Journal of Cultural Heritage xxx (2013) xxx–xxx

Available online at
SciVerse ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en

Original article

The varnished truth: The recipes and reality of tintype coatings

Corina E. Rogge*

Department of Art Conservation, State University of New York Buffalo State College, 1300, Elmwood Avenue, Buffalo, 14222 New York, United States

ARTICLE INFO

Article history:
Received 16 November 2012
Accepted 4 February 2013
Available online xxx

Keywords:
Tintype
Pyrolysis-GC-MS
Varnishes
Resins
Photography

ABSTRACT

The most popular photographic technique in the USA between 1856 and 1900 was the tintype, with millions of these objects created by photographers in established studios, by itinerant artists in portable workshops, and by amateurs working from 'how-to' manuals and journal articles. Whereas the fundamentals for this photographic process (collodion binder on a japanned metal support) were largely invariant, historical documents recommended a wide variety of protective varnish materials. A collection of 221 tintypes was analyzed using pyrolysis gas chromatography-mass spectrometry (py-GC-MS) to compare the components of actual tintype varnishes with recipes from the historical literature. Several resins in published tintype varnish recipes, including mastic, copal, and amber, are entirely absent from this collection and only five constituents – shellac, *Pinaceae* resin (Canada balsam or colophony), dammar, sandarac, and camphor – are detected alone or in combination. Each detected resin appears in historical recipes, but just 24% of the samples have varnish layer constituents consistent with published tintype varnish recipes. Forty-four percent of the tintypes have varnish constituents consistent with formulations recommended for other collodion images, but the varnishes of the remaining samples have no direct literature equivalents. The preponderance of shellac- and *Pinaceae*-based varnishes suggests that these correspond to inexpensive commercial varnishes, but tintypists may have developed their own preferred mixtures or simply used what was at hand. This first in-depth technical analysis of tintype materials suggests that the cheapest and most readily available materials were employed in the varnishing process and that the artists were not bound by literature recommendations.

1. Research aims

The aims of this work were to identify the resinous constituents of varnishes on 19th and early 20th century tintypes by pyrolysis gas chromatography-mass spectrometry (py-GC-MS) and to determine the degree to which the materials actually used correspond to those recommended in the contemporaneous literature.

2. Introduction

The invention of photography in the 19th century provided the lower and middle classes with the first economical means of portraiture. Whereas daguerreotypography was the first commercially successful technique, Frederick Scott Archer's discovery of the wet collodion (nitrocellulose) process led to the development of less expensive ambrotypes, positive images on glass, which quickly supplanted daguerreotypes in terms of popularity [1]. However, ambrotypes suffered from the inherent fragility of glass and – like daguerreotypes – had to be framed or cased to protect against breakage and preserve the image. In 1856 Hamilton Lanphere Smith, a Professor of Natural Philosophy at Kenyon College, in Ohio, USA, patented the production of wet collodion photographic images on metal surfaces coated with a black 'japanning' layer, which usually consisted of linseed oil and lampblack or asphaltum [2]. This method grew out of work Smith performed with Peter Neff, Jr., a student at Kenyon College and assignee of the patent [3]. Initially marketed by Neff under the name 'melainotypes' and also termed 'ferrotypes', these images later became known as tintypes, the name commonly used today (Fig. 1a) [3].

The tintype is a multilayer image consisting of an iron or steel plate, a black japanning layer, the collodion or nitrocellulose binder that holds the silver image particles, and a protective varnish coating (Fig. 1b). The whites of the image are caused by diffuse reflectance off the silver image particles and the blacks are due to the exposed japanning layer (Fig. 1c). The images are always positive and unless taken through a special camera are also reversed.

The metal support greatly improved both the profit margin of the photographer and durability of the image, and in the United States tintypes quickly became the most popular form of photographic portraiture, spurred on by the social demands of the

* Tel.: +1 716 878 4646; fax: +1 716 878 5039.
E-mail address: roggece@buffalostate.edu

1296-2074/$ – see front matter © 2013 Elsevier Masson SAS. All rights reserved.
http://dx.doi.org/10.1016/j.culher.2013.02.002

American Civil War. Becoming a tintypist was seen as a profitable career move, and in 1862 a war correspondent reporting on two brothers wrote

> "They have followed the army for more than one year, and taken, the Lord only knows how many thousand portraits. In one day since they came here, they took in one of the galleries, so I am told, 160 odd pictures at $1.00 (on which the net profit was probably ninety-five cents each). If anybody knows an easier and better way of making money than that, the public should know it" [4].

Books, 'how to' manuals, and journal articles describing the process enabled individuals to establish their own tintype studios. The japanned supports were commercially available, and the collodion and silver compounds generally standardized, but the varnishing materials recommended were quite diverse. Some authors recommended the use of 'patent' formulations such as Anthony's Diamond Varnish [5] while others provided recipes to enable tintypists to make their own, and literature recommendations on effective varnishes sometimes included warnings of the perils of using poor or inappropriate materials.

To correlate the published varnish recipes with what tintypists actually used, the varnish layers of tintypes dating from the 1860s to the early 20th century were analyzed by py-GC-MS to determine their resinous constituents. The findings were compared to publish historical tintype varnish recipes as well as varnish recipes recommended for ambrotypes and wet collodion negatives, sister techniques to the tintype.

3. Historical recipes

Table 1 presents a compilation of the formulations explicitly recommended in the historical literature for tintype varnishes and the number of occurrences of each resin or resinous mixture. The recipes involve a wide variety of materials including shellac, sandarac, dammar, mastic, copal, and amber. It should be noted that 'amber' in this context might not mean true fossilized amber, but rather the semi-fossilized resin copal [6] or a mixture of sandarac and mastic [7].

