



Article: Technical Investigation of a 20th Century Hand-Colored Opaltype

Author(s): Greta Glaser

Topics in Photographic Preservation, Volume 15.

Pages: 222-238

Compiler: Jessica Keister

© 2013, The American Institute for Conservation of Historic & Artistic Works. 1156 15th St. NW, Suite 320, Washington, DC 20005. (202) 452-9545, www.conservation-us.org.

Under a licensing agreement, individual authors retain copyright to their work and extend publication rights to the American Institute for Conservation.

Topics in Photographic Preservation is published biannually by the Photographic Materials Group (PMG) of the American Institute for Conservation of Historic & Artistic Works (AIC). A membership benefit of the Photographic Materials Group, *Topics in Photographic Preservation* is primarily comprised of papers presented at PMG meetings and is intended to inform and educate conservation-related disciplines.

Papers presented in *Topics in Photographic Preservation, Vol. 15*, have not undergone a formal process of peer review. Responsibility for the methods and materials described herein rests solely with the authors, whose articles should not be considered official statements of the PMG or the AIC. The PMG is an approved division of the AIC but does not necessarily represent the AIC policy or opinions.

Technical Investigation of a 20th Century Hand-Colored Opaltype

Greta Glaser

*Presented at the 2013 AIC & ICOM-CC Photographs Conservation
Joint Meeting in Wellington, New Zealand.*

Abstract

This technical study investigates a 1930s, hand-colored opaltype of a young boy from the Winterthur/ University of Delaware Program in Art Conservation (WUDPAC) study collection. The object remains in fair condition but without any identifying documentation in the WUDPAC files. Analysis was undertaken using X-ray fluorescence (XRF), scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, gas chromatography- mass spectrometry (GC-MS), infrared reflectography (IR), long-wave and short-wave ultraviolet illumination (UV), fiber optic reflectance spectroscopy (FORS), cross-section microscopy, and polarized light microscopy (PLM). Results show that the support is a non-lead fluorine-opacified glass, the photographic process is a silver-gelatin photograph, and the following pigments were used to color the portrait and the background in an oil binder: vermilion, Prussian blue, and iron oxide in the background, ultramarine blue and zinc white in the clothing, and iron oxide and madder lake in the flesh. Analysis of the housing components was not a critical goal of this study but helped assign economic context to the object. Analysis of the housing components has shown the materials to be of mass-market quality: a gilded brass frame, leaded cover-glass, and a poor-quality paperboard back mat. The results of this study help place this object within the history of opaltype manufacture and help inform future treatment decisions for this object and for others of its kind.

I. Introduction

Opaltypes

Opaltypes, also called opalotypes, were a popular form of portraiture from the late nineteenth century through the 1930s and 1940s but are now quite rare in photograph collections. They can be made from a number of photographic processes on an opaque white glass and resemble the miniature portraits that were often painted on opacified glass, ivory, and other similarly colored materials long before photography became widely available to the public. They were favored for their permanence as well as their appearance (Gernsheim 1969, 342). Opaltypes were so desirable in the nineteenth century that on April 10 1866 Victor Griswold introduced an “opaltype” which was more an “opal ferrotype” or a tintype made to look like an opaltype by coating plate iron with white, opaque collodion. This process was claimed to be cheaper than the traditional opaltype and unsusceptible to cracking (Schimmelman 2007, 81-21). Opaltypes could also be created by “burning-in” the image by firing the plate in a kiln. However, this process usually changed the tonality of the image and the majority of opaltypes were not processed in this manner (Gernsheim 1969, 342).

Glass Manufacture

Glass has been used as a photographic support since 1847, when Niépce de Saint-Victor used albumen as a binder on a glass support. Although the first documented use of opal glass as a photographic support was in 1856 by James Good Tunny, Glover and Bold of Liverpool first patented opaltypes in 1857. Two types of opal glass were commonly used: “pot” or “pot metal” glass which is opaque white throughout, and “flushed” glass which is not a true opaque or opalescent glass but has one or more layers of opaque glass that have been flashed onto a clear glass. Pot opal was apparently the choice material for making opaltypes in the US and is the type of glass examined in this study (Egunnike 2005, 8-9). Opal plates were usually sold in packs [of six], and often already prepared by the manufacturer, such as “Cowan’s Organic Chloride Opals” sold by Marion & Co., or Scovill’s glass which were made to be used with Eastman’s Transferotype Paper (Werge 1973 and Scovill & Adams 1890, 81). The opaltype examined for this study is considered a 1/6 plate (3 1/4” x 2 3/4”).

Hundreds of formulae for opal glass manufacture were available by the 1930s. The physical and chemical characteristics of individual glass plates can vary greatly from one another. In industrial glass manufacture, two kinds of glass are typically made – soda-lime glass (silica, soda, and lime) and lead glass (silica, lead oxide, and sodium or potash) – by melting the respective ingredients in various proportions in a pot in a furnace with the opacifying agent(s) included. Opacifiers are a number of tiny inclusions in the glass that diffuse light, making the glass appear white but still translucent. Since the eighteenth century, glass manufacturers have been using white metal opacifiers such as lead arsenate [$\text{Pb}_3(\text{AsO}_4)_2$], and phosphates (such as sodium phosphate [Na_2HPO_4]) (Vogel, W 1985, 266 and Doremus 1973, 102). These technologies continued throughout the nineteenth and twentieth centuries.

Clair Tragni examined several opaltypes in her study of ultraviolet-induced visible fluorescence in photographic materials for the advanced residency program at the George Eastman House. She found that only opaltypes identified as gelatin and that were produced in the twentieth century exhibited a dull rose color when examined under shortwave ultraviolet illumination and a dull violet color in long wave illumination. The glasses in Tragni’s report were then examined using X-ray diffraction to identify the opacifiers, and were found to have a greater content of feldspar and alumina (and therefore classified as fluorine opal due to the fluorine-based opacifying agents) than earlier opaltypes that were made on leaded glass. These earlier glasses appear bright blue in ultraviolet illumination (Tragni 2005, 43).

Preparation for Photography

Glass plates require a fair amount of preparation before they can be used as supports for photographic processes. Preparation includes cleaning, subbing (with dilute albumen or gelatin if necessary) and cutting to the desired shape. Cleaning was done either by hand or machine using several methods, including alcohol and whiting (calcium carbonate) or rottenstone, or by soaking the plate in lye, sulfuric acid, and nitric acid sequentially. A more detailed description of the cleaning process can be found in Towler’s *The Silver Sunbeam* (Towlder 1864, 129). Subbing involves applying a layer of dilute albumen or gelatin to the surface of the glass before application of the image-bearing layer in order to help one adhere more thoroughly to the other. Subbing could be done overall or only at the edges. (Egunnike 2005, 13-16). Three distinct surface finishes for opal glass were popularly used: patent plate opal (the plate is ground then

polished), egg-shell finish (the plate is left unfinished), and smoothed opal (the plate is ground but not polished). The level of polish can be easily distinguished by the naked eye, and hand polishing was considered to be higher quality, although a certain amount of “tooth” was sometimes desired for hand coloring (Egunnike 2005, 13-14).

