# CYANOTYPE



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 www.getty.edu/conservation

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Front cover: Cyanotype photograph, 1909. Photographer unknown.

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# CYANOTYPE

English: cyanotype, blueprint, ferro-prussiate process, blue process French: *cyanotype* German: Cyanotypie, Zyanotypie, Eisenblaudruck, Blaupause

### HISTORICAL BACKGROUND

The cyanotype process (a print example is shown in fig. 1) was invented by the astronomer and chemist John Frederick William Herschel (British, 1792–1871) and featured in his paper "On the Action of the Rays of the Solar Spectrum on Vegetable Colours and on Some New Photographic Processes," which was presented to the Royal Society of London on June 16, 1842.

The name *cyanotype* was derived from the Greek name *cyan*, meaning "dark-blue impression." Color changes of solution of iron salts were noticed first by Count Bestuscheff in 1725 and more precisely described in 1831 by Johann Wolfgang Doebereiner (1780–1849). The inorganic pigment Prussian blue (hydrated iron hexacyano ferrate complex), which is the image-forming material of cyanotypes, was prepared first by Heinrich Diesbach in Berlin between 1704 and 1710 and



**Figure 1** Cyanotype photograph, 1909. Photographer unknown.



was used after about 1730 as a pigment in oil paintings and watercolors. Herschel experimented with the cyanotype process in the 1840s and inspired Anna Atkins, daughter of his friend Dr. John Children, to illustrate her botanical studies with cyanotype photograms. The three volumes of her book Photographs of British Algae: Cyanotype Impressions (1843-53) represent the earliest examples of books illustrated with photogenically produced images.

The cyanotype process was seldom used until the 1880s, when it became a cheap proofing process for collodion, dry gelatin plates, and gelatin roll film before the final printing, which used more expensive silver- or platinum-based photographic processes. From the 1870s until about the 1950s, when it was replaced by diazo-based reprographic processes, the cyanotype process and its variants were the primary processes used by engineers and architects to copy plans.

The first commercial cyanotype paper became available in 1872 in France, where it was produced by Marion et Cie in Paris under the name papier ferro-prussiate. Students at the Massachusetts Institute of Technology have been instructed in the use of cyanotype for reprographic purposes (blueprints) since 1875. The first commercial blueprint machine made in Switzerland was introduced into the United States at the Philadelphia Centennial Exposition of 1876. Sensitized cyanotype paper is still available today for student instruction and as an educational toy. Kits for making cyanotypes are also available.

The cyanotype process, together with a number of other, older photographic processes, was revived by contemporary photographers in the 1960s. The older processes were considered alternatives to the silver gelatin process using commercial photographic material. It is interesting to note that today, as digital photography replaces all applications of classic "chemical" photography, the silver gelatin process itself will soon be considered an alternative photographic process.

#### Commercial Cyanotype Material

French Satin Jr., Ideal, Eastman's Blue Print, Opto, E.A. Ferroprussiate Paper Eastman blueprint postcard Silkdown (cyanotype fabric)

Two types of commercial cyanotype material available during the early twentieth century are seen in figure 2. A historical timeline of the cyanotype process is given in figure 3.

> Figure 2 Two types of blueprint photographic paper commercially available in the 20th century.





Figure 3 Timeline of the cyanotype process.

#### **Process Description**

The general principle of the cyanotype process is the photochemical reduction of iron (III) salts to iron (II) salt that reacts with potassium ferricyanide (red prussiate of iron), forming an intensely blue complex. The process has several simple steps:

- 1. Selected paper or other material is coated with a mixture of iron (III) salt (today mostly of ferric ammonium citrate) and potassium ferricyanide. The coating must be applied under dim light due to light sensitivity.
- 2. The resulting yellow-greenish layer of sensitized material is dried in the dark.
- 3. The dried, sensitized material is exposed under a negative or other partially or fully opaque material (when creating photograms) to strong light (sun or an artificial UV light source), usually in a printing frame that assures good contact between the negative and the sensitized material.
- 4. Light exposure is aided by simultaneous exposure of a sensitometric wedge or timed based on exposure and development of a series of test samples.
- 5. The exposed material is transferred to a water bath to complete the formation of Prussian blue in areas exposed to light and to dissolve any unexposed mixture of sensitizing compounds. Full development of the blue image can be aided by the addition of a hydrogen peroxide solution to the bath. Otherwise, the blue image can be assessed only after the material is fully dried and oxidized by exposure to air.



