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## Thickness Measurements of Clear Coatings on Silver Objects using Fiber Optic Reflectance Spectroscopy

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### ABSTRACT

Polymer films have been used extensively to coat heritage metal objects to provide protection against atmospheric oxidation and tarnish. Coating performance is directly proportional to coating thickness, but current methods used to measure coating thickness for quality control during treatment are qualitative at best. This paper demonstrates how fiber optic reflectance spectroscopy (FORS) was used to accurately determine coating thicknesses on a number of nitrocellulose-coated silver objects at Winterthur Museum. FORS appears to be significantly more accurate than other common methods used to measure film thickness, such as magnetic/eddy current techniques, but is limited to transparent or semi-transparent coatings. FORS is a simple, accurate method for measuring the thickness of protective coatings on a wide range of cultural heritage metal objects.

### RÉSUMÉ

Les films de polymères ont été fréquemment utilisés comme recouvrement pour les objets métalliques patrimoniaux, afin de les protéger de l'oxydation et de la ternissure. L'efficacité de cette protection est directement proportionnelle à son épaisseur, mais les approches habituellement utilisées pour le contrôle de la qualité pendant le traitement ne sont, au mieux, que qualitatives. Cet article explique comment la spectroscopie de réflectance par fibre optique (FORS) a été utilisée pour évaluer l'épaisseur de la protection de nitrocellulose appliquée sur des objets en argent au Winterthur Museum. Cette approche semble beaucoup plus précise que d'autres pour mesurer l'épaisseur du film de protection, tel que la technique de courants magnétiques de Foucault, mais elle est limitée aux revêtements transparents ou semi-transparentes. La spectroscopie de réflectance par fibre optique est une approche simple et précise pour l'évaluation de l'épaisseur des revêtements de protection sur une vaste gamme d'objets patrimoniaux métalliques. Traduit par André Bergeron.

### RESUMO

Filmes de polímeros têm sido usados extensivamente para revestir objetos metálicos patrimoniais para fornecer proteção contra oxidação atmosférica e manchas. O desempenho do revestimento é diretamente proporcional à espessura do revestimento, mas os métodos atuais usados para medir a espessura do revestimento para controle de qualidade durante o tratamento são qualitativos, na melhor das hipóteses. Este artigo demonstra como a espectroscopia de refletância por fibra óptica (FORS) foi usada para determinar espessuras de revestimentos em uma série de objetos de prata revestidos de nitrocelulose no *Winterthur Museum* (Museu Winterthur). O FORS parece ser significativamente mais preciso do que outros métodos comuns usados para medir a espessura do filme, como técnicas magnéticas/de correntes parasitas, mas é limitado a revestimentos transparentes ou semitransparentes. FORS é um método simples e preciso para medir a espessura dos revestimentos de proteção em uma ampla gama de objetos metálicos patrimoniais. Traduzido por Carla Coelho.

### RESUMEN

Las películas poliméricas se han utilizado ampliamente para revestir objetos patrimoniales de metal para brindar protección contra la oxidación atmosférica y el deslustre. La efectividad del revestimiento es directamente proporcional a su espesor, pero los métodos actuales utilizados para medir dicho espesor con el fin de realizar un control de calidad durante el tratamiento son, en el mejor de los casos, cualitativos. Este artículo demuestra cómo se utilizó la espectroscopia de reflectancia de fibra óptica (FORS) para determinar con precisión los espesores de recubrimientos de nitrato de celulosa en varios objetos de plata del Museo de Winterthur. FORS parece ser significativamente más preciso que otros métodos comunes utilizados para medir el espesor de la película, como las técnicas de corrientes magnéticas / de Foucault, pero se limita a

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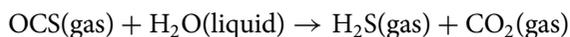
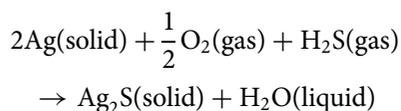
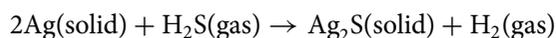
### KEYWORDS

Coating thickness; fiber optic reflectance spectroscopy (FORS); silver coatings; protective coatings; nitrocellulose; Agateen; metal conservation

revestimientos transparentes o semitransparentes. FORS es un método simple y preciso para medir el espesor de los revestimientos protectores en una amplia gama de objetos metálicos del patrimonio cultural. Traducción: Amparo Rueda; revisión: Silvia Centeno y Diana Díaz.

## 1. Introduction

Silver objects in museum environments are susceptible to corrosion through the formation of tarnish, which significantly impacts their appearance. The formation of tarnish is due to chemical reactions between silver (Ag) and atmospheric pollutants such as hydrogen sulfide or carbonyl sulfide (Ankersmit, Tennent, and Watts 2005; Franey, Kammlott, and Graedel 1985; Graedel et al. 1985; Lilienfeld and White 1930; Rice et al. 1981; Saleh, Xu, and Sanvito 2019; Volpe and Peterson 1989) which, aided by the presence of water and perhaps oxygen, react to produce tarnish (silver sulfide, Ag<sub>2</sub>S) via the following possible chemical reactions:



Typical atmospheric concentrations of H<sub>2</sub>S and OCS are very low, on the order of parts-per-trillion to parts-per-billion-volume (Pope, Gibbens, and Moss 1968; Graedel, Kammlott, and Franey 1981; Rice et al. 1981). Nevertheless, bare silver will develop a 5 nm thick Ag<sub>2</sub>S layer in a matter of days to months at these low atmospheric concentrations (Graedel, Kammlott, and Franey 1981). Thus, tarnish formation is a serious issue in museum collections such as those at Winterthur Museum, Garden & Library in Delaware, where the silver objects are on open display. Since abrasive polishing to remove tarnish also removes silver (Selwyn 1990; Costa 2001), frequent polishing is not only time intensive, but can also cause damage, especially if fine details or thin platings are present (Polidori and Rovito 2018; Grayburn and Wagner 2019). Implementing environmental controls to eliminate offending gases is difficult, since tarnishing gases are present at such low concentrations and are not only present in air external to the museum, but can be generated by other materials located within the museum itself (Reedy et al. 1999; Sease et al. 1997). Short of storing silver objects in hermetic display cases, polymer coatings have been found to provide an effective method to slow the tarnishing process to rates that are much slower than for uncoated silver (Heller 1983; Pouliot et al. 2013).