Photographic Processes Used on Opaltypes

Almost any photographic process could be applied to opaque glass to produce an opaltype, from albumen and collodion to carbon and silver gelatin. Trends in processes used on opaltypes parallel the popularity of processes used on paper (Egunnike 2005, 2). Collodion opaltypes were typical from the 1860s to the early 20th century, albumen from about 1860 to 1890, carbon transfer from the mid 1860s until 1940, and silver gelatin from the 1880s until about 1940. The two processes most popular during the date attributed to the opaltype examined in this study (1935) were gelatin and carbon transfer. The process for creating a gelatin opal is essentially the same as the dry plate negative process (credited to John Burgess of London in 1873). The sensitized gelatin – the light-sensitive halide being chloride, bromide, or “chloro-bromide” – is applied to the plate either by transfer paper or directly to the plate by machine. The plate can then be exposed in the camera (a direct positive), in contact with a negative, or by an enlarger. It is then developed and the binder hardened with a chrome alum solution and fixed with sodium thiosulfate (which must be thoroughly washed after fixing to prevent deterioration) (Egunnike 2005, 49-52).

Hand-Coloring Photographs

Photographs were often colored by hand to compensate for the challenges of capturing realistic color in the 19th and early 20th centuries. Various methods were available and some were favored over others depending on the photographic process. For example, daguerreotypes and ambrotypes were most commonly colored with dry pigments that were dusted onto under-bound gum Arabic or isinglass. Albumens were also sometimes colored in this manner. In contrast, tintypes and opaltypes were more often colored with opaque oils or watercolors (Henisch 1996, 104 and 119). Even though laborious color photography processes had been available to consumers since the mid-19th century, hand coloring remained a popular method of achieving life-like images as evidenced by the number of hand colored photographs found in collections. During the gelatin opal period, heavily hand-colored opaltypes received a generous amount of attention as they mimicked the painted portrait miniature.

Hand coloring with oil, watercolor, crayon, or dry pigments and even a varnish layer was common on gelatin opaltypes above other photographic processes (Egunnike 2005, 7). Opal glass, or milk glass, was desirable for hand colored photographs because it is smoother than paper and highly reflective – traits which add to the visual sense of depth and volume in two-dimensional images. Several manuals on coloring photographs were available by the turn of the 20th century; however, those that address coloring of opaltypes specifically are rare. The earliest handbook regarding opaltypes is by Delacy & Son and aptly titled *The Secret of Coloring Photographs on Glass, to which is added the Best Formula Yet Discovered for Making the Silver Bath, the Developing and Fix for Direct Positives, and the Cause of and How to Remedy Stains, Markings, Fogging, etc.* (Henisch 1996, 119). Three nineteenth century handbooks were studied for this investigation: A. N. Rintoul's *A guide to painting photographic portraits, draperies, backgrounds, etc, in water colours*, George Ayres' *How To Paint Photographs In Water Colors*

and In Oil, and J. S. Templeton's and A.H. Wall's *The Guide to Miniature Painting and Colouring Photographs*, as well as a twentieth century photographic magazine *The Photo Miniature* edited by James Tennant. Although these manuals predate the opaltype examined in this report, they were selected because they provide detailed instructions for painting photographic portraits, and more specifically portraits of children.

Ayres' manual includes the most specific instructions for painting portraits of women and children. Special attention is given to "flaxen hair" for which he recommends first a wash of ocher, shaded by Roman ocher and sepia, and shadowed with raw umber, roman ochre, sepia, or bistre (Ayres 1878, 71). Templeton recommends more simply for "the lighter and warmer hair of all the various hues" burnt sienna, Italian ochre, lake, raw or burnt umber, and ultramarine in various combinations (Templeton 1867, 31). Rintoul also suggests a combination of Roman ochre, yellow ochre, raw sienna, carmine, or "any of the yellows which may be modified with sepia to suit the various shades" (Rintoul 1870, 50). Of particular note in Ayres' manual are his suggestions for blue eyes:

If they are light blue, use thin cobalt; shadow delicately with the same and a touch of indigo; add white to cobalt for the illuminated part of the iris – if it is not left sufficiently clear in the photograph. If they are dark blue, use a deeper tint of cobalt and shadow with indigo. If deeply, darkly, beautiful blue (as are some children's eyes), the effect can be heightened by using French Blue, but carefully, as it is a powerful color (Ayres 1878, 77).

Tennant, on the other hand, suggests that pupils should be painted with sepia and black, and made larger than they appear in the photograph without altering their shape or position. Whites can be painted with Chinese white (zinc oxide) tinted slightly with gray (Tennant 1902, 370). Flesh tones recommended for fair-skinned women and children are further broken down into areas of general flesh tone, cheek, and lip by the three selected authors. Ayres and Tennant instruct the reader to paint women and children with Indian yellow and pink madder or vermilion, the cheeks in a similar mixture of pink madder and vermilion, but cautioning that children require more vermilion in both the cheek and lip (Ayres 1878, 62, 72 and Tennant 1907, 526). Rintoul similarly comments that a fair complexion should be created by rose madder and raw sienna, and in the flesh of children vermilion (Rintoul 1870, 46).

Clothing is only regarded in Tennant's magazine. He recommends that it should be painted in plain colors and shaded with a deeper tint of the same color, or by mixing a little black in the blues and grays and dark brown in the reds (Tennant 1907, 526). The authors also make specific points regarding the painting of backgrounds. Templeton writes: "Plain backgrounds in all their varieties, from warm to cold and from the deepest toned to the most transient hue, may be produced by the use of sepia, ultramarine, light red, and Italian ochre" (Templeton 1867, 44). Ayres also shares his opinion on backgrounds: "The figure should always stand prominently before the background, which should consequently be unobtrusive and retiring, with but few details, and no pure colours; dark backgrounds give the most forcible effect" (Ayres 1878, 36). All of the authors agree that backgrounds should be quiet and harmonious with the subject. Preparation beyond washing the print is hardly mentioned in the nineteenth-century manuals, but

Tennant declares that a sizing of white glue must be laid on a gelatin photograph before oil painting (Tennant 1902, 379).

