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Fluorescence Fails: the Color of UVA-Induced Visible Fluorescence of Tintype Varnishes does not Discriminate between Varnish Materials

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Abstract: In order to determine if the commonly used technique of UVA-induced visible fluorescence could accurately identify varnish materials, a study collection of over 200 tintypes with known varnish materials was digitally imaged. The CIE L*a*b* values of the fluorescence in the lightest light and darkest dark areas of the images were obtained and showed that there was no correlation between resins present and the color of the fluorescence, even for quite disparate materials such as shellac and dammar. False color reflected UVA images also failed to differentiate resins. Thus, this commonly used examination technique should not considered a reliable identification method.

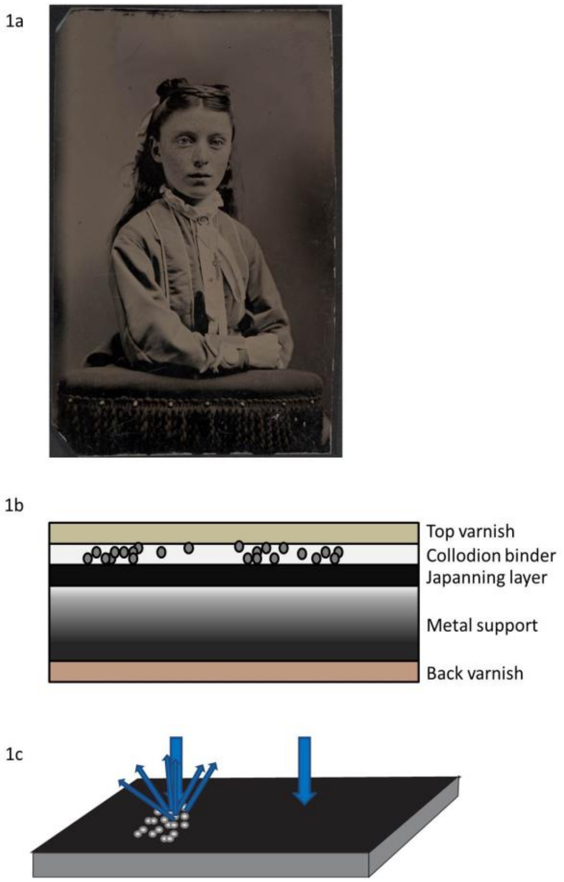

Fig. 1. (a) a 1/6 plate tintype from the study collection; (b) the layer structure of a tintype, image particles are indicated in the collodion layer; (c) darks are caused by the absorption of light by the exposed japanning layer while highlights are caused by diffuse reflectance off the silver image particles.

Introduction:

The tintype, also known as the melainotype or ferrotype, was the most popular type of photographic image in the United States of America from the 1860s to the early 1900s, due to their low cost and durability (Shimmelman 2007). This status was additionally driven by the social imperatives of the American civil war and the increased purchasing power of the middle class who sought to document their lives (Fig. 1a). Thus, tintypes provide a glimpse into the lives of everyday citizens and are of historic and sociological interest.

Tintypes were made using the wet collodion method first developed by Frederick Scott Archer (Archer 1851), but instead of glass the support material was a japanned metal plate (Smith 1856). In their final state tintypes are multilayered composite structures; the metal support plate was japanned on one side, with the colored japanning layer providing the darks of the final image (Fig. 1b-c). The plate manufacturers also applied a protective varnish to the verso of the plate to help prevent rusting of the support (Shimmelman 2007). The artist would purchase these plates from photographic supply houses, and then apply the collodion binder as well as a protective top varnish layer to help prevent physical damage and oxidation of the image.

The popularity of tintypes led to the publication of 'how to' monographs, such as *The Practical Ferrotyper* by A.P. Trask (Trask 1872), which provided instruction in the mechanics of taking tintypes, in how to create pleasing portraits, and in running a commercially successful studio. The most variable step of the photographic process was the artist-applied top varnish: some authors recommended that the artist make their own varnish, while others recommended the use of commercially available varnishes from photographic supply houses (Rogge 2013). These recommended varnishes contain a wide range of components, with different solubilities and solvent sensitivities that should be handled differently by conservators, so identifying the top varnish used in a given tintype is a critical step in its treatment.