For the case of silver objects or silver-plated objects, nitrocellulose (Figure 1) has been the polymer of choice to reduce tarnish formation to acceptable levels over significant periods of time, on the order of 10–30 years (Selwitz 1988; Pouliot et al. 2013). This protection is due to the presumed low permeability of nitrocellulose coatings to gases such as hydrogen sulfide or carbonyl sulfide (De Witte 1973; Reedy et al. 1999).

The permeability  $P$  of nitrocellulose films to small molecules such as H<sub>2</sub>S is determined by two parameters: the diffusivity  $D$  and the solubility coefficient  $S$  of the molecules in the polymer (Heilman et al. 1956; Crank 1998, chapter 4; DeLassus 2002),

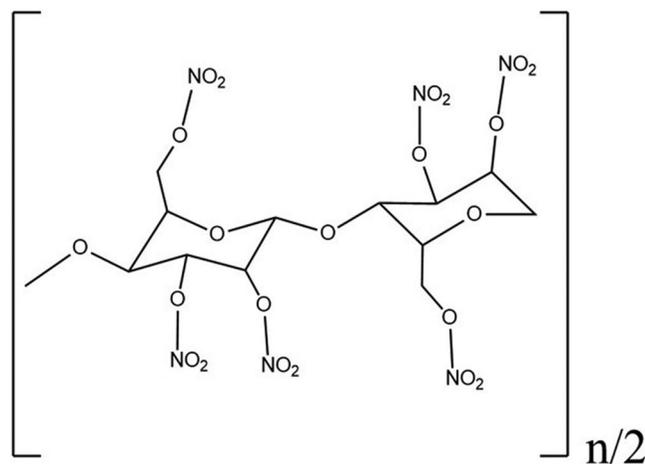
$$P = D \times S. \quad (1)$$

Diffusivity determines how fast the molecules diffuse through the polymer film, while the solubility coefficient determines the equilibrium concentration of the molecules in the film.<sup>1</sup>

The transport of small molecules through polymer films can be described by a variation of Fick's first law (Heilman et al. 1956; Stern and Frisch 1981; Neogi 1996; DeLassus 2002; Feldman 2002; Stern and Fried 2007),

$$\Delta M / \Delta t = PA\Delta p / d \quad (2)$$

where  $\Delta M$  is the mass of molecules transported through an area  $A$  of the film in time  $\Delta t$ ;  $P$  is the permeability of the



**Figure 1.** Chemical structure of nitrocellulose with the maximum degree of nitrate substitution  $DS = 3$ . Commercial nitrocellulose lacquers have lower  $DS$  values, on the order of 2.3, to render them non-explosive but still maintain solubility in organic solvents.

film given by equation (1);  $\Delta p$  is the difference in pressure or concentration of the molecule across the film; and  $d$  is the film thickness (so  $\Delta p/d$  is then the pressure or concentration gradient). For a given polymer and permeant, such as nitrocellulose and  $H_2S$ , the only parameter in equation (2) that can be readily adjusted to control transport of the molecule through the polymer film is the film thickness  $d$ . For that reason, accurate measurements of film thickness and uniformity are needed to support the design and implementation of effective coating techniques for tarnish prevention.

At Winterthur, conservators apply nitrocellulose (Agateen Lacquer #27) either by brush application (1:1 lacquer to Agateen Thinner #1) or by spray application (1:2 lacquer to thinner). Winterthur has been employing this approach to its silver collection for over 30 years (Pouliot et al. 2013), and it recently completed the second phase of a multi-yearlong project funded by the Institute of Museum and Library Services (IMLS) to recoat hundreds of silver pieces in the collection. Over 1,000 silver pieces were re-coated between 2015 and 2019. These intensive projects have allowed the conservators and scientists to closely evaluate their methods and seek better strategies to lengthen the lifetimes of coatings and limit cases of lacquer failure (see Selwitz 1988 and Ziegler et al. 2014 for discussions of nitrocellulose stability).

The Winterthur protocol regularly employs three methods for evaluating the thickness and thickness uniformity for a freshly applied coating. First, the coating is examined under normal visible light<sup>2</sup> against a white background to help make noticeable any areas of iridescence in the coating. This often indicates that the coating may be too thin in that region, or not well-adhered to the silver surface, such as when there is a greasy residue not adequately removed prior to coating. In addition, it is a sign that tarnish may still be able to form under this thinned area of the coating. A second evaluation method employs a conductivity tester on the object. Such a tester indicates conductivity where there is no film (lacunae) or the film is too thin (often with visible iridescence); conversely, no indication from the meter indicates a film thick enough to prevent conductivity. The conductivity tester is often used to confirm observed iridescence or areas with suspected lacunae. Finally, starting in 2016, Winterthur conservators began adding a UV-fluorescent dye, coumarin 6, to their lacquer mixtures to visualize coating integrity; this produces a bright yellow-green auto-fluorescence under long-wave UV and shows lacunae or areas that may be too thin, even if they were not exhibiting iridescence in normal visible light.

While these methods have improved the ability to empirically assess a freshly applied coating, they do have significant limitations. Iridescence can be difficult

to see, especially on silver with intricate surfaces; and although it is a fairly reliable indicator, a coating that is “too thin” (i.e., will allow passage of enough atmospheric sulfur to cause visible tarnish) may not necessarily exhibit detectable iridescence. The conductivity tester also has drawbacks, as each end of the circuit must be in contact with uncoated metal within one object, and these areas can be difficult to identify or access. Finally, though the UV-fluorescent dye has greatly improved coating evaluation capabilities, it can still be difficult to tell how thin is “too thin,” even if the area does not light up when checked with a conductivity tester. All this to say, our current methods of evaluating coating thickness are subjective.