Coloring kits produced by suppliers of photographic materials were commonly available since the 1850s. The amateur photographer or even the collector could color their own photographs as a pastime instead of going directly to the professional studio. Advertisements for photo colors are rampant in photographic supply catalogues and painting manuals. These advertisements often mention pigments by common name or simply refer to the number of opaque or translucent “tinting” colors available rather than list the specific pigments.

Housing Opalatypes

Opaltype housings follow the styles appropriated for other cased photographs of the same time periods (daguerreotypes, ambrotypes, and tintypes). A popular frame style for smaller plates, such as the one examined in this study, is the stamped metal frames designed to stand alone (Egunnike 2005, 53).

This Investigation

A small, hand-colored opaltype and its housing components (including a metallic frame, a cover glass, and a textile back-mat with a stand) belong to the Winterthur/ University of Delaware Art Conservation Program (WUDPAC) study collection (figure 1). The photograph is a portrait of a young boy, around the age of 5, seated in a $\frac{3}{4}$ turn with his face turned to the front, his eyes focused somewhere beyond the camera’s lens. The boy’s face and costume have been delicately painted in vibrant, opaque colors, while the background has been enhanced with touches of red, blue, and green paint. The object was separated from its housing prior to this investigation; its components include a curved cover glass, a decorative metallic frame with a hanging loop at the top edge, and a black back-mat with an attached stand. This back-mat/stand element is constructed from a poor-quality paper board, covered on the presentation side by a black velvet textile and on the interior (non-presentation) side by a two types of black paper: one with a faux-leather texture that is found directly under the textile turn-ins, and a secondary smooth black paper that appears to have been more hastily cut and applied to the back-mat and stand. Three straight pins are inserted into the stand, and a red ribbon with evidence of red paint extends from a hole in the back of the back-mat.



Fig. 1. WUDPAC Opaltype

No correspondence could be found regarding this object. However, a somewhat legible inscription on the reverse includes the date “9/10/1935.” Although it is unclear whether this date is the date of the object’s manufacture, the boy’s costume can be used to infer that the photograph was taken around that time period. Although the half portrait does not reveal the lower portion of the boy’s outfit, it appears to be closely related to the “buster” suit in which the boy’s shorts are attached to the blouse at the waist by buttons. The button-down blouse has wide,

rolled sleeves embellished with delicate designs, which would have likely been embroidered on the sitter's costume. This style of boys' clothing remained popular through the 1930s and 1940s (Rose 1989, 141-144 and Martin 1978, 139-144).

Condition

The opaltype is in relatively good condition. Minor losses in the support and image occur at each of the four corners, most notably the bottom two. A fragment of one of these losses with some binder and paint still intact remains with the object. Minor edge loss of the hand-coloring and image binder is found on all four edges of the image but it appears to be in otherwise good condition. It is difficult to assess the condition of the image material and binder through the presence of the opaque hand-coloring in most areas, although the image appears to have a warm, brown tonality overall.

The housing components are in overall poor to fair condition. The cover glass is broken into two pieces and suffers some minor losses in the upper corners. The metallic frame has evidence of wear, most notably on the vertical edges, but remains in otherwise good condition. The black back-mat/ stand element is in poor condition. The join at the upright stand is weak and should be handled with caution. Some fading and wear of the black textile is evident on the sides of the stand element. It is not entirely evident whether the three straight pins in the stand are original to the object, but numerous holes in the back-mat, stand, and red ribbon suggest that they were once used to hold the stand in position so the object could remain upright for viewing. These holes have caused losses in both of the black papers on the mat's non-presentation side.

II. Experimental

Infrared Reflectography (IR)

Infrared reflectograms provide information regarding the absorbance of pigments used in the hand-coloring on the opaltype and may help clarify the inscription on the verso of the glass plate. Images will be captured using an ALPHA NIR Infrared Camera with National Instruments Labview Frame Grabber using Indigo Systems Corp. IRvista 2.51 software. The camera is equipped with an indium gallium arsenide (InGaAs) detector with a 320x 256 focal plane array and a spectral response from 0.9 to 1.7 μm .

Cross-Sectional Analysis

A small edge fragment containing some paint from the opaltype was already detached from the object when it was selected for this study. Although it is unclear precisely where this fragment originally belonged on the object, it can be assumed that, because it contains some of the paint layer, it also contains some of the binder layer and image-forming material as well. This sample was halved with a diamond-tipped scribe and the segment with more paint was mounted in Extec polyester resin and polished using 150 grit silicon carbide paper to 12,000 grit Micromesh silicon carbide paper to reveal the sample in cross section (cross-section 1). During handling and examination, a second, smaller fragment became detached from the upper right edge. This was also mounted and polished (cross-section 2). The cross sections were examined using a Nikon Eclipse 80i microscope equipped with a Nikon digital camera DXM1200F at 100x, 200x, and 400x magnification in both visible light and ultraviolet illumination (using a BV-2A cube, excitation from 400-440nm, barrier 470nm, dichroic mirror wavelength 455), as well as with the

B-2A filter cube (excitation 450-490nm, Barrier 520nm, dichroic mirror wavelength 505) and with the G-1B cube (excitation 546-510nm, barrier 590nm, dichroic mirror wavelength 575). They were stained with the following fluorochrome stains for medium identification:

- 0.02% Rhodamine B [Sigma: R6626] in denatured ethanol. A positive reaction for the presence of oils is indicated by a red fluorescence when viewed with the G-1B filter cube.
- 4% Triphenyl Tetrazolium Chloride (TTC) [Sigma: T-8877] in anhydrous methanol. A positive reaction for the presence of carbohydrates is indicated by a red/brown when viewed with the BV-2A filter cube.
- 0.2% Alexafluor 488 [Molecular Probes] in a 0.5% Sodium Barate buffer of pH 9.0. A positive reaction for the presence of proteins is indicated by green fluorescence when viewed with the B-2A filter cube.

Energy Dispersive X-ray Fluorescence (XRF)

Qualitative ED-XRF spectroscopy was performed to gather data regarding the elemental composition of the opal glass, pigments used in the hand-coloring, and the elemental composition of the framing elements (particularly the metallic frame); no sample preparation was necessary. Analysis was performed with the Artax μ XRF spectrometer using a molybdenum x-ray tube (700 μ A current, 50kV voltage, 100 seconds live time irradiation, approximately 70-100 micron spot size) with element range of potassium (K) to uranium (U). Spectra were interpreted and labeled using the Artax Basic version 5.3.21.0 software. Graphic documentation of the areas analyzed was obtained using an integrated CCD camera.

