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# COATINGS ON PHOTOGRAPHS

## Materials, Techniques, and Conservation

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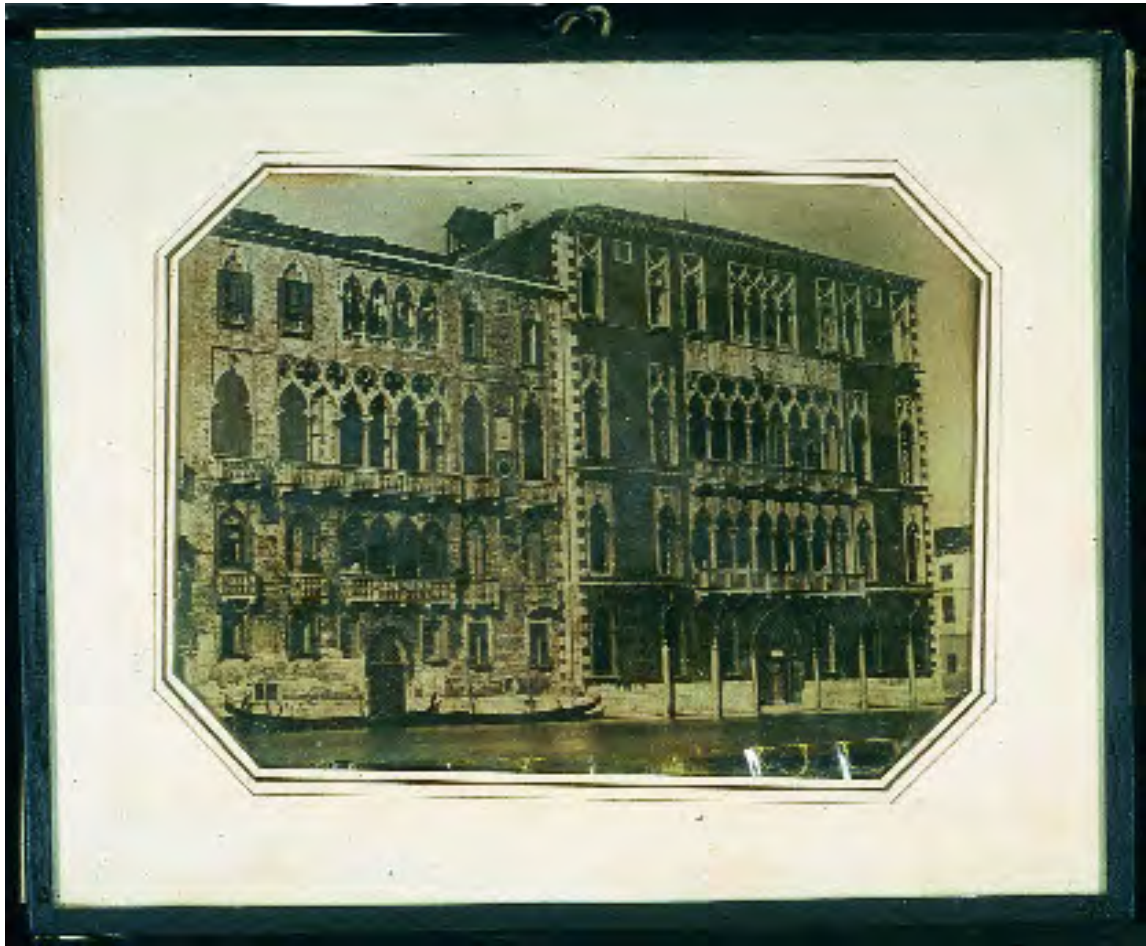
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## Case Studies



## A History of Zapon Lacquer Coating and Its Use on the Daguerreotypes in the Albertina Photograph Collection

Andreas Gruber  
Taiyoung Ha



Figure 1. *Opposite*: Josef Wawra, *Palazzo Foscari in Venice*, 1848. Daguerreotype coated with Zaponlack. Half plate, plate size 4.25 x 6.38 in. (10.8 x 16.2 cm). Courtesy Albertina, permanent loan of the Höhere Graphische Bundes- Lehr- und Versuchsanstalt, Vienna (GLV2000/10064).

Figure 2. *Above*: Ascribed to Félix Jaques-Antoine Moulin, *Two Female Nudes*, 1850. Daguerreotype with Zaponlack coating. Half plate, plate size 4.72 x 6.34 in. (12.0 x 16.1 cm). Courtesy Albertina, permanent loan of the Höhere Graphische Bundes- Lehr- und Versuchsanstalt, Vienna (GLV2000/10207).

The Albertina Museum in Vienna, Austria is the repository of nearly 450 daguerreotypes, one of the country's largest and most important collections of its kind. The Albertina collection of daguerreotypes contains images by many prominent photographers from the former Austrian monarchy, Germany, and France, and features diverse subjects that include scientific, artistic, documentary, and commercial images. The formats range from gem size to stereo to larger than full plate. A few of the images are cased, but most are mounted behind glass or in ornamental *passe-partouts* with cardboard backings and decorative paper seals. Many images are also framed. The daguerreotypes are part of the Eder Collection, named for the Austrian photographic chemist and historian Josef Maria Eder (1855-1944). Eder founded the world's first state-run institution for education in photographic and reproduction techniques in Vienna in 1888, the K.k. Lehr- und Versuchsanstalt für Photographie und Reproduktionsverfahren. He and his successors acquired more than 40,000 photographs, 25,000 books, and approximately 3,000 pieces of photography equipment for teaching and research purposes. In the year 2000, the collection was transferred from the Höhere Graphische Bundes-Lehr- und Versuchsanstalt (GLV), as the school is called now,<sup>1</sup> to the Albertina, on the basis of a permanent loan.<sup>2</sup>

A number of the daguerreotypes from the Eder Collection were chosen to be displayed in the Albertina's first photographic exhibition in 2003, *Das Auge und der Apparat, Eine Geschichte der Fotografie* (*The Eye and the Camera, A History of Photography*),<sup>3</sup> which presented highlights of the museum's photograph collection. Prior to the exhibition, the selected daguerreotypes went through conservation treatment. In the course of the treatment it became evident that most of the daguerreotypes had been treated previously, some several times. The original seals were broken and replaced by newer materials such as gummed paper seals or pressure-sensitive adhesive tape. The plates showed evidence of cleaning, and distinctly visible coatings were present (figs. 1, 2, and 3). The authors found no recorded documentation regarding the cleaning methods employed, with the exception of the date of the respective restoration, which had been noted by hand on the paper envelopes in which the objects were stored. The signature of the restorer and the word "Zaponlack" were often found on the envelopes. These clues, gathered by the authors at the time the collection was examined, provided direction for further research.



Figure 3. Anton Martin, *Portrait of a Young Girl*, test shot taken with the first Voigtländer camera, c. 1840-1841. Daguerreotype coated with Zaponlack. Round plate, plate size 3.82 in. (9.7 cm) diameter. Courtesy Albertina, permanent loan of the Höhere Graphische Bundes-Lehr- und Versuchsanstalt, Vienna (GLV2000/9677).

The authors conducted a literature search using the Albertina's extensive historical library in order to learn what cleaning methods had been popular in German-speaking countries, and to discover what treatments might have been employed for this collection. Special attention focused on source material concerning the use of protective coatings for daguerreotypes. This report concentrates primarily on these coatings.