Measurements of the protective coating thicknesses on heritage metal objects are not commonplace. Thicknesses have occasionally been measured using magnetic/eddy current techniques developed for measurements of coatings that are generally considerably greater than the typical thicknesses expected for protective coatings on heritage metal objects. For example, in one study of coatings on brass coupons it was found that the eddy current technique was not accurate for films less than approximately 20  $\mu m$  thick, requiring a complex calibration procedure that still provided uncertain accuracy (Heginbotham et al. 2014). In a different study of the efficacies of various coatings to protect silver from  $H_2S$ , an eddy current thickness gauge was used to determine the coating thicknesses on a series of flat silver coupons (Grissom et al. 2013). The authors highlighted the importance of accurate thickness measurements for such laboratory studies, but also recognized the difficulty of applying eddy current thickness gauges to actual artifact surfaces where the relatively large, flat areas needed ( $\sim 1 \text{ cm}^2$ ) for each measurement are not often present. Further, the eddy current thickness measurements were found to have poor reproducibility, in particular for Agateen coatings less than 13  $\mu m$  thick, and especially for coatings below 5  $\mu m$  thick. Most of the Agateen coatings we measured in this study have thicknesses that are less than 13  $\mu m$ , and many have regions that are less than 5  $\mu m$  thick.

In a recent study, x-ray fluorescence spectroscopy (XRF) was used to determine the thicknesses of organic coatings on metal objects (Porcinai and Ferretti 2018). This technique relies upon the presence of measurable differential absorption between two x-ray fluorescence spectral lines from the substrate, which will be attenuated to differing degrees as they pass through a polymer coating. After calibration, film thicknesses were measured for a series of test films to evaluate the accuracy of the method. For films more than 20  $\mu m$  thick, the accuracy was good, on the order of a few percent. However, for

films below 10  $\mu\text{m}$  thick, the accuracy was on the order of 10% or greater.

Thus, there is a clear need for a simple, rapid technique to measure film thicknesses on cultural heritage objects such as silver. Since the nitrocellulose films used to protect silver objects are transparent, the use of optical techniques to determine film thicknesses is potentially a more accurate method than eddy current or XRF techniques. For that reason, Winterthur conservators and scientists evaluated fiber optic reflectance spectroscopy (FORS) as a method to determine nitrocellulose coating thicknesses. If successful, FORS could be used to correlate coating thickness with the observed timescale for coating failure and lead to better optimized coatings. It would provide an additional quantitative evaluation method beyond typical visual clues of a flawed coating, such as iridescence. We used FORS to evaluate film thicknesses for a number of silver objects with old or new nitrocellulose coatings. Based on our results, we expect this technique can be readily applied to silver or other metal objects protected by a wide range of transparent polymer coatings, including acrylics.

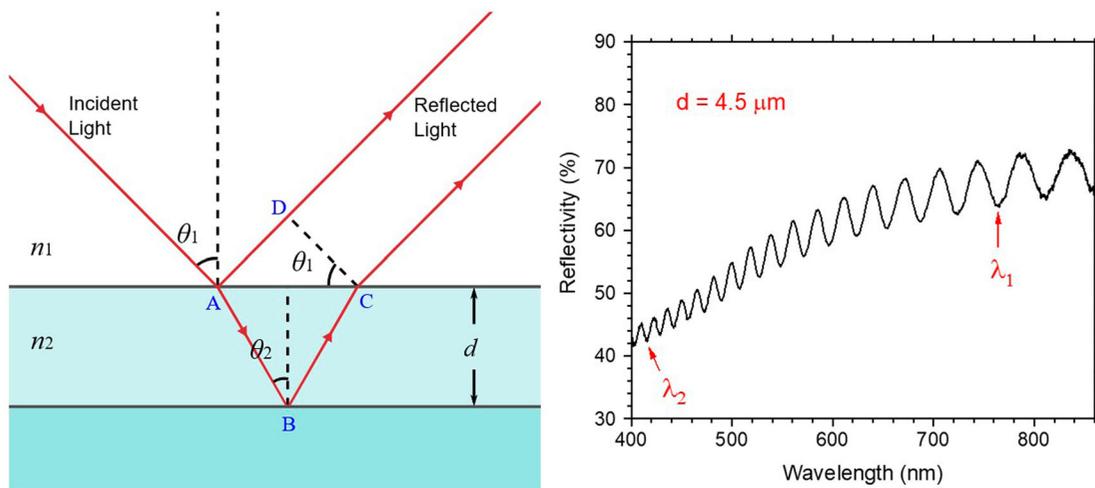
## 2. Materials and methods

### 2.1. Theory

A schematic of the FORS film thickness measurement appears in Figure 2 (left). If white light is incident on the nitrocellulose/silver surface from the fiber optic, a

small amount (approximately 4%) is reflected at the air/nitrocellulose interface. The remainder of the light is transmitted through the film, where most of it is then reflected from the nitrocellulose/silver interface before traveling through the film again and then exiting the film at the top surface. The two reflected light beams travel paths of different lengths before they undergo constructive or destructive interference upon recombining as they leave the film. The reflected light, collected by a fiber optic probe, is then dispersed by a small UV-vis spectrometer, yielding a typical spectrum as shown in Figure 2 (right). The periodic oscillation of the reflected light intensity versus wavelength is due to the interference of the reflected light beams, and the distance between oscillations is inversely proportional to the coating thickness.

The interference oscillations (hereafter referred to as interference fringes, or more simply, fringes) shown in Figure 2 (right) can be analyzed to determine the film thickness, as described in Born and Wolf 1999; Hecht and Zajac 1979; Fowles 1989; Heavens 1991. There is an angular phase shift of  $\pi$  (equal to a  $\lambda/2$  shift of distance) when light is incident from a medium of lower refractive index (in our case, air) to one of higher refractive index (nitrocellulose), i.e. at the air/nitrocellulose interface. However, negligible phase shift occurs when the reflection occurs at the nitrocellulose/silver interface since silver has a lower refractive index (see for example Jiang, Pillai, and Green 2015 and references therein) than



**Figure 2.** (left) Schematic of FORS measurement of thickness of a thin film on a silver surface.  $n_1$  and  $n_2$  are the refractive indices of air ( $n_1 = 1$ ) and nitrocellulose ( $n_2 = 1.51$ ), and  $d$  is the film thickness (Credit: Nicoguaro under CC BY 4.0). (right) FORS spectrum of a nitrocellulose coating on a silver kettle (Winterthur Museum, 1958.1965a-d). The intensity oscillations are due to interference of the light reflected from the top surface of the coating (ray A-D) with the light reflected from the bottom surface (ray A-B-C). The oscillations can be analyzed to determine the coating thickness according to Eq. 5. In applying Eq. 5 we selected the two reflectivity minima shown, far apart to minimize the impact of small errors associated with determining the wavelength value at each minimum. We used values of  $n = 1.51$ ,  $\Delta m = 15$ , and the wavelengths shown in the figure ( $\lambda_1 = 764.8 \text{ nm}$  and  $\lambda_2 = 415.5 \text{ nm}$ ), in Eq. 5 to calculate the coating thickness  $d = 4.5 \mu\text{m}$ .

