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# THREE DECADES LATER: A STATUS REPORT ON THE SILVER LACQUERING PROGRAM AT WINTERTHUR

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## ABSTRACT

30 years ago, Winterthur began its first museum-wide campaign of cellulose nitrate lacquer application to its collection of historical silver objects displayed predominately in open period room settings, i.e., not in display cases. This coating was chosen after testing demonstrated that it could protect the silver from tarnishing for up to 28 years under regular museum conditions. The lacquering program continues at Winterthur today for over 2,000 silver objects on permanent display in period rooms and in the study collection.

The authors discuss a project currently underway, which began with a survey of 1,500 lacquered pieces to determine the effectiveness of the coating over the years. The results of this survey, which indicated that the coating had begun to fail on 42% of the silver pieces, were instrumental in the development of an intensive second campaign of cellulose nitrate lacquering that began in August 2011. As part of this initiative, funded in part by a grant from the Institute of Museum and Library Services, 550 silver objects will be relacquered, focusing on pieces where the lacquer is oldest or has failed. This article presents the results of many observations made during the project to better understand the behavior of cellulose nitrate coatings on silver objects, its progressive change over time, the reasons why it may or may not fail, and the methods used for the removal of old coatings and reapplication of new ones. This includes preliminary analytical results of a study of failed/discolored cellulose nitrate coatings and the corrosion that develops underneath or within them.

Coating with cellulose nitrate, a material with inherent chemical instability, may at first seem counterintuitive in conservation; to that effect, other preventive methods exist and are successfully in use at Winterthur to retard silver tarnishing. Yet, the results of this study demonstrate how effective cellulose nitrate coatings have been within the open environment of Winterthur's period rooms so long as the coating is properly applied, the objects appropriately handled, the environment controlled, and with a plan and resources in place for the coating's eventual and inevitable reapplication.

## 1. SILVER AT WINTERTHUR AND A HISTORY OF SILVER LACQUERING

Winterthur's collection of about 11,600 silver objects includes 2,150 silver and silver-plated objects on open display. This includes historic interiors, gallery spaces, and the collection study area. The silver represents a unique collection of colonial and pre-industrial era silver made or used in America, including both prestigious and common items, from incredibly elaborate soup tureens to stylish eyeglasses. Other highlights include a rare set of six matching tankards made by Paul Revere Jr. and the largest extant collection of British fused-plate lighting devices in the world. Henry Francis du Pont, the museum founder, encouraged access and study of the collection, and it has been well researched and published, for instance by Quimby (1995) who included the results of extensive x-ray fluorescence spectroscopy (XRF) analysis completed in large part by the late Janice H. Carlson, a scientist at Winterthur for 30 years.

Care of the silver was a concern of the conservation department from the moment it was officially established in 1970. Most of the silver is on display in the museum's period rooms and would quickly tarnish without a protective coating. It was clearly understood that regular polishing would be untenable. Even the gentlest polishing methods remove some silver, resulting over time in a softening and eventual loss of design and the appearance of the base metal on plated objects (fig. 1). In addition, the time requirements for repeated polishing and the risks associated with the move and deinstallation of objects would also be immense, considering the scope of the collection. Given these factors, coating was deemed the best option.



Fig. 1. Two objects in the Winterthur collection showing extensive wear to the silver surface due to repeated polishing. Left: engraved initials now barely legible. Joseph Jr. and Nathaniel Richardson, teapot, 1771–1791, silver and wood, H: 15 cm, W: 10.5 cm, Winterthur Museum, 1998.0019; Right: copper base metal showing where silver plating is worn away. Unknown maker, England, candlestick, 1815–1830, fused silver plate over copper, H: 30.5 cm, W: 15 cm, Winterthur Museum, 1965.0067.002 (Courtesy of Winterthur Museum)

The true father of the lacquering program is Don Heller, a silversmith and then conservator at the museum from 1974 to 1992. He was also a professor in the art conservation program. Throughout the 1970s, he conducted research and experiments on different lacquer formulations and application methods, evaluating properties such as visual intrusion, adherence, durability, and tarnish protection, ultimately concluding that cellulose nitrate lacquers were the best choice (Heller 1983). Following observations made over 25 years on items he owned, Heller recommended that a cellulose nitrate coating should ideally be replaced every 10 years, suggesting that if well applied and properly handled within a controlled museum environment, it could last up to 28 years. His findings are supported by Luxford and Thickett (2007), who determined via accelerated aging tests that cellulose nitrate coatings applied to silver exposed to low to mid relative humidity (RH) environments have a longevity of at least 20 years.

From 1982 to 1987, with the support of grants from the National Endowment for the Arts, Heller and two trainees, Don Williams and Helen Stetina, cleaned and lacquered over 1,000 objects. During this time, they refined techniques and developed lacquer application protocols that remain pertinent to this day.