The use of coatings in art conservation has been studied extensively. Many historic and artistic works, such as paintings, sculpture, and furniture, are often coated with a wide variety of coating materials. Coatings can have a primarily aesthetic function or be applied for both physical and environmental protection. Ideally, when a coating is used for protective purposes, it should not alter the object's appearance. Further, it should be reversible in an appropriate solvent, possess sufficient flexibility, and be chemically and physically stable.<sup>4</sup>

Since daguerreotypes were generally placed behind glass in frames and cases and were thus relatively well protected from abrasion and scratches, the goal of coating was probably less to protect the physical surface and more to prevent silver oxidation. To

this end, a coating had to fulfill the following criteria: it had to be colorless, leave the image unaltered, and be impermeable to oxidizing gases. It also needed to be nonreactive with the material it was meant to protect, possess good aging characteristics, and remain reversible. Most of the usual resins, varnishes, and lacquers were unable to fulfill these criteria for daguerreotypes. Many experts believed that only cellulose nitrate varnish, specifically Zapon lacquer, seemed to match the criteria. The large number of objects in the Eder Collection that had been coated with Zapon lacquer presented a unique opportunity to study the effects of this coating on daguerreotypes.

### Zapon Lacquer

In general, Zapon lacquer is a highly viscous cellulose nitrate lacquer with amyl acetate as its primary solvent, and is unlike the more dilute modern cellulose nitrate lacquers. The origin of the term "Zapon" is derived from the Japanese pronunciation of the metal finishes, namely "Japans," that were prevalent in the late nineteenth century.<sup>5</sup> That term was adopted as a product name for a cellulose nitrate lacquer made by the Fredric Crane Chemical Company in the 1890s (see below). The word "Zaponlack" (a direct translation of Zapon lacquer into German) has, at least in German-speaking countries, become a generic name for clear cellulose nitrate lacquers that are generally used for varnishing metal or wood.<sup>6</sup> Today, the name Zapon is a trademark of the German BASF Company.

### History of Cellulose Nitrate Coatings

In 1846 Christian Friedrich Schönbein, a chemist from the University of Basel, discovered guncotton when investigating the behavior of nitric and sulfuric acid in relation to organic substances.<sup>7</sup> The following year, several individuals, including Flores Domonte, Louis Ménard, Marc-Antoine Gaudin, and John Parker Maynard, independently found that different types of pyroxylin, as soluble guncotton was then described, could be formed by variations in the degree of the cotton's nitration. Nitrocellulose was divided into ether-alcohol insoluble and soluble types. Maynard named the pyroxylin in ether-alcohol solution "collodion," from the Greek "κόλλαω" (to glue).<sup>8</sup> He suggested the use of cellulose nitrate in ether-alcohol as a protective coating for wounds.<sup>9</sup> In 1851 Frederick Scott Archer was the first to use collodion successfully as a photographic binder for the wet collodion process, which was used until the 1880s as the main photographic negative process. At the 1862 International Exhibition in London, Alexander Parkes introduced a

new material based on cellulose nitrate mixed with camphor<sup>10</sup> and vegetable oils, which he called Parkesine. The addition of camphor made it possible to produce more uniform, shrink-resistant, and flexible cellulose nitrate materials in solid form.<sup>11</sup> However, the Parkesine Company did not prosper and was dissolved in 1868.<sup>12</sup> That same year John Wesley Hyatt of Albany, New York, also manufactured a cellulose nitrate that contained camphor, from which he produced imitation ivory billiard balls. He called his product Celluloid. In 1872 he established the Celluloid Manufacturing Company in Albany.<sup>13</sup> The term "Celluloid" quickly became a generic name for cellulose nitrate plastics. Sheets or flakes of Celluloid were also used as raw material for making cellulose nitrate lacquer.

The large number of formulas and products that date from the mid-1850s<sup>14</sup> indicate that the use of cellulose nitrate as a lacquer must have been popular in both Europe and North America. The first successful commercial uses of cellulose nitrate lacquer seem to date from the 1880s and were sold in America under such names as "Crystalline" and "Victoria Varnish."<sup>15</sup> In 1884 Richard Hale and his sons-in-law, Frederick Crane and Leonard Richards, formed the Frederick Crane Chemical Company in Springfield, New Jersey, in order to manufacture and sell a lacquer called "Zapon" for finishing plated goods, brass beds, and metalware.<sup>16</sup> In Germany, J. Perl was one of the first large-scale producers of cellulose nitrate lacquers.<sup>17</sup> Later, especially during and after World War I, its composition was modified with additives such as resins and plasticizers. The automobile industry, in particular, stimulated cellulose nitrate lacquer production by developing a higher quality and more economical product and a better-understood material.<sup>18</sup>

### Uses for Zapon Lacquers

Since their introduction in the 1880s, Zapon lacquers provided extremely strong commercial competition for the spirit lacquers (e.g. shellac) that were highly common at that time. This was particularly true in the metalware industry and in the applied arts. Spirit lacquers gave the underlying metal a particular gloss, while Zapon lacquers neither affected the highly polished sheen of metals nor endowed the support with a gloss of its own.<sup>19</sup> Wood and metal parts were often given thin protective celluloid coatings, or even thick, enamel-like ones, which protected iron from rust and filled the pores of wood. Papers, drawings, documents, pictures, game boards, and maps were "protected against decay" with Zapon-like lacquers. Additives

such as castor oil, rubber, and resinous solutions created lacquers that made textiles and paper waterproof or especially resistant to high humidity. Highly colored Zapon lacquers were used to decorate polished celluloid, imitation tortoise shell, buffalo horn, and leather.<sup>20</sup> Toys, dolls' heads, and everyday objects of all kinds were coated with colored, opaque, or transparent Zapon lacquers. The addition of matting agents allowed Zapon-like lacquers to be used for a variety of purposes, such as a matte varnish for light bulbs.<sup>21</sup> Although cellulose nitrate lacquers have been largely replaced by newer and more stable synthetic materials, they are still used today as a varnish material for wood and metal objects.<sup>22</sup>

Until around 1920, the use of Zapon lacquers for conservation applications was restricted to a few special uses, such as coatings for silver and bronze objects.<sup>23</sup> Zapon lacquers were recommended as a fixative for watercolors in the early twentieth century. For a short time they were also used as an isolating varnish for paintings until they were found to discolor with age. Another unsuccessful use of Zapon lacquer was as a consolidant for documents degraded by iron gall ink.<sup>24</sup>

### Composition

The composition of a cellulose nitrate lacquer can be divided into five components: film-forming materials, solvents, diluents, plasticizers, and additives. Solvents and diluents are volatile materials that do not remain in the final lacquer form.

There are two main film-forming materials in ordinary commercial cellulose nitrate lacquer products: cellulose nitrate and gums or resins. Cellulose nitrate is produced when cellulose molecules are chemically altered by means of strong nitric and sulfuric acids. The material thus produced has been used to make a wide range of materials, including explosives, adhesives, film bases, and varnishes. The principal differences between the various materials can be described in terms of the degree of nitration of the cellulose molecule.<sup>25</sup> It is recognized that as the number of nitrate groups increases, the cellulose nitrate becomes less stable. However, in order to create the polarity required for adhesion, film formation, and solubility, sufficient nitrogen content is required.<sup>26</sup> Cellulose nitrate with a nitrogen content below 11.2% is used for adhesives. In lacquers, the nitrogen content is between 11.5% and 12.3%. Products with still higher nitrogen contents are used, for example, as explosives.<sup>27</sup> Guncotton, a cellulose nitrate in which all of the hydroxyl groups have been replaced by

nitrate, cannot be used for the manufacture of lacquer.<sup>28</sup> Excessive nitrogen content generates either no film at all or films that are too thick and uneven, whereas an insufficient amount of nitrogen results in thin, opaque, and brittle films.<sup>29</sup> Older formulations of 5% nitrocellulose solutions were quite viscous, whereas modern lacquers are sufficiently thin-bodied, even in concentrated solutions, and are easily applied as coatings.<sup>30</sup>