nitrocellulose. As described in Heavens 1991, this situation leads to minima in the reflected intensity at wavelengths  $\lambda_1$  and  $\lambda_2$  that are directly related to film thickness  $d$  according to equation (3):

$$2 n_2 d \cos\theta_2 = \frac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)}, \quad (3)$$

where  $\theta_2$  is the angle between the light propagation direction and the vector perpendicular to the nitrocellulose/silver interface, as shown in Figure 2 (left). More specifically, equation (3) applies to minima that are adjacent in wavelength. If instead we select minima that are separated by  $\Delta m$  interference fringes, a more accurate estimate of film thickness is obtained since the larger fringe separation reduces the impact of inaccuracies in the determination of  $\lambda_1$  and  $\lambda_2$ . However, in this case, an additional factor of  $\Delta m$  must be introduced in equation (3), leading to

$$2 n_2 d \cos\theta_2 = \Delta m \frac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)}. \quad (4)$$

For light that is incident perpendicular to the film surface ( $\theta_2 = 0$ , so  $\cos\theta_2 = 1$ ), the film thickness  $d$  is given by

$$d = \frac{\Delta m}{2n_2} \frac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)}. \quad (5)$$

We used equation (5) to determine the thicknesses of nitrocellulose films on silver objects. For the refractive index of nitrocellulose, we used  $n_2 = 1.51$ . This is roughly the average value for the refractive index of nitrocellulose determined by ellipsometry over the 400–760 nm wavelength range (Cai et al. 2013).

See Supplementary Material 1 and 2 for additional discussion and for thickness calibration measurements on several thin films supplied as thickness standards by Filmetrics.

## 2.2. FORS Instrumentation

Data was collected using a portable Ocean Optics USB2000 FORS spectrometer in the UV-visible (400–860 nm) spectral range and an Ocean Optics near-IR (NIR) Quest 2000 spectrometer for the 900–2200 nm spectral range. A tungsten-halogen light source was used for all measurements.

A reference spectrum was first collected from a bare silver mirror (Edmund Optics), which was assumed to have 100% reflectivity, followed by a measurement of the silver object with a nitrocellulose coating. The ratio of the two measurements ( $(R_{\text{object}}/R_{\text{ref}}) \times 100 = \% \text{ reflectivity}$ ) was recorded. The minimum integration time of 3 ms was used due to the high intensity of the light reflected from the silver reference mirror and most silver objects; ten

scans were averaged to obtain better quality spectra. However, averaging time was intentionally limited to about one second by the need to position the fiber probe and manually hold it steady during each measurement. The distance between the end of the optical fiber and the silver mirror or silver object surface was adjusted and maintained using a small one-hole rubber stopper that could be placed over the end of the fiber, then positioned in gentle contact with the surface so that the reflected signal was maximized but not saturated, as indicated by the spectrometer software. Thus it was necessary to maintain the orientation of the fiber with respect to the object surface but the distance was fixed by the stopper.

See Appendix for additional discussion and images of the FORS instrumentation and setup.

## 3. Results

FORS was used to measure the thickness of a variety of coatings on 32 silver and silver plate objects from the Winterthur collection (Table 1).

Of these 32 coated objects tested with FORS, all but three are coated with nitrocellulose. The thickness variations shown by the FORS measurements of the three Paraloid B-48N-coated objects are generally much higher than those collected from nitrocellulose-coated surfaces. All three acrylic coatings were achieved through spray application. Whether this represents difficulty achieving coating thickness uniformity by spray application, or simply that the viscosity of the Paraloid B-48N lacquer was not optimized for spray application is not known.

Just over half the coatings tested displayed areas of iridescence. Those that did display iridescence had an average coating thickness between 0.69 and 8  $\mu\text{m}$ ; those that did not had average thicknesses in a slightly narrower range of 2.5–6.9  $\mu\text{m}$ . However, the median thickness for coatings displaying iridescence is thinner (3.6  $\mu\text{m}$ ) compared to those coatings that do not (4.75  $\mu\text{m}$ ). This small margin confirms the aforementioned difficulty of objectively determining coating thickness by visual observation of iridescence during treatment. However, this statement is based on coating thickness averages across an entire object (only part of which may be displaying iridescence). In Case Study 2 and Supplementary Material 3, we examine coating thicknesses in several local areas of iridescence on an object.

Looking at the dataset in Table 1, we can make some correlations between date of application and coating thickness. Coatings applied most recently (<1 year) range from 2.5–5.3  $\mu\text{m}$ . Coatings applied 19–22 years ago have a similar thickness range: 2.7–6  $\mu\text{m}$ . The oldest campaigns (28–35 years ago) have the broadest range of average thicknesses: 0.7–13.5  $\mu\text{m}$ .

**Table 1.** FORS measurements of nitrocellulose and three Paraloid B-48N coating thicknesses on silver or silver plate objects, sorted first by coating material and method (brush or spray), and second by coating age when measured (oldest to youngest). Table entries with a blue background are Paraloid B-48N; all others are either Agateen #27 or of unknown composition. However, where the coating material is unknown, it is most likely Agateen Lacquer #27 or another nitrocellulose formulation. Table entries with a gray background are Agateen #27 applied by spraying, all others were applied by brushing.