Working with an inherently chemically unstable material was always perceived as a calculated risk, and this is reflected in the museum's silver coating history. While Agateen Air Dry Lacquer #27 has been the main lacquer for silver since 1982, a different Agateen lacquer, #2B-4, was also used between 1982 and 1996. This lacquer is tinted yellow and provides a somewhat antique appearance. Conservators who followed Heller at Winterthur in the 1990s, including Julie Reilley, Debbie Long, and Margaret Little, experimented with acrylic coatings, using mostly Paraloid B-48N, though they also tried Paraloid B-72 on a few pieces. In 1997, observations were made on the rapid retarnishing of several pieces coated with acrylics. Supported by research done by Reedy and others in 1999 at the University of Delaware demonstrating the superior tarnish prevention ability of cellulose nitrate over acrylic coatings, Agateen #27 became from then on the only lacquer applied to silver at Winterthur.

## 2. THE 2009 SURVEY

In the summer of 2009, with Don Heller's prediction for a 28-year maximum lifetime approaching for pieces lacquered in 1982, a systematic survey of the silver on display was undertaken. Each object's report was consulted and then all objects were examined to determine what kind of coating, if any, was present (table 1), and the condition of the majority of the pieces lacquered between 1982 and 2009 was assessed. Much comparative data were generated (La Duc and Peirce 2009), and only the most significant findings are indicated here.

The lacquer on 42% of the pieces had moderate to major issues, enough that relacquering was deemed necessary (table 2). Most significantly perhaps, poor condition of the coating did not relate to the date or method of application, or to the composition of the silver substrate, but instead to how well the lacquer had been applied, and how multipart or ornamented the objects are. Examples of typical

Table 1. Survey Results Indicating the Number and Percentage of Objects Coated with the Different Lacquers Used at Winterthur between 1982 and 2009, versus Uncoated Objects

|                            | Number | Percentage |
|----------------------------|--------|------------|
| Objects Surveyed           | 1514   |            |
| Coated with Agateen #27    | 989    | 65%        |
| Coated with Agateen # 2B-4 | 164    | 11%        |
| Coated with Paraloid B-72  | 12     | <1%        |
| Coated with Paraloid B-48N | 42     | 3%         |
| Uncoated                   | 307    | 20%        |

Results of a separate survey done on 39 additional pieces in the Dorrance Gallery and completed by B. Pouliot in 2013 were added to this table, as this group included the only pieces lacquered with Paraloid B-72.

Table 2. 2009 Survey Results Indicating Percentages of Coating Failure

|                      | Number | Percentage |
|----------------------|--------|------------|
| Objects with coating | 1168   |            |
| Intact Coating       | 444    | 38%        |
| Minor issues         | 234    | 20%        |
| Moderate issues      | 444    | 38%        |
| Major issues         | 46     | 4%         |

Minor issues represented coatings with very minimal tarnish caused by defects in the lacquer, while moderate and major issues represented coatings with significant failure and having developed enough tarnish to warrant a reapplication of the lacquer.



Fig. 2. Examples of typical lacquer failure on silver. Upper left: fingerprint left prior to application of the lacquer. Lower left: brush marks and areas of gray tarnish formed where lacquer is too thin. Right: lacunae in the coating; those circled in red are associated with indentations in the design where the lacquer application did not reach, while the area circled in blue indicates abrasion of the lacquer, likely through handling (Courtesy of Winterthur Museum)

lacquer defects are presented in figure 2. Application defects, such as fingerprints, brushmarks, and lacunae, were much more common than coating failures associated with abrasion and handling. Coating failures were present on nearly 85% of pieces with moving parts or heavily ornamented surfaces.

Yellowing of the coating was a difficult factor to properly assess, particularly as most of the survey was conducted in period rooms where lighting options are limited, but it was anticipated and found. However, in basically all cases, it did not correlate with an increased incidence of coating failure. Tarnish formation was found in many instances where the coating was too thin and slightly iridescent in appearance. Taking this and other findings from the survey into consideration, the main conclusion was that so long as it is well applied, cellulose nitrate lacquer can remain effective at preventing tarnish on silver even over 20 years after application, especially on less complex objects and surfaces.

### 3. THE 2011–2013 RELACQUERING PROJECT

The next step in the project was to gather the resources necessary to launch a large relacquering campaign. Armed with the survey data, a two-year grant was obtained in 2011 from the Institute of Museum and Library Services (IMLS). Careful orchestration was planned for all activities including object movement, documentation, cleaning, relacquering, and analysis, while minimally interfering with year-round tours and public programs (table 3). Beyond those in the conservation department, the project required involvement from the curator, registrar, art handlers, photographer, and others in development, public programs, and finance.