Many conservators use UVA light in the examination of artifacts and it is commonly accepted that the color of the visible fluorescence can help identify varnish materials (Rivers 2003; Tragni 2005; Grant 2010; Stoner 2012). However, discussions with photograph conservators suggest that misidentification of varnish materials based upon fluorescence color is common and in some cases has led to treatment issues. A previous study utilizing pyrolysis-gas chromatography mass spectrometry (py-GC-MS) to identify the components in the top varnishes of a study collection of tintypes found a wide range of components, some of which were distinct from literature recipes (Rogge 2013). 24% of the varnishes had materials specifically recommended for tintypes, 44% of the varnishes had materials recommended for other wet-collodion images, and the remaining 32% of the tintypes were mostly varnished with mixtures of shellac and *Pinaceae* resin, which likely represent commercially available varnishes. This corpus of diverse and definitively-identified varnishes made an ideal collection to assess whether UVA-induced visible fluorescence provides an accurate, non-destructive way to determine varnish identities. Accordingly, digital images of the visible fluorescence of the study collection tintypes were obtained and processed in Adobe Photoshop® to extract CIE $L^*a^*b^*$ values for the lightest light and darkest dark areas, which were compared to the varnish compositions. False color reflected UVA imaging was also explored as another possible means for non-contact, non-destructive identification of varnish materials. Both methods show poor correlations between image colors and varnish composition in this collection of 221 tintypes. The failure of these methods to identify varnish materials indicates that they cannot be used as reliable analytical tools for tintypes, and the use of more definitive analytical techniques such as FT-IR or GC-MS is necessary.

Materials and Methods:

Objects: A study collection of 221 unprovenanced, undated tintypes ranging in size from gems (19 x 27 mm) to 1/6 plates (64 x 89 mm), was purchased from local and online vendors. Based upon the clothing of the sitters they are presumed to date from the 1860s to early 1900s.

Digital Imaging:

Normal illumination: UV-VIS-IR modified Nikon D700 camera (36 x 23.9 mm CMOS sensor) with a 60 mm 1:4 UV-VIS-IR apo macro lens equipped with a PECA 918 filter. The camera was white balanced using a neutral grey card and the camera settings were as follows: ISO 200; aperture f/11; shutter speed 1/10 s; exposure adjustment -0.2. The tint and temperature were adjusted in the RAW (NEF) format to -34 and 2050, respectively. Illumination was provided by two Cole Palmer single light guide fiber optic lamps, EKZ 30W/10.8V/3100K (MR-16) and a Leica twin light guide fiber optic EJA 150W/21V/3400K (MR-16) and the irradiance at the object was 267 footcandles.

UVA-induced visible fluorescence imaging: digital photographs of the tintypes were taken with a Nikon D700 camera (36 x 23.9 mm CMOS sensor) with a Nikon AF Micro Nikkor 105 mm 1:2:8 D lens equipped with PECA 918 + 2E (gelatin) filters. The camera settings were as follows: ISO 200; aperture f/8; shutter speed 1.6 s; no exposure adjustment. The white balance was set to shade and the tint and temperature were adjusted in the RAW (NEF) format to +35 and 10000, respectively. Radiation was provided by two UV Systems Inc. Superbright II 3000 series LW lights with primary wavelengths of 370 nm and the irradiance at the object was 516 W/m^2. The lights were positioned at a 32^o angle on foamcore supports in order to provide an even wash of light across the image surface; this method was adapted from one developed by J.J. Chen (2012) for documentation of UVA-induced visible fluorescence.

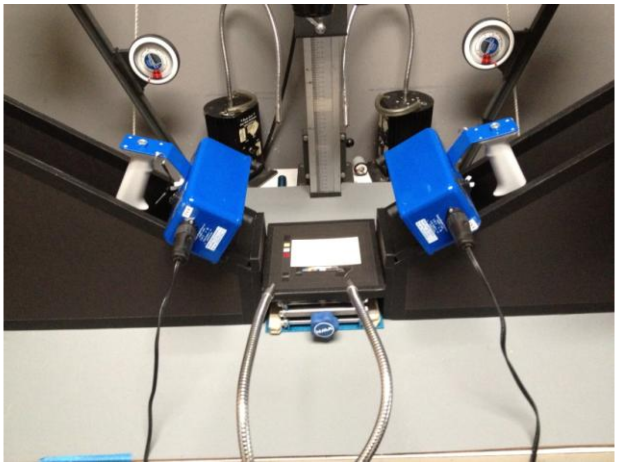

Fig. 2. Lighting set up for photographic documentation of UVA-induced visible fluorescence, the fiber optic lights for normal illumination are also shown.