To improve the film formation and the workability and elasticity of the lacquer, various other film-forming materials were and still are added to the cellulose nitrate lacquer, and may include natural resins (usually dammar), altered natural resins (e.g. maleate resin modified with colophony), or synthetic resins (alkyd resins, acrylates, etc.). Today, natural and synthetic resins make up a large percentage of the components found in cellulose nitrate lacquers.<sup>31</sup> There are also modern so-called Zapon lacquer products that do not contain any cellulose nitrate at all, but are actually acrylic-based.<sup>32</sup>

The pyroxylin used for Zapon lacquer is soluble in the usual ketone-ester and ether types of solvents. Apart from butyl acetate, amyl acetate was often used as the main solvent because many users associated the distinctive quality of Zapon lacquer with its characteristic banana smell. However, in modern nitrocellulose ester lacquers, the solvent has been replaced with butyl acetate because it is cheaper and has a more neutral aroma.<sup>33</sup> Complex solvent mixtures (ketones, alcohols, aromatics, and esters) are also used as components of the varnish.<sup>34</sup> In some formulations, the rapidly evaporating ester-like solvent cyclohexanol acetate is also used. The simpler alcohols, methanol and ethanol, are also used as solvents to produce rapidly evaporating or low-viscosity lacquers.<sup>35</sup>

The diluents ordinarily employed in lacquer manufacture fall into two general groups, namely alcohols and hydrocarbons. While diluents are used, as the name implies, to dilute the lacquers and decrease the cost of production, they may also serve as carrier solvents for gums that are not soluble in the solvents ordinarily used to dissolve cellulose nitrate.<sup>36</sup>

Plasticizers are ideally non-volatile materials that are completely miscible with the other lacquer components and impart plasticity to the dry film. The most commonly employed plasticizers, sometimes comprising up to 45% of the weight of the cellulose nitrate portion, are non-volatile esters. The earliest plasticizer used for cellulose nitrate is camphor, using usually two parts cellulose nitrate with up to one part of camphor. Camphor is a nine-carbon cyclic ketone

and as such a good solvent for nitrocellulose. However, celluloid loses camphor at a very slow rate and after thirty to forty years reaches a state where the amount of camphor remains at a constant 15% level.<sup>37</sup> When its relatively high volatility was recognized, it was replaced by more suitable substances. Before World War II camphor was replaced by phosphates (e.g. triphenyl- and tricresyl-phosphate), but phthalates (e.g. dibutyl-, diisooctyl-) were also frequently used as early as the 1920s.<sup>38</sup>

Additives such as pigments were usually the only solids used in cellulose nitrate lacquer as colorants. Some modern lacquers also contain other additives such as UV stabilizers.<sup>39</sup>

### Properties

Despite its well-known negative qualities relating to chemical and physical instability, Zapon lacquer was popular because it was easy to work with, dried quickly and thereby reduced the inclusion of dust particles, and had good film-forming qualities. Suitably composed layers of cellulose nitrate varnish were very resistant to chemical and atmospheric influences and provided a better barrier to water and hydrogen sulfide (H<sub>2</sub>S) than other well-known coating materials, such as methacrylates or polyvinylacetates.<sup>40</sup> Zapon's most important quality was that it coated metals and other materials with a very thin, firmly adhering film, which was essentially invisible, leaving the appearance of the surface unaltered.<sup>41</sup> Its reversibility is considered to be adequate, and cellulose nitrate lacquers can be relatively stable when stored in the dark.<sup>42</sup>

### Application

The application of Zapon lacquers was simple, although it did require some practice to achieve a good coating. Even if ideally suited products were used, improper application techniques could result in flawed coatings. If applied too thinly, the coating, once dry, may not be completely impermeable. Iridescence was observed in coatings from overly diluted Zapon. However, the same phenomenon also appeared when ready-to-use undiluted Zapon was applied with a dry brush or applicator, because the substrate was insufficiently wetted. The likelihood of the formation of iridescent colors was more common with metal substrates that were not completely free of grease, which was very often the case with highly polished metal. If the substrate was not sufficiently prepared, then adhesion problems arose due to insufficient de-greasing. Layers that were applied too thickly often displayed an orange-peel surface. Reasons for this may be

mistakes in solution preparation or thick varnish application, which causes the surface to dry more rapidly than the underlying coating. Dust inclusions were also very common, so it was recommended that varnishing be performed in a dust-free area. However, compared to other coatings, Zapon lacquer dried very rapidly, which was a great advantage.<sup>43</sup>

### Stability

In addition to application errors, another primary problem associated with cellulose nitrate lacquers is lack of stability. Cellulose nitrate is a chemically unstable material that can result in poor aging characteristics and is subject to thermal, chemical, photochemical, and physical degradation. Cellulose nitrate decomposition mechanisms include acid-catalyzed ester cleavage, homolytic scission of the nitrogen-oxygen bond, and ring disintegration. These mechanisms cause cellulose nitrate to become yellow, tacky or brittle, or have other negative effects.<sup>44</sup> Finally, the dry film is susceptible to abrasion.

### Zapon Lacquer as a Protective Coating on Daguerreotypes

The daguerreotype surface is easily damaged by physical contact, and even Louis Jacques Mandé Daguerre, the inventor of the process, experimented with protective coatings.<sup>45</sup> However, Daguerre found that none of the commonly available resins, gums, or varnishes produced satisfactory results:

The application of varnish, of whatever kind it might be, significantly weakened the highlights and contrast in the images and at the same time diminished their vividness and strength.<sup>46</sup>

A 1991 study by Susan Barger<sup>47</sup> stated that recommendations for protective coatings on daguerreotypes were frequently found in the nineteenth century, whereas few modern references exist. However, the authors of this chapter conducted a more recent literature search of historical photographic texts from Eder's library at the Albertina; the search focused on the many previously unexplored German-language sources. The twentieth-century publications regarding daguerreotype restoration are surprisingly rich with recommendations for the use of coatings, specifically the use of Zapon lacquer.

The use of cellulose nitrate lacquer on daguerreotypes became established in the German-speaking countries at the beginning of the twentieth century.

The probable starting point for this development is marked by one of the earliest reports on the use of cellulose nitrate lacquer on daguerreotypes, written by A. J. Jarman in *The Photographic Times* in 1907.<sup>48</sup> In this article, Jarman's main focus was the creation of "electrotype" copies from daguerreotypes, which involved a galvanic process. In the course of his writing he mentioned that "the surface of any daguerreotype can be preserved and any further damage occurring from sulphurization will be stopped by employing amyl acetate collodion as a varnish."<sup>49</sup> In subsequent years Josef Maria Eder and others quoted this report in abbreviated form in German-language photographic journals.<sup>50,51</sup>

However, the most extensive exploration of the idea of using Zapon lacquer as a protective coating was undertaken by Dr. Erich Stenger in his 1920 work *Wiederherstellung alter photographischer Bilder*.<sup>52</sup> Stenger also quoted Jarman, among others, indicating the general lack of experience in using collodion as a varnish for daguerreotypes, yet spoke of his own positive experiences using Zapon lacquer on surface-silvered glass mirrors. He recommended the use of a Zapon lacquer from the Pillnay Company in Dresden,<sup>53</sup> and emphasized, above all, the purity of the lacquer for obtaining optimal results:

