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Author(s): Krista Lough
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Characterization of a Surface Tarnish Found on Daguerreotypes under Shortwave Ultraviolet Radiation

Krista Lough

Presented at the PMG session of the 2014 AIC Annual Meeting in San Francisco, California.

Abstract

A characteristic fluorescent tarnish can be observed on some daguerreotypes under shortwave ultraviolet radiation. The fluorescence can be seen in several distinct patterns: edge tarnish, rings, and continuous films. The tarnish has been observed on the fronts and backs of daguerreotypes on electroplated and roll-clad plates. The tarnish also can be seen on the backs of brass mats and on mat bevels. The fluorescent tarnish was observed on heavily tarnished plates as well as plates that showed minimal tarnish. In some cases the fluorescence corresponded to brown staining on the daguerreotype under normal and specular illumination. Test plates were created based on early experiments by Lee Ann Daffner (1996) and Claire Buzit Tragni (2005). A fluorescent tarnish, similar to the tarnish seen on historic plates, formed on bare copper plates exposed to a solution of sodium cyanide. Dispersive Raman spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) were applied to characterize and identify the fluorescent compound on the test and historic plates. Raman spectroscopy identified the characteristic peak for copper cyanide, CuCN, at 2172 cm^{-1}. Elemental k-ratio maps of the SEM analysis indicated an increase in copper, carbon and nitrogen in the area of fluorescence. Powder XRD was capable of identifying the copper cyanide compound on a test plate but was not sensitive enough for detection on a historic daguerreotype. Cyanide could have been introduced to the daguerreotype process by at least six different historical procedures in its creation as well as restoration.

Introduction

Ultraviolet radiation is a common technique employed to examine art and artifacts; and is used to examine a variety of materials including paintings, objects, paper, and photographs (Grant 2000). Shortwave radiation was first used to examine daguerreotypes in 1992 at Buffalo State College, State University of New York (Daffner et al.1996). It was observed that the shortwave radiation of daguerreotypes produced a bright green fluorescence. Early research on this phenomenon documented the occurrence of this fluorescence in daguerreotype collections, and made advancements in its initial identification. The purpose of this research is to continue in the characterization of the fluorescence through different analytical techniques, including dispersive Raman spectroscopy, scanning electron microscopy (SEM) using elemental k-ratio maps, and Powder X-ray diffraction (XRD). The focus is to analyze the fluorescent tarnish itself and not to document its occurrence. Therefore, only nine daguerreotype plates, all exhibiting the fluorescing tarnish, were observed and documented. The plates selected for analysis exhibited strong fluorescence, possibly indicating a greater amount of the fluorescent compound.

There are two potential methods of analysis that can be used in attempting to identify the cause of the witnessed fluorescence, in-situ analysis and removing a small sample for invasive testing. In-situ analysis can be performed directly on the plate without removing the tarnish and it has benefits and weaknesses. The analysis is performed directly on the plate so there is no direct sampling required but the plate itself and other forms of deterioration can affect, or interfere with the analysis and interpretation of the resulting data. In addition, some analytical techniques, like Raman spectroscopy, have the potential to thermally degrade the area of analysis causing damage, however minor. Alternately, a small amount of the fluorescent tarnish could be removed from the surface for analysis. Although this is suggested as a preferred method for specific identification, this research focuses on in-situ analysis to avoid removing the tarnish, limiting the damage to the plate itself, and suggest a non-invasive method of identification for other researchers.

Early Literature

The use of shortwave radiation for the investigation of daguerreotypes was first discussed in 1996 by Daffner, Kushel, and Messinger. This article includes a description of a witnessed tarnish that occurs on some daguerreotypes, its analysis and preliminary identification. Their research included a study of the rate of occurrence of the fluorescent tarnish on a group of 110 daguerreotypes where it was observed that 50% of the plates exhibited the fluorescent tarnish. The bright fluorescence observed with shortwave radiation was first identified in 1992. They observed the fluorescence in primarily three forms, edge tarnish, rings, and continuous films. Under normal illumination it was not always possible to discern the exact location of the fluorescent areas. The fluorescence occasionally corresponded to a brownish color, visible under normal illumination.

The methods of analysis used in their research were; scanning electron microscopy (SEM), Fourier transform infrared analysis (FTIR), and solvent tests. The solvent spot tests showed that the fluorescence was eliminated by xylene, and N,N-dimethyl formamide. The fluorescence was not affected by water, ethanol, hydrochloric acid, and ethylemedianimetetraacetic acid (EDTA). Their SEM and FTIR analysis detected copper and cyanide ions suggesting that the fluorescent material may be a copper cyanide compound but they were not conclusive in this determination. Their paper outlines the various cyanide procedures used on daguerreotypes.

Tragni (2005) conducted an extensive research project on the use of ultraviolet induced visible fluorescence for the examination of photographs and a component of this study involved the continuation of the earlier research by Daffner, Kushel, and Messinger (1996). Tragni investigated an additional 180 daguerreotypes using shortwave radiation. It was noted that the fluorescent tarnish was observed on a large number of the daguerreotypes, however the percentage was not listed. New observations made during this research included the finding of fluorescent tarnish on the back of several daguerreotypes. The fluorescence on the back was observed on electroplated and roll-clad plate (Sheffield plate). Electroplated procedures often included the use of cyanide but the roll-cladding technique does not involve a cyanide compound (Barger and White 1991). Modern daguerreotypes produced by Grant Romer were also observed and fluorescence was visible on the back of all ten of the modern plates. This indicated that in some situations, the fluorescence could be seen soon after the creation of the daguerreotype. Fluorescence was also observed on two of the brass mats. Shortwave radiation was used to document the fluorescence before and after the treatment of a daguerreotype with ammonium hydroxide. After treatment the fluorescence disappeared completely. ATR-FTIR analysis of the back of a roll-clad daguerreotype, where a strong fluorescence existed, indicated the presence of cyanide. Two daguerreotypes that exhibited the fluorescence were treated with ammonium hydroxide. After the treatment the fluorescence was no longer visible under UVC. The cleaning solution was examined under shortwave radiation and the fluorescence was not detected. Fluorometric readings were performed on the cleaning solution of one of the plates and an absorption peak in the shortwave spectrum was observed. This suggests that the fluorescent compound was removed from the plate and in the cleaning solution.

Daguerreotypes
The discovery of the daguerreotype was announced at the meeting of the French Academy of Scienes in Paris in 1839. Daguerreotypes are a one-of-a-kind image on a highly polished, silver-plated sheet of copper. The polished plate is exposed to iodine vapors to create a light-sensitive surface on the silver. After the plate is exposed to light in the camera it is developed over hot mercury. The image is fixed with sodium thiosulfate and then gilded with gold chloride. The polished silver surface of the daguerreotype is subject to tarnish. Daguerreotypes were usually placed in a protective packaging consisting the daguerreotype, paper or metal mat, glass, all bound together with paper tape. The sealed package was then placed in a small case. The history, conservation and preservation of daguerreotypes is extensively covered in other liturature, and is not the focus of this reasurch (Barger and White 1991).