In addition to recommending varnishes some texts also warned against the use of certain resins; in The Practical Ferrotyper [8] Trask noted that

> "Some use gum sandarac for varnish; but it has one fault, which I call a serious one and very injurious to the trade, namely, any dampness coming in contact with the picture will cause it to turn a milky white, sometimes spreading over the whole picture, completely obliterating it. And by carrying a picture in the

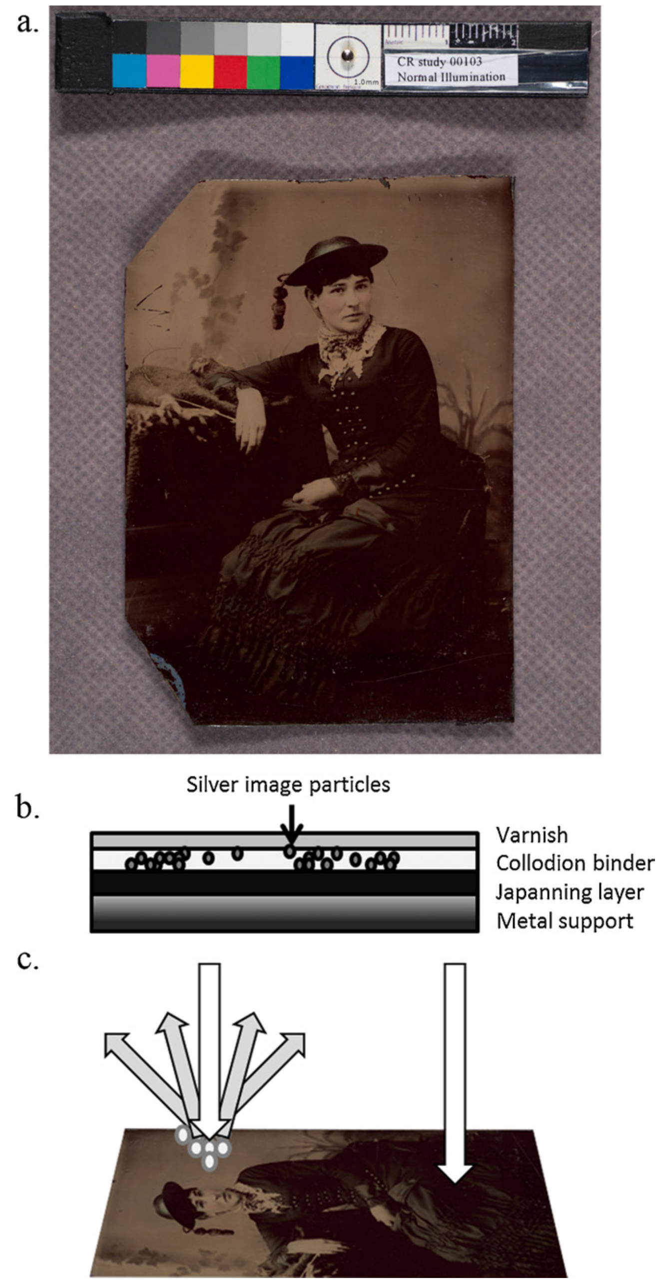

Fig. 1. (a) a 1/6 plate tintype, the scale bar is in cm; (b) the layer structure of a tintype; (c) black areas are formed by absorption of light by the japanning layer, highlights are caused by diffuse reflectance off the silver image particles.

Table 1
Historical tintype varnish formulations.

Resinous materials	Occurrences of this recipe in the literature	% of resinous components in varnish by weight[b]	Reference(s)
Shellac[a]	2	100	[5,8]
Shellac, oil of lavender	2	99 shellac, < 1 oil of lavender	[39–41]
Shellac, camphor, Canada balsam	1	94 shellac, 3 camphor, 3 Canada balsam	[42]
Dammar[a]	4	100	[42–45]
Mastic	1	100	[46]
Copal[a]	1	100	[42]
Amber[a]	3	100	[42,47]
Sandarac, oil of lavender[a]	1	56 sandarac, 44 oil of lavender	[42]
Sandarac, white turpentine (gum)	1	50 shellac, 50 turpentine	[48]
Collodion[a]	1	100	[49]

[a] Also recommended for ambrotypes or wet collodion negatives.
[b] Calculated by summing the weight of all materials other than solvents. Note that many of the formulations record weight as drachms, of which there were two types; the apothecary drachm is equivalent to 3.89 g and the avoirdupois drachm is equivalent to 1.77 g. All calculations were performed assuming the apothecary unit.

Please cite this article in press as: C.E. Rogge, The varnished truth: The recipes and reality of tintype coatings, Journal of Cultural Heritage (2013), http://dx.doi.org/10.1016/j.culher.2013.02.002

Table 2
Some examples of 'patent' tintype varnishes.

Commercial name	Reference(s)
Anthony's diamond varnish	[5,10]
Rose varnish	[50]
Holmes' lustrous ferrotype varnish	[51]
Mountfort's self drying crystal varnish	[52]
Lewis and Holt's adamantine varnish	[42]
The American amber varnish	[53]
French diamond varnish	[54]
Reid's ferrotype varnish	[55]

pocket, where it came near the body, it would change in the same way".

Dammar and copal were seen as being too soft for these oft-handled objects:

"In the choice of a varnish, avoid the white varnish made of benzole and gums dammar or copal. It is disagreeable and dangerous to work with, and utterly unfit for ferrotypes or negatives. Gum dammar is a very soft resin, becomes "tacky" and will soften under the heat of the hand. It is one of the most fusible, if not the most fusible, of all the resins, and for this and other reasons should be discarded" [9].