Table 3. Schedule of Completion for IMLS-Funded Grant to Relacquer Approximately 550 Silver Objects in the Winterthur Collection between August 2011 and July 2013

|  |  | IMLS SILVER GRANT<br>SCHEDULE OF COMPLETION |     |     |     |     |     |      |     |     |     |     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |
|--|--|---|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|  |  | 2011  |     |     |     |     |     | 2012 |     |     |     |     |     | 2013 |     |     |     |     |     |     |     |     |     |     |     |     |
| Activity   |  | Jul   | Aug | Sep | Oct | Nov | Dec | Jan  | Feb | Mar | Apr | May | Jun | Jul  | Aug | Sep | Oct | Nov | Dec | Jan | Feb | Mar | Apr | May | Jun | Jul |
| Hire/Train Technicians                           |  | █   | █   | █   |     |     |     |      |     |     |     |     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |
| Hire Asst Conservator                            |  | █   | █   | █   |     |     |     |      |     |     |     |     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |
| Establish Art Handling Schedule                  |  |   | █   | █   |     |     |     |      |     |     |     |     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |
| Install Fume Hood                                |  |   | █   | █   |     |     |     |      |     |     |     |     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |
| Art Handlers: Move Objects In/Out of Lab         |  | █   | █   | █   | █   | █   | █   | █    | █   | █   | █   | █   | █   | █    | █   | █   | █   | █   | █   | █   | █   | █   | █   | █   | █   |     |
| Silver Objects Clean & Recoat                    |  |   |     |     |     |     |     |      |     |     |     |     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |
| 8th floor (study)                                |  |   |     | █   | █   | █   |     |      |     |     |     |     |     |      |     |     |     |     |     |     |     |     |     |     | █   |     |
| 7th floor  |  |   |     |     |     | █   | █   |      |     |     |     |     |     |      |     |     |     |     | █   | █   |     |     |     |     |     |     |
| 6th floor  |  |   |     |     |     |     |     |      |     |     |     | █   | █   | █    |     |     |     |     |     |     |     |     |     |     |     |     |
| 5th floor  |  |   |     |     |     |     |     | █    | █   |     |     |     |     |      |     |     |     |     |     |     | █   | █   |     |     |     |     |
| 4th floor  |  |   |     |     |     |     |     |      |     | █   | █   | █   |     |      |     |     |     |     |     |     |     |     |     |     |     |     |
| 3rd floor  |  |   |     |     |     |     |     |      |     |     |     |     |     |      |     | █   | █   |     |     |     |     |     |     |     |     |     |
| Galleries  |  |   |     |     |     |     |     |      |     |     |     |     |     |      |     |     |     |     |     |     | █   | █   | █   |     |     |     |
| SRAL Sampling, Analysis, Compiling Data          |  |   |     | █   | █   | █   | █   | █    | █   | █   | █   | █   | █   | █    | █   | █   | █   | █   | █   | █   | █   | █   | █   | █   | █   |     |
| Production of Prof. Publications & Presentations |  |   |     |     |     |     |     |      |     |     |     |     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |
| Update Website                                   |  |   | █   |     |     |     |     |      |     | █   |     |     |     |      |     |     |     |     |     |     |     | █   |     |     |     |     |
| Treatment Photography                            |  |   |     |     |     |     |     |      |     |     |     |     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |
|  |  |   |     |     |     |     |     |      |     |     |     |     |     |      |     |     |     |     |     |     |     |     |     |     |     |     |

Objects from specific floors are treated during particular months to facilitate object movement and reduce impact on public tours and programs. An objective was to make this project broadly accessible and details are available on the Winterthur website. (Winterthur 2014)

The focus was on three categories of objects. First, all objects lacquered in 1985 or prior were treated. These were easy to recognize because of the obvious numbering system formerly in place, whereby the date of the lacquer application was painted on the object in blue acrylic paint. Second, those with significant coating failure or application defects were treated, regardless of the year of application. A third category addressed objects that were never lacquered. These were typically complex objects that have silver associated with and adjacent to other materials.

The procedures for relacquering the objects were carefully standardized, as the goal was to diminish the percentage of application defects so apparent in the 2009 survey. For that purpose, the two conservation assistants hired for the project were trained for two months on simpler objects, like a group of porringers from the study collection, before moving on to more complex forms from the display areas. The main steps in the treatment protocol are shown in figure 3. As it is not possible within this text to fully detail these procedures, focus will be on the most important lessons learned and the main materials used.