The lacquer is diluted with five or six times the amount of pure amyl acetate, well mixed and filtered into a narrow, high glass-stoppered vessel rinsed out with amyl acetate . . . . The fluid should fill the vessel, which is well-sealed and should stand completely motionless for three to four weeks and thus allow all the dust particles, as well as the traces of a white sediment as fine as flour, to be deposited on the bottom. The remaining fluid is carefully poured out and preserved in the dark, because a yellow color appears after some time in the light. This protective solution leaves behind a very fine invisible coating.<sup>54</sup>

Josef Maria Eder and Eduard Kuchinka<sup>55</sup> list the aforementioned experiments in the short chapter on "Protective Coatings on Daguerreotypes" in their volume on the daguerreotype as part of Eder's *Ausführliches Handbuch der Photographie*. It is primarily Stenger's methods that are quoted.<sup>56</sup>

Also based on Stenger's description, Prof. Dr. Ernst Rüst, of the Photographisches Institut der Eidgenössischen Technischen Hochschule Zürich

in Switzerland, wrote a report in 1933 regarding his own experiences in using Zapon lacquer on daguerreotypes.<sup>57</sup> In the report, he first discussed typical lacquer defects such as interference colors and wavy surfaces, as well as how to avoid them. Rüst recommended that daguerreotypes that had been cleaned with his hydrochloric acid/dichromate method be protected from further influences in the air by coating them with Zapon lacquer according to Stenger's proposal. Rüst wrote:

However, I only dilute the purchased solution with pure amyl acetate to the extent that, after it has run off, it no longer dries to a wavy surface. In the case of a stronger dilution (four to five times), such as Stenger records, the plate displays interference colors after drying. If one were to dilute so much that the thickness of the remaining layer is smaller than the wavelengths of daylight, the interference colors would probably not occur. However, I prefer a thicker layer for safety reasons. The Zapon lacquer used has to be colorless and the dilution has to be tested, because the solutions that are available display different viscosities. Since the lacquer has to be completely clear and free of dust, one pours it through a filter made of cotton wadding or, if necessary, of paper.<sup>58</sup>

Rüst also gave exact details of the actual lacquering process:

For lacquering one holds the plate without grasping it at the edge, horizontally on three fingers, and pours the Zapon lacquer onto the middle, until the circle of the spreading liquid touches the sides, letting the lacquer flow into the corners by slightly inclining the plate and pouring it off from the last corner into a filter, which one has placed above the bottle of Zapon lacquer. Afterwards, one places the plate in dust-free air on a plate stand to dry. Should it still display a weak interference color after drying one can once again pour lacquer over it. If the lacquer was deficient or if dust has stuck to it, then one rinses the lacquer away with amyl acetate and lacquers the plate one more time.<sup>59</sup>

These methods greatly resemble the application technique used in the preparation of collodion nega-

tives and positives. It is interesting that Stenger and the other authors previously quoted, except Rüst, do not seem to regard the instructions for lacquering as worth mentioning. One reason for this might be that, at the time, the practices of flowing varnishes on negatives and coating glass plates with collodion lay in the not-too-distant past.

Martin Hansch was the official photographer of the American Military Headquarters in Frankfurt in 1946. In the 1970s and 1980s he became the foremost authority on photograph restoration in the German-speaking countries, having acquired a profound knowledge of formulas dating from the early days of photography. Hansch described the use of Zapon lacquer in a series of articles entitled "The Restoration of Old Photographs" in *Photo-Antiquaria*, the specialist journal of the German photo-historical association Club Daguerre.<sup>60</sup> A revised version of the articles was published in book form in a limited edition in 1985.<sup>61</sup> In these articles, which date from the 1970s, Hansch recommended the following procedure as a finishing measure, subsequent to cyanide cleaning: "Zapon lacquer of a water-white quality is poured over the image side of the daguerreotype in a dilution that excludes the formation of bubbles. In doing so, move the plate so that the lacquer reaches the whole surface and can then run down via a corner." In his later book from 1985 he no longer recommended this method as a general protective measure for daguerreotypes, but rather made specific recommendations according to methods of chemical treatments and types of sealing. After cleaning with hydrochloric acid/dichromate according to Rüst's formula, Hansch further advised that, above all, a coating of Zapon lacquer be applied as protection against corrosion: "Varnish with thinned Zapon lacquer and if it fails, remove with amyl acetate." In his opinion, daguerreotypes whose presentation or format do not allow them to be sealed with strips of paper, which is frequently the case with brooches, should also be treated with Zapon lacquer as an additional protective measure.

Hansch was responsible for the care of Erich Stenger's considerable photograph collection, which was acquired by the Agfa Company in 1955, and was probably the first to study the durability of their coatings, which he briefly discussed in his essays. While he noted that the cellulose nitrate coatings provided excellent protection against atmospheric influences, he was also well aware of the fact that they have poor aging characteristics and can yellow severely when exposed to light. He therefore recommended that if the image was subjected to light, the coatings should

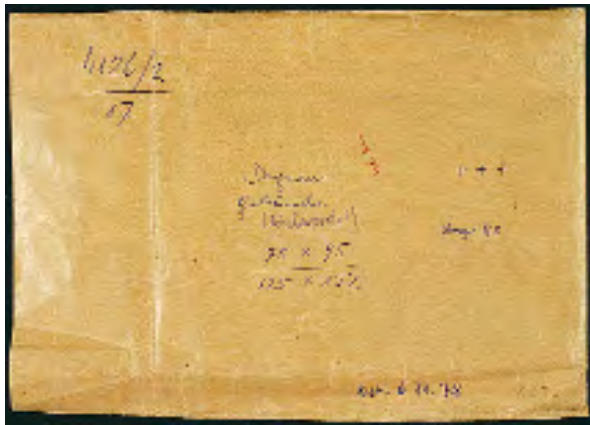


Figure 4. Typical paper envelope in which the Albertina Collection of daguerreotypes were stored. The lower edge shows the handwritten date of restoration.

be removed with amyl acetate every twenty to thirty years and replaced with new Zapon lacquer coatings.<sup>62</sup>

The most valuable account of coating daguerreotypes with Zapon lacquer was written in 1962 by the man who actually treated the Eder daguerreotype collection: Franz Dirnhofer. The collection's storage envelopes were inscribed with the restoration data as well as the initials "Di." or "D". In the course of assessing the condition of all the daguerreotypes, the complete name was identified as Franz Dirnhofer, a lecturer in photography at the Graphische Lehr- und Versuchsanstalt in Vienna and the custodian of its photograph collection. In his description of the collection's daguerreotype cleaning project,<sup>63</sup> he recommended that daguerreotypes that had been subjected to chemical treatment with cyanide should generally be coated with Zapon lacquer in order to avoid any chemical changes to the freshly restored images, as well as to prevent any physical abrasion of the plate.

### Survey of the Albertina's Daguerreotypes

In 2001 the authors completed a thorough examination and prepared condition reports for all 442 daguerreotypes in the Albertina collection. A digital database was then created to analyze the treatment methods that had been used in the past. The database contains brief descriptions of the objects and all the treatment-related information that was found on the storage enclosures. The database also includes a description of the condition of the objects, with notes on particularly endangered daguerreotypes that required urgent treatment, that is, the seal was not intact, the cover glass had deteriorated, etc.

The following descriptive information was recorded for each object:

- Inventory numbers: both current and historic
- Technical information: size of object, plate format, sealing materials
- Restoration data, including the date
- Condition, with sections for distinct types of damage and deterioration, including pressure-sensitive tapes, coatings, glass corrosion, and housing, with a brief description of the extent of the deterioration or damage
- Level of risk: active deterioration or stable condition.