In addition to self-made varnishes, tintypists also had the option to employ a number of 'patent' varnishes sold by photographic supply companies (Table 2). Unfortunately these varnishes were not actually patented and so their constituents are unknown (apart from Anthony's diamond varnish, which was reported to be made of mastic and Venice turpentine [10]).

Ambrotypes and wet collodion negatives were also often varnished in order to protect the vulnerable image layer [11]. Some materials recommended for tintype varnishes were also recommended for ambrotypes or wet collodion negatives (Table 1), but the compiled recommendations for varnishing these objects include a wider variety of constituents – oil of bergamot, New Zealand gum, bezoin, castor oil, and linseed oil – and often more complex formulations (Table 3) than those for tintypes.

4. Materials and methods

4.1. The artworks

A study collection of 221 tintypes, varying in size from gems (19 × 27 mm) to 1/6 plates (64 × 89 mm), was purchased from local and online vendors. The photographs derive mostly from the Midwestern and Eastern United States, and date from the 1860s to early 1900s based upon the style of garments worn by the sitters.

4.2. Pyrolysis gas chromatography-mass spectrometry (py-GC-MS) analysis

4.2.1. 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 microscope. Care was taken to ensure that the japanning layer was not co-sampled.

4.2.2. Pyrolysis instrumentation and method

Three to five micrograms 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 [12]. 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.

Table 3
Historical ambrotype and wet collodion negative varnish recipes.

Resinous materials	% of resinous components in varnish by weight[a]	Reference(s)
Shellac, camphor	88 shellac, 12 camphor	[56]
Shellac, sandarac, oil of bergamot	5.5 sandarac, 94.5 shellac, < 0.05 oil of bergamot	[42]
Shellac, sandarac, Canada balsam, oil of lavender	39 shellac, 39 sandarac, 19 oil of lavender, 3 Canada balsam [30], or 49 shellac, 33 sandarac, 16 oil of lavender, 2 Canada balsam [31]	[57,58]
Shellac, sandarac, Canada balsam, oil of lavender, camphor	39 shellac, 39 sandarac, 19 oil of lavender, 3 Canada balsam	[56]
Shellac, sandarac, Canada balsam	62 shellac, 31 sandarac, 7 Canada balsam	[59]
Shellac, sandarac	50 shellac, 50 sandarac	[60]
Shellac, New Zealand gum, copal	50 New Zealand gum, 25 shellac, 25 copal	[61]
Shellac, sandarac, benzoin, Venice turpentine, castor oil, oil of lavender	57 sandarac, 28 shellac, 7 benzoin, 7 Venice turpentine, ≈ 0.5 castor oil, ≈ 0.5 oil of lavender	[62]
Amber, linseed oil, turpentine, shellac	Unrecorded	[63]
Amber, linseed oil, turpentine	Unrecorded	[63]
Sandarac, camphor, castor oil, Venice turpentine	72 sandarac, 14 castor oil, 7 camphor, 7 Venice turpentine	[64]
Sandarac, Venice turpentine, turpentine	57 sandarac, 29 turpentine, 14 Venice turpentine	[64]
Sandarac, dammar	50 sandarac, 50 dammar	[56]
Sandarac, castor oil	85 sandarac, 15 castor oil	[65]
Sandarac, shellac, castor oil	59 sandarac, 33 shellac, 8 castor oil	[66]
Sandarac, mastic (note-called amber varnish)	80 sandarac, 20 mastic	[7]
Sandarac, shellac, castor oil, oil of lavender	57 sandarac, 29 shellac, 12 castor oil, 2 oil of lavender	[65]
Sandarac, turpentine, oil of lavender	66 sandarac, 26 turpentine, 8 oil of lavender	[59]
Sandarac, benzoin	50 sandarac, 50 benzoin	[67]
Sandarac, mastic, benzoin	93 benzoin, 4 sandarac, 3 mastic	[59]
Sandarac, mastic, benzoin, Jalap resin[b]	47.5 benzoin, 47.5 Jalap resin, 2 sandarac, 3 mastic	[59]
Copal, turpentine, drying oil	Unrecorded	[68]
Dammar, castor oil	86 dammar, 14 castor oil	[69]

[a] Calculated by summing the weight of all materials other than solvents. Note that many of the formulations record weight is drachms of which there were two types; the apothecary drachm is equivalent to 3.89 g and the avoirdupois drachm is equivalent to 1.77 g. All calculations were performed assuming the apothecary unit.
[b] Jalap resin is normally used for medicinal purposes as a purgative or laxative, not as an artists' material [70].

4.2.3. Gas chromatography-mass spectrometry (GC-MS) instrumentation and analytical 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 × 0.25 mm × 0.25 μm) 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 [12]. 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.

4.2.4. 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 included the hydroxydehydroabietic acid (DHA) series in *Pinaceae* resins such as Canada balsam and colophony [13,14], aleuritic, butolic, jalaric and shellolic acids present in shellac [15,16], larixol and larixyl acetate in Venice turpentine [15,17], totarol and ferruginol in sandarac [17], dammaranes, ursanes, oleananes, and ocotillones in dammar [18,19], moronic acid in mastic [17], α- and β-amyrin in elemi [20], cinnamic acid present in benzoin [21], fenchyl alcohol and succinic acid in fossilized amber [22], agathic acid in Manila copal [23], sandaracopimarol in Kauri copal [24], *enantio*-biformene in Congo copal [25], ricinoleic acid and its degradation product, 9,12-dihydroxyoctadecanoic acid in castor oil [26], linalool and linalyl acetate in bergamot and lavender oils [27] and lavender oil has been reported to contain borneol, while bergamot oil does not [28,29]. Each of these specific marker compounds was readily detectable in unaged control samples of the indicated resins at the expected positions and masses.