Scanning Electron Microscopy – Energy-Dispersive X-Ray Spectroscopy (SEM-EDS)

SEM-EDS was used to identify elements that are either too low atomic number or in too small a quantity to be detected using Winterthur's Artax XRF. The elements found using SEM-EDS can also be mapped in order to visualize their locations and relative quantities. In preparation for analysis, the edges of cross-section 1 were coated with a layer of SPI-Chem carbon suspension particles in order to prevent charging while in the SEM vacuum chamber. The sample was mounted on a SPI-Supplies pure carbon 15mm mounting stub using double-sided carbon tape. It examined at 1000x magnification using a Topcon ABT-60 scanning electron microscope with a Bruker Quantax 200 XFlash EDS detector, an accelerating voltage of 20kV, and a working distance of 22mm. The software used to process the BSE images and X-ray spectra was Bruker Quantax Esprit version 1.8.2.

Raman Spectroscopy

The opaltype was placed directly on the microscope stage, which minimized the need for sampling in image areas (particularly the sitter's face and hair). Pigment samples that were taken for the purpose of polarized light microscopy were also analyzed before they were mounted. The instrument that was used to analyze the pigments is a Renishaw in Via Raman spectrometer with a 785 nm diode laser or a 514 nm argon laser with a vibrational spectral range of 100 – 3200 cm^{-1} , a microscope equipped with a 10x, 20x, and 50x objectives (with magnifying capabilities up to 500x) and an approximately 3" x 15" x 4.5" stage. Areas of the opaltype's surface measuring approximately 1 μ by 20 μ were scanned using a range of laser powers (0.1% - 10% for the 785 nm laser which is Watts) for 30 seconds per scan at accumulations of 1 to 4 scans. Published Raman spectroscopic libraries, including the University of College London's online library and

the Tate Museum Tom Learner Organic Pigments library, and articles were used for reference spectra to gather information about the pigments used to color the opaltype.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was used to help characterize the binding media of the photograph and the paint, and possibly the fluorescing layer between the photographic layer and the support. Small samples were collected from the existing unmounted fragment (FTIR 1) and from the edges where paint could be scraped without deforming the image (PLM 1-5) using a stainless steel scalpel. The sample was then transferred to a diamond half cell and rolled flat with a steel micro-roller to make the film even and appropriately transparent to perform absorption spectroscopy. The sample was viewed and analyzed with a Thermo Scientific Nicolet 6700 FTIR spectrometer with a Nicolet Continuum FTIR microscope. The spectra were obtained using Omnic 8.0 software (Thermo Scientific) in the spectral range of 600 to 4000 cm^{-1} with a 4 cm^{-1} resolution; spectra were analyzed in comparison with SRAL's collection of commercial reference spectral libraries and the IRUG database.

Gas Chromatography – Mass Spectroscopy (GC-MS)

A small sample was removed from the upper right edge of the opaltype in an area of existing damage using a stainless steel scalpel under magnification and was placed in a glass vial. The sample was derivatized with 100 μL of 1:2 MethPrep II reagent (Alltech): benzene in the glass vial. This mixture is used to convert carboxylic acids and esters to methyl ester derivatives. The vial is then heated to 60°C for one hour, and then allowed to cool to room temperature. The instrument used in this analysis was a Hewlett Packard 6890 series GC system equipped with a HP5973 mass selective detector, a HP7683 automatic liquid injector, and a HP59864B ionization gauge controller. Agilent Technologies MSD ChemStation control software was used to collect and analyze the chromatogram and mass spectrum gathered from the sample. The inlet temperature and the transfer line temperature to the MSD (SCAN mode) were set to 300°C. A sample volume of 1 μL was injected onto a 30m x 250m x 0.25 μL film thickness HP-5MS column (5% phenyl methyl siloxane) at a flow rate of 1.5mL/minute. The oven temperature was held at 50°C for two minutes, then programmed to increase by 10°C every minute until a temperature of 325°C was reached and held for 10.5 minutes, a total run time of 40 minutes.

Near Infrared - Fiber Optic Reflectance Spectroscopy (NIR-FORS)

Visible reflectance spectra were collected using an Ocean Optics NIR FORS spectrometer equipped with an Ocean Optics tungsten halogen lamp (LS-1), which was calibrated against a Labsphere reflectance standard (TiO_2). Spectra were collected and analyzed using Ocean Optics SpectraSuit software.

Polarized Light Microscopy (PLM)

This technique was performed last because it involves destructive sampling. Scrapings were removed from the sitter's clothes at the lower edge (PLM 1), lower left arm (PLM 2), two areas of the background including yellow-green and blue samples from the right edge (PLM 3 and PLM 4), and at the top left corner where the paint has extended beyond the plane of the image (PLM 5). Fiber samples of the velvet textile (PLM 6), black papers (PLM 7 and PLM 8), and board (PLM 9) were removed from the backmat. Pigment samples were mounted onto glass slides using Cargille Meltmount (refractive index 1.66) and analyzed using a Leitz Laborlux 12

polarizing light microscope with a transmitted visible light source, equipped with 10x oculars and 4x, 10x, 25x, and 40x objectives. Fiber samples were mounted on glass slides with water and were analyzed using the same microscope. Distinguishing characteristics were noted and compared to personal reference samples as well as Gettens's and Stout's *Painting Materials*.

III. Results

Visual Examination

Magnification revealed several indications of the object's manufacture. For example, the pebbled texture of the object's recto (painted side), and the smooth finish on the object's verso are more easily distinguished under magnification, as well as the delicate and deliberate lines in the sitter's face and costume, most notably around eyes and buttons (figure 2). Brush strokes in the brown background paint can be seen curving around the boy's shoulders. The brown paint appears to have been scumbled over the blue paint fields on the sides of the object. This handling of the brown paint contrasts with the dots of red and yellow in these areas.

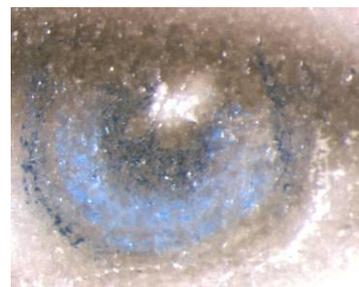


Fig. 2. Detail of the boy's proper left eye, 40x.

Ultraviolet Examination

The opaltype examined for this study exhibited the same dull violet color in long wave illumination and a rose color in short wave illumination as those in Tragni's report. The paint fluoresces bright yellow in the sitter's clothing and background in both long wave and short wave illumination, and a blue, fluorescing layer can be seen around the edges. The areas containing flesh tones do not fluoresce but appear deep blue or purple as a result of the glass support. It can be inferred that this brightly fluorescing material seen in cross section 1 is only found at the edges. Jennifer Jae Gutierrez found similar results when observing two 1929 opaltypes with ultraviolet fluorescence (Mentzer 2003, 5). Two small areas on the top and bottom of the metal frame fluoresce orange in longwave illumination. The cover glass did not fluoresce in longwave illumination, but appeared bright white in shortwave illumination. The backing stand did not exhibit any notable fluorescence in either longwave or shortwave illumination.