Complete removal of old lacquer is crucial, as recent research by Thickett and Hockey (2003) has clearly demonstrated. This can be more time-consuming for coatings that are visibly degraded, as they are more difficult to remove. Two methods work well for this, a portable steamer used at 60 PSI or a 1:1 acetone:denatured alcohol solution. Most often the two methods are used in conjunction to appropriately



Fig. 3. Different steps in the silver treatment process. Upper left: a wooden handle protected with Parafilm M. Here the edges of the film are lifted to allow for local removal of old lacquer. Upper middle: removing old lacquer with a portable steamer. The steamer nozzle is kept at least 2 cm away from the object surface. Upper right: polishing the surface with a calcium carbonate slurry and cotton cloth. The entire surface is lightly polished in preparation for the application of new lacquer. Lower left: after polishing, the first rinse with a 0.2% Triton XL-80N solution. Lower right: second rinse in deionized water using soft brushes and cotton pads to ensure that all polishing materials are removed. This is followed immediately by drying with compressed air, not shown. (Courtesy of Winterthur Museum, except upper left by Courtney von Stein)

address sensitive surfaces and associated, nonmetallic materials, for instance a wooden handle. Complete protection of associated materials is essential and requires full attention through the entire relacquering process. Parafilm M is a versatile material used successfully for this purpose.

Regarding polishing materials, a precipitated calcium carbonate slurry in a 1:1 deionized water:denatured alcohol solution works well for basically all objects and most degrees of tarnishing. Localized areas of dark tarnish that form in areas of coating failure require an aluminum oxide (typically 0.3 micron in size) slurry, otherwise a shadow of the former tarnish tends to remain visible, particularly after the application of new lacquer. Mars Staedtler plastic erasers are used occasionally adjacent to water-sensitive or hard-to-rinse components. Removal of all polish and greasy residues from the silver surface requires many steps, including rinsing in water, drying with compressed air, degreasing with acetone, and buffing with a Selvyt cloth. All are essential to ensure good adhesion of the lacquer.

With lacquer application, meticulous attention must be paid to the preparation of the space and equipment, and a careful strategy considered in terms of where to begin and end. Brushing works best on

smaller pieces and objects with complex surfaces, while spray application is ideal for smooth surfaced objects. Brushing edges and deep indentations is essential, even on objects that are otherwise spray lacquered. Lacquer is not applied to the interior of pieces with a top or a lid, as it is unnecessary in those areas and difficult to both apply well and remove entirely later on. In most cases, lacquer was applied soon after polishing to preserve the bright silver appearance desired for display in historic homes.

After application, it is essential to carefully examine the lacquer within the first hour for imperfections, and again after 24 hours, particularly for iridescence (fig. 4), which indicates a coating that is too thin to effectively retard tarnish. A continuity tester is a useful and inexpensive tool to identify lacunae in the coating. It is also important to allow enough time for the lacquer to fully dry. While it will be dry to the touch within an hour after application, full solvent evaporation is not achieved for several days and a minimum period of two to three weeks is recommended before objects are moved back to display. Toward the end of this period, a comparative visual examination of entire groups of objects is useful to ensure overall good appearance and again to identify potential application defects.



Fig. 4. Iridescence visible on punch bowl, indicating that the cellulose nitrate lacquer was applied too thinly. Typically tarnish will become visible in these areas within a few months after application of the lacquer. John Burt, punch bowl, 1740–1745, silver, H: 10.1 cm, D: 19.2 cm, Winterthur Museum, 2004.0052 (Courtesy of Winterthur Museum)

#### 4. SCIENTIFIC ANALYSIS

Another goal of the project was to understand better how the lacquer ages, and what happens to the silver underneath as it does. Two silver tea sets in private collections, both lacquered with Agateen #27 in the 1980s and displayed in home environments, provided the necessary degradation phenomena for investigation. These tea sets showed extensive discoloration of the lacquer and on one tea set, a brownish-pink tarnish not observed to that extent on any museum object.

One from each tea set, a teapot and creamer, served as the focus of a multianalytical study to investigate coating degradation and to identify the resulting silver corrosion products formed. The degraded lacquer was removed with a steamer and pieces of cohesive film samples were retained for subsequent analyses (fig. 5). While the films were obviously discolored, a fair amount of corrosion products was also observed directly on the silver surface. This suggests that the silver was reacting with pollutants in the air beneath the deteriorating films.

The initiating reaction of the degradation mechanism of cellulose nitrate is the splitting of the nitro ( $-O-NO_2$ ) bonds of the secondary nitrate group joined to carbon atoms 2 and 3 of the glucopyranosyl ring,



Fig. 5. Both upper images show the objects with the deteriorating cellulose nitrate coatings, while the corresponding images on the bottom show samples of the discolored film after it was removed from the object with a portable steamer. Upper left: Sheffield, England, teapot, 19th century, silver fused plate over copper and wood, H: 16.5 cm, W: 12 cm, private collection. (Courtesy of Bartosz Dajnowski). Upper right: Allen Armstrong, creamer, 1806–1817, silver, H: 17.8 cm, W: 12.7 cm, private collection. (Courtesy of Becky Kaczowski) (Bottom photographs courtesy of Catherine Matsen)