5. Results

Only five resinous materials – camphor, dammar, *Pinaceae*, sandarac, and shellac – were found on the study collection tintypes. The most common constituents are shellac, which is found on 149 samples, and *Pinaceae*, which is found on 173 samples; interestingly, the only samples that contain neither shellac nor *Pinaceae* are varnished with pure dammar. Pure shellac was found 16 times, and pure *Pinaceae* once, but all other varnishes are mixtures. The more exotic resins such as benzoin, mastic, Congo copal, Kauri copal, Manila copal, and amber that are recommended in published varnish recipes were not detected. Given the vagaries of pyrolysis and derivatization [14,30] and the variations in naturally occurring materials aged under different environments [23,31] it is difficult to assess the lower detection limit of this method; however, polyaromatic hydrocarbons can be detected at 5 ppm [32] and fatty acids at 10 ng level [33] using pyrolysis GC-MS, and abietic acid and ursolic acid can be detected at 1 ppm levels using an extractive GC-MS procedure [34], so a conservative estimate indicates that resins should be detected if they constitute more than 1% of the material. Tables 1 and 3 show that with the exception of oils (lavender, bergamot, and castor) the resinous materials in historical recipes contribute at least 2% to the total weight of the varnish (excluding solvent) and so would most likely be within the detection limits of py-GC-MS. We therefore conclude that these undetected materials are unlikely to be present, at least as significant varnish constituents. The underrepresentation of the more exotic resins is probably due to the economics of the tintype trade, with artists choosing to use cheaper resins on these relatively inexpensive photographs in order to maximize their profit.

The prevalence of both sandarac (44% of samples) and dammar (14% of samples) in these varnishes is interesting given that certain authors warned specifically against their use. Sandarac is a constituent in five of the 12 observed formulations despite being considered inferior by Trask due to its moisture sensitivity. It should be noted that sandarac is one of the most recommended materials

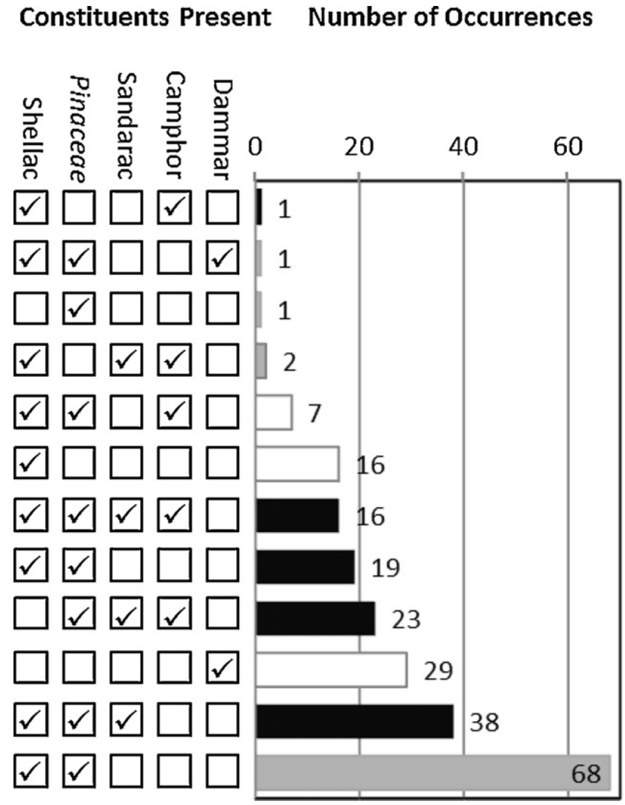

Fig. 2. The number of occurrences of different resins and resinous mixtures found on study collection tintypes. Mixtures corresponding to recommend tintype varnishes are shown in white, those corresponding to ambrotype and/or collodion negative varnishes are shown in black and unrecorded formulations are shown in grey.

for varnishing ambrotypes and wet collodion negatives, occurring in 15 of the 20 formulations, and it may be that the photographers' familiarity with it led them to disregard the lone warning. Dammar and copal were also seen as being inferior but dammar was found on the study collection materials in significant amounts whereas copal was entirely absent. The contemporaneous use of dammar as a lantern slide varnish [35] and the continued use of dammar as a painting varnish suggest that, as with sandarac, tintypists' decisions to use dammar may have been influenced by practical experience with this material in other contexts. The unfavorable literature review of dammar may also have resulted from case of mistaken identity on the part of that author as some soft copals were termed dammar copals [36].

Although each of the five resinous materials identified on these tintypes is listed in one or more of the literature varnish formulations, few of the observed combinations of constituents correspond to those in the literature. As can be seen on Fig. 2, fewer than one quarter of the tintypes (52 total) were varnished with materials specifically recommended for tintypes, and thus it is abundantly clear that the artists were not strictly adhering to the recommended formulations. However, 43% of the collection was varnished with materials recommended for other collodion-based processes, suggesting that they did not venture very far afield in their choice of varnishing materials. The remaining 33% of the collection was varnished with mixtures that do not correspond to any of the recorded historical recipes, and the most predominant of these was a shellac and *Pinaceae* mixture that accounts for nearly 31% of the tintypes analyzed. Given the preponderance of this mixture and the relatively inexpensive nature of the materials, it is likely that this group corresponds to commercial varnish formulations [37]. Fig. 3 is a histogram showing the number of occurrences of different relative ratios of shellac to *Pinaceae* as determined by the fractional peak