Object	Metal(s)	Coating material and method	Coating age when measured	Iridescence observed?	Number of FORS measurement sites	Average coating thickness and standard deviation ( $\mu\text{m}$ )
Fish server <i>1954.0079.051</i>	Nickel silver	Agateen Lacquer #27, likely brushed	35 years	Yes	30	$3.2 \pm 0.9$
Baby feeder <i>1982.0313</i>	Silver	Agateen Lacquer #27, likely brushed	34 years	No	5	$5.4 \pm 2.1$
Oil lamp <i>1964.1206a-c</i>	Silverplate (fused plate silver on copper)	Agateen Lacquer #27, likely brushed	32 years	No	58	$3.2 \pm 1.2$
Dish warmer <i>1987.0020a-c</i>	Silver or silver plate	Agateen Lacquer #27, likely brushed	32 years	No	37	$6.9 \pm 2.4$
Needlework tool <i>1955.0136.079</i>	Silver	Agateen Lacquer #27, likely brushed	31 years	Yes	6	$1.4 \pm 0.5$
Case with bottle <i>1975.0016a</i>	Silver	Agateen Lacquer #27, brushed	31 years	Yes	38	$4.0 \pm 2.0$
Argand lamp <i>1959.1600</i>	Silverplate (fused plate silver on copper)	Agateen Lacquer #27, likely brushed	21 years	Yes	40	$2.8 \pm 2.0$
Candlestick <i>1971.1526.001ab</i>	Silverplate (fused plate silver on copper)	Agateen Lacquer #27, brushed	20 years	Yes	10	$4.5 \pm 2.6$
Candlestick <i>1971.1526.002ab</i>	Silverplate (fused plate silver on copper)	Agateen Lacquer #27, brushed	20 years	Yes	30	$6.0 \pm 2.8$
Tankard <i>1978.0157</i>	Silver	Agateen Lacquer #27, brushed	19 years	Yes	33	$3.0 \pm 1.4$
Tea kettle <i>1958.1965a-d</i>	Silverplate (electroplate silver on copper)	Agateen Lacquer #27, brushed	1 year	No	41	$3.8 \pm 2.0$
Buckle <i>1977.0169.001</i>	Silver	Agateen Lacquer #27, brushed	< 1 year	No	7	$4.6 \pm 3.1$
Buckle <i>1977.0169.002</i>	Silver	Agateen Lacquer #27, brushed	< 1 year	No	7	$5.3 \pm 4.0$
Argand lamp <i>1961.1410.001</i>	Silverplate (fused plate silver on copper)	Agateen Lacquer #27, sprayed	21 years	Yes	81	$2.7 \pm 1.5$
Tray <i>1983.0108.001</i>	Silver	Agateen Lacquer #27, sprayed	6 years	Yes	12 (near-IR); 17 (UV-vis)	$4.0 \pm 1.7$ ; $3.6 \pm 0.9$
Charger <i>1966.1053</i>	Silver	Agateen Lacquer #27, sprayed	< 1 year	No	50	$2.5 \pm 0.8$
Tray <i>1983.0108.001</i>	Silver	Agateen Lacquer #27, sprayed	<1 year	No	80	$3.5 \pm 1.4$
Spectacles <i>1958.2971</i>	Silver	Agateen Lacquer #2B-4, likely brushed	30 years	No	6	$5.8 \pm 3.9$
Spectacles <i>1959.2915</i>	Silver	Agateen Lacquer #2B-4, likely brushed	30 years	No	5	$4.8 \pm 2.3$
Watch case <i>1964.2142a</i>	Silver	Agateen Lacquer #2B-4, likely brushed	30 years	Yes	14	$2.2 \pm 0.8$
Beaker <i>1977.0131</i>	Silver	Agateen Lacquer #2B-4, likely brushed	28 years	Yes	20	$7.1 \pm 2.6$
Miniature flatware <i>1959.0996b-s</i>	Silver	Unknown*	32 years (minimum)	Yes	54	$0.69 \pm 0.24$

(Continued)

**Table 1.** Continued.

Object	Metal(s)	Coating material and method	Coating age when measured	Iridescence observed?	Number of FORS measurement sites	Average coating thickness and standard deviation ( $\mu\text{m}$ )
Needlework tool 1953.0165.003	Silver	Unknown*	30 years	No	5	$5.0 \pm 4.2$
Needlework tool 1959.0556a	Silver	Unknown*	30 years	Yes	6	$6.8 \pm 2.3$
Needlework tool 1959.0557	Silver	Unknown*	30 years	Yes	6	$8.0 \pm 7.8$
Needlework tool 1959.0560a	Silver	Unknown*	30 years	Yes	5	$6.9 \pm 2.2$
Tea canister 1970.1028	Silver	Unknown,* likely brushed	30 years	Yes	66	$2.7 \pm 1.0$
Chatelaine 1959.0153	Silver	Unknown*	22 years (minimum)	No	6	$3.1 \pm 1.4$
Pitcher 2017.0017.004a	Gold-plated silver (electroplate gold on silver)	Nitrocellulose (confirmed by FTIR)	Unknown	No	5 (near-IR); 5 (UV-vis) (only 4 used)	$4.7 \pm 0.6$ ; $5.0 \pm 1.2$
Coffee Pot 1983.0108.002	Silver	Paraloid B-48N, sprayed	24 years	No	10 (near-IR); 10 (UV-vis)	$6.0 \pm 4.9$ ; $5.2 \pm 3.5$
Cream Pot 1983.0108.003	Silver	Paraloid B-48N, sprayed	24 years	No	10 (near-IR); 4 (UV-vis)	$9.2 \pm 6.4$ ; $7.8 \pm 1.7$
Sugar Bowl 1983.0108.004	Silver	Paraloid B-48N, sprayed	24 years	No	5	$13.5 \pm 8.9$

The average thicknesses for brushed and sprayed Agateen #27 coatings were calculated from the values given in Table 1. The average thickness of the two types of coatings is effectively the same, within one standard deviation, although it was found that on average, spray-applied nitrocellulose coatings were slightly thinner ( $3.1 \mu\text{m}$ ) than brush-applied coatings ( $4.0 \mu\text{m}$ ). This result suggests that the two techniques will provide similar levels of protection and selecting one or the other can be dictated by the needs or limitations of the object. Of course, it is also important to optimize the lacquer formulation for each technique to enable similar results for both methods.