Some of the survey results are particularly noteworthy as they quantify the number of coated plates, the treatment records, and the dates of treatment, and summarize the condition of the collection. Special attention is given to the coatings and their relation to the condition of the objects' binding materials, cover glasses, and daguerreotype plates.

### The Number of Coated Plates

The presence of a coating was established by visual examination and with the aid of a microscope and artificial illumination. Treatment records were also consulted (see the section on identification for more details). The objects were not removed from their original mountings for this examination because the



Figure 5. Backing of a daguerreotype (GLV/10027). Handwritten inscription with ballpoint pen: ZAPONLACK, Rest(ored):15.VII.68 Di(rnhofer).

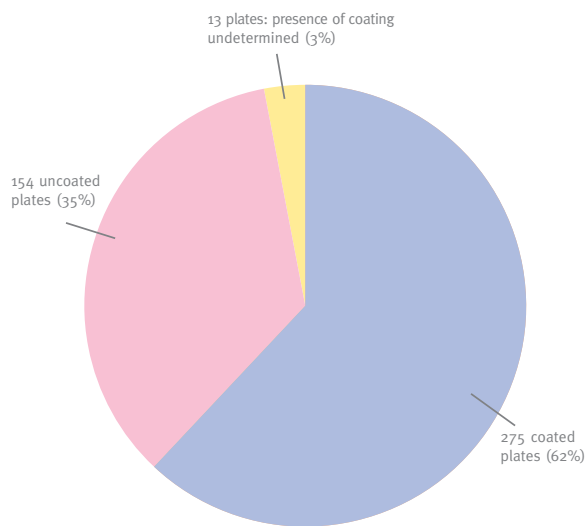


Figure 6. Survey of the Albertina's daguerreotypes.

surfaces could generally be viewed through the cover glass. The inscription "Zaponlack," written in graphite or ballpoint pen, was frequently found on the envelopes that housed the objects and/or on cardboard backings of the objects (figs. 4 and 5). Every plate was examined in order to ensure the survey was accurate, especially because the accuracy and consistency of the treatment records were unknown.

The survey results indicated that 275 plates were coated and 154 plates were uncoated. The results were inconclusive for 13 plates, possibly because the coating was extremely thin or no coating was present. Furthermore, examination of some of the plate surfaces was impossible due to severe corrosion of the cover

glasses (fig. 6). Given the considerable number of coated plates and the information about their treatments, the authors conducted further research on the coatings of the Albertina daguerreotypes.

### The Collection's Treatment Records

According to the records found within the collection of 442 plates, 223 plates were treated once, 190 plates were treated twice, and 21 plates were treated three times. No treatment records exist for eight of the plates. The following chart gives an overview of the treatment dates according to the treatment records and presents the authors' comments regarding the presence of coating (Table 1).

Most of the plates coated with Zapon lacquer were treated from 1962 to 1980, and the treatments were carried out by Franz Dirrhofer. In May 1962 he published his article on daguerreotype restoration and recorded the treatment of seven plates from the collection. From 1962 onward, restorations were not carried out annually or daily, but appear to have been performed randomly. Dirrhofer treated three to six plates in a day during the years he performed the treatments. The condition and thickness of the coatings did not appear to be related to the date of coating in any significant way. It may be assumed that the restorer did not experiment with different coating formulas, and that the thickness of the coating is related more to the technique and viscosity of the coating rather than the ingredients of the coating solution. No treatment records dating from 1969 to 1976 were found, and the restoration of the daguerreotypes resumed in 1977. No restorer signatures were found

Table 1. Dates of Treatment

Year	Number of Plates Treated	Restorer	Comment
1895	1	Unsigned	No coating treatment
1962	7	Dirrhofer	All coated
1964	3	Dirrhofer	All coated
1968	25	Dirrhofer	23 coating treatments
1977	23	Unsigned	All coated
1978	120	Unsigned	97-99 coating treatments
1979	186	Unsigned, 19 Dirrhofer sig. 167	114-118 coating treatments
1980	169	Unsigned, 5 Dirrhofer sig. 164	Last recorded by Dirrhofer on 28 May 4 coating treatments
1981	48	Unsigned	No coating treatments
1982	51	Unsigned	3-9 coating treatments
1983	21	Unsigned	1 coating treatment

for the treatments carried out from 1977 to 1978, but the presence of the coating and the housing method used lead to the conclusion that Dirnhofer was the restorer, or that he supervised the restoration projects. The last indication of his involvement with the restoration of the collection is his signature on May 28, 1980 on four daguerreotype housings. It is uncertain whether Dirnhofer re-treated his work of the 1960s with new coatings. The authors found records by other restorers for treatments dating from 1980 to 1983. From that point until 2001, the year that marks the start of the authors' treatments on the collection, no other treatment records were found.

### **Condition of the Enclosure Materials, Coatings, and Daguerreotype Plates**

With the exception of 47 objects, the 395 cover glasses exhibited moderate to severe glass decomposition. Glass decomposition products were found on the surfaces of the coated plates, but no specific pattern of plate or coating deterioration could be established based on the presence of these deposits. Glass deterioration occurred regardless of the presence or condition of other housing materials such as cases, frames, or bindings. Furthermore, the good condition of some cover glasses appeared unrelated to the condition of other housing materials. These observations demonstrate that there was no significant correlation between glass decomposition and the condition of the housings. Moreover, there was no significant correlation between glass decomposition and the condition of the coating.

The condition of the bindings, frames, and cases of 64 plates was fair, while the housings of 380 plates had deteriorated moderately to severely. One of the main reasons for the poor housing condition was that original seals, mats, backing boards, etc., had been removed during previous treatments and replaced by modern, low-quality boards and pressure-sensitive tapes. Many of the plates with bindings in fair condition were themselves in fair condition as well. Furthermore, numerous plates with bindings in poor condition were themselves in poor condition. Thus, there was significant correlation between the condition of plates and the condition of their housings.

The visual appearance of many of the coated daguerreotypes was severely affected because all the coatings were in poor condition due to discoloration and "irregularities," presumably related to application. All the coatings seem to have yellowed over time. Thickly applied coatings show more prominent yellowing than the thinly applied coatings. Yellowing may have occurred in dark storage without exposure

to daylight or ultraviolet irradiation; it is possible that the coatings might have been somewhat yellow from the beginning. Except for yellowing, no other well-known signs of cellulose nitrate deterioration were evident such as brittleness or stickiness.

Finally, the coated daguerreotypes showed substantially less tarnishing than the uncoated plates. Even the thinly coated plates that showed interference colors were well protected from retarnishing. In addition, some coated plates appear to have been protected from glass decomposition products and minor abrasion. However, some hand-colored daguerreotypes that were coated showed some color bleeding into the lacquer layer. The condition of the plate bears a significant correlation to the coating. Many samples showed that the image remains in good condition even if the coating is deteriorated, as was revealed after the removal of the coatings. Interestingly, no distinctive differences were observed in the condition between plates that had been treated once and plates that had been treated several times.

### **Identification of Cellulose Nitrate Coatings on Daguerreotypes**

#### ***Visual Examination***

The simplest way to recognize if a daguerreotype has been coated with cellulose nitrate is by its deterioration characteristics. When the coating is present, the discoloration associated with the aged lacquer is often obvious to the naked eye. Although only cellulose nitrate coatings were examined during this study, it should be mentioned that many of the identifying features that are described here may also apply to other coatings as well.



Figure 7. Detail of a coated daguerreotype displaying iridescent color formation (GLV2000/10027).