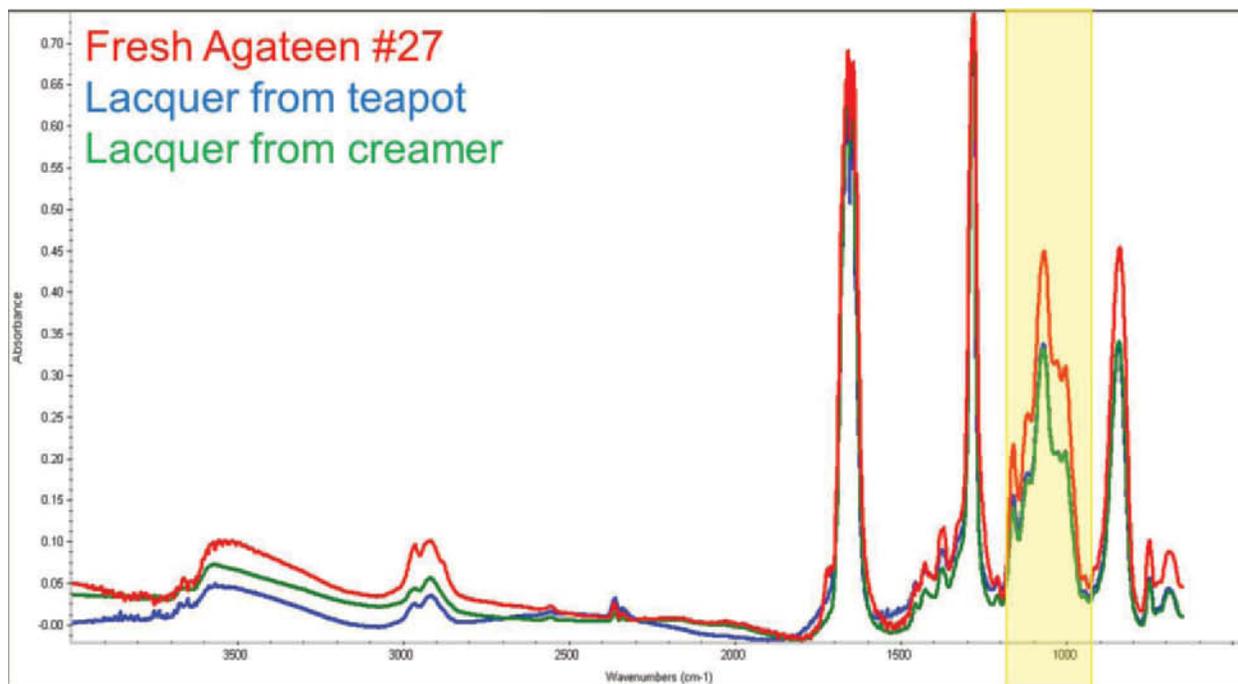


Fig. 6. FTIR spectra of fresh Agateen #27 film (red spectrum) overlaid with discolored lacquer from teapot (blue spectrum) and from creamer (green spectrum). The area highlighted in yellow indicates the spectral region where the degradation of the cellulose nitrate film is evident for the lacquer samples from the two objects. (Courtesy of the Scientific Research and Analysis Laboratory at Winterthur Museum)

which produces nitrous oxide. The nitrous oxide then fuels an autocatalytic degradation of the cellulose nitrate and causes accelerated corrosion of adjacent materials, such as silver and copper, which are both present in historic silver alloys. This deterioration is accelerated by increased temperatures, elevated RH, and acidic conditions. Ultraviolet light exposure can cause degradation of the cellulose ring, breaking down the polymer into shorter oligomers and thus causing a rapid decrease in molecular weight (Shashoua et al. 1992).

The discolored cellulose nitrate films from the teapot and creamer were compared to a sample of fresh Agateen #27 using FTIR. The sample was analyzed using the Thermo Scientific Nicolet 6700 FTIR with Nicolet Continuum FTIR microscope (transmission mode); data were acquired for 128 scans from 4000 to 650  $\text{cm}^{-1}$  at a spectral resolution of 4  $\text{cm}^{-1}$  with Omnic 8.0 software. No dramatic difference was observed in the spectra (fig. 6), suggesting that the formation of degradation products is below the minimum detection limit, or approximately 10 wt% of the sample composition. A slight decrease in the carbon–oxygen vibrations of the glucopyranose ring in the spectral region between 1200 and 950  $\text{cm}^{-1}$  indicates some breakdown of the cellulose nitrate polymer within the discolored films. Py-GC-MS (pyrolysis–gas chromatography–mass spectrometry) was performed to detect any plasticizers or additives in the Agateen #27 lacquer that may possibly interfere with interpretation of the FTIR data, but nothing was found. Cellulose nitrate completely combusts with py-GC-MS to form carbon dioxide ( $\text{CO}_2$ ; 44 amu), nitrogen ( $\text{N}_2$ ; 28 amu), and ammonia ( $\text{NH}_3$ ; 17 amu); the mass spectrometer is set to detect masses  $\geq 33$  amu and so  $\text{CO}_2$  is the only remnant of cellulose nitrate detected. Py-GC-MS was performed with the Frontier Lab EGA/PY-3030D mounted to a Hewlett-Packard 6890 gas chromatogram equipped with 5973 mass selective detector (MSD). Agilent Technologies MSD ChemStation 2004 control software was used with Winterthur PYGC method with conditions as follows: pyrolysis temperature was 600°C, interface temperature to the column was 320°C, and transfer line temperature to the MSD (SCAN mode) was 300°C. A 30 m  $\times$  250  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$  film thickness HP-5MS column (5% phenyl methyl siloxane at a flow rate of 1.5 mL/minute) was used. The oven