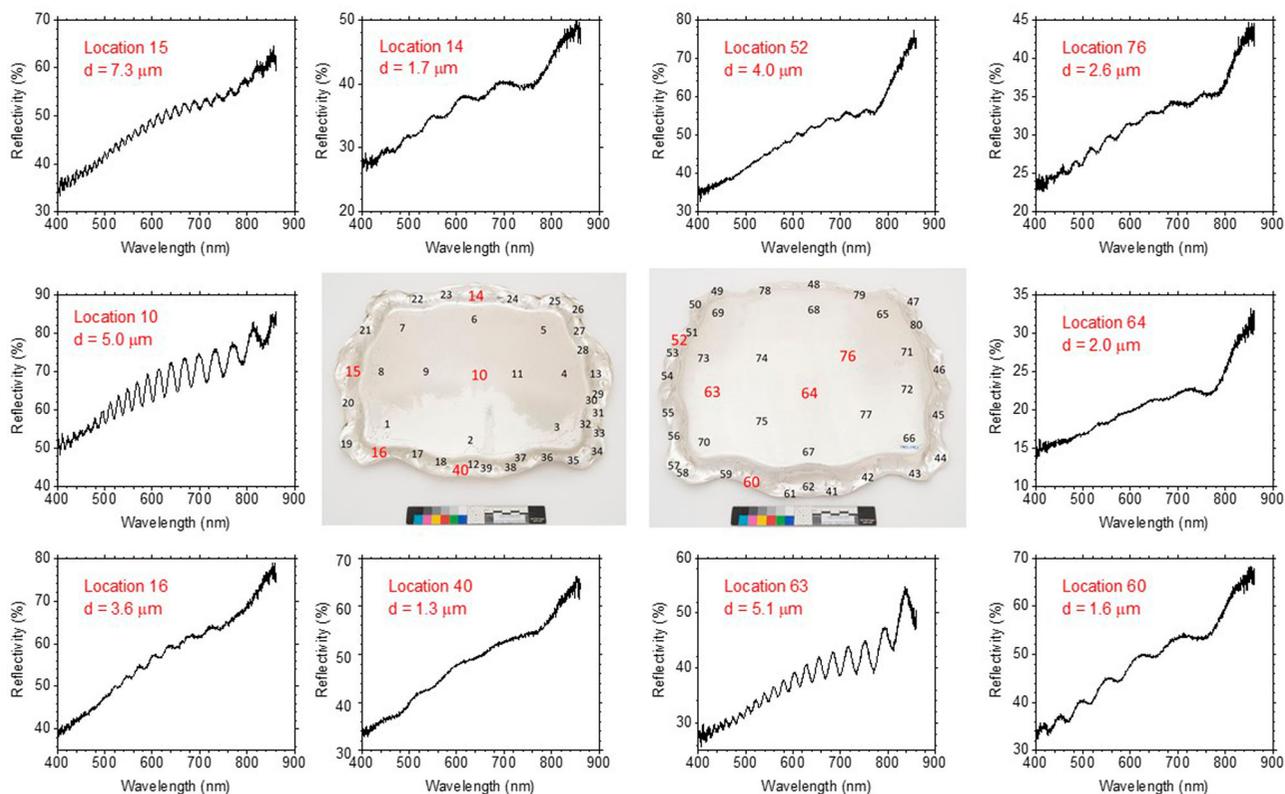
The following two case studies more closely examine the results from two objects listed in Table 1.

**Case study 1: Thickness measurements of a new nitrocellulose coating on silver tray 1983.0108.001**

This tray (Figure 3) is one of a four-piece coffee set that was made in 1903 by the Gorham Manufacturing Company. Though the tray was recently coated in 2013 with Agateen #27, the multiple drips, lacunae, and visible iridescence throughout made it a candidate for re-coating. After removing the old coating with pressurized steam and lightly polishing the surface, the tray was spray-lacquered with 1:2 Agateen Lacquer #27:Agateen Thinner #1 dosed with coumarin 6 UV-fluorescent dye. After two lacquer applications, the coating still exhibited visible iridescence, indicating that the lacquer was still too thin. A third layer of

the Agateen was spray-applied. After lacquering, the tray was examined under long-wave UV. A few thin areas in the coating were observed on the outer edges. These spots were touched up by brush-applying a 1:1 mixture of Agateen Lacquer #27 and Agateen Thinner #1. It is possible that areas touched up with a brush have a thicker coating than the rest of the object.

Eighty FORS measurements were taken from various points on the tray, both on the large flat surfaces and on the engraved edges; selected raw data and calculated thicknesses are shown in Figure 3. Figure 4 shows the values and distribution of thicknesses for all points on the tray. The average film thickness is  $3.5 \pm 1.4 \mu\text{m}$ . The thickest film was measured at position 30 at the tray edge where a touch-up had been later brush applied. Overall, some of the thickest areas of coating do correlate with areas of strongest UV fluorescence (Figure 5) on the inner edge of the tray (positions 12–40). However, the fluorescence intensities in the image will reflect not only the local coumarin areal densities (coumarin molecules/cm<sup>2</sup>, determined primarily by the local film thickness), but also by how uniform the intensity of the UV excitation is over the imaged area. We have not corrected the fluorescence image for this intensity distribution but believe the image in Figure 5 provides at least a rough indication of the distribution of coating thickness. We plan to test improved arrangements to collect coumarin 6 fluorescence images.



**Figure 3.** FORS measurement locations for the top (left) and underside (right) surfaces of a silver tray (1983.0108.001) with a new Agateen #27 coating applied by spraying with brush touch-up on the edges. Locations where the FORS spectra shown were collected are labeled in red in the photographs. The locations labeled in black were also measured and all the data are summarized in Table 1 and Figure 4.