Infrared Reflectography

Silver does not absorb in the IR region of the electromagnetic spectrum, and therefore does not appear in the reflectogram. However, certain pigments used in the opaltype's hand-coloring absorb radiation in wavelengths roughly between 750nm and 1mm, and therefore appear dark in the reflectogram. The sitter's hair appears especially dark, along with the background (most notably at the left and right edges), and portions of the sitter's costume. Because the glass is transparent in IR, the pigments can also be seen in the image of the verso (figure 3).

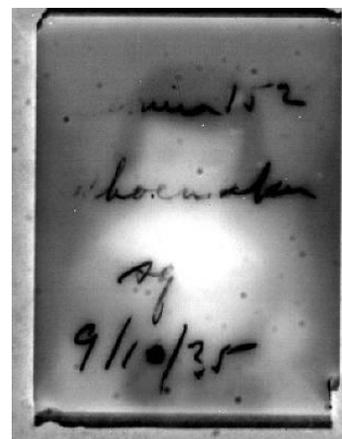


Fig. 3. Opaltype verso in IR

Cross-Sectional Analysis

In visible light and ultraviolet illumination at 200x magnification the cross section exhibited four layers: the glass substrate, a relatively thick (about five times thicker than the image-bearing layer) and bright, blue-fluorescing layer, a thin binder layer containing silver particles (the image material), and a dark paint layer. When the opaltype is examined under long wave ultraviolet illumination this fluorescing layer can be seen around the edges under the paint layer but does not apparently exist evenly under the entire image layer. Stains for oils (Rhodamine B) appeared positive in the paint layer in both cross sections and for proteins (Alexa488) in the image-binder layer and the larger layer beneath.

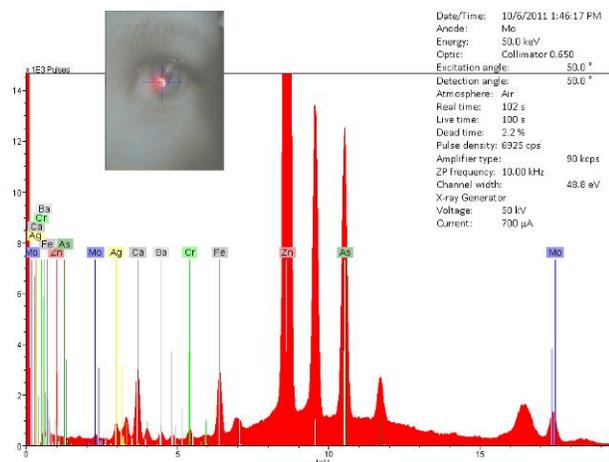


Fig. 4. XRF spectrum from the boy’s proper left eye; peaks shown include arsenic (As), barium (Ba), chromium (Cr), iron (Fe), and zinc (Zn). Molybdenum appears in the spectrum as the source of radiation.

XRF

A summary of the elements found using XRF is in Table 1. Areas chosen for analysis included the verso of the glass, high and low image densities, and at least one sample from every visible color. Calcium (Ca) and arsenic (As) appear in all spectra taken from the opaltype.. Silver (Ag) was also found in all of the spectra taken from the image side of the opaltype. The cover glass spectrum showed peaks for lead (Pb), calcium, and arsenic. Figure 4 shows the spectrum taken from the boy’s left eye.

Location	Elements found	Location	Elements found
Glass verso, center, no pigment	Ca, As, K, Ti, Fe, Zn	Left edge (background), blue, red, and yellow pigments	Ca, As, Ba, Cr, Fe, Zn, Ag, Hg
Proper left eye, blue pigment	Ca, As, Ba, Cr , Fe, Zn	Proper left cheek, flesh tones	Ca, As, Si, Ba, Fe, Zn, Ag
Lower lip, red pigment	Ca, As, K, Ba, Cr , Fe, Zn, Ag		
Proper left arm (clothing), flesh tone	Ca, As, K, Ba, Cr , Co , Fe, Zn, Ag	Cover glass	Ca, As, Pb , Fe, Si
Forehead, flesh tone	Ca, As, K, Fe , Zn, Ag	Frame - Upper right corner	Cu, Zn, Fe
Hair highlight, yellow pigment	Ca, As, Si, Ti, Fe , Zn, Ag	Frame - Upper edge center	Cu, Zn, Fe, Sn, Au
Hair shadow, yellow pigment	Ca, As, Fe , Zn, Ag	Back-mat/Stand	Ca, Ba, Cu, Zn, Fe

Table 1. Elements found using energy dispersive XRF; major elements are in bold.

SEM-EDS

Table 2 summarizes the elements found in cross section 1 using SEM-EDS and the energy-dispersive x-ray fluorescence spectrum taken from the SEM microscope can be seen in figure 6. A false color x-ray map of the major elements found in Cross Section 1, which was taken from the detached fragment which contained some earth-toned paint found in the background, is shown in figure 5.

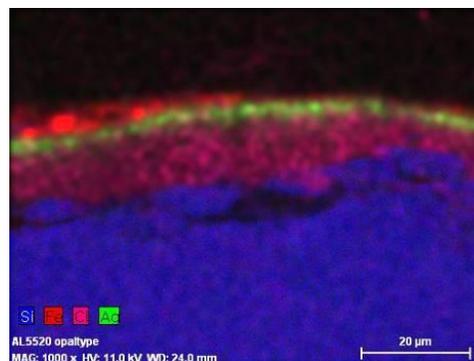


Fig. 5. Cross section 1 at 1000x, elemental map showing, from bottom to top, layers of silicon, chlorine, silver, and iron.

Location	Elements Found
Paint	As, Ca, F, Fe , Zn
Image-layer	Ag , S
Fluorescent layer	Cl
Glass support	Al , As , Ca , F , K , O, Si, Zn

Table 2. Elements found using SEM-EDS on cross-section 1; major elements are in bold.