Figure 4 shows a schematic cross section of a typical cyanotype print.



#### Main Application of the Cyanotype Process

- Cheaper, simpler, more stable alternative to silver albumen, silver collodion, and silver gelatin photographic printing processes. The blue color of a final photograph can be used creatively (Henry Peter Bosse, German American photographer, 1844–1903) or considered aesthetically unacceptable (Peter Henry Emerson, British photographer, 1856–1936).
- Proofing medium for photographic negatives
- Main reprographic process between 1870 and about 1950
- One of the processes used to produce photographs on textile
- One of the main alternative photographic processes since the 1960s practiced by some contemporary photographers
- Production of postage stamps and banknotes (during the Siege of Mafeking, Boer War, 1899–1900)

#### Noted Photographers Using the Cyanotype Process

- John Frederick William Herschel (see above) discovered and experimented with the cyanotype process in the 1840s.
- Anna Atkins (1799–1871; see above) later collaborated with Anne Dixon.
- Hippolyte Bayard (1801–1887) made a series of cyanotype photograms similar to Talbot's photogenic drawing photograms.
- Henri Le Secq (1818–1882) worried about the longevity of his photographic work; after 1870, he reprinted his negatives using the cyanotype process.
- Henry Peter Bosse (see above) used the cyanotype process exclusively; he was well known for his Mississippi River series.
- Edward Sheriff Curtis (1868–1952) used the cyanotype process for proofing of negatives.
- Eadweard Muybridge (1830–1904) used the cyanotype process to make working proofs of his human and animal motion series.
- Edward Jean Steichen (1879–1973) produced a series of combination prints using both the cyanotype and palladiotype processes.



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#### **Cyanotype-Related Patents**

A. Baudesson and P. Houzeau, English Patent 2,526 (Oct. 13, 1864) Preparation of Prussian blue and treatment for toning of images to black, violet, and red colors

## **IDENTIFICATION: CYANOTYPES**

#### **Visual Signatures**

#### Visual Characteristics

Visual identification of cyanotype photographs is rather simple. Once identified, there is often no further need for any microscopic or analytical investigation. Depending on the chemistry of the process and the paper substrate used for printing, cyanotype photographs can be found in many shades of blue, from light blue and gray blue to a bright and intense navy blue. The highlights of cyanotype photographs are light blue or white, and the dark areas are in various intensities of blue. When tilted and observed under a raking light, most cyanotype photographs exhibit a matte surface in both the blue and white areas of the image. A very slight sheen in some white areas, if any, can be attributed to sizing of the paper before printing. Some, namely modern, cyanotype images have signs of hand coating clearly visible in the image or hidden under a framing matte.

#### **Microscopic Characteristics**

Under a stereomicroscope, cyanotype photographs exhibit a typical one-layer structure that shows a mass of blue particles and particle clusters. These clusters coat fibers in the paper substrate that are clearly visible under high magnification (figs. 5a-5c). Some glossiness of paper fibers in white areas of the photograph can be seen under higher magnification. Its presence is attributed to the natural glossiness of cellulosic fibers and to the glossiness added due to the sizing of the paper substrate. No baryta layer is present when inspecting the edges and corners of cyanotype photographs.

#### **Analytical Signatures**

#### XRF

The elemental composition of untoned cyanotype photographs printed on clean paper substrates is rather simple. The key element that should be present in all cyanotype photographs is iron from the cyanotype blue complex pigment. The amount of iron should vary between the Dmax and Dmin areas. Figure 6 shows a modern cyanotype photograph printed on an archival paper substrate. Comparison of the XRF spectra recorded at the Dmax and Dmin areas of the image (figs. 7a, 7b) show different amounts of iron depending on how much of the cyanotype blue complex pigment is present. The XRF spectrum recorded at the Dmin area of the image shows a very low concentration of iron. This is typical even for a well-processed, cleared, and washed cyanotype image.

Some commercially available cyanotype printing paper was also available for making cyanotype postcards (figs. 8a, 8b). Figure 9 shows the XRF spectrum of the Dmax area of the postcard.

For postcard production, the cyanotype chemistry was coated onto a heavier paper stock. The small amount of lead recorded in the XRF spectrum is present in the paper substrate.