### Case study 2: Iridescence from thin films: an old coating on tea canister 1970.1028

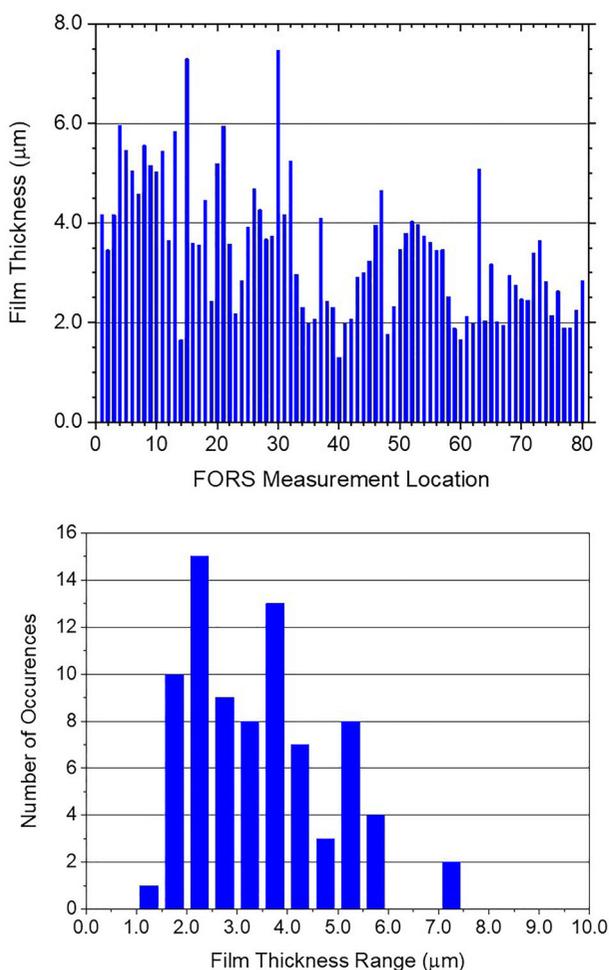
The tea canister (Figure 6) was made between 1906 and 1925 for retail in New York City but possibly manufactured in England. It is attributed to Philip Oriel and Arthur S. Vernay, both of whom are listed as manufacturers and sellers. There was no previous treatment record on file for the tea canister; however, “\*5/89” was written in blue acrylic paint on the underside of the canister, a Winterthur practice that indicates it was coated in May 1989. Since there was no other record of previous treatment, the coating material was not confirmed. However, due to the fact that the coating was easily removed with pressurized steam, it is likely that the coating applied in 1989 was Agateen #27. This is also consistent with historical approaches to silver lacquering at Winterthur.

In order to determine the actual film thicknesses of regions exhibiting iridescence on silver objects, a prominent example of iridescence on the tea canister was chosen for measurement (see also Supplementary Material 3 for more photographs of iridescence for this object). A series of 66 FORS measurements were made, 12 of which lay along the line shown in Figure 6. The results, plotted as a histogram in Figure 7, show that the

iridescence is associated with a relatively thin coating, from 1.5–3.5  $\mu\text{m}$  thick with an average thickness of  $2.3 \pm 0.6 \mu\text{m}$ . The average coating thickness for all 66 measurements is  $2.7 \pm 1.0 \mu\text{m}$ , one of the thinner coatings we encountered. It is not surprising that these thinner coatings are associated with iridescence and coating failure. The photos of this object taken before and after treatment highlight the presence of an overall yellow-tan discoloration before treatment, likely due to formation of a thin layer of tarnish beneath the coating (SM (in online version)). In addition, localized regions of darker tarnish, presumably thicker than the yellow-tan regions, are visible in SM (in online version). This is likely due to a higher prevalence of defects such as pinholes or cracks in thin regions over surface topography, as well as to the overall increased permeability to sulfur molecules of thinner films.

## 4. Discussion

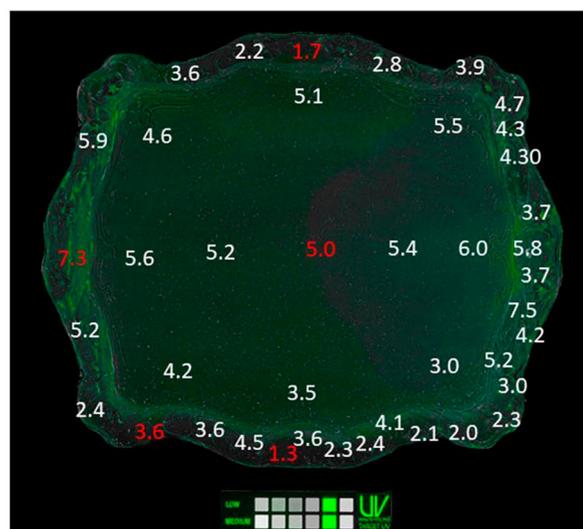
Nitrocellulose films on silver objects have prevented significant tarnish formation over periods of 10–30 years (Heller 1983; Pouliot et al. 2013). These timescales are long enough that, together with our accurate thickness measurements, we can conclude that diffusion of sulfur



**Figure 4.** (top) Agateen film thickness values for the top (locations 1–40) and underside (locations 41–80) surfaces of a silver tray (1983.0108.001) measured for the 80 locations indicated on the photograph in Figure 3. (bottom) Distribution of film thickness values.

compounds through the films is clearly not the rate-limiting step in tarnish formation.<sup>3</sup> As shown by equations (1) and (2), the permeability of nitrocellulose to H<sub>2</sub>S or OCS is the product of the diffusion constant and the solubility coefficient for those gases in nitrocellulose. To our knowledge, there are no direct measurements of permeability, diffusion, or solubility coefficients for hydrogen sulfide or carbonyl sulfide in nitrocellulose, but such measurements would clearly be very useful for better understanding how nitrocellulose inhibits tarnish formation.

It is also possible, if water plays a significant role in the formation of tarnish, as suggested by Lilienfeld and White 1930; Graedel et al. 1985; and Franey, Kammlott, and Graedel 1985, that a low water permeability through nitrocellulose is a second important factor to suppress tarnish formation. However, a measurement of H<sub>2</sub>O permeability through nitrocellulose (Hsieh 1963) yielded an