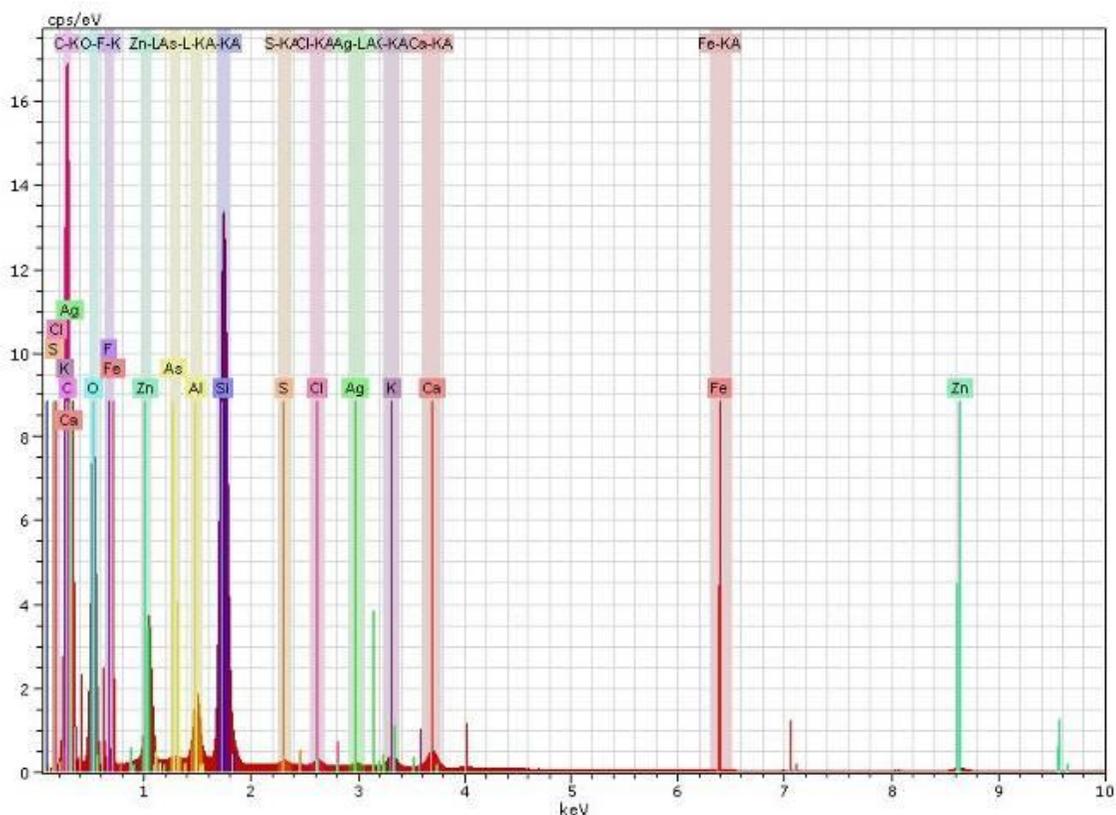


Fig. 6. XRF spectrum of Cross Section 1(taken from the fragment with earth-toned paint found in the background) obtained using the scanning electron microscope; elements present include Ag, As, C, Ca, Cl, F, Fe, K, O, S, and Zn.

Raman Spectroscopy

Raman spectroscopy was helpful in identifying a handful of pigments used in the opaltype's hand-coloring. Vermilion was identified in the red areas of paint in the background, showing peaks at 252, 282, and 343 cm^{-1} clearly (figure 7). Also found in the spectrum taken from both the pigment samples from the background were peaks at 2102 and 2154 cm^{-1} which indicate Prussian blue (figure 8). The spectrum obtained from the boy's proper left arm exhibits peaks at 224, 291, and 407 cm^{-1} , which correspond with Raman spectra of synthetic iron oxides (such as Mars red and Mars orange) (figure 9). The spectrum obtained from the boy's lower lip most closely resembles the spectrum of PR83: Corbrite Madder Lake, a hydroxyanthraquinone, with peaks seen at 484, 1191, 1294, 1328, and 1481 cm^{-1} (figure 10). Only one peak in the spectrum obtained from the pigment sample from the boy's blue clothing corresponds to lazurite or ultramarine: 548 cm^{-1} (figure 11). This peak does not correspond to other blue pigments in SRAL's spectral libraries such as the RRUFF database.

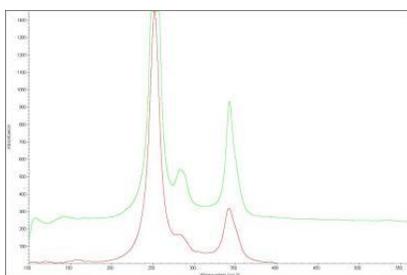


Fig. 7. Red pigments in background (top) showing a match for vermilion (bottom).

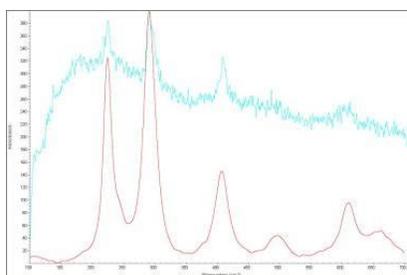


Fig. 9. Yellow pigments in boy's arm (top) showing a match for iron oxides (bottom).

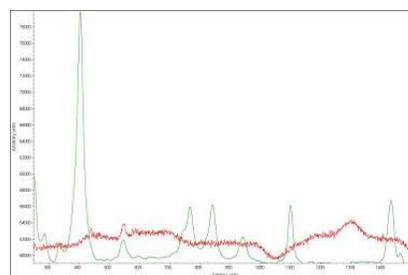


Fig. 11. Blue pigments in the boy's clothing (top) showing a match for ultramarine (bottom).

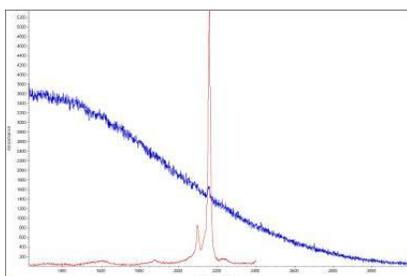


Fig. 8. Blue pigments in background (top) showing a match for Prussian blue (bottom).

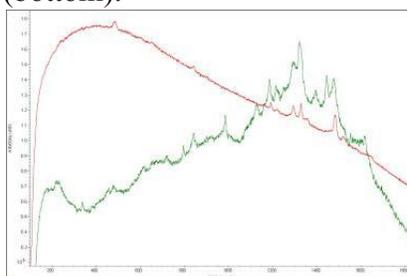


Fig. 10. Red pigments in boy's lips (bottom) showing a match for madder lake (top).