Please cite this article in press as: C.E. Rogge, The varnished truth: The recipes and reality of tintype coatings, Journal of Cultural Heritage (2013), http://dx.doi.org/10.1016/j.culher.2013.02.002

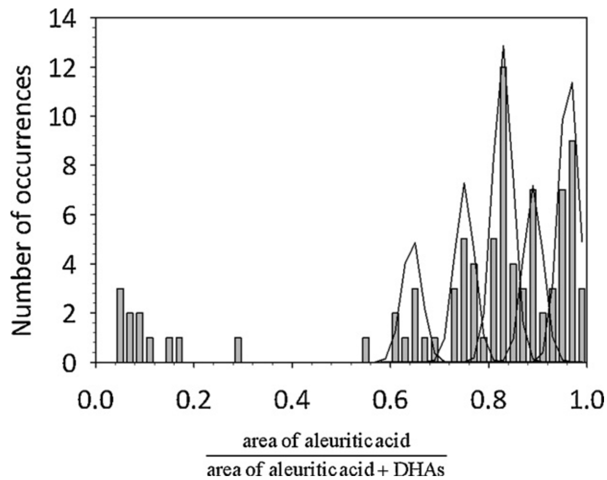

Fig. 3. Histogram showing the ratio of the area of the derivatized aleuritic acid marker peak of shellac to the sum of the areas of peaks arising from the DHA series (methylated derivatives of dehydroabietic acid, 6-dehydroabietic acid, 7-methoxydehydroabietic acid, 15-methoxydehydroabietic acid, 7,15-dimethoxydehydroabietic acid, 7-oxodehydroabietic acid, 15-methoxy-7-oxodehydroabietic acid, and methyl abietate). The clustering at certain shellac peak area fractions suggests that a small set of distinct recipes, perhaps commercial formulations, were applied to these samples. The region above 0.53 can be fit to a set of five Gaussian functions (solid lines) whose centers and heights were allowed to vary while the widths were held constant at 0.019. The chi-squared and reduced chi-squared values for the fit are 9.59 and 0.44, respectively.

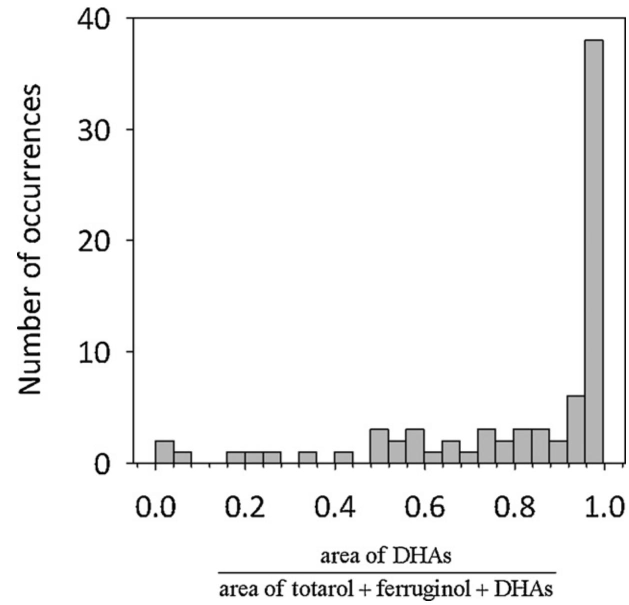

Fig. 4. Histogram showing the ratio of the areas of the DHA series peaks to the sum of the area of the totarol/ferruginol peak of sandarac and the areas of the DHA series peaks. Many varnishes have large DHA to totarol/ferruginol ratios and thus likely represent the deliberate mixture of sandarac and *Pinaceae*.

areas for the aleuritic acid derivative marker for shellac compared to the sum of the aleuritic acid and DHA series areas. These shellac fractional peak areas do not strictly correspond to the fraction of shellac in the samples, since raw py-GC-MS areas are skewed by many factors including variation in derivatization efficiency, but it is clear that a wide range of ratios of shellac to *Pinaceae* were employed by the tintypists who made these 88 samples. The clustering at certain shellac peak area fractions (0.08, 0.16, 0.65, 0.75, 0.83, 0.89, 0.96) and the avoidance of wide ranges (only a single sample between 0.18 and 0.54) suggests that a small set of distinct recipes, rather all possible random ratios of shellac and *Pinaceae*, were applied to these samples. The portion of the data with ratios greater than 0.53 can be well fit to five histograms, as shown on Fig. 3. These recipes probably correspond to a few commercially available varnishes, or perhaps to recipes that were shared by word of mouth instead of through the published literature.

Pinaceae resin, as identified by the presence of the hydroxydehydroabietic acid series, is one of the most frequently encountered resins on the tintypes, occurring on 78% of the samples. Tintypists have used it to dilute not only shellac, an insect resin, but also sandarac, another diterpenoid-containing tree resin. Indeed, all but two samples that contain sandarac also contain the DHA markers indicative of *Pinaceae*. Although there are conflicting reports on the presence of abietic acid species in sandarac [23,24,38] with one group reporting trace amounts of these compounds [24], the sandarac reference material obtained from Kremer Pigmente is devoid of these compounds. Two samples from the collection contain sandarac markers but not hydroxydehydroabietic acids, further indicating that not all sandarac resins contain detectable levels of abietic acids. Fig. 4 is a histogram showing the number of occurrences of different relative ratios of sandarac to *Pinaceae* as determined by the fractional peak areas for the DHA series compared to the sum of totarol/ferruginol and DHA series areas. It is evident that many varnishes have very large amounts of the abietic acid series relative to the sandarac markers and thus likely represent the deliberate mixture of sandarac and *Pinaceae*. The three samples with very low relative amounts of the DHA series may either represent a deliberate addition of very small amounts of *Pinaceae* or naturally occurring trace amounts of DHAs in sandarac from a different source than the Kremer sample and the two non-DHA containing samples.