Table 4. Elements Detected from XRF and SEM-EDS Analyses of the Discolored Cellulose Nitrate Films Removed from the Teapot and Creamer

|         | XRF                    | SEM-EDS  |
|---------|------------------------|--|
| Teapot  | <b>Ag</b> , Cu, Fe, Zn | <b>Ag</b> , Cu, Fe, Zn, C, N, O, Al, Si, S, Cl |
| Creamer | <b>Ag</b> , Cu, Fe     | <b>Ag</b> , Cu, Fe, C, N, O, Al, Si, S, Cl     |

Most strongly detected element (Ag) shown in bold font.

temperature was held at 43°C for 2 minutes, then programmed to increase at 10°C/minute to 320°C where it was held for 5 minutes for a total run time of 37 minutes.

XRF and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) analyses were performed to identify the elemental composition of any corrosion products that may have formed within or have migrated into the cellulose nitrate film. XRF analysis was performed with the ArtTAX  $\mu$ XRF spectrometer using a rhodium tube (600  $\mu$ A current, 50 kV voltage, 100 seconds live time irradiation, approximately 70–100- $\mu$ m spot size) with element detection range of potassium to uranium; spectra were interpreted using the Intax software. SEM-EDS analysis was performed on cross sections of the discolored cellulose nitrate films from the teapot and creamer. The cross sections were mounted to a carbon stub with double-sided carbon tape adhesive. Carbon paint was applied on the side and top surfaces of casting medium, without covering the cross section itself, to prevent charging. The sample was examined using the Topcon ABT-60 scanning electron microscope at an accelerating voltage of 20 kV for the electron beam, stage height of 22 mm, and sample tilt of 20°. The EDS data were collected for 10 minutes for each sample with the Bruker AXS X-flash detector 4010 and analyzed with Quantax 200/Esprit 1.8.2 software.

Elements detected are indicated in table 4 for each analysis. Silver is the major element detected in both films with minor amounts of copper and iron; zinc is detected in the film from the teapot, likely present as an impurity remaining from silver ore refining. Carbon, nitrogen, and oxygen are detected from the cellulose nitrate. Aluminum, silicon, and iron are present in the films from surface dirt, sulfur is introduced from the air (from H<sub>2</sub>S among other sources) and likely part of the corrosion products, and chlorine is present likely from fingerprint salts due to handling.

Because of its low detection limit, FTIR spectroscopy was not adequate to further analyze the corrosion products within the films. Micro-Raman spectroscopy is another technique that has been used successfully to provide reference spectra for silver corrosion products (Martina et al. 2012). In this case, it only produced peaks attributed to cellulose nitrate or the cellulose nitrate caused fluorescence oversaturation to the detector, and peaks for common silver corrosion products were not detected. Time of flight–secondary ion mass spectrometry (TOF-SIMS), a technique widely used in material sciences for the study of polymers, pharmaceuticals, and semiconductors, proved however to be an ideal technique here. This technique involves bombardment of the sample with a high energy primary ion beam that desorbs and ionizes molecules from its surface. These molecules are then characterized by mass spectrometry. Analysis was conducted using an ION-TOF TOF-SIMS IV system equipped with a bismuth source. Data were collected using the “high-current bunched” mode with a primary beam of Bi<sup>3+</sup> ions at 0.27 pA current at the target surface. Multiple 50  $\mu$ m  $\times$  50  $\mu$ m analysis spots were examined, each to the static SIMS limit beam dosage (1  $\times$  10<sup>12</sup> ions/cm<sup>2</sup>). The angle of incidence of the beam was 45°, and TOF takeoff was normal to the surface. The data were smoothed using a second-order polynomial Savitzky-Golay smoothing with a 100-channel window.