*Note:* The back of the cyanotype postcard (see fig. 8b) contains information that can help date the image even when there is no direct date on the postcard. The undivided back of the postcard



**Figure 5a** Photomicrograph of a cyanotype photograph at 10× magnification, showing blue particles and particle clusters.



**Figure 5b** Photomicrograph of the same photograph at 25× magnification, showing clearly visible fibers in the paper substrate.

#### Figure 5c

Photomicrograph of the same photograph at 40× magnification, showing glossiness in the white areas.



Figure 6 Modern cyanotype photograph printed on archival paper substrate.





**Figure 7a** XRF spectrum of fig. 6, recorded at the Dmax area.



**Figure 7b** XRF spectrum of fig. 6, recorded at the Dmin area.

**Figure 8a** Recto of a cyanotype postcard printed on commercially available material.



**Figure 8b** Printed back of the cyanotype postcard in fig. 8a.

FOR THE



**Figure 9** XRF spectrum of the Dmax area of the cyanotype postcard in fig. 8a.

image was used in the United States until 1907. The address was to be written across the entire back of the postcard, and any message had to be incorporated into the image area on the front of the postcard. The area for the stamp on the back calls for a one-cent stamp, another visual clue in dating the image.

XRF analysis of the card-mounted cyanotype image in figure 10 shows the presence of additional elements (figs. 11a, 11b): iron, chromium, and lead. All of these are contained in the mounting board of the photograph. An independent analysis of the mounting board, together with spectral subtraction, can be used to separate the spectral contributions of the cyanotype image from the mounting board.

#### FTIR

ATR-FTIR analysis confirms the presence of the cyanotype blue complex not only in typical cyanotype photographs but also in modified or toned cyanotype images that lack the blue visual signature of the process. Figure 12 shows the ATR-FTIR spectrum of the Dmax area of the cyanotype photograph in figure 6.



**Figure 10** Card-mounted cyanotype photograph, date unknown.



**Figure 11a** XRF analysis of fig. 10, recorded at the Dmax area.



**Figure 11b** XRF analysis of the mounting board used in fig. 10.



Figure 12 ATR-FTIR spectrum of the cyanotype photograph in fig. 6.

The most important feature in figure 12 is the presence of a well-defined cyano (carbon nitrogen stretch)( $C \equiv N$ ) peak at 2070.7 cm<sup>-1</sup>. This peak is easy to locate and identify because this part of the midrange of the infrared spectrum does not exhibit any important spectral overlaps. Another important feature of the cyanotype photograph is the presence of a broad spectral envelope between about 1400 cm<sup>-1</sup> and 900 cm<sup>-1</sup>. This feature is typical for a paper substrate and other cellulosic materials.

#### **Identification Problems**

Identification problems are as follows:

- Blue mordant dye-toned silver gelatin photographs
- Gold-toned silver gelatin photographs
- Blue pigment "carbon" prints
- Blue pigment "pigment" prints
- Blue pigment Woodburytypes

#### **Post-Process-Treated Cyanotypes**

#### **Bleaching or Reduction**

Prussian blue pigment is rather stable in neutral or acidic environments, but it is quickly decomposed (hydrolyzed) by the presence of alkaline materials (ammonia, sodium carbonate) forming iron (III) hydroxide. Light-blue stains can be removed using a diluted solution of oxalic acid.

#### Intensification

In the case of underexposure, some intensification of a cyanotype photograph can be achieved by dipping into a weak solution of iron (III) chloride FeCl<sub>3</sub>. The intensification process is difficult to control. In general, it is better to deal with overexposure than with underexposure when it comes to cyanotype photographs.

#### **Toned Cyanotypes**

Some photographers were not satisfied with the blue color of cyanotype images. A number of chemical toning procedures were proposed to change the color.

#### Black

The cyanotype photograph is bleached in a solution of ammonia, and the photograph is toned in a solution of tannic or gallic acid. The black cyanotype image shows the presence of the cyano complex when analyzed using ATR-FTIR. XRF analysis shows the presence of iron.

#### Warm Black

The photograph is bleached in a weak solution of potassium hydroxide, then washed and bathed in a weak solution of silver nitrate. The photograph is placed in a hydroquinone developer.