FTIR

Analysis of FTIR 1, taken from the same edge fragment as Cross Section 1, revealed a protein with a broad peak near 3300 cm^{-1} (N-H stretching), peaks at 1650 and 1550 cm^{-1} (N-H scissoring) and 1240 cm^{-1} (C-N stretching) (figure 12). The paint included in the sample was too thick for analysis using transmitted FTIR, so additional spectra were collected from the background scrapings taken for PLM analysis (PLM 3 and 4). Both spectra contain a peak near 2100 cm^{-1} which is characteristic of the C=N bond in Prussian blue, as well as peaks in the 1000 cm^{-1} to 1200 cm^{-1} range that are characteristic of silicates, and peaks near 2930 cm^{-1} and 2850 cm^{-1} (C-H stretching) that suggest the presence of an oil likely the binder for the hand painting.

These spectra also show peaks between 1300 cm^{-1} and 1750 cm^{-1} that correspond to cobalt driers (figure 13).

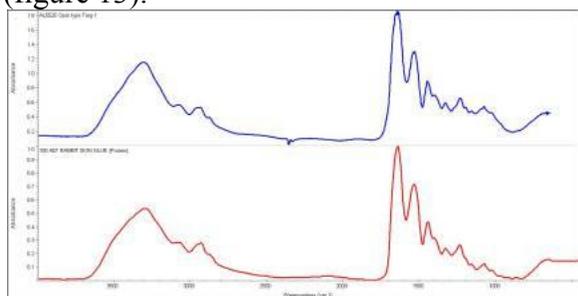


Fig. 12. Protein in the binder layer (top) characterized by FTIR library match (bottom).

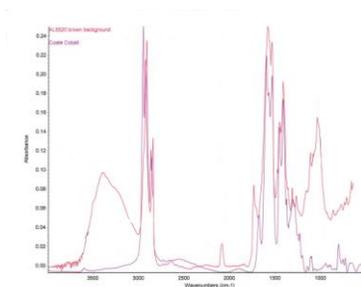


Fig. 13. Cobalt driers found in the background paint sample.

GC-MS

GC-MS analysis of the scrapings from the background paint revealed a very faint signal for oil, which is more likely a contaminant than a positive result for the presence of an oil binding media.

NIR-FORS

The spectra obtained using NIR-FORS did not reveal significant information to derive the presence of any particular pigment or colorant used in the opaltype's manufacture.

PLM

PLM successfully characterized pigments used to color the opaltype and fibers in the back-mat by examining their morphological characteristics (color, shape, and opacity) and refractive index in plane-polarized light (ppl) and birefringence and extinction in crossed-polarized light (xpl). Analysis of the background samples confirmed the presence of iron oxides (red and yellow), as well as a carbon black pigment. Analysis of the sample from the costume revealed the presence of an isotropic, synthetic ultramarine in a matrix of white pigment particles which are most likely zinc due to their cool gray-brown tone in xpl and black masses in ppl. The velvet textile and the red ribbon on the back-mat are both cotton, while all three paper fiber samples revealed bast-fibers (i.e. linen) and soft wood pulp.

IV. Discussion

Opal Glass Support

The results of ultraviolet illumination, XRF, and SEM-EDS analysis show that the opaltype examined for this study contains the opacifying agents sodium fluoride and alumina, both usually found in opal glasses. It also contains arsenic which is often found in the presence of lead in opal glasses although lead is absent in this glass. Arsenic is used both as an opacifying agent and also as a fining agent to reduce the formation of bubbles in a glass. SEM-EDS helped confirm that aluminum, arsenic, calcium, fluorine, potassium, and zinc in the glass substrate are present in greater proportion than other layers of the object, such as a subbing layer or the paint layers. The composition of this opal glass is a complicated formula that could be better understood with X-ray diffraction (XRD), which would provide phase information of the inorganic elements in the glass.

Photographic Process

Silver was found in areas of high image density, and FTIR confirmed the presence of a protein. A silver gelatin process is in keeping with the trends during this opaltype's date of manufacture. However, the presence of the bright fluorescing layer remains a confounding element in this object. Proteins have a bright blue fluorescence, but the significant amount of chlorine found by SEM-EDS in this layer gives little to no indication of its function in the object's manufacture. Dilute albumen and gelatin were often used as subbing layers on opalotypes but one would expect a subbing layer to be very thin in comparison to the other image-forming layers (Egunnik 2005, 14). Because Cross Section 1 was taken from a fragment that was already detached, it is also difficult to relay its information to the entire object. It appears that the fluorescence does not occur throughout this proteinaceous layer, but is only found around the edges, possibly due to natural aging where the layer has been exposed.

Paint and Pigments

The two most common photograph-coloring media were watercolors and oil, and analysis of the binding medium on this opaltype strongly points to oil. Although the results from GC-MS analysis were too faint to be conclusive, the positive staining with Rhodamine B in the cross-sections and the presence of cobalt driers and oil in FTIR analysis are all indicative of an oil-based medium. Without a larger sample for GC-MS, the origin of the oil cannot be discerned (i.e. linseed, etc.). All of the pigments found (iron oxide, Prussian blue, lamp black, zinc white, synthetic ultramarine blue, and madder lake) are all consistent with photograph coloring literature from the nineteenth and early twentieth centuries. This evidence, and the lack of any contemporary dye material from the early twentieth century, may also suggest that the paints used on this object were sold by a photographic supplier as a kit for both amateur and professional use. The use of two different blue pigments for the clothing and the background is of particular interest and may suggest that two different blues were used to color the sitter's eyes, which were too delicate for sampling (see figure 1). FORS was primarily attempted to identify or characterize the blue pigments in order to reduce the need for sampling. However, the absence of evidence for the presence of the blue pigments with FORS may be due to the high tinctorial power of blue pigments and therefore their relative lack of abundance. This may be an unreliable technique for detection of blue pigments in hand-colored photographs and PLM proved to be a more conclusive technique in this study. This result should not be discouraging: the use of non-destructive techniques for the investigation of hand-colored photographs should be studied in greater depth, especially for photographs that do not lend themselves to sampling.

V. Conclusions

The analyses of this object suggest that, although it was intended for a private audience, this *kind* of object was intended for *many* private audiences. In other words, the manufacture of this photograph, however delicate and precious it may seem, was made to save expense with common materials, particularly the silver gelatin photographic process on the fluorinated, opaque glass. Even though color photographic processes were available to the public in the 1930s, hand-coloring was still popular until the dyes in chromogenic prints were finally made more stable in the 1960s. The pigments found in paint on this photograph comply with traditional photograph-coloring materials and may have possibly been sold as a kit for both professionals and amateurs.

More hand-colored opatypes and painting materials of this era should be studied in greater depth to produce more conclusive results about the niche into which this object fits.