Dehydroabietic acid passes through a well-characterized oxidation pathway and the relative amounts of different species detected by py-GC-MS can be used to assess the index of degree of oxidation, or IDOX value [14], which ranges from 0 to 1 with smaller values representing less oxidized samples. The IDOX values for the *Pinaceae*-containing tintype samples are shown on Fig. 5 and cluster around a value of 0.35. The IDOX values obtained for these objects,

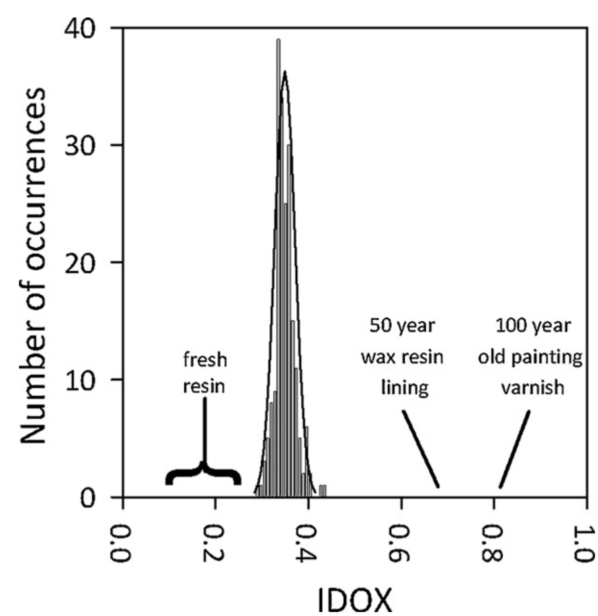

Fig. 5. Histogram of the IDOX values of the hydroxydehydroabietic acids arising from *Pinaceae* resins in the tintype varnishes. The black line is a Gaussian fit of the data centered at 0.35. Also indicated are the IDOX values for *Pinaceae* resins discussed in [14]. The lower IDOX values of the tintype varnishes compared to contemporaneous painting materials suggest that storage and display conditions may influence the oxidation of abietic acid.

most of which are between 100 to 150 years old, are relatively low compared to the values found for a 100 year old painting varnish (0.81) and 50 year old oil-resin lining (0.67) and are instead much closer to the values reported for fresh resin samples (0.1 to 0.25) [14]. Since it is unlikely that any, let alone all, of these images would have been cleaned and re-varnished, the low oxidation index may be due to these images having been stored in albums, cabinets or other relatively closed containers that limit photo-oxidation and slow gaseous diffusion. The enclosed storage may have protected the varnish materials from oxidation compared to previously described samples of painting varnish and lining adhesive, which would have been exposed to both light and gases for extended periods of time.

6. Conclusions

This study represents the first large-scale analysis on the manufacture of tintypes and provides a unique glimpse into the working habits of photographers of the nineteenth and early twentieth centuries. The poor correlation between recommended tintype varnishes and the materials detected on the historical samples serves as a warning to art historians, conservators, and conservation scientists that practices and processes described in the contemporary literature were not necessarily followed by the artists of the day.

Acknowledgements

Many thanks to Gwenanne Edwards (Buffalo State College) for taking the digital image shown on Fig. 1a, to Michael Schilling (Getty Conservation Institute) for sharing his py-GC-MS expertise, analytical method, and database, to Kevin MacKenzie for his help with the Excel fitting shown in Fig. 3, and to Klaas Jan van den Berg and Henk van Keulen for helpful discussions on the issue of abietic acid in sandarac. Funding was provided by a Buffalo State College Provost's Incentive Grant (2010), and the Andrew W. Mellon Foundation.