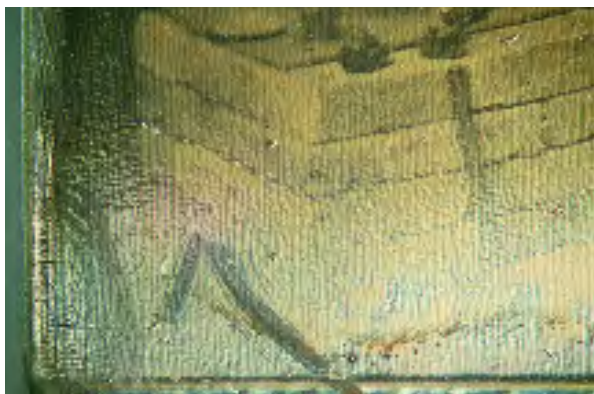


Figure 8. Detail of a coated daguerreotype displaying wavy surface (GLV2000/10049).

In general, a coated daguerreotype image appears weak and dull with very low contrast. Yellow or brown coloration is particularly evident in the highlights, as seen in figures 1, 2, and 3. In the case of thin coatings, pink and green interference can be observed very easily under fluorescent illumination (fig. 7). Thicker layers almost always have a wavy or rippled surface, which can be observed easily with specular illumination (fig. 8). A thicker layer of lacquer may be present along one or more of the edges and on the backs of the daguerreotypes. Indications of the coating in the form of drips or ridges from the applied liquid may be seen and may provide excellent candidates for analytical sampling. There may also be uncoated areas similar to those seen on collodion plates, which are usually restricted to one or more corners. The uncoated areas of the plate frequently display evidence typical of silver corrosion, ending abruptly where the coating begins (fig. 9). Dust inclusions are almost always present and are most easily distinguished from other surface dirt under magnification because the layer of Zapon lacquer is somewhat thicker around the embedded dust fibers (fig. 10).

#### **Diphenylamine Test**

The diphenylamine test requires minute samples of the coating to determine if cellulose nitrate is present. Note that proper health and safety precautions must be taken when using diphenylamine and sulfuric acid.

In this test, a 0.5% solution of diphenylamine is prepared with 90% sulfuric acid. A drop of the diphenylamine solution is placed on a microscope slide. A small rod capable of absorbing the solvent, such as a thin bamboo or wood stick, is dipped in acetone until the tip is soaked. Using the rod, the coating is touched to dislodge a small sample from an inconspicuous location, such as the reverse side of the plate. When the sample is dipped in the diphenylamine solution,

a blue-violet color appears if the material contains cellulose nitrate.<sup>64</sup> This test works well, although it may be difficult to purchase diphenylamine in some countries, as it is regarded as highly toxic. Consequently, the authors cannot recommend this test as a general identification tool.

#### **Fourier-transform Infrared Spectroscopy (FTIR)**

The coatings on two daguerreotypes in the Eder Collection were analyzed and identified using Fourier-transform infrared spectroscopy (FTIR).<sup>65</sup> When the spectrum of a cellulose nitrate coating on one daguerreotype (inventory number GLV9799) was compared with a sample FTIR spectrum (sr0004.sp) from the Infrared and Raman Users Group (IRUG)<sup>66</sup> database, the FTIR bands in the two spectra confirmed that the coating could be identified as cellulose nitrate<sup>67</sup> (fig. 11). The analytical results of the second daguerreotype were similar to the first plate that was examined, so the analysis of the one daguerreotype is discussed here.

#### **Ultraviolet Fluorescence**

Cellulose nitrate typically fluoresces green under ultraviolet light, as seen on a daguerreotype from the Eder Collection (fig. 12). Deteriorated cellulose nitrate is supposed to fluoresce bright green to yellow.

#### **Solubility Tests**

Cellulose nitrate coatings are soluble in acetone, methyl ethyl ketone, ethyl acetate, butyl acetate, and amyl acetate. The coating does not dissolve completely in ethanol. Samples swelled only slightly in butanol, a longer chain alcohol. No changes in the samples were observed with non-polar solvents and distilled water.

The authors reviewed other tests that require heating or burning a sample to assess the odor or melting behavior of the sample.<sup>68</sup> However, due to



Figure 9. Detail of a coated daguerreotype displaying a corroded area that was not coated (GLV2000/10023).

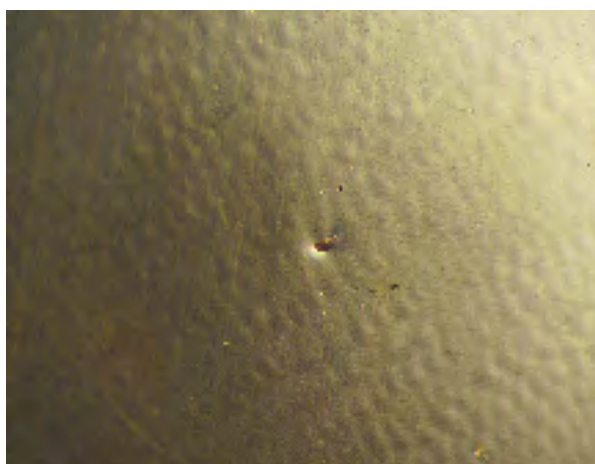


Figure 10. Detail of a coated daguerreotype displaying wavy surface and embedded dust particle (GLV2000/10023).

the impracticality of these tests and concerns regarding safety, the authors of this chapter did not find them suitable for the purpose of this project. Additional test methods used to identify cellulose nitrate are described in the chapter by McGlinchey and Maines in this volume.

## Conservation Treatments of the Albertina Daguerreotypes

### *Franz Dirnhofer's Early Restoration Treatment Procedure*

In his 1962 study Franz Dirnhofer wrote, "In the historical collections of the GLV there are a large number of significant daguerreotypes that are, from time to time, restored in order to preserve them for posterity. Private persons also sometimes submit daguerreotype images, in order to subject them to thorough expert restoration."<sup>69</sup> He further described unbinding and washing the plates before treating them with a potassium cyanide solution to remove the silver corrosion products. Concentrations of 0.5%, 1%, and 2% were used, beginning with the weakest, using successively stronger solutions if the corrosion products did not disappear.<sup>70</sup> In order to minimize a subsequent chemical change of the freshly restored daguerreotype images, and as protection against physical damage, he recommended coating the chemically treated plates with Zapon lacquer.

Interestingly, he did not use one of the ready-made commercial coatings that were available in the 1960s, but instead proposed his own coating formula:

15g colorless celluloid or collodion cotton  
100g acetone  
200g amyl acetate  
add 100g benzene after all is in solution.<sup>71</sup>

He also advised attaching a note to the back of the frame to record the date of the restoration, the method used, and the type of protective lacquer. Dirnhofer's inscriptions on the Eder Collection storage enclosures indicate that he restored the daguerreotypes in the years between 1962 and 1980.