VI. Acknowledgements

This technical study would not have been possible without the assistance of the staff at Winterthur's Scientific Research and Analysis Laboratory (SRAL), University of Delaware staff, and visiting scholars. I sincerely offer my gratitude to the following individuals for their dedication and hard work: Dr. Joseph Weber (Associate Professor, WUDPAC), Dr. Jennifer Mass (Senior Scientist, Winterthur Museum), Catherine Matsen (Associate Scientist, Winterthur Museum), Dr. Caitlyn O'Grady (Mellon Fellow, WUDPAC) and Dr. Chris Petersen (Consulting Scientist, Winterthur Museum) for all of their assistance with the technical analysis involved in this study. Thanks are also due to Barbara Lemmen (Head Photograph Conservator, Conservation Center for Artifacts and Historic Artworks, Philadelphia) for her loan of her privately owned opaltype and Melanie Gifford (Research Conservator, National Gallery of Art) for her helpful interpretation of pigment samples. I would especially like to extend my thanks to my major supervisor Jennifer Jae Guiterrez (Assistant Professor, WUDPAC), Bruno Pouliot (Objects Conservator, Winterthur Museum), and Debra Hess-Norris (Chair, WUDPAC) for suggesting this topic and all of their guidance and support with this project.

VII. References

- Ayres, G. 1878. *How to paint photographs in water colors and in oil, how to work in crayon, make the chromo-photograph, retouch negatives and instructions in ceramic painting*. New York: D. Appleton.
- Burband, R. 1891. *Photographic Printing Methods: A Practical Guide to the Professional and Amateur Worker*. New York: Scovill & Adams Co.
- Doremus, R. 1973. *Glass Science*. New York John Wiley & Sons.
- Egunnike, L. 2005. *Opatypes: Their Evolution and Care*. Rochester: George Eastman House International Museum of Photography and Film.
- Gernsheim, H. 1969. *The History of Photography: from the camera obscura to the beginning of the modern era*. New York: McGraw-Hill Book Company.
- Grabow, N. 2002. *A Technical Study of Five Opaque Glasses*. Winterthur Museum/ University of Delaware.
- Henisch, H.K. and Henisch, B.A. 1996. *The Painted Photograph 1839 – 1914 Origins, Techniques, Aspirations*. University Park, PA: The Pennsylvania State University Press.
- Martin, L. 1978. *The Way We Wore; Fashion Illustrations of Children's Wear 1870-1970*. New York: Charles Scribner's Sons.

Mentzer, J. 2003. *The Technical Study of Two Opaltypes*. Winterthur Museum/ University of Delaware.

Messier, P. June 2011. "Photographic Papers in the 20th Century: Methodologies for Research, Authentication, and Dating." *Fotoconservación* 2011. Logroño, Spain.

Rintoul, A. c. 1870 *A guide to painting photographic portraits, draperies, backgrounds, etc. in water colours with concise instructions for tinting, paper, glass, & daguerreotype pictures and for painting photographs in oil colours and photo-chromography*. 7th edition. London: Barnard & Son.

Rose, C. 1989. *Children's Clothes Since 1750*. London: B.T. Batsford Limited.

Schimmelman, J. 2007. *The Tintype in American 1856-1880*. Philadelphia: The American Philosophical Society.

Scovill & Adams. 1890. *How to make photographs: with a descriptive catalogue of cameras, lenses, tripods, plate-holders, printing frames, plates, trays, chemicals, etc. and all requisites of the amateur photographer*. New York: Scovill & Adams Company.

Scovill & Adams. 1895. *Scovill & Adams Company of New York Catalogue of Photographic Goods and All Articles Pertaining to Photography*. New York: Scovill & Adams Company.

Templeton, J. and Wall, A. 1867. *The guide to miniature painting and coloring photographs: with a few words on portrait painting in water colours*. London: G. Rowney.

Tennant, J. 1902. "Coloring Photographs." *The Photo Miniature* IV, no. 44. New York: Tennant and Ward.

Tennant, J. 1907. "Coloring Lantern Slides." *The Photo Miniature* VII, no. 83. New York: Tennant and Ward.

Towler, J. [1864] 1969. *The Silver Sunbeam*. Reprint, New York: Morgan & Morgan.

Tragni, C. B., Chen, J.J. and Kushel, D. 2005. *The Use of Ultraviolet-induced Visible Fluorescence for the Examination of Photographs*. Rochester: George Eastman House International Museum of Photography and Film.

University College of London. 2009. Raman spectroscopic library of natural and organic pigments. <http://www.chem.ucl.ac.uk/resources/raman/index.html>

Vogel, W. 1985. *Glass Chemistry* 2nd ed. Michigan: Springer-Verlag.

Werge, J. 1973. *The Evolution of Photography*. New York: Arno Press.

VIII. Bibliography

Centino, S., Buisan, V., and Ropert, P. 2005. "Raman study of synthetic organic pigments and dyes in early lithographic inks (1890-1920)." *Journal of Raman Spectroscopy* 37: 1111-1118

Chen, K., Leona, M., Vo-Dinh, K., Yan, F., Wabuyele, M., and Vo-Dinh, T. 2005. "Application of surface-enhanced Raman scattering (SERS) for the identification of anthraquinone dyes used in works of art." *Journal of Raman Spectroscopy* 37: 520-527.

Chipman, A. 2010. *A Technical Study of Hand-Painted Tintypes*. Winterthur Museum/ University of Delaware.

Gettens, R. and Stout, G. [1942] 1966. *Painting Materials A short encyclopedia*. Reprint, New York: Dover.

Hoppe, J. 2010. *Spectroscopic Analysis of Hand-Colored Photographs and Photographic Hand-Coloring Materials*. Winterthur Museum/ University of Delaware.

Neblette, C.B. 1952. *Photography: Its materials and processes*. 5th edition. Princeton: Van Nostrand.

Ricciardi, P. and Delaney, J. 2011. "Combining visible Spectroscopy with sitespecific, in-situ techniques for material identification and mapping." *Revista de Historia da Arte Serie W*, No.1. 253-261.

Saverwyns, S. 2009. "Russian avant-garde... or not? A micro-Raman spectroscopy study of six paintings attributed to Liubov Popova." *Journal of Raman Spectroscopy* 41: 1525-1532.

Scherrer, N., Stefan, Z., Françoise, D., Annette, F., and Renate, K. 2008. "Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection." *Elsevier, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*.

Skoog, D. and Leary, J. 1993. *Principles of Instrumental Analysis*. 4th ed. New York: Saunders.

Weber, J. and Mass, J. 2012-2013. Unpublished presentation notes and handouts for ARTC 672 and 673: Advanced Analytical Techniques. Winterthur/ University of Delaware Program in Art Conservation.

Greta Glaser

Washington D.C., USA

Papers presented in *Topics in Photographic Preservation, Volume Fifteen* have not undergone a formal process of peer review.