References

[1] J.M. Reilly, Care and Identification of 19th Century Photographic Prints, Eastman Kodak, Rochester, 1986.
[2] H.L. Smith, W.M. Neff, P. Neff, Jr., Photographic pictures on japanned surfaces, United States of America Patent 14300, 1856.
[3] J.G. Shimmelman, The Tintype in America, 1856–1880, American Philosophical Society, Philadelphia, 2007.
[4] Anonymous, New York Tribune August 20 (1862).
[5] E.M. Estabrook, The Ferrotype and How to Make it, 12th ed., The Anthony and Scoville Company, New York, 1903.
[6] M. Leonard, N. Khandekar, D.W. Carr, 'Amber varnish' and Orazio Gentileschi's 'Lot and His Daughters', Burlington Mag. 143 (2001) 4–10.
[7] A. Pringle, Lantern-Slides by Photographic Methods, The Scovill & Adams Company, New York, 1897.
[8] A.K.P. Trask, The Practical Ferrotyper, Benerman & Wilson, Philadelphia, 1872.
[9] T.H. Kane, Ferrotypes, Photogr. Times Am. Photogr. 17 (1887) 93.
[10] J.F. Bodtker, Mode of coloring photographs, United States of America Patent 38144, 1863.
[11] C. McCabe (Ed.), Coatings on Photographs: Materials, Techniques, and Conservation, Photographic Materials Group of the American Institute for Conservation of Historic and Artistic Works, Washington, D.C, 2005.
[12] A. Heginbotham, M. Schilling, New evidence for the use of Southeast Asian raw materials in seventeenth-century Japanese export lacquer, in: S. River, R. Faulkner, B. Pretzel (Eds.), East Asian lacquer: Material Culture, Science and Conservation, Archetype Publications, London, 2011, pp. 92–106.
[13] K.J. van den Berg, I. Pastorova, L. Spetter, J.J. Boon, State of oxidation of diterpendoid Pinaceae resins in varnish, wax lining material, 18th Century resin oil paint, and a recent copper resinate glaze, in: Proceedings of ICOM, 11th Triennial Meeting, Edinburgh, September 1–6, James & James, London, 1996, pp. 930–937.
[14] K.J. van den Berg, J.J. Boon, I. Pastorova, L.F.M. Spetter, Mass spectrometric methodology for the analysis of highly oxidized diterpenoid acids in Old Master paintings, J. Mass Spectrom. 35 (2000) 512–533.
[15] L. Wang, Y. Ishida, H. Ohtani, S. Tsuge, Characterization of natural resin shellac by reactive pyrolysis-gas chromatography in the presence of organic alkali, Anal. Chem. 71 (1999) 1316–1322.
[16] M.P. Colombini, I. Bonaduce, G. Gautier, Molecular pattern recognition of fresh and aged shellac, Chromatographia 58 (2003) 357–364.
[17] J.S. Mills, R. White, The Organic Chemistry of Museum Objects, 2nd ed., Butterworth & Heinemann, Oxford, 1994.
[18] G.A. van der Doelen, K.J. van den Berg, J.J. Boon, Comparative chromatographic and mass-spectrometric studies of triterpenoid varnishes: fresh material and aged samples from paintings, Stud. Conserv. 43 (1998) 249–264.
[19] S. Watts, E.R. de la Rie, GCMS analysis of triterpenoid resins: in situ derivatization procedures using quaternary ammonium hydroxides, Stud. Conserv. 47 (2002) 257–272.
[20] G. Chiavari, S. Montalbani, V. Otero, Characterisation of varnishes used in violins by pyrolysis-gas chromatography/mass spectrometry, Rapid Commun. Mass Spectrom. 22 (2008) 3711–3718.
[21] R. Stevanato, M. Rovea, M. Carbini, D. Favretto, P. Traldi, Curie-point pyrolysis/gas chromatography/mass spectrometry in the art field. Part 3: the characterization of some non-proteinaceous binders, Rapid Commun. Mass Spectrom. 11 (1997) 286–294.
[22] J.S. Mills, R. White, L.J. Gough, The chemical composition of Baltic Amber, Chem. Geol. 47 (1984) 15–39.
[23] D. Scalarone, M. Lazzari, O. Chiantore, Ageing behavior and analytical pyrolysis characterization of diterpenic resins used as art materials: Manila copal and sandarac, J. Anal. Appl. Pyrol. 68–69 (2003) 115–136.
[24] K.J. van den Berg, J. Ossebaar, H. van Keulen, Analysis of copal resins in 19th century oil paints and resin/oil varnishes, in: R. van Griecken, K. Janssens, L. Van't dack, G. Meersman (Eds.), Art 2002: 7th International Conference on Non-destructive testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, Antwerp, June 2–6, University of Antwerp, Antwerp, 2002, pp. 1–10.
[25] K.J. van den Berg, J. van der Horst, J.J. Boon, Recognition of copals in aged resin/oil paints and varnishes, in: J. Bridgland, J. Brown (Eds.), Proceedings of ICOM, 12th Triennial Meeting, Lyon, August 29–September 3, James & James Ltd, London, 1999, pp. 855–861.
[26] M.S. Copley, H.A. Bland, P. Rose, M. Horton, R.P. Evershed, Gas chromatographic, mass spectrometric and stable carbon isotopic investigations of organic residues of plant oils and animal fats employed as illuminants in archaeological lamps from Egypt, Analyst 130 (2005) 860–871.
[27] P.J. Marriott, R. Shellie, C. Cornwell, Gas chromatographic technologies for the analysis of essential oils, J. Chromatogr. A 936 (2001) 1–22.
[28] S. Salido, J. Altarejos, M. Nogueras, A. Sánchez, P. Luque, Chemical composition and seasonal variations of spike lavender oil from southern Spain, J. Essent. Oil Res. 16 (2004) 206–210.
[29] E. Dellacassa, D. Lorenzo, P. Moyna, A. Verzera, A. Cavazza, Uruguayan essential oils. Part V. Composition of bergamot oil, J. Essent. Oil Res. 9 (1997) 419–426.
[30] W.C. Kossa, J. MacGee, S. Ramachandran, A.J. Webber, Pyrolytic methylation/gas chromatography: a short review, J. Chromatogr. Sci. 17 (1979) 177–187.
[31] D. Scalarone, J. van der Horst, J.J. Boon, O. Chiantore, Direct-temperature mass spectrometric detection of volatile terpenoids and natural terpenoid polymers in fresh and artificially aged resins, J. Mass Spectrom. 38 (2003) 607–617.
[32] T.P. Wampler (Ed.), Applied Pyrolysis Handbook, 2nd ed., CRC Press Taylor & Francis Group, Boca Raton, 2007.
[33] J.M. Challinor, Review: the development and applications of thermally assisted hydrolysis and methylation reactions, J. Anal. Appl. Pyrol. 68–69 (2001) 3–34.
[34] A. Andreotti, I. Bonaduce, M.P. Colombini, G. Gautier, F. Modugno, E. Ribechini, Combined GC/MS analytical procedure for the characterization of glycerolipid, waxy, resinous and proteinaceous materials in a unique paint microsample, Anal. Chem. 78 (2006) 4490–4500.
[35] Anonymous, Varnish for lantern slides, Photogr. News 53 (1908) 317.
[36] M. Doerner, The Materials of the Artist and Their Use in Painting: With Notes on the Techniques of the Old Masters, Mariner Books, Orlando, 1949.
[37] M.E. Wieseman, A Closer Look: Deceptions and Discoveries, National Gallery Co., London, 2010.
[38] G. Cartoni, M.V. Russo, F. Spinelli, F. Talarico, GC-MS characterization and identification of natural terpenic resins employed in works of art, Ann. Chim. (Rome) 94 (2004) 767–782.
[39] W.T. Brannt, Varnishes, Lacquers, Printing Inks and Sealing Waxes: Their Raw Materials and Their Manufacture to Which is Added the Art of Varnishing and Lacquering, Including the Preparation of Putties and of Stains for Wood, Ivory, Bone, Horn and Leather, Henry Carey Baird & Company, Philadelphia, 1893.
[40] Anonymous, Notes and Queries, Scientific American (1891) 123.
[41] H.R. Berkeley, W.M. Walker, Practical Receipts for the Manufacturer, the Mechanic & for Home Use, Spon & Chamberlain, New York, 1902, pp. 76.
[42] J. Towler, The Silver Sunbeam: a practical and Theoretical Textbook on Sun Drawing and Photographic Printing: Comprehending all the Wet and dry Processes at Present Known, with Collodion, Albumen, gelatin, Wax Resin and Silver; as [sic] also Heliographic Engraving, Joseph H. Ladd, New York, 1864.
[43] G. Smee, Ferrotype photography, Wilson's Photogr. Mag. 51 (1914) 161–162.
[44] Anonymous, Questions and answers, The camera an independent magazine devoted to the advancement of photography 17 (1913) 552.
[45] C.W. Gamble, An Introduction to the Practice of Wet Collodion Photography, Hazel, Watson and Viney, Ltd., Ludgate Hill, 1895.
[46] M.H. Kelleher, Am. Photogr. 2 (1908) 353–354.
[47] T.F. Hardwich, A Manual of Photographic Chemistry, Including the Collodion Process, 4th ed., John Churchill, London, 1857.
[48] W.H. Tipton, A good varnish, in: E.L. Wilson, M.C. Lea (Eds.), Photographic Mosaics, Benerman and Wilson, Philadelphia, 1875, p. 41.