In order to interpret the data obtained, it is important to understand the two mechanisms by which corrosion products develop on uncoated historic silver objects. The first is through the reaction of the silver alloy surface with atmospheric gases, and the second is due to reaction with the inorganic and organic components found in fingerprint residues from handling. These phases include, in the case of atmospheric

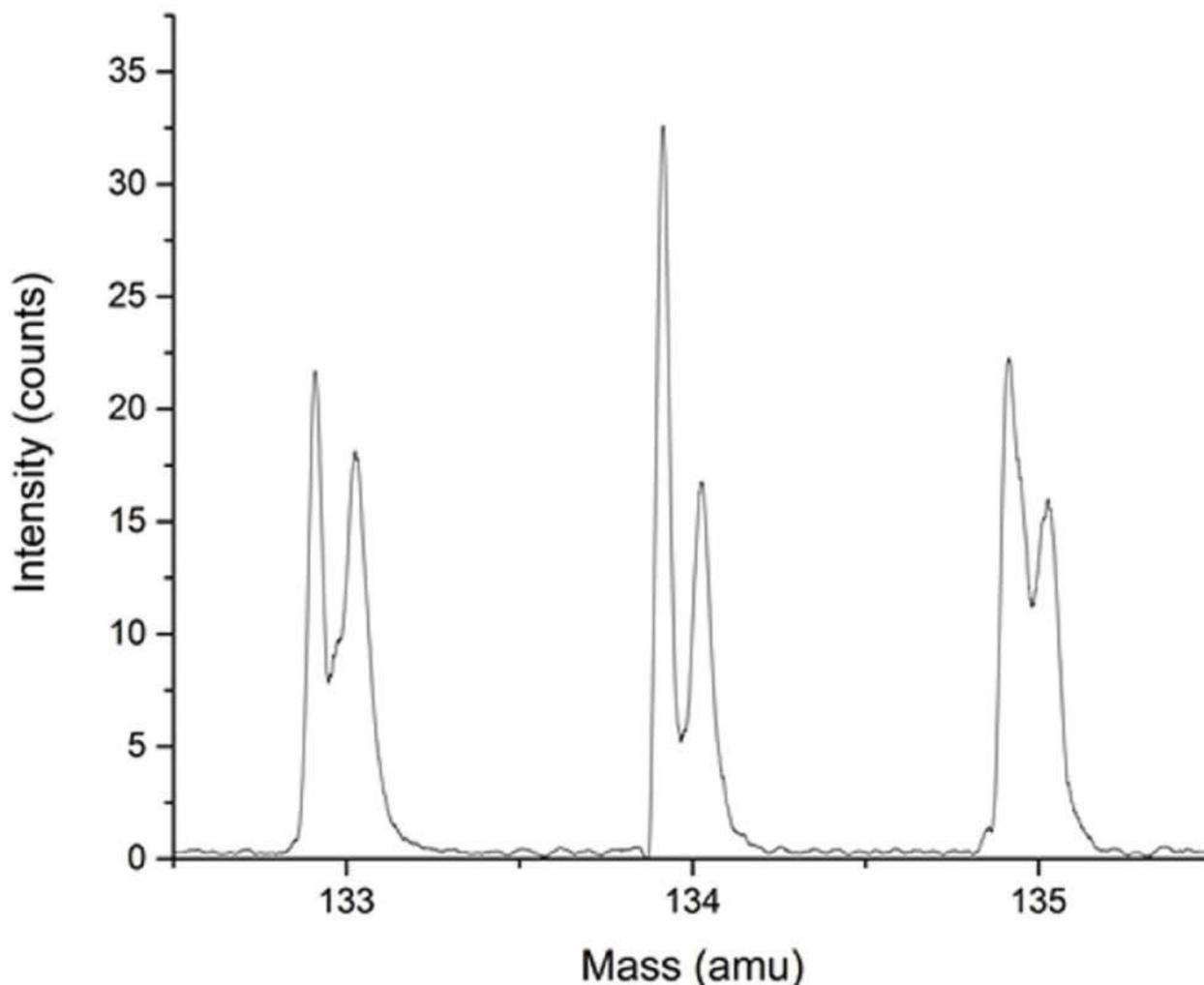


Fig. 7. TOF-SIMS mass spectrum from discolored cellulose nitrate film from teapot; peaks at 132.9 and 134.9 amu indicate the presence of silver cyanide (Courtesy of the Surface Analysis Facility, University of Delaware Department of Chemistry and Biochemistry)

gases, silver sulfides, copper sulfides, silver oxides, silver sulfates, copper oxides, silver carbonates, silver chlorides, and mixed silver-copper sulfides (Hallett et al. 2003; Dowsett et al. 2005). Corrosion due to fingerprints has been shown to produce copper oxychlorides, silver chlorides, sodium chloride deposits, and short chain fatty acid deposits (Cheel et al. 2010). TOF-SIMS analysis of the cellulose nitrate films from the teapot and creamer identified silver chlorides, silver cyanides, silver oxides, silver sulfates, and copper oxides. These can be present as corrosion products on uncoated silver, except for silver cyanide ( $\text{AgCN}$ ). It is represented by peaks at 132.9 and 134.9 amu (fig. 7). While silver cyanide is an uncommon finding on uncoated silver, it was consistently found in our study, and suggests two hypotheses for its formation: the cyanide source is either derived from cellulose nitrate degradation or more likely it originates from a previous silver cyanide-based treatment of the object. Cyanide-containing solutions were and are still commonly used in the strike bath, a process that deposits a thin layer of metal that serves as foundation for electroplating (Chamberlain and Hogaboom [1936] 1994; Mohler and Sedusky 1951; Lins 2013). They are also traditionally used as cleaning dip solutions in commercial silver shops (Strahan 1986; Drayman-Weisser 2013). These cyanide-containing cleaning solutions also deposit a thin layer of silver that hides the firescale pattern, which is often revealed later through repeated polishing of the object (Lins 2013).