The daguerreotypes selected for this research all exhibited fluorescence under shortwave radiation. The plates are a mixture of bare plate and incased daguerreotypes. The incased daguerreotypes selected for this research had either no tape present or tape with a broken seal. No sealed daguerreotype packages were opened for the purpose of this research.

Ultraviolet Radiation
Ultraviolet induced visible fluorescence is a common non-destructive technique used in art conservation for the examination of objects. Ultraviolet radiation is not visible to the human eye. It falls at 10 to 400 nanometers, between visible light and X-rays, on the electromagnetic spectrum. Ultraviolet light can be broken down into four regions:

- UVA, also known as longwave ultraviolet radiation, near-ultraviolet, black light, or Wood's light (between 320 and 400 nm)
- UVB, also known as middlewave ultraviolet radiation (between 280 and 320 nm)
- UVC, also known as shortwave ultraviolet radiation, far-ultraviolet, or germicidal UV (between 180 and 280 nm)
- Vacuum UV (between 10 and 180 nm)

UVA and UVC are the most useful for the examination of museum objects. Ultraviolet induced visible fluorescence refers to the emission of visible light from a substance being exposed to ultraviolet radiation. In the fluorescence process a material temporarily absorbs energy, which is then reemitted as lower-energy radiation in the visible light region (Grant 2000). The color and intensity of the fluorescence is a response to several factors including: the nature and amount of the material, the extent of degradation, and the excitation source (wave-length intensity). Therefore, a material may show no fluorescence under one region of the ultraviolet spectrum and show a strong fluorescence under a different region.

Shortwave radiation has been shown to be a useful tool in the examination of daguerreotypes. The emission peak of the ionized mercury for UVC is in 254 nm and is the strongest of the ultraviolet emission peaks. Shortwave ultraviolet is not transmitted by glass. Therefore all of the daguerreotypes examined have to be removed from their package for analysis. Overtime, long exposure to ultraviolet radiation can potentially change the fluorescent behavior of an object. The amount of exposure of ultraviolet radiation should be limited to the object.

Methods

Daguerreotypes are inherently fragile and conducting in-situ analysis on their surface should be completed only after safe methods are determined. A series of mock-ups were created in order to gain a greater understanding of the fluorescent tarnish and to develop secure procedures for the in-situ analysis of the daguerreotypes.

Mock-ups

The procedure for the construction of the mock-ups was referenced from Tragni's paper (2005). Her experiment was a reproduction of the experiment performed by Daffner, Kushel, and Messinger (1996).

Experiment with potassium cyanide, KCN

Four plates were dipped in a solution of 0.2 molar potassium cyanide in distilled water to try and reproduce the fluorescence found on the daguerreotypes (Figure 1). The plates used for the construction of the mock-ups were as follows: two silver electroplated copper sheets, one electroplated copper sheet with the back of the plate blocked out to expose the copper, and one bare copper sheet. The samples were dipped into the solution for 30 sec. and then rinsed with distilled water and left to air dry. None of the plates showed significant alteration in visible light. Under shortwave ultraviolet radiation no fluorescence was observed on any of the plates.

Experiment with sodium cyanide, NaCN

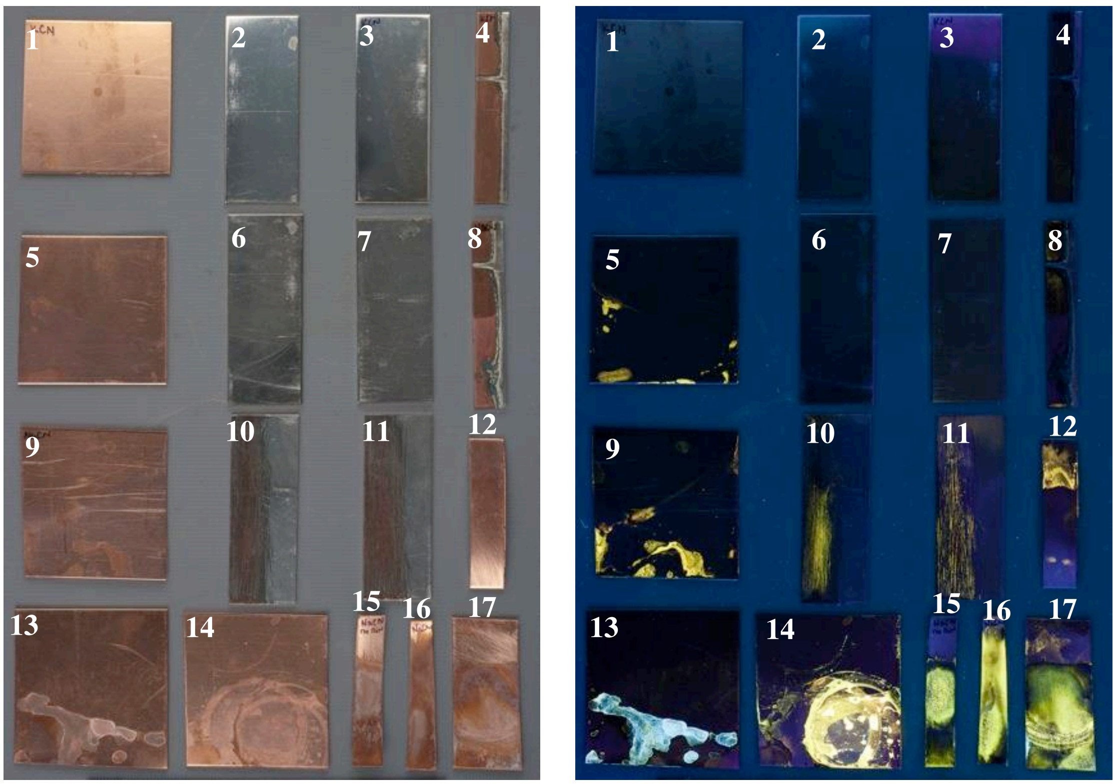
Thirteen plates were dipped in a solution of 0.2 molar sodium cyanide in distilled water to try and reproduce the fluorescence found on the daguerreotypes (Figure 1). The plates used for the construction of the mock-ups were as follows: two silver electroplated copper sheets, one electroplated copper sheet with the back of the plate blocked out to expose the copper, two sanded and filed electroplated copper sheets, four bare copper sheets, and four sanded copper sheets. The copper plates were sanded with 200-grit sandpaper to create a larger surface area. The samples were dipped into the solution for 30 sec. and then all but one of the plates were rinsed with distilled water and left to air dry.