### Restorations in the 1980s

A further treatment campaign occurred in 1983. The paper envelope of the plate *Exploded Locomotive* (inventory number GLV2000/10169), includes handwritten notes outlining the individual steps of the treatment, with a different restorer's signature. Upon contacting the restorer, the authors learned that the Zapon lacquer of this plate was removed using acetone before chemical cleaning, which was carried out according to Ruth K. Field's thiourea formula.<sup>72</sup> The restorer had learned the method of chemical cleaning with thiourea through his contacts with Hansch and the German Club Daguerre. As an opponent of "Zaponisation," the restorer had refrained from performing it

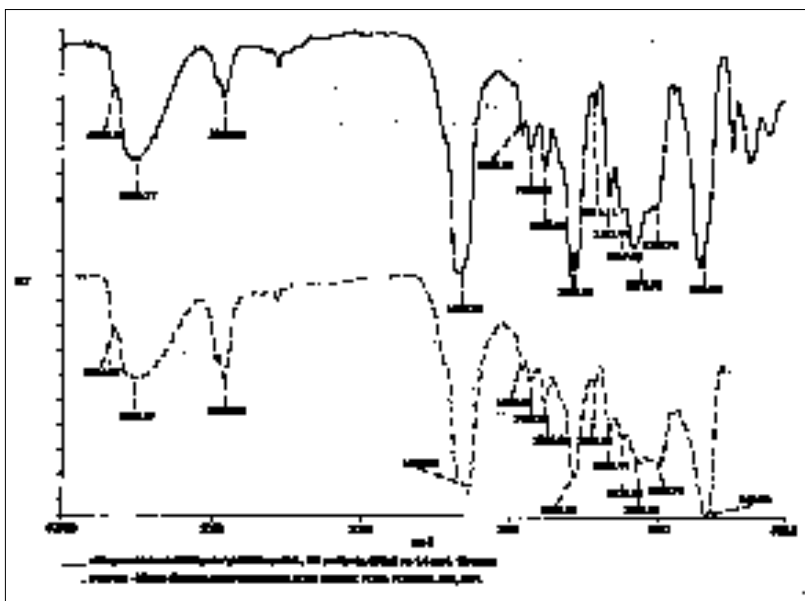


Figure 11. The FTIR spectrum of a cellulose nitrate coating on a daguerreotype (GLV 9799) in comparison with FTIR spectrum of a reference sample of cellulose nitrate (sr0004.sp) from the Infrared and Raman Users Group (IRUG) database. The agreement of the FTIR bands in the two spectra confirms that the coating can be identified as cellulose nitrate.



Figure 12. Comparison of a coated and uncoated daguerreotype observed with UV fluorescence. The Zaponlack-coated daguerreotype on the left shows a greenish fluorescence.

again, since in his opinion the best protection was afforded by carefully sealing the object, monitoring it, and perhaps restoring it at regular intervals. According to the restorer (who preferred to remain anonymous), the conservation activities of the early 1980s focused primarily on improving bindings and resealing due to concerns about the long-term stability of chemical and coating treatments.

### Recent Conservation Treatment

#### *Removal of the Coatings*

In order to prepare some of the Albertina daguerreotypes for display in *The Eye and the Camera* exhibition, the coatings were removed from a selected group of daguerreotypes. The coatings had been poorly applied, were discolored, and presented surface irregularities that impaired the viewing of the images. Full photographic and written documentation was performed for all treatments.

#### *Choice of Solvent*

As mentioned earlier, cellulose nitrate lacquer is soluble in esters (e.g. amyl acetate, ethyl acetate), ketones, and alcohol-ether mixtures.<sup>73</sup> Solubility tests showed that the coating could be removed most effectively using ethyl acetate or acetone. However, previous experience treating daguerreotypes with acetone resulted in the formation of whitish residues. Therefore, ethyl acetate was chosen as the solvent for this project. Among the esters, this solvent poses the fewest health risks and does not leave behind any white residues. In general, the solubility of the lacquers that were encountered was not impaired by aging. While constant light exposure leads to degradation of cellulose nitrate

varnishes and ultimately to poor solubility, the fact that the Eder Collection daguerreotypes had very little exposure to light may explain the ease of solubility.

#### *Varnish Removal*

The cleaning procedure began with careful documentation and removal of each plate from its frame and binding. The plate was then bathed in water to reduce surface dirt and glass corrosion products. Each plate was placed in a tray of distilled water at about 20° C, and agitated continuously by gently rocking the tray. The coating was not affected by the distilled water bath. The plate was occasionally lifted from the water bath to remove any water-soluble adhesive residue from the reverse using a soft brush. After ten minutes of washing, the plate was removed from the bath and set aside to air dry.

Working in a fume hood, the conservator placed the dry daguerreotype in a 1 cm-deep ethyl acetate bath in a glass tray for approximately five minutes with the image side facing up. The duration of cleaning in the first bath was determined by the thickness of the lacquer. In order to achieve the most effective and efficient cleaning effect, the bath was kept in slight but constant movement. The plate was then placed in a second bath of fresh ethyl acetate for another five minutes. As the final step in the cleaning process, the plate was held at an angle and fresh ethyl acetate was poured uniformly over the surface using a pipette.

A hair dryer was used to dry the plate, using care to be sure the plate did not become too hot. Sudden and extreme changes in temperature can threaten the adhesion of the silver metal layer to the copper substrate due to differential expansion of the two metals.



Figure 13. Anonymous, *Still Life with Laboratory Utensils*, 1845. Two ninth-plate daguerreotypes (stereoview). Plate size: 2.87 x 1.57 in. (7.3 x 4.0 cm) each. The plate on the left is shown with its Zaponlack coating. The plate on the right is shown after treatment, with its coating removed. Courtesy Albertina, permanent loan of the Höhere Graphische Bundes-Lehr- und Versuchsanstalt, Vienna. (GLV2000/10049).



Figure 14. Anonymous, *Sculptor Hans Gasser in His Studio*, 1855-1857. Daguerreotype with Zaponlack coating before treatment. Quarter plate, plate size 6.22 x 5.24 in. (15.8 x 13.3 cm). Courtesy Albertina, permanent loan of the Höhere Graphische Bundes-Lehr- und Versuchsanstalt, Vienna. (GLV2000/9989).



Figure 15. The same daguerreotype shown in figure 14 after removal of the coating.

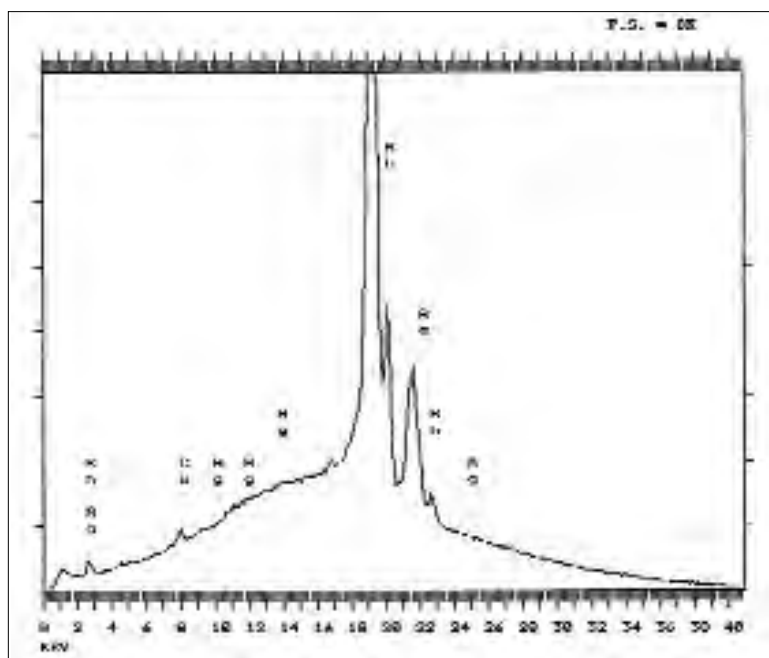


Figure 16. EDXRF spectrum of the evaporated solution showing only minimal amounts of copper. Analysis performed with Tracor Spectrace 5000. Tube voltage: 50 KV. Tube current: 0.05 mA. Atmosphere: Air. Filter used: none. Livetime: 300 seconds. Vertical scale: 8000 counts (y scale).