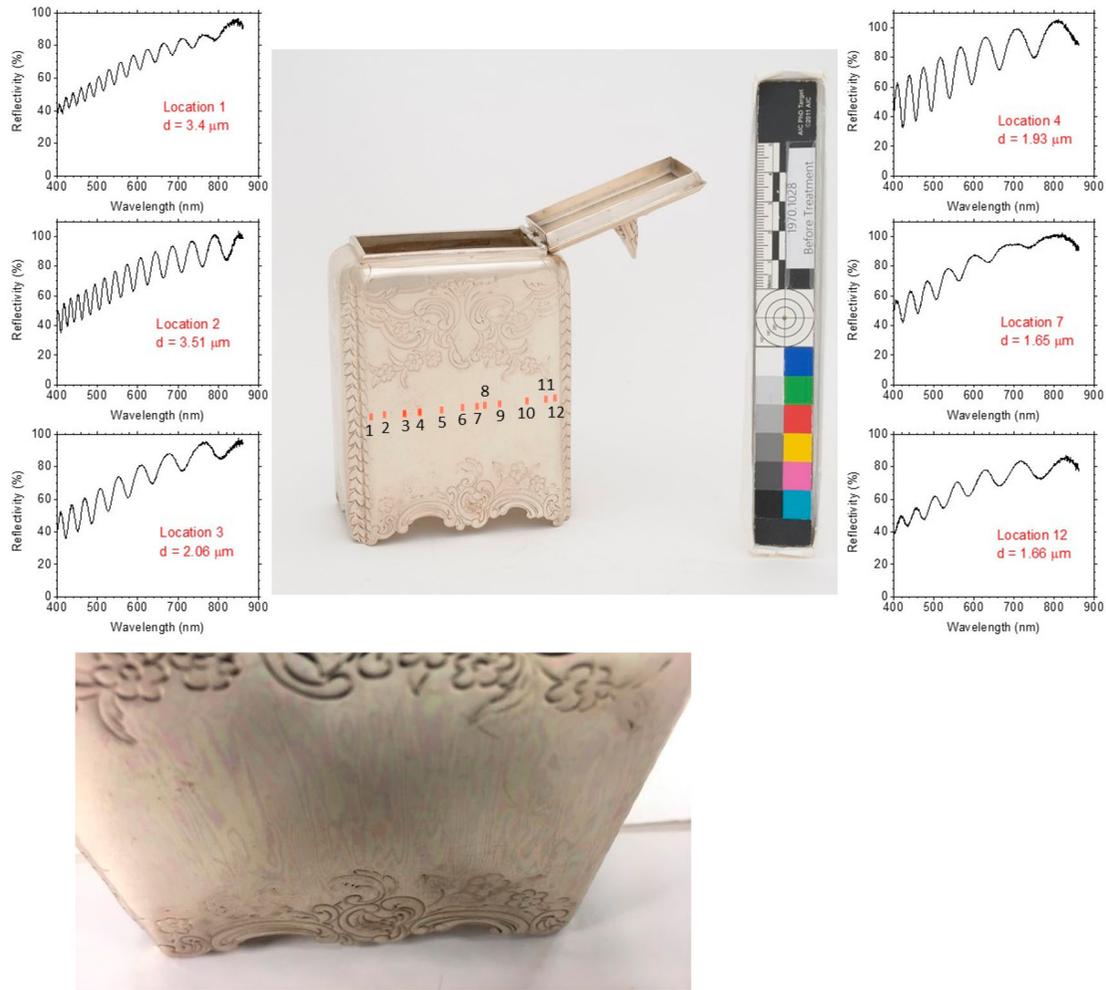


**Figure 5.** UV-fluorescence image of the top surface of the silver tray. The image was adjusted in Photoshop to show only green light to roughly correspond to the dye coumarin 6 fluorescence spectrum. The tray was spray-coated but touched up by brush along some of the edges, which can be clearly seen in the fluorescence image. Also shown on the fluorescence image are the thickness values determined by FORS at the locations numbered on the photograph in Figure 3 (left). The fluorescence image was captured with a Nikon D850 camera with a 20-mm lens, Peca 918 filter, UV filter (similar to Kodak Wratten 2E gel filter), a 30-second integration time, and a 365-nm UV light source.

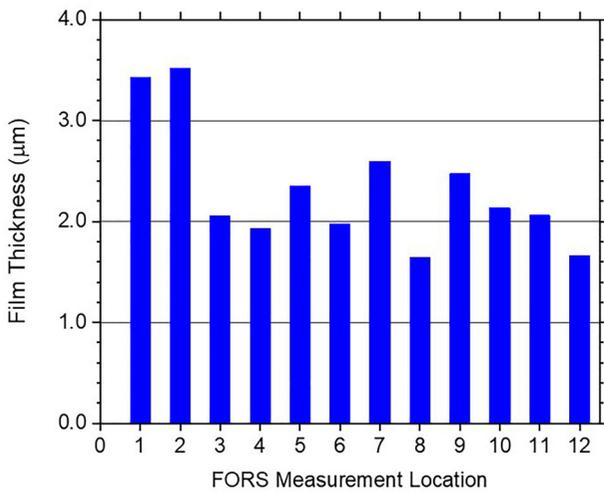
anomalously large value ( $P = 6.3 \times 10^{-6} \text{ cm}^3 \text{ mm/sec cm}^2 \text{ cm Hg}$ ). Additional measurements of H<sub>2</sub>O permeability in nitrocellulose are also desirable.

FORS measurements of iridescent regions of a nitrocellulose film on a tea canister showed film thicknesses on the order of 1.5–3.5 μm. It is interesting that we do not observe a direct correlation between the presence of iridescence and average film thickness or film uniformity (Table 1), as we might expect if the iridescence is simply due to thin film interference from the nitrocellulose coating. Whether this is because we did not intentionally sample the thinner iridescent regions of those coatings, or because the cause of the iridescence is not always the nitrocellulose film itself, requires further study. All objects showing iridescence in Table 1 had aged coatings, suggesting that thin layers of tarnish that have formed beneath the nitrocellulose films or that partial loss of adhesion between the silver and nitrocellulose over long periods of time can also lead to iridescence. Laboratory studies of new nitrocellulose films on fresh silver substrates could provide the needed correlation between nitrocellulose film thickness and iridescence without the presence of such other complicating factors.

Since the H<sub>2</sub>S permeation rate is inversely proportional to film thickness, as shown by equation (2), thinner films will allow faster formation of tarnish.



**Figure 6.** (top) 1970.1028 BT tea canister plus typical FORS spectra measured at the specified locations. (bottom) Detail of the lower portion of the tea canister (side 1) showing iridescence due to the presence of a thin nitrocellulose film. The FORS measurements yield thicknesses from 1.6–3.5  $\mu\text{m}$  across this region. The color changes are due to variations of the film thickness around the average value of  $2.3 \pm 0.6 \mu\text{m}$ . Positions of FORS measurements are shown as numbered red squares.



**Figure 7.** Results of FORS thickness measurements at the locations indicated in Figure 6 for the 1970.1028 tea canister.

However, for thinner films, the probability to form film defects, such as lacunae and pinholes that can function as entrance points for corrosive gases, will also increase. More careful examination of the surface distribution of tarnish on coated objects, correlated with coating thickness measurements, would also help identify the primary failure mode(s) for nitrocellulose coatings.

Coating thickness is determined by a number of factors, many of which are not under the direct control of conservators. For example, the nitrocellulose polymer used in a formulation can be characterized by its weight average and number average molecular weights, polydispersity, and degree of nