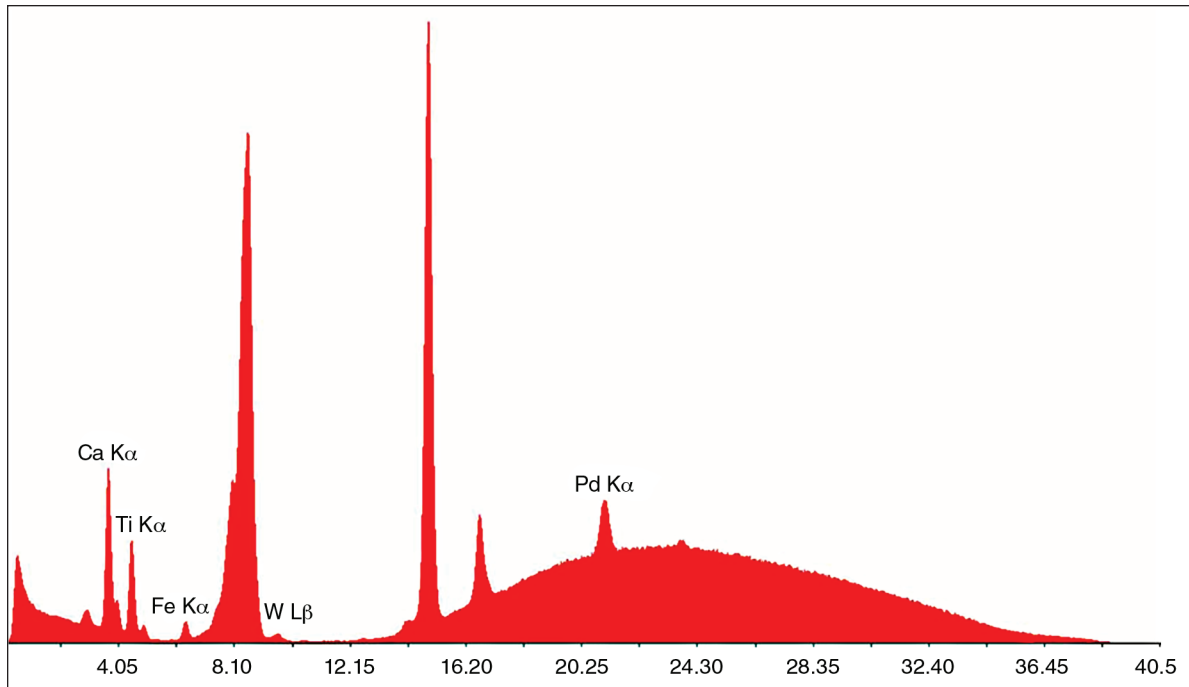
## IDENTIFICATION: ZIATYPES

Standard Ziatype photographs do not exhibit any unique visual, microscopic, or analytical signatures that would allow differentiating them from old or new palladium-based photographs. XRF analysis would detect palladium as the main imaging metal and a small amount of iron left in the photograph after clearing and washing (fig. 39). Only when potassium dichromate is used to adjust the contrast of the final print can a very small amount of chromium be detected. When the final tonality is modified by including compounds of tungsten, gold, or small amounts of cesium, these compounds may then be found. Detecting these chemical elements together with palladium and iron may represent strong evidence that the analyzed photographs are Ziatypes.

## Identification Problems

Ziatype images look similar to other iron-based photographic processes (palladiotype, kallitype, toned cyanotype). XRF or another technique is usually needed to determine which of these processes was used to create the image.

Around the turn of the twentieth century, platinum photographs were widely used both for art photography and for high-end commercial portraiture, and the look of platinum photographs was very much in fashion. This and the later increase in price of platinum precipitated the development of several variations of photographic processes that produced visual effects close



**Figure 39** XRF spectrum of the Ziatype print in fig. 38.

to platinotypes. Matte-collodion photographs, Satista paper photographs, and later photographs made using Gevaluxe paper are some examples of these processes and may be easily misidentified as platinum photographs when relying only on visual observation. Using a microscope alone or in combination with analytical methods (XRF) usually allows for the precise identification of prints.

## INTERPRETATION GUIDE

**Table 2** Summary of the main microscopic and analytical signatures of the platinum class of photographs and some processes commonly misidentified as platinum. The information below is for typical versions of each process. Exceptions to each entry may exist but are rare.

Platinotype Prints														
Tonality	Process	Surface Coating	Paper Fibers	Pt	Pd	Fe	Ag	Au	Ba	Other Inorganics	Cellulose	Gelatin	Collodion	Other Organics
Black	Platinotype	-	X	X	-	X	-	-	-	(Ti)*	X	-	-	-
	Pt / Pd	-	X	X	X	X	-	-	-	(Ti)*	X	-	-	-
	Varnished Pt	X	X	X	-	X	-	-	-	(Ti)*	(X)	-	-	X***
	Matte collodion	-	-	(X)	-	-	X	(X)	X	Sr	-	-	X	-
	Gevaluxe	-	X**	-	-	-	X	-	(X)	(Sr)	X	-	-	-
	Satista	-	-	X	-	X	X	-	-	-	-	X	-	-
	Palladiotype	-	X	-	X	X	-	-	-	(Ti)*	X	-	-	-
Brown	Hot dev. Pt	-	X	X	-	X	-	-	-	(Ti)*	X	-	-	-
	Pt / Pd	-	X	X	X	X	-	-	-	(Ti)*	X	-	-	-
	Hg toned Pt	-	X	X	-	X	-	-	-	Hg, (Ti)*	X	-	-	-
	Matte collodion	X	-	(X)	-	-	X	(X)	X	Sr	-	-	X	-
	Silver gelatin	X	-	-	-	-	X	(X)	(X)	(Ti)*	-	X	-	(coatings)
	Kallitype	-	X	-	-	X	X	-	-	(Ti)*	X	-	-	-
	Tannin toned	-	-	-	-	-	-	-	-	(Ti)*	-	-	-	-
	Cyano	-	X	-	-	-	X	-	-	-	X	-	-	CN
	U toned Pt	-	X	X	X	-	X	-	-	U, (Ti)*	X	-	-	-
	Ziatype	-	X	-	-	X	X	-	(X)	X <sup>†</sup> , (Ti)*	X	-	-	-

X Present  
 - Absent  
 ( ) May be present  
 X\*\* Unique image structure under a microscope  
 X\*\*\* Often wax or linseed oil  
 X<sup>†</sup> May contain W or Cs from toning; Cr from contrast adjustment  
 (Ti)\* Some modern prints on 20th- and 21st-century substrates containing TiO<sub>2</sub>



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