Silver cyanide is itself a colorless to gray-white compound, but if mixed with the reddish cuprite also identified during the analysis, it could result in the formation of the pink to brown color observed on the creamer and teapot. Silver cyanide also darkens with exposure to light and may be mistaken for silver sulfide. As a way to further define the source of the silver cyanide, more TOF-SIMS analyses will be conducted on discolored cellulose nitrate films from museum objects that have likely never been cleaned or replated with a cyanide-containing solution.

## 5. RECOMMENDATIONS AND CONCLUSION

In conclusion, this study shows that the silver lacquering program that began at Winterthur in 1982 has been successful. Where coatings did fail, the causes were in vast majority because of application defects, and the removal of old coatings and the minimal tarnish that formed underneath was not problematic. Although there was hesitation at first about starting a new coating campaign using cellulose nitrate, observations on hundreds of objects demonstrate that it is effective at retarding tarnish formation within the open room settings at Winterthur. So far, no evidence has been found that it has enhanced tarnish or corrosion formation. Yet, it is important to emphasize how other methods using appropriate scavengers are effectively in use in the museum's gallery spaces and are preferred whenever objects with silver components can be displayed in sealed cases.

It can realistically be expected that within the museum's controlled environment, properly applied lacquer will be effective and will not visibly deteriorate for up to 25–30 years. This will be true however mostly for objects that are relatively simple, and if the lacquer application was done impeccably. This also assumes that the coating is protected from exposure to excessive ultraviolet radiation, high RH, and heat. For lacquered objects displayed in less controlled environments such as private homes, the lifetime of the lacquer will be much shorter. As the relacquering project wrapped up with 515 pieces completed, the following list of recommendations can be made for others involved in similar projects.

First, it is crucial that lacquered silver be clearly identified and properly handled. Lacquered silver objects may have a particular numbering system, for example, a specific color is used to write the accession numbers on lacquered pieces at Winterthur. Lacquer is susceptible to abrasion, particularly where there are moving parts or components that fit tightly against each other. At Winterthur, a layer of Renaissance microcrystalline wax is applied to moving parts to minimize lacquer abrasion. Shock caused by contact with a hard material, for instance, a ring on a finger, can also cause lacquer loss that will later allow local tarnishing.

Second, it cannot be emphasized enough how important it is for institutions to instigate recurring monitoring and assessments of their lacquered silver. Pieces with complex surfaces or multiple components should be assessed more frequently, possibly every 5–10 years. During the 2009 survey, it was found that the coating on the majority of these types of pieces failed within a 10 to 15 year period.

Third, specific dates for lacquer reapplication need to be set in place every time a coating is applied. Removing old cellulose nitrate lacquer is an essential component of the retreatment process, and depending on the piece, it can be quite complicated and time-consuming. The resources and time necessary to institute and maintain a silver lacquering program are significant and need to be well accounted for in short- and long-term institutional planning.

Finally, it is essential that ongoing efforts and research continue toward finding alternate coating options that will provide adequate protection against silver tarnishing. Recent and ongoing efforts at the Smithsonian Institute (Grabow et al. 2007; Grissom et al. 2013) and Walters Art Museum<sup>1</sup> (Drayman-Weisser 2013; Gates 2013) are applauded. Their results combined with observations made during this project will continue to influence decisions made at Winterthur, since a second major relacquering project for another group of over 500 silver objects lacquered in the late 1980s must be undertaken as early as 2016.

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## NOTES

1. More information on this project can be found on the Walters Art Museum website. <http://articles.thewalters.org/saving-silver/> (accessed 05/22/15)

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## SOURCES OF MATERIALS

Agateen #2B-4 Lacquer, Agateen #27 Lacquer

Agate Lacquer Tri-Nat LLC  
824 South Avenue  
Middlesex, NJ 08846  
(732) 968-1080  
Agateen #2B-4 now discontinued

Alpha Alumina, Gamma Alumina

LECO Corp.  
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St. Joseph, MI 49085  
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301 Poplar St.  
Hanover, PA 17331  
(717) 632-4261  
[www.chreed.com](http://www.chreed.com)

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