The XRF spectrum of warm black-toned cyanotypes shows the presence of iron and silver. Finding these analytical signatures together with the presence of the  $C \equiv N$  peak in the ATR-FTIR spectrum strongly indicates that the analyzed image is a toned cyanotype.

#### Green

To produce green-tone cyanotypes, the image has to be toned in a solution of iron (II) sulfate acidified with sulfuric acid, then washed in water and dried.

There is no good analytical signature specific for green cyanotype images, but some conclusion, even if not 100%, can be made when detecting both iron (XRF) and  $C \equiv N$  functional groups in a green image that also exhibits all of the microscopic attributes of cyanotype images (matter surface, visible paper fibers, etc.).

#### **Bluish Lilac**

Bluish lilac-toned cyanotype images are produced by bathing photographs in a dilute solution of borax or potassium oxalate, followed by toning the resulting image in a diluted solution of potassium sulfocyanide.

XRF analysis detects iron, and ATR-FTIR analysis of the Dmax areas of the image may show the presence of a weak spectral peak of the C $\equiv$ N spectral group at around 2165 cm<sup>-1</sup>.

#### **Violet Tones**

Cyanotype photographs can be toned to violet tones by treating with a warm solution of lead acetate. XRF analysis of the resulting toned cyanotype image shows the presence of high concentrations of lead. The identification of the violet-toned cyanotype is confirmed by detecting the  $C \equiv N$  spectral group using ATR-FTIR analysis.

#### **Mordant Toning of Cyanotypes**

Mordant toning of cyanotype photographs was developed by John Mercer (1791–1866). Bleached cyanotypes were treated in a solution of organic dyes. XRF analysis of these types of toned images shows the presence of iron. ATR-FTIR analysis should detect the presence of the C $\equiv$ N spectral peak but is usually not sensitive enough to detect the low concentration of organic dyes. Visual identification of the bright color images, in combination with the results of the XRF analysis (iron) and ATR-FTIR analysis (C $\equiv$ N peak), leads to the proposal that the image might be a mordant-toned cyanotype.

### IMPORTANT VARIANTS OF THE CYANOTYPE PROCESS

Pellet's process The new cyanotype (Ware) Cyanotype Rex (King)

#### **Formula-Based Variants**

At first John Frederick William Herschel experimented with the cyanotype process using only the low sensitivity of potassium ferricyanide. The process resulted in a weaker cyanotype image but required very long exposure times. A great number of different cyanotype formulas were described in the photographic and scientific literature. With the exception of formulas that include the addition of other inorganic materials (silver nitrate, potassium dichromate) or organic material (gelatin) to the basic cyanotype formula, there is no easy or proven way to relate the appearance, microstructure, and chemical composition of a cyanotype image to the different formulas that could have been used by an artist.

A major change in the basic cyanotype chemistry occurred after 1897, when the Austrian chemist Eduard Valenta introduced the green form of ammonium ferric citrate, which quickly replaced the brown form. Green ammonium ferric citrate was found to increase the light sensitivity of cyanotype material, but the final chemical composition of cyanotype images resulting from using either form of ammonium ferric citrate is identical.

#### Pellet's Process (Positive Cyanotype)

Positive cyanotype was invented by Henri Pellet (French) in 1877.

#### **Process Description**

The basic idea for the direct positive cyanotype was developed early by Herschel, who conducted a series of initial experiments but did not achieve reproducible results. A more usable version of the process was invented and patented in 1877 by Henri Pellet.

Paper is coated with a mixture of solutions of gum arabic, ammonium ferric citrate, and ferric chloride. The dried and sensitized paper is exposed to strong light in contact with line drawings, continuous transparent images, or translucent positive images. In the areas exposed to light, photochemical reduction of iron (III) salts takes place. Only areas protected from light still retain some amounts of unreduced iron (III) that react with the developing solution of potassium ferrocyanide (yellow prussiate or ferro-prussiate), forming the Prussian blue pigment. The process was used from 1877 to the 1940s, though it was much more difficult and delicate than the basic cyanotype process.

#### **Visual Characteristics**

The visual characteristics of Pellet's process include positive image when using positive transparency; negative image when exposing using a negative; blue lines on a white background when copying black-line drawings or plans.

#### **Microscopic Characteristics**

Pellet's process is identical to cyanotype.