All of the plates dipped in sodium cyanide exhibited a distinct line seen in visible light. The surface became more reflective where the plate was exposed to sodium cyanide and as the solution dried significant staining was viewed on the surface. Under shortwave ultraviolet radiation a green fluorescence was observed in the areas of solution staining.

In order to create more fluorescent material a bare copper plate was dipped in the sodium cyanide solution and was not rinsed. This however, did not create more fluorescent material but a material that exhibited a different kind of fluorescence, a blue fluorescence. This blue fluorescence is most likely a result of excess sodium cyanide. Sodium cyanide crystals were observed under UVC and exhibited a strong blue fluorescence.

The four sanded copper sheets were created to try and maximize the surface area to obtain as much green fluorescence as possible. One of the samples was not rinsed and it exhibited a bright green fluorescence under UVC. The other samples showed little to no fluorescence. These plates were all dipped back into the solutions for 30 sec. and then only one was rinsed with distilled water.

A large un-sanded copper sheet was dipped in sodium cyanide and then left un-rinsed for a few minutes. The plate was observed under UVC and exhibited a bright blue fluorescence. Then the plate was rinsed after the solution dried for several minutes and observed again under UVC. After the plate was rinsed it exhibited a yellow-green fluorescence.



1 Bare copper sheet, KCN, rinsed
2 Silver sheet, KCN, rinsed
3 Silver sheet, KCN, rinsed
4 Plated copper with stopped-out back, KCN, rinsed
5 Bare copper sheet, NaCN, rinsed
6 Silver sheet, NaCN, rinsed
7 Silver sheet, NaCN, rinsed
8 Plated copper with stopped-out back, NaCN, rinsed
9 Bare copper sheet, NaCN, rinsed
10 Filed silver sheet, NaCN, rinsed
11 Filed silver sheet, NaCN, rinsed
12 Sanded bare copper sheet, NaCN, rinsed
13 Bare copper sheet, NaCN, not rinsed
14 Bare copper sheet, NaCN, rinsed after 20 Min.
15 Sanded bare copper sheet, NaCN, not rinsed
16 Sanded bare copper sheet, NaCN, not rinsed
17 Sanded bare copper sheet, NaCN, not rinsed

Fig. 1. Test plates under normal illumination (left) and shortwave-induced visible fluorescence (right).

Documentation and Shortwave Ultraviolet Radiation
Prior to instrumental analysis, nine daguerreotypes were documented with normal and specular illumination, and shortwave ultraviolet radiation.

The normal and specular illuminated photographs were taken with a UV-VIS-IR Modified Nikon D700 camera with a Nikon 105 mm lens with a PECA 918 filter. The light source was one GTI graphic light box, with 2 fluorescent bulbs (F20T12, 20W), D5000. For normal illumination white foam core was used to fill the light onto the other side of the plate. For specular illumination a sheet of glass at a 45-degree angle was used to create a specular light and block the cameras reflection from appearing on the reflective surface. The settings on the camera were as follows: ISO 200, with white-balance taken with the gray card, Aperture Priority, with an aperture set to F8 or F11.

The UVC-induced visible fluorescence photographs were taken with a UV-VIS-IR Modified Nikon D700 camera with a Nikon 105 lens with PECA 918 and a Kodak 2E filters. Visible fluorescence was induced with one UV Systems SuperBright II UVC lamp peak/254 nm. The UVC lamp was held at different distances for each plate depending on the size. The closest distance the UVC lamp was held to the daguerreotype was 12 ¾”. The settings on the camera for the UVC-induced visible fluorescence images were as follows: ISO 200, the white balance set to “Shade,” Aperture Priority, with an aperture set to F8 or F11. The temperature and tint settings were adjusted individually to match the appearance of the visible fluorescence observed in each daguerreotype.

Dispersive Raman Spectroscopy
Dispersive Raman spectroscopy was used to examine: a green fluorescent area on a test plate, and the green fluorescent areas on the front and back of two daguerreotypes. The spectra were collected with a Bruker Senterra Raman Spectrometer. Spectral resolution was 3-5 cm^{-1} across the spectral range analyzed. Spectral spikes due to cosmic rays were removed and baselines adjusted as necessary using Opus 6.5 software.

The spectra of the green fluorescent areas on the test plate and the daguerreotypes were collected using a 633 nm excitation laser operating at a power of 0.83 mW at the sample. A 100x ultra-long working distance objective was used to focus the excitation beam to an analysis spot of approximately 1 μm directly on the surface of the objects under study. The resulting Raman spectra are the average of 5 scans at 2 sec integrations each.

Scanning Electron Microscopy (SEM)
Scanning electron microscopy (SEM) with a silicon drift detector (SDD) energy-dispersive (EDS) X-ray spectrometer was used to examine a green fluorescent area on a daguerreotype. The analysis was performed with a mapping SEM/SDD-EDS instrument, TESCAN tFEG with four 30 mm^2 SDD-EDS detectors. Elemental k-ratio maps were collected at beam energy of 5 kV to maximize sensitivity to nitrogen and other light elements. The background and peak-interference corrected k-ratio maps are presented in the logarithmic three-ban color encoding which enables sensible inter-comparison of the images. The data cubes were compiled with the image analysis program Lispix (Bright 2012).

X-Ray Diffraction (XRD)
X-ray diffraction (XRD) was collected using a Rigaku Ultima X-ray Diffractometer to analyze the green fluorescence on a test plate and on a daguerreotype. The plates were placed directly in the diffractometer, so no sample was taken. The measurement conditions for the test plate were 40 kV at 44 mA with a .5 deg/min scan speed, a sampling step at 0.03 deg, and a measurement axis of 2ƒÆ/ƒÆ. The scan range for the test plate was 20-39.41 deg. The scan range for the daguerreotype was 20-40.01 deg.

Results and Observations

Tarnish Visible in Normal Illumination and Shortwave Ultraviolet Radiation
The fluorescent tarnish described in the early literature by Daffner, Kushel, and Messinger (1996) was clearly observed and documented. The tarnish was observed to occur primarily in three forms; edge tarnish, rings, and continuous films. The research performed by Tragni (2005) documented the fluorescent tarnish in the three forms described previously, the back of electroplated and roll-clad plates, and on the brass mat. The nine daguerreotypes observed and documented in this experiment exhibited all of the forms of fluorescence described in early research, and additionally tarnish on the bevel of the brass mat was identified.