Reflected UVA: digital photographs of the tintypes were taken with a UV-VIS-IR modified Nikon D700 camera (36 x 23.9 mm CMOS sensor) with a 60 mm 1:4 UV-VIS-IR apo macro lens equipped with B+W 403 (18A) + BG38 (B+W 2mm thick screw-in) filters. The camera settings were as follows: ISO 200; aperture f/11; shutter speed 2.0 s; exposure adjustment +0.30. The white balance was set to shade and the tint and temperature were adjusted in the RAW (NEF) format to +2 and 7300, respectively and the saturation was set to -100. Radiation was provided by two UV Systems Inc. Superbright II 3000 series LW lights with primary wavelengths of 370 nm and the irradiance at the object was 536 W/m^2.

Image Analysis:

CIE $L^*a^*b^*$ Analysis: Tiff images were opened in Adobe Photoshop®. A 3 mm selection circle was used to select and copy three areas of the lightest lights and three areas of the darkest darks of the images to a new layer. The blur tool, set at 100% strength and a size of 6 pixels, was used to homogenize the selected swatches by sweeping the brush in a circular fashion from the center of the swatch outward. The color sampling tool set to a 5x5 pixel sample size was then used to take three reading from each swatch, and the CIE $L^*a^*b^*$ valued were recorded.

Fig. 3. A selection of tintypes displaying different induced fluorescence colors under UVA light.

False color UVA-induced visible fluorescence analysis: Tiff images were opened in Adobe Photoshop® and the reflected UV image was converted into grayscale. The contrast of this image was optimized using Auto Levels, bringing the N8 patch on the color chart to 120 RGB, and this modified image was saved as a Tiff. The visible light image was then opened and the following channel substitutions were made: G to R; B to G; and UV grayscale to B.

Py-GC-MS Analysis:

Sampling: Samples of the varnish layers of the tintypes were obtained by scraping the surface with a 0.5 mm tip microchisel (Ted Pella) or #15 scalpel blade under a stereo-microscope. Care was taken to ensure that the japanning layer was not co-sampled.

Pyrolysis instrumentation and method: 3-5 μg samples were placed into a 50 μL stainless steel Eco-cup (Frontier Laboratories) and 3 μL of a 25% methanolic solution of tetramethylammonium hydroxide (TMAH) was introduced for derivatization (Heginbotham 2011). After 3 minutes an Eco-stick (Frontier Laboratories) was fitted into the cup, and the cup was placed into the pyrolysis interface of a Frontier Lab Py-2020D double-shot pyrolyzer where it was purged with He for 3 minutes. Samples were pyrolyzed using a single-shot method at 550 °C for 6 seconds and then passed to the GC-MS through an interface maintained at 320 °C.

GC-MS instrumentation and method: The pyrolyzer was interfaced to an Agilent Technologies 7820A gas chromatograph coupled to a 5975 mass spectrometer via a Frontier Vent Free GC/MS adapter. An Agilent HP-5ms capillary column (30 m x 0.25 mm x 0.25µm) was used for the separation with He as the carrier gas set to 1 mL per minute. The split injector was set to 320 °C with a split ratio of 50:1 and no solvent delay was used (Heginbotham 2011). The GC oven temperature program was 40 °C for 2 minutes, ramped to 320 °C at 20 °C per minute, followed by a 9 minute isothermal period. The MS transfer line was at 320 °C, the source at 230 °C, and the MS quadropole at 150 °C. The mass spectrometer was scanned from 33-600 amu at a rate of 2.59 scans per second. The electron multiplier was set to the autotune value.