#### **Analytical Signatures**

**XRF** Pellet's process is identical to cyanotype.

#### FTIR

There is a theoretical possibility of detecting the presence of the gum arabic coating in blue areas of the image. However, the analytical signal of gum arabic is very weak, and it is in a spectral region highly prone to spectral interferences.

#### **Identification Problems**

Modern so-called blueprint reprographic copies that provide blue lines on a white background are actually based on the light sensitivity of diazo compounds.

#### The New Cyanotype (Ware)

The new cyanotype was invented by Mike Ware (British) in 1994.

#### **Process Description**

Faced with several shortcomings of the basic cyanotype process (long light exposure, short-term stability of mixed sensitizer, peptization of Prussian blue pigment during washing, and staining



of highlights), Mike Ware developed a new variant of the cyanotype process based on the light sensitivity of ammonium ferric oxalate and its reaction with ammonium ferricyanide that is produced during the preparation of the sensitizing solution. The major change in the chemistry of the new cyanotype process, in comparison with the basic cyanotype process that can be utilized for the identification of the new cyanotype photograph, is the frequently used addition of a solution of ammonium dichromate to the sensitizing solution.

#### **Visual Characteristics**

The new cyanotype is similar to a basic cyanotype.

#### **Microscopic Characteristics**

The new cyanotype is similar to a basic cyanotype.

#### **Analytical Signatures**

#### XRF

The presence of chromium can be an indication that Ware's new cyanotype process was used.

#### FTIR

The new cyanotype is identical to the ATR-FTIR signature of the basic cyanotype process.

*Note:* The cyanotype process was used when making postage stamps and banknotes (Siege of Mafeking, Boer War, 1899–1900). Figure 13 shows an example of a Mafeking Blue stamp. XRF analysis of the stamp detected iron, calcium, chlorine, potassium, and lead (fig. 14).

The likely source of all of the elements—with the exception of iron—is the paper on which the stamp was printed. This cannot be confirmed, however, without taking a sample from the stamp and performing EDX-SEM or a similar type of analysis.



**Figure 13** A Mafeking Blue cyanotype stamp.

**Figure 14** XRF spectrum of the Mafeking Blue stamp in fig. 13, showing the presence of iron, calcium, chlorine, potassium, and lead.

INTERPRETATION GUIDE

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

<b>Cyanotype Prints</b>	rints														
Process	Image Structure	Surface Coating	Paper Fibers	F	Ag	Ba	Ħ	Other Inorganics	Cellulose	Gelatin	Collodion	CN	Other Organics	Tonality	Notes
Cyanotype	Photograph	I	i×	iх	I	I	*(X)	I	ix	I	I	iХ	I		
Blue toned gelatin	Photograph	(X)	I	×	×	×	I	I	I	×	I	×	(coatings)		
Blue (gold) toned gelatin	Photograph	(X)	I	I	×	×	I	Au	I	×	I	I	(coatings)		Under special conditions gold may produce a blue or red tone
Blue pigment carbon	Photograph	×	(X)	8	I	I	I	ර්	I	×	I	8	I		Blue pigment Woodburytypes were described in literature but are rare
Blue pigment gum	Photograph	I	×	8	I	I	I	ර්	×	I	I	8	Gum arabic (Iow)	(light to dark)	For analytical signatures of gum arabic, see the Gum Dichromate section (forthcoming)
Blue pigment oil	Photograph	I	(X)	8	I	I	I	ර්	(X)	×	I	8	Ester bonds (low), inks		For analytical signatures of oil, see the Oil section (forthcoming)
Blue pigment bromoil	Photograph	I	I	8	Ι	×	I	Cr, (Cu)	I	×	I	8	Ester bonds (low), inks		For analytical signatures of bromoil, see the Bromoil section (forthcoming)
Blue ink photo- mechanical	Photo- mechanical	I	**(X)	8	I	8	(X)	(Ca), (Sr)	(X)	I	8	***(X)	I		
X Present - Absent	<u> </u>	May be present Key signature	sent ıre	(X) (X) (X) (X)		ne mode ner fibers st early b	rn prints are not olue print	Some modern prints on 20th- and 21st-century substrates containing ${\rm Ti0}_2$ Paper fibers are not visible when a paper "clay" coating is present Most early blue printing inks contain Prussian blue pigment	l 21st-centur a paper "clay ain Prussian l	y substrate " coating is blue pigmer	s containing <sup>]</sup> present it	710 <sub>2</sub>			

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