Please cite this article in press as: C.E. Rogge, The varnished truth: The recipes and reality of tintype coatings, Journal of Cultural Heritage (2013), http://dx.doi.org/10.1016/j.culher.2013.02.002

[49] C. Gravier, The preservation of the photographic image, Wilson's Photogr. Mag. 33 (1896) 523.
[50] W.M. Madock & Co., American Photography 2 (1908) c.
[51] W.B. Holmes, The photographer' friend: a practical independent magazine 1(1871) xxxi.
[52] J. Towler, Dry Plate Photography or the Tannin Process, Made Simple and Practical for Operators and Amateurs, Joseph H. Ladd, London, 1865.
[53] J. Towler, The Negative and the Print, or the Photographer's Guide in the Gallery and in the Field; Being a Text-Book for the Expert and Amateur, Joseph H. Ladd, London, 1870.
[54] C. Waldack, P. Neff Jr., Treatise of Photography on Collodion, 2nd ed., Longley Brothers Printers, Cincinnati, 1858.
[55] J.T. Taylor, The Photographic Amateur: A Series of Lessons in Familiar Style for those who Desire to Become Practically Acquainted with this Useful and Fascinating Art, Scovill Manufacturing Company, New York, 1881.
[56] E.L. Wilson, Wilson's Cyclopaedic Photography: A Complete Handbook of the Terms, Formulae and Appliances Available in Photography, E.L. Wilson, New York, 1894.
[57] W. Crookes, T.C. Hepworth, The wet collodion process, Photogr. News 28 (1884) 240.
[58] Anonymous, The wet collodion process, Sci. Am. Suppl. 351 (1882) 5602.
[59] H. Greenwood, Photographic varnishes, Br. J. Photogr. 14 (1867) 206.
[60] L. Pine, Negative and positive varnish, Photograph. News 10 (1866) 488.
[61] N.G. Burgess, The Photograph and Ambrotype Manual: The Art of Taking Positive and Negative Photographs on Glass, Commonly Known as Photography in All its Branches, 5th ed., Wiley & Halstead, London, 1858.
[62] Anonymous, Preparing varnishes for negatives, paper prints, and retouching mediums, Photogr. J. Am. 52 (1915) 394.
[63] R. Hunt (Ed.), Ure's Dictionary of Arts, Manufactures and Mines, vol. 1, Longmans, Green & Company, London, 1867.
[64] J.B. Schriever, T.H. Cummings, Complete Self-Instructing Library of Practical Photography, vol. 7, American School of Art and Photography, Scranton, 1909.
[65] J.T. Taylor, The Photographic Amateur, 2nd ed., Scovill Manufacturing Company, New York, 1883.
[66] C.G.W. Lock (Ed.), Spon's Encyclopedia of the Industrial Arts. Manufactures and Commercial Products, E & F.N. Spon, London, 1882.
[67] H. Greenwood, Sandarac and benzoin varnish, Br. J. Photogr. 21 (1874) 310.
[68] H. Greenwood, Removal of the varnish, Br. J. Photogr. 29 (1882) 729.
[69] W.J. Smith, E.L. Turner, Wet collodion photography V.- varnishes, Process Engravers' Mon. 27 (1920) 145–146.
[70] J.H. Langenheim, Plant Resins: Chemistry, Evolution, Ecology, Ethnobotany, The Timber Press, Portland, 2003.