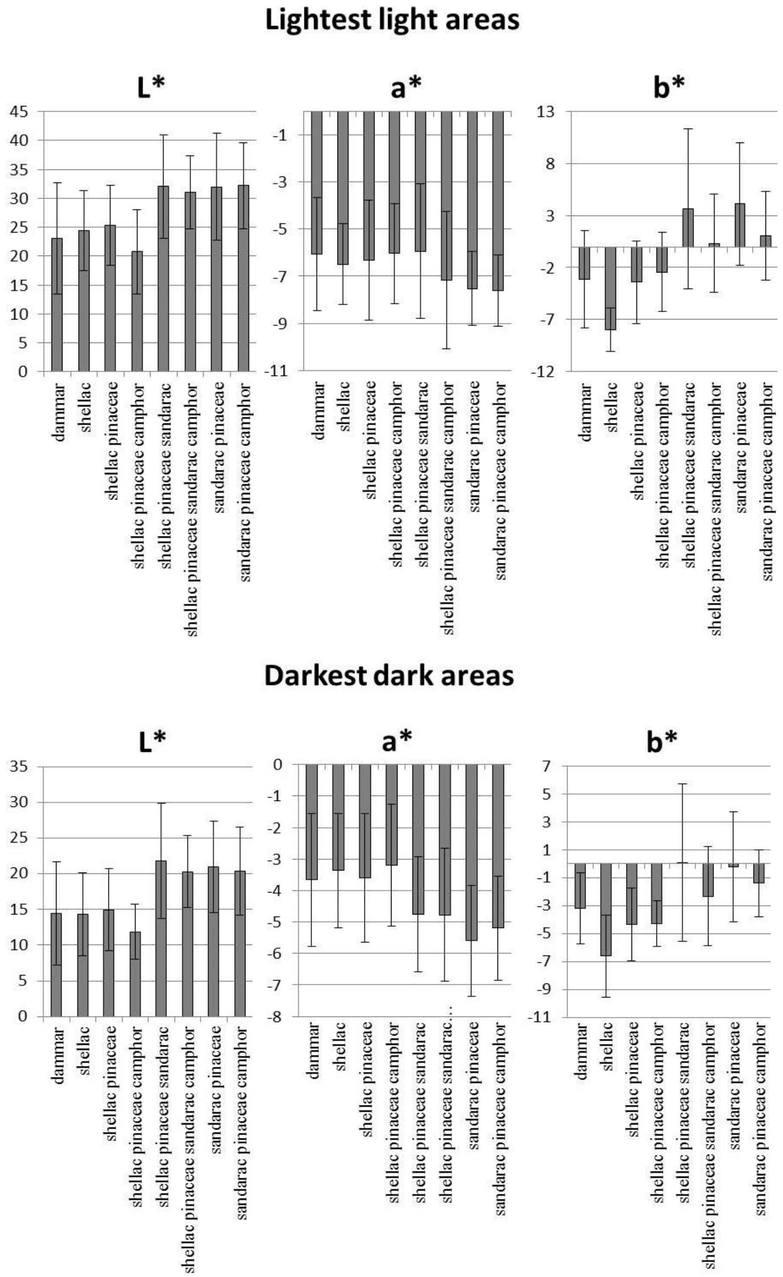

Fig. 4. CIE L*a*b* values of the lightest light (top) and darkest dark (bottom) areas of the digital images of the UVA-induced visible fluorescence of tintype varnishes.

Data analysis: Sample identification was aided by searching the National Institute of Standards and Technology (NIST) MS library, and by comparison to pyrograms and mass spectra of reference materials (Kremer Pigmente) and published literature. Specific marker compounds searched for have been previously published by Rogge (2013).

Results:

The tintypes displayed a wide range of fluorescence colors including blue, yellow, orange or white under UVA light (Fig. 3). However, color sampling of the lightest light and darkest dark areas of the digital images of the UVA-induced visible fluorescence failed to show any correlation between the CIE L*a*b* values of the fluorescence and the varnish components (Fig. 4). All varnishes exhibit similar ranges of L* and a* values in the lightest light and darkest dark areas of the image. Sandarac containing varnishes have a more yellowish tone in the lightest light areas indicated by the positive b* values, but the correlation is not significant enough to permit positive identification of this material, and this difference is not present in the darkest dark areas.

Fig. 5. Two tintypes varnished with a combination of shellac, sandarac and *Pinaceae* resin. Only the one on the left displays the orange fluorescence commonly expected of shellac.

Despite the large percentage of the collection that contains shellac in the varnish layer (59 %), only two tintypes displayed the orange color typical of the insect resin (Fig. 5). Instead, most of the varnish materials containing shellac fluoresced a bluish-green, as indicated by the negative a* and b* values. This suggests that the tintypists were using decolorized shellac to minimize the typical yellowish tonality of the varnish. During the time of these tintypes' manufacture shellac was most commonly decolorized by bleaching with chlorine gas or sodium hypochlorite or by passage through an adsorbent material such as charcoal (Sutherland 2010). The chlorine bleaching process results in formation of trace levels of chlorinated compounds that are detectable by mass spectroscopy (Sutherland 2010); however these compounds were not detected in the shellac varnishes on the study collection tintypes. This may be due to the concentrations of these marker compounds being below the detection limit of the instrument, or due to a deliberate choice on the part of the artists to use carbon decolorized shellac. Literature reports on the early production of bleached shellacs suggest that these become insoluble with age and were unsuitable for use on photographic materials, for instance H. Greenwood (1882) wrote of chlorine bleaching saying "This process, though it produces a pale resin of great value for many economical purposes, causes the resin to lose many of those properties that specially fit orange lac for use in photographic varnish." And "Experimenters with "bleached," or as it is often called, "white lac," must know that unless it be properly stored it practically loses its solubility in spirit of wine…" While Nash (1867) reported on adverse reactions of chlorine bleached shellac with silver image material: "…I studiously avoid the use of chlorine, phosphatic compounds or chromates, as any of these coming into contact with silver or its salts enter readily into combination, forming chloride, phosphates, and chromates of the metal; and solutions of shellacs or gums treated with any of the above chemicals will, to the most casual observer, be seen to be an injury to a print, or in fact in any instance where silver is present." Thus, contemporary photographers were well aware of the importance of varnish quality and may reasonably be supposed to have deliberately used non-chloride containing photographic grade materials.

False color reflected UV photography (FCUV) is a method that combines a reflected UVA image with two visible light channels, and offers a potential method to differentiate between materials similar in appearance (Warda 2011). This technique was first developed in 2004 by Aldrovandi (2004) for non-destructive analysis of pigments and has since been applied to easel and wall paintings (Albrovandi 2005), works of art on paper (Coccolini 2010), and textile dyes (Conti 2008), but analysis of resinous materials has not yet been reported. In order to determine if this method would offer a means to differentiate between the different varnish materials, a subset of tintypes that had different varnish materials but similar UVA-induced visible fluorescence colors was chosen and imaged. Figure 6 shows FCUV images of two tintypes, one varnished with shellac and *Pinaceae* and the other varnished with dammar, which are nearly identical color; thus, this method too fails to distinguish between insect and plant resin materials.

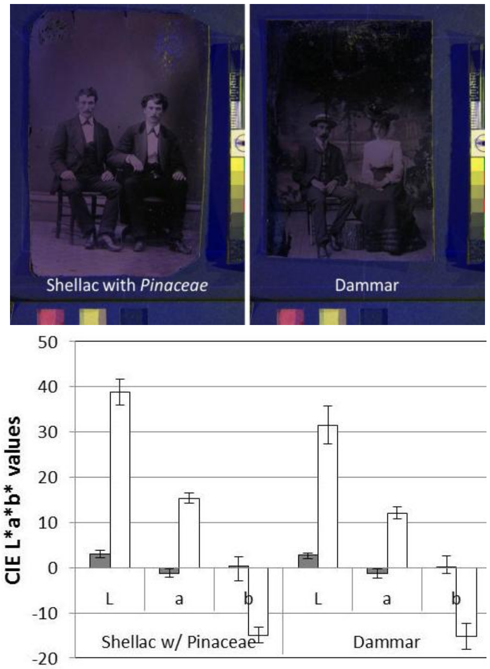

Fig. 6. Top: False color reflected UVA images of tintypes varnished with shellac and *Pinaceae* resin (left) or dammar (right). Bottom: average CIE $L^*a^*b^*$ values for the lightest lights (white) and darkest darks (grey) of the images above. The false color images have very similar tonality despite the presence of completely different varnish materials.

Fig. 7. Normal (left) and UVA-induced visible fluorescence (right) images of a tintype. The image on the right clearly shows how the presence of a paper holder altered production of fluorophores.

The failure of fluorescence to distinguish dammar, shellac and sandarac is likely due to a variety of causes. Fluorophores in materials can be initially present in the material or can form upon aging; shellac is highly fluorescent as obtained from the insect (Larsen 1991), but many plant varnishes display increased fluorescence upon aging (de la Rie

1982b), which is often used to detect modern overpaint on easel paintings (de la Rie 1982a). Decolorization can remove the fluorophores initially present (Sutherland 2010), and may also influence the type and quantity of fluorophores created upon aging. Aging conditions may also influence the types of fluorophores produced. For instance, many tintypes were originally housed in carte de visite sized paper holders although when purchased the tintype shown in Figure 7 did not have such a case. However, the UVA-induced visible fluorescence image of this tintype shows a difference in fluorescence between the edges of the tintype and the central portion and clearly delineates the shape and size of the window of the now missing holder; the window area is significantly more yellow in tone than the areas that were once covered. The storage and display history of this object are unknown, and the difference in fluorescence could result from different levels of light exposure, materials present within the mount, or both, but it is evident that the life of an object can dramatically influence its fluorescence color.

Conclusions:

Fluorescence of varnish materials is not indicative of the type of resinous materials present. Di-, tri-, and sesquiterpenoids all display a range of colors under UVA radiation and thus the color of UVA-induced visible fluorescence should not be considered an analytical tool capable of identifying varnishes present.

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