The varnish removal was very effective, even stunning, and the images usually regained a remarkable freshness. After drying, the surface of the plate was thoroughly inspected. The presence of any interference colors indicated that traces of the coating were still present on the surface. In such cases the cleaning procedure was repeated again after the plate had cooled. It should be noted that once the darkened and discolored lacquer was removed some brown corrosion stains on the plates became more clearly visible (figs. 13, 14, and 15).

#### Testing for Image-forming Particles with EDXRF

The appearance of the plates improved dramatically following the removal of the varnish, but it was impossible to know how the plates appeared before the coating was first applied. Further, it was unknown if removal of the varnish—or coatings that may be applied in the future and their subsequent removal—might have a negative impact on the image structure. To learn whether image particles were removed during the process, the ethyl acetate used to remove the lacquer was analyzed. The goal was to find any traces of silver, mercury, or gold that might comprise an image particle. This test was carried out using energy-dispersive x-ray fluorescence analysis (EDXRF).<sup>74</sup> The examinations were carried out by university professors M. Schreiner, Ph.D., and D. Jembrih-Simbürger, Ph.D., at the Institute for the Natural Sciences and Technology in Art at the Academy of the Fine Arts in Vienna. The spectra of three experimental arrange-

ments indicate that only minimal amounts of copper were detected, the source of which was probably the back of the daguerreotype. The presence of silver or mercury in the solution was not detected. This analysis indicates that it is unlikely that image particles were removed during the coating removal. It is possible, however, that image materials could not be detected using this equipment under the measurement conditions (fig. 16).

#### Additional Conservation Measures

Other important steps in the conservation of the daguerreotypes included the removal of considerable pressure-sensitive tapes from bindings, backs, and sometimes from the image sides of the plates. The preservation of the original packaging and binding materials was a priority, even if they were no more than fragments. The reconstruction of historical seals or missing parts from frames, cases, or *passe-partouts* was performed if enough evidence existed to provide guidance for treatment. Deteriorated or broken cover glasses were replaced with new glass or, in the case of painted cover glasses, cleaned and reutilized. Finally, the plates were sealed within a protective package consisting of the original mounting boards in combination with new museum-quality boards or archival papers in direct contact with the plates. Paper or mat board spacers were used if possible so that no mounting materials or *passe-partouts*, old or new, would touch the delicate surface of the plates. The resealed plates were returned to their original frame or case.

Figure 17. Josef Wawra, *Palazzo Foscari in Venice*, 1848. The same daguerreotype shown in figure 1 after conservation treatment, with the coating removed. Courtesy Albertina, permanent loan of the Höhere Graphische Bundes-Lehr- und Versuchsanstalt, Vienna. (GLV2000/10064).



After treatment, the daguerreotypes were housed in custom-made archival boxes (fig. 17).

### Results and Considerations

The Zapon lacquer coatings were successfully removed from the selected plates in the Albertina Collection, considerably improving the visual appearance of the images. The surfaces beneath the coatings were in very good condition, indicating that the coatings had provided very good protection. The daguerreotypes were not given new protective coatings of cellulose nitrate lacquer for three key reasons:

1. Such coatings visually mar the images if not applied in a controlled manner. The effects may include such visual imperfections as: a reduction of the range of tonal values, an irregular surface, the appearance of interference colors, and dust inclusions on the surface.
2. Cellulose nitrate coatings are not stable and have to be removed regularly, which may cause physical damage to the image layer during the removal and reapplication of the lacquer, although the results of EDXRF on the solutions used for this study do not seem to indicate such damage occurred.
3. Other potential coating materials should be studied further. Certain methacrylates and polyvinyl acetates have been recommended by other conservators as protective coatings for silver surfaces. In addition, sputtered coatings are mentioned in recent literature.<sup>75,76</sup>

The possibilities of utilizing these other materials as protective coatings for daguerreotypes, as well as using a more controlled cellulose nitrate application, need to be tested prior to reapplying the coatings.

The silver surfaces of the treated daguerreotypes are very sensitive to air pollutants. Daguerreotypes that have been subjected to repeated treatment with cyanide, and therefore display slightly etched and damaged surfaces, are very susceptible to corrosion. For this reason, attention should focus on preventive measures, such as optimal sealing and archival housings. Furthermore, a controlled storage environment is absolutely imperative for the future preservation of these objects.

### Acknowledgments

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## Notes

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13. Hyatt's crucial contribution to the product was the use of heat and pressure. Heat melted the camphor, making it into a solvent for the cellulose nitrate (which diminished the need for additional solvents), and eliminated many of the previous problems associated with producing large quantities of volatile solvents. Furthermore, Hyatt was able to develop machinery to work the new material. Plastics Historical Society, 2004.
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16. With the British Patent 6542 in 1892, Frederick Crane secured the first patented manufacture of Zapon varnish according to a certain formula. The Zapon Company of Stamford, Connecticut, large producer of lacquers, leather cloth, and rubberized materials, was the successor of the

- companies that originated lacquer and leather cloth in the United States, namely, The Frederick Crane Chemical Company; Tannette Company; and the Evans Artificial Leather Company. Several years later, the company name was changed to Celluloid Zapon Company and the factory moved to Stamford. In 1917, the Zapon Company's stock was purchased by the Atlas Powder Company of Wilmington, Delaware. The factory site at Stamford included fifteen acres located on Long Island Sound. Around 250 men were employed in 1935. Bingham 1935, 1718.
17. Zimmer 1931, 2.
18. Brown and Crawford, 1928.
19. Zimmer 1931, 52.
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42. de la Rie 1992, 62-82.
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44. Reilly 1991, 145-162.
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54. Stenger 1920, 17.
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68. Kathrin Kessler, "Celluloid—Ein Werkstoff zersetzt sich," in *Kunststoff als Werkstoff: Celluloid und Polyurethan-Weichschaum. Material-Eigenschaften-Technik*, vol. 13 of *Kölner Beiträge zur Restaurierung und Konservierung von Kunst- und Kulturgut* (Munich, 2001), 89-93.
69. Dirnhofer 1962, 1.
70. Dirnhofer 1962, 5. In his report, Dirnhofer refers to the enormously poisonous nature of these solutions, only a few milligrams of which could prove fatal. Nevertheless, potassium cyanide was to his knowledge the sole substance that dissolved silver sulfide. The average duration of the treatment was ten minutes, yet when the concentration of the potassium cyanide bath rose to 2%, as in the case of particularly tenacious patches, the treatment time may have lasted as long as one hour.
71. Dirnhofer did not distinguish between celluloid and collodion cotton in his recipe.
72. Charles van Raavenswaay, "An Improved Method for the Restoration of Daguerreotypes," *Image*, 5, no. 7 (September 1956): 156-159.
73. Selwitz 1988, 10.
74. The examinations were carried out using the XRF equipment Tracor Spectrace 5000 and analyzed both the ethyl acetate solution, an ethyl acetate solution restricted to about 5%, and the insoluble deposits that existed in the original solution. Measuring parameters: Tube voltage: 50 kV, Tube current: 0.01 mA, Atmosphere: air, Filter: -, Tubes: Rh, Detector: Si(Li).
75. Susan Barger et al., "Protective Surface Coatings for Daguerreotypes," *Journal of the American Institution for Conservation*, 24 (Washington, 1984): 72.
76. Mogens S. Koch and Anker Sjøgren, "Behandlung von Daguerreotypen mit Wasserstoffplasma," *Maltechnik* 4 (Munich, 1984), 58-64. The authors recommend the spraycoating of plasma-treated daguerreotypes with Incralac, an acrylic-based lacquer.