Several of the plates exhibited a combination of the forms of tarnish. A plate with a strong concentration of fluorescence along the edges could also have several fluorescent rings in the center (fig. 2). A plate with several rings could also have areas of fluorescence in continuous film (fig. 3). On a couple of the plates a clear connection between the fluorescence and brown spots or stains could be seen (figs. 2, 4). The connection between the brown stains and the fluorescence could be more easily determined on plates with less visible tarnish. The fluorescence was also observed on the back of electroplated and roll-clad daguerreotypes (figs. 5, 6). Fluorescence was observed on the back of five brass mats. The tarnish on the back of the mats was primarily a continuous film (fig. 7). The fluorescence was also seen on the bevel of three of the brass mats (fig. 8).

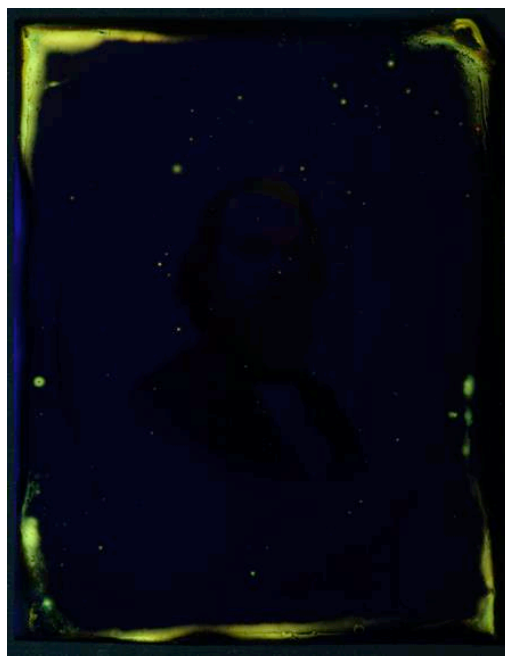


Fig. 2. Daguerreotype under normal illumination *(top)* and under shortwave ultraviolet radiation *(bottom)*. The plate exhibits tarnish along the edge and in rings. The rings and some of the edge tarnish correspond to brown stains on the plate.

Fig. 3. Daguerreotype under normal illumination *(left)* and shortwave ultraviolet radiation *(right)*. The fluorescent tarnish is visible in a continuous film and in rings.

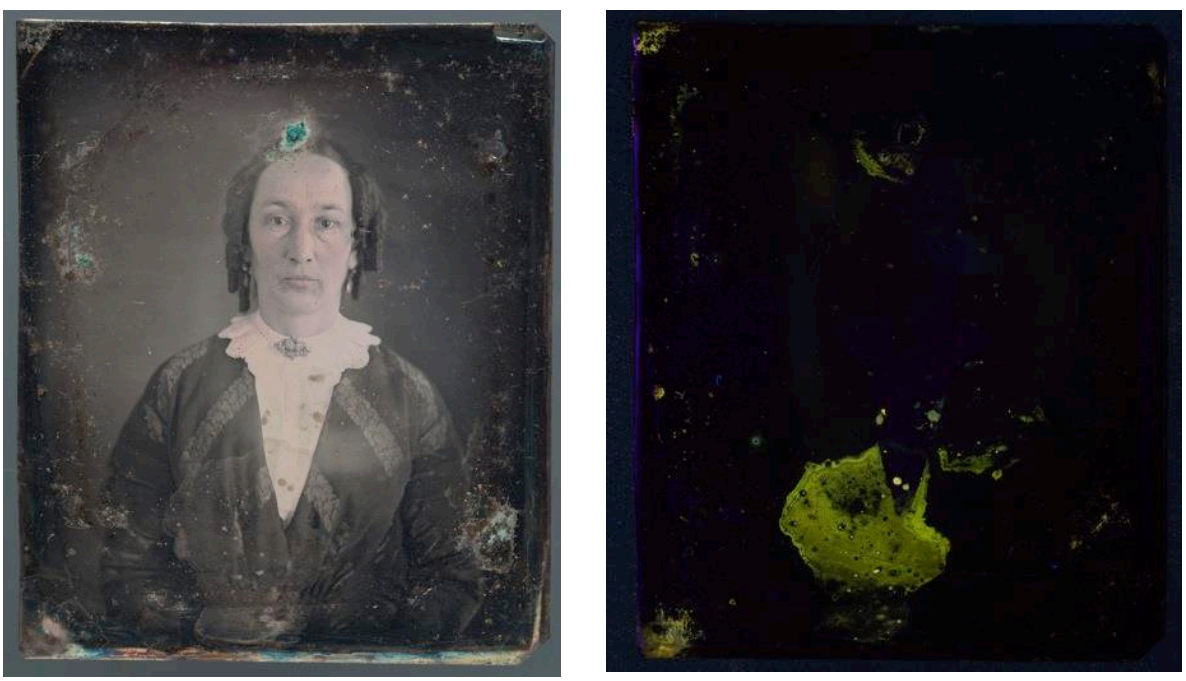


Fig. 4. Daguerreotype under normal illumination *(left)* and shortwave ultraviolet radiation *(right)*. The fluorescent tarnish is visible in a continuous film with some spots. The areas of fluorescent tarnish correspond to brown stains.

Fig. 5. The back of an electroplated daguerreotype under normal illumination *(left)* and shortwave ultraviolet radiation *(right)*. The fluorescent tarnish is a thin film over the entire back of the plate. Areas with heavy green and purple corrosion, see under normal illumination, do not show fluorescence.

Fig. 6. The back of a roll-clad daguerreotype under normal illumination *(left)* and under shortwave ultraviolet radiation *(right)*. Fluorescence is present with less intensity and slightly different tone. Areas of bare copper seem to show the strongest fluorescence.

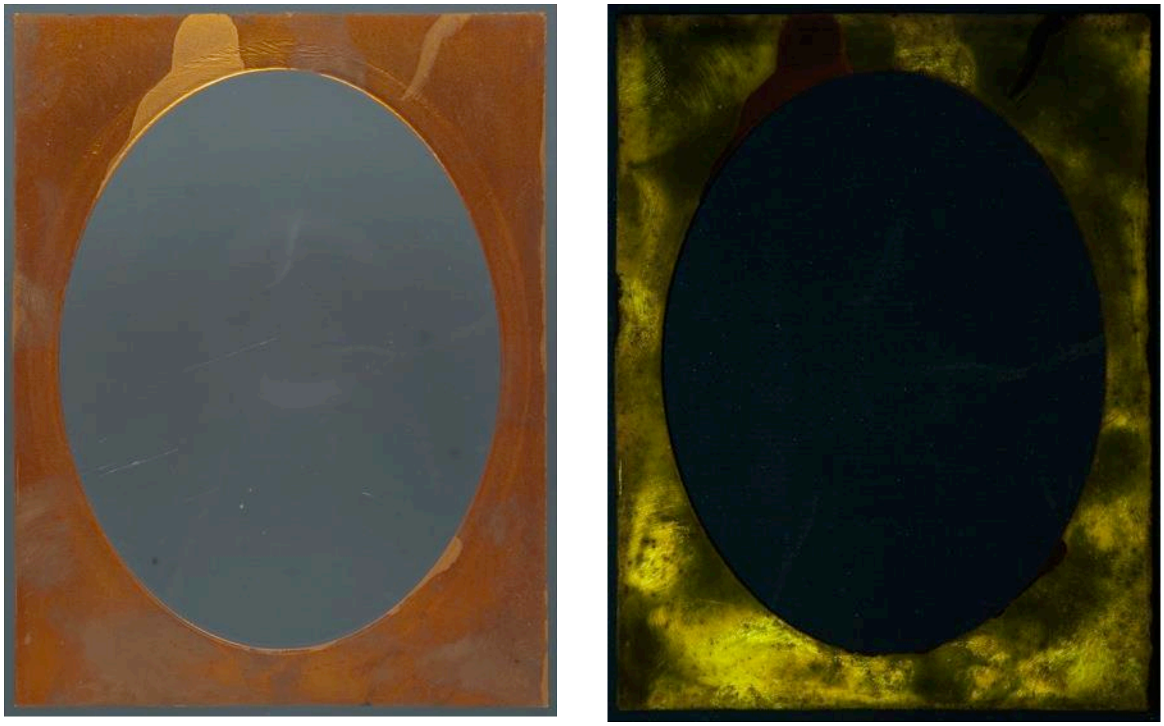


Fig. 7. The back of a brass mat in normal illumination *(left)* and shortwave ultraviolet radiation *(right)*. A strong thin film of fluorescence is present. Fluorescence is concentrated in areas with grey tarnish visible in normal illumination.

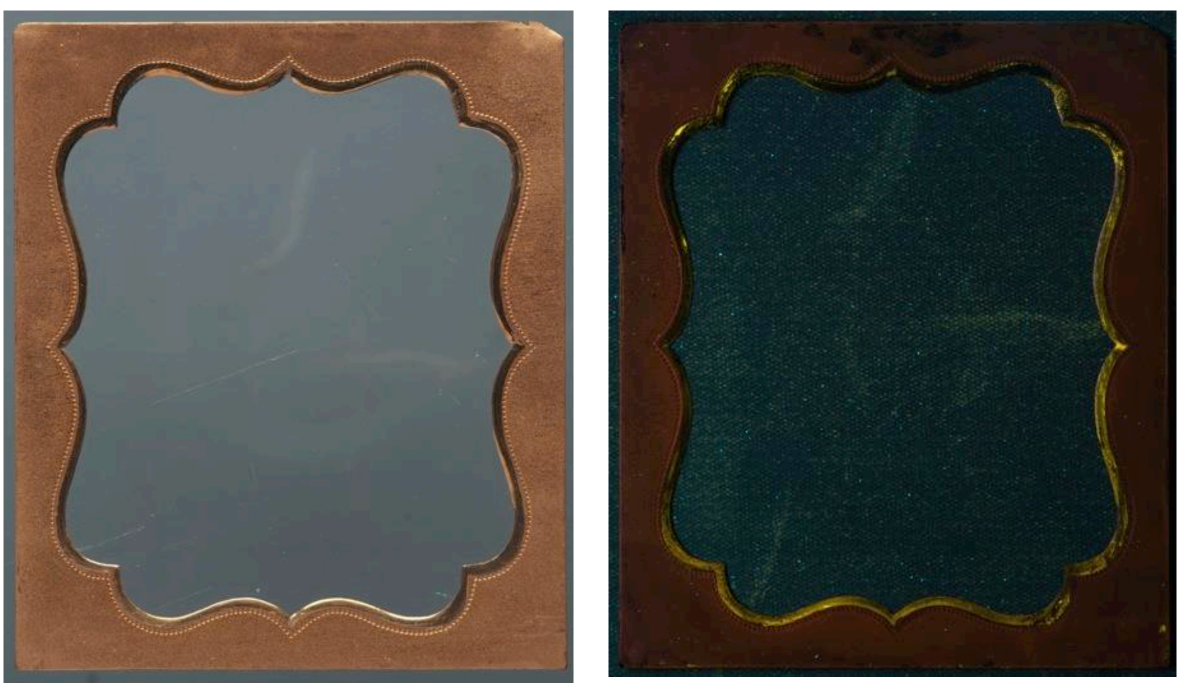


Fig. 8. Brass mat under normal illumination *(left)* and shortwave ultraviolet radiation *(right)*. Fluoresce is observed on the bevel of the mat.

Dispersive Raman Spectroscopy

The Raman spectrum for the green fluorescence on one of the test plates is presented in Figure 9a. The peak at 2172.40 cm^{-1} is close to the literature value for copper cyanide, which for solid CuCN occurs at a wavelength of 2174 cm^{-1} (Lukey et al. 1999). The significant intensity of the peak to background could be a result of the metallic surface of the daguerreotype creating a surface-enhanced Raman scattering effect (Centeno et al. 2008).

Surface-enhanced Raman scattering (SERS) has been a useful technique for examining dyes and organic pigments (*ibid)*. SERS involves removing a small sample and placing the sample in contact with the appropriate SERS substrate, such as citrate or hydroxylamine-reduced Ag colloids, a Tollens mirror, or Ag nanoisland films (*ibid*). The significant increase of peak to background is enhanced on the daguerreotypes due to the mirror like surface of the plate. The fine silver surface is inherently a SERS substrate. In a study of the use of Raman on daguerreotypes the natural SERS surface allowed the detection of some deterioration products that were below the detection limit of scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS) (*ibid*). There are some potential problems, which may limit the SERS effect on daguerreotypes. This includes the level of deterioration or tarnish on the surface, which can reduce the enhancement provided by the silver substrate.

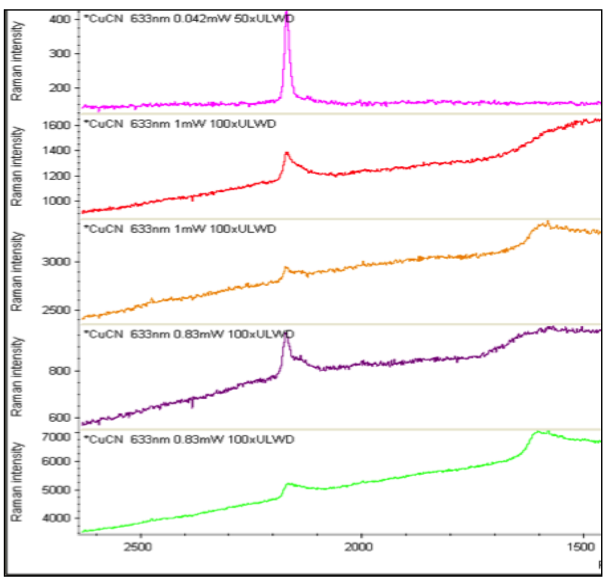


Fig. 9. Raman spectra (a) test plate, (b) front of plate, (c) back of plate, (d) front of plate, and (e) back of plate.

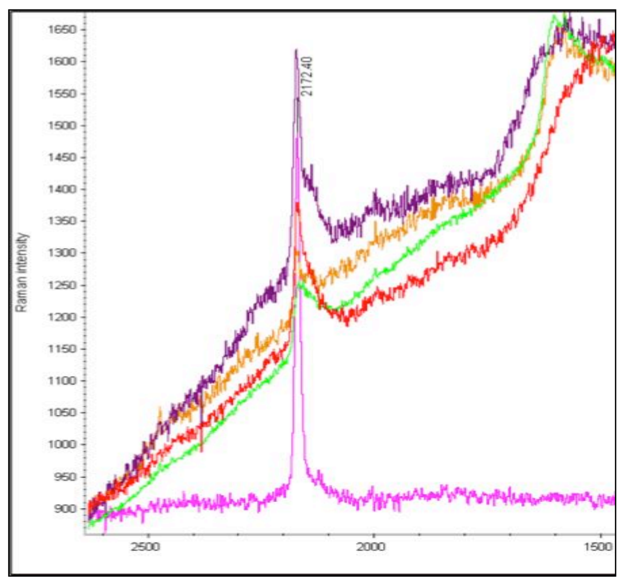


Fig. 10. Stacked spectra of fig. 9.

A fluorescent area on the front and back of a daguerreotype was tested. The front of the plate showed a peak from CuCN at 2174.50 cm^{-1} (Figure 9b). The back of the plate had a peak for CuCN at 2175.00 cm^{-1} (Figure 9c). The Raman spectra of the fluorescence on the front and back of a significantly tarnished daguerreotype were also collected. The front of the plate showed a peak for CuCN at 2175.203 cm^{-1} (Figure 9d). The back of the plate showed a peak for CuCN at 2172.00 cm^{-1} (Figure 9e). When the peaks are overlapped (Figure 10) it is apparent that Raman is detecting the same compound on the test plate and the daguerreotypes.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS) was used to analyze several fluorescent spheres that appeared as brown stains under normal illumination (Figure 11). Elemental analysis is encoded in a logarithmic multiband color scale with three distinct color bands: trace (blue), minor (green), and major (red) (Figure 12). The color bands run from pure color at the low end of the scale to pastel color to the high end of the scale (Newbury and Bright 1999). A k-ratio map shows an increase in copper, carbon, and nitrogen, in the location of the fluorescence, which are the elemental components of copper cyanide. The k-ratio maps also showed a decrease of silver and gold indicating degradation of the image material. In the same region, the map also shows an increase of oxygen and sodium. The sodium increase is seen as a ring around the tarnish and is likely related to a previous sodium cyanide treatment.

Fig. 11. Location of the SEM analysis

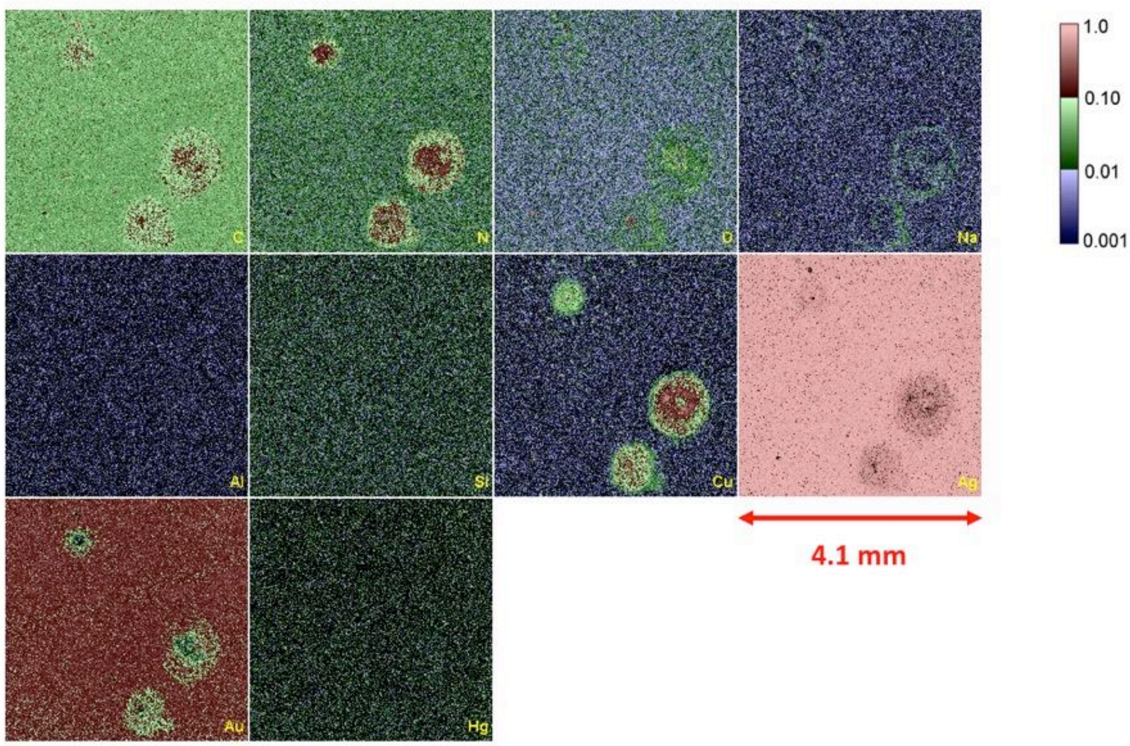


Fig. 12. Elemental k-ratio map collected at beam energy of 5 keV. The background and peak-interference corrected k-ratio maps are presented in a logarithmic three-ban color encoding scale.

X-Ray Diffraction (XRD)

The X-ray diffraction analysis for the test plate is presented in Figure 13. The spectrum indicated one peak at 2-theta (deg) 29.6291. This peak corresponded to the most intense peak of copper (I) cyanide, seen in the ICSC pattern. The most intense peak for copper (I) cyanide has a 2-theta at 29.90. Copper (I) cyanide has a trigonal crystal system with cell parameters of: Alpha=90.000, Beta=90.000, and Gamma 120.000 (Reckeweg et al. 2012).

The X-ray diffraction analysis for the daguerreotype is presented in Figure 14. The spectrum detected two peaks: one with 2-theta 32.669, the second peak has a 2-theta of 38.524. The first peak with a 2-theta of 32.669 corresponds to a peak of silver sulfide (Grocholl 2003), which is the most common tarnish found on daguerreotypes. The second peak with a 2-theta at 38.524 corresponds to a peak of silver (*ibid*), which is related to the substrate. The daguerreotype was analyzed in the area with the strongest fluorescence, the same area as the Raman spectrum in Figure 9b. The amount of fluorescence on the plate is probably below the detection limit of the powder XRD.

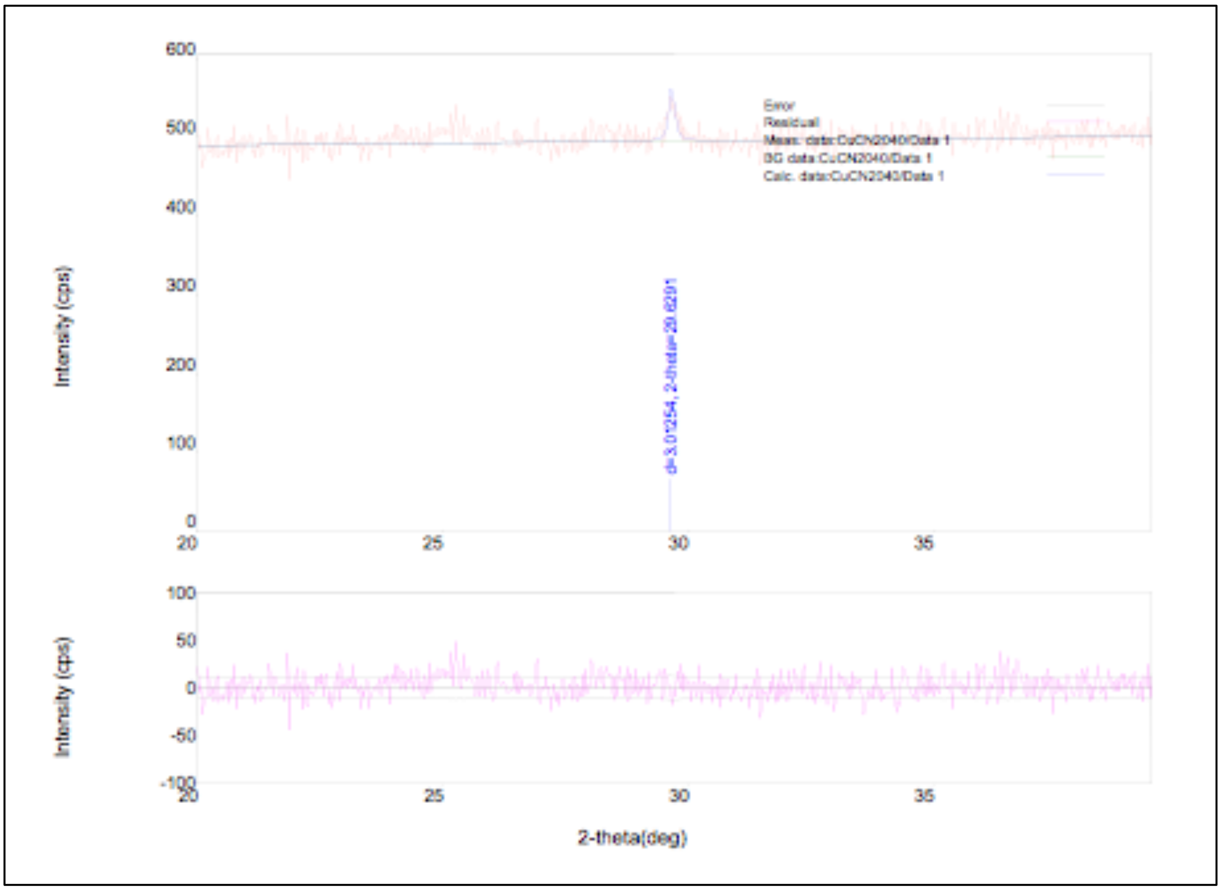


Fig. 13. X-ray diffraction of the green fluorescence on a test plate. The peak present is an indication of the presence of copper (I) cyanide.

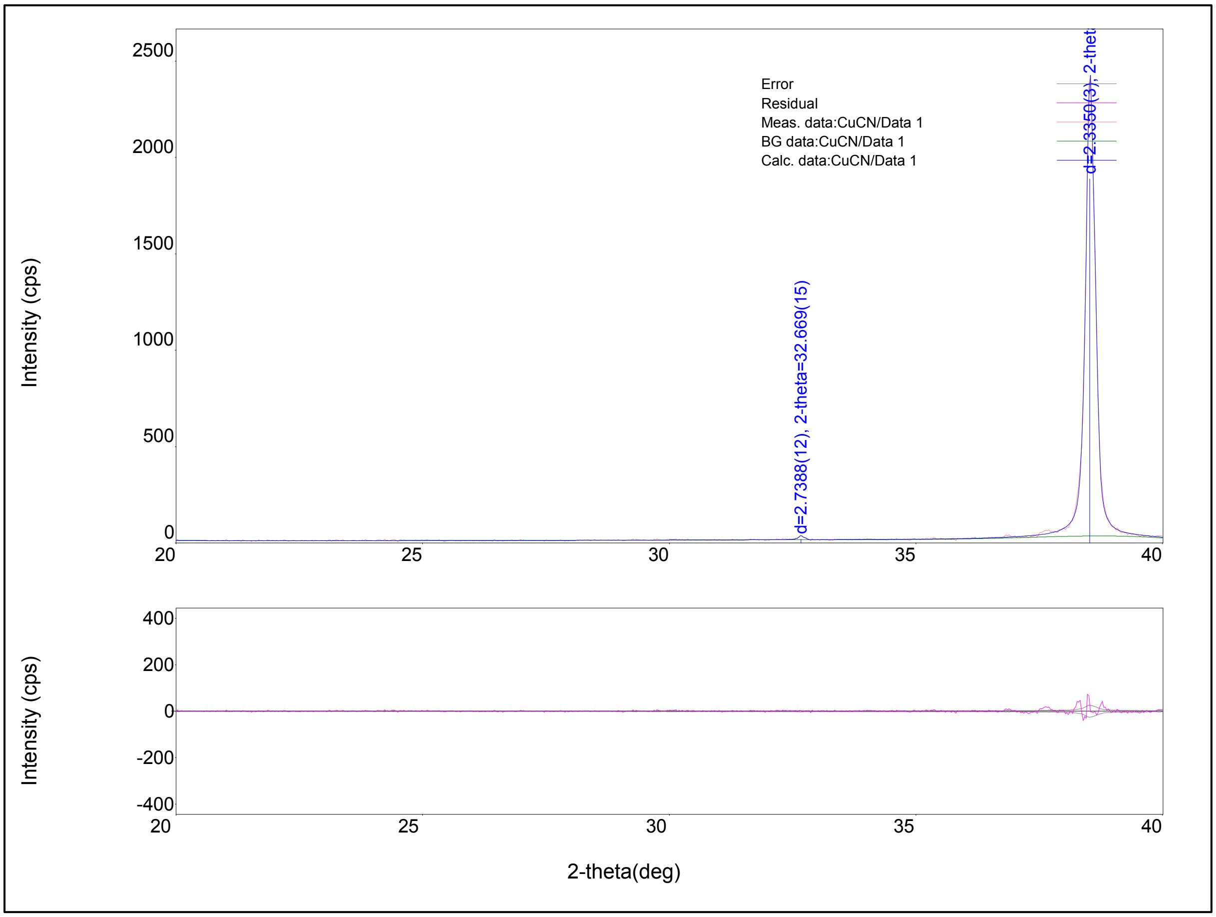


Fig. 14. X-ray diffraction of the green fluorescence on a daguerreotype. The peaks present are an indication of the presence of silver sulfide and silver.

Discussion

The fluorescent tarnish on daguerreotypes seen under shortwave radiation can exist in several forms including: edge tarnish, rings, and continuous films. The tarnish has been observed on the front and back of the daguerreotype and on electroplated and roll-clad plates. The tarnish can also be seen on the back of the brass mat and on the mats bevel. The fluorescent tarnish was observed on heavily tarnished plates as well as plates that showed minimal tarnish. The fluorescence was observed in some cases, but not all, to correspond to brown staining on the daguerreotype under normal and specular illumination. Comparisons of the analytical testing including: dispersive Raman spectroscopy, scanning electron microscopy, and X-ray diffraction, all confirm that the fluorescent compound is composed of copper cyanide.

One concern is that the fluorescence relates to copper cyanide and not silver cyanide. This may indicate some level of deterioration to the silver surface in the location of the fluorescence. On a couple of the daguerreotypes the fluorescence appeared in areas that did not show noticeable deterioration to the silver under specular illumination. An alternative explanation is that the copper cyanide was formed and deposited on the surface of the daguerreotype. These deposits may be what relate to the brown staining on the silver surface.

Cyanide in the Daguerreotype Process

Historical literature discusses the use of cyanide in several aspects of the daguerreotype process. As mentioned by Daffner, Kushel, and Messinger (1996) there are six procedures discussed in early literature in which cyanide can be introduced to the daguerreotype. The procedures include: electroplating, gilding or gold toning, brightening, fixing, "engraving by Galvanism", and cleaning. Of the six procedures, electroplating and cleaning were the most prevalent cyanide procedures used in the daguerreotype process. It is important to note that photographers experimented greatly with the photographic process and it is possible that cyanide could have been introduced into the daguerreotype process through other procedures.

Copper Cyanide and its Toxicity

Copper (I) cyanide, cuprous cyanide, is a white powder and does not absorb light in the visible region. It has only two distinct absorbance peaks at 237 nm and 208 nm (Reddy et al. 2010), in the shortwave ultraviolet fluorescent region. Copper (I) cyanide is the most stable oxidation state for copper in the cyano compound. Copper (I) cyanide is diamagnetic and melts at 473ºC (Sharpe 1976). CuCN is insoluble in all common organic solvents and is soluble in aqueous ammonia.

Copper cyanide is very toxic and with chronic exposure it can cause damage to the blood, kidneys, lungs, nervous system, liver, and mucous membranes. Copper cyanide is extremely dangerous when ingested or inhaled and can be a very hazardous irritant when in contact with skin (Sciencelab.com, Inc. 2012).

Future Work

Research into the fluorescent tarnish observed on daguerreotypes under shortwave radiation is ongoing and new insights can be made onto this phenomenon with additional analysis. At this time the fluorescence on the brass mat has not been analyzed, so currently it is unclear if the fluorescent compound is the same on the brass mat and on the daguerreotype. It is not apparent if the copper cyanide will continue to affect the condition of the daguerreotype. It may be possible that after its initial formation the fluorescence does not alter with time. It is currently unknown if it is necessary to remove the copper cyanide from the surface of the daguerreotype or if its removal would create additional problems. The fluorescent compound was only examined and identified on three plates and with out further testing it is uncertain if the fluorescence under shortwave radiation always indicates the presence of copper cyanide or if a different compound also forms a strong fluorescence under UVC. Additional micro X-ray diffraction analysis may help to detect the copper cyanide compound on an actual daguerreotype.

Conclusions

Shortwave radiation is a useful tool for the examination of daguerreotypes and can yield new information about their tarnish patterns. Under shortwave radiation a characteristic bright fluorescence can be observed that appears to indicate the presence of copper cyanide. Early research into the phenomenon by Daffner, Kushel, and Messinger (1996) indicated a high concentration, around 50%, of the fluorescent tarnish when observing a large daguerreotype collection.

Dispersive Raman spectroscopy indicated a clear presence of copper cyanide in the areas of fluorescence on the front and back of two daguerreotypes. The characteristic peak at 2172 cm^{-1} for copper cyanide was observed. The presence of copper cyanide in the fluorescence was confirmed with scanning electron microscopy. The analysis indicated an increase in copper, carbon, and nitrogen in the area of fluorescence. Copper, carbon and nitrogen are the elemental components of copper cyanide and their presence helps to confirm the Raman data. X-ray diffraction was collected on a test plate and on a daguerreotype. Powder X-ray diffraction was able to indicate the presence of copper cyanide on the test plate but was not sensitive enough to detect its presence on the daguerreotype.

Shortwave ultraviolet radiation is a powerful tool and its proper use is crucial in ensuring the safety of the object and the examiner. Shortwave radiation cannot penetrate glass therefore daguerreotypes observed under UVC will have to be removed from their packages. Bare plate daguerreotypes are extremely fragile and require extra care when handled. Gloves should always be worn when handling bare plate daguerreotypes not only for the objects safety but for the examiner as well.

After the initial discovery of the fluorescent tarnish in 1996 there has been few advancements into understanding and characterizing the fluorescent compound. From this research a few new developments were made to aid in the understanding of the nature of the compound. It is hopeful that research into this phenomenon can continue and provide a greater understanding of the first commercially successful photography process.

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Krista Lough
Andrew W Mellon Fellow in Photograph Conservation
The Art Institute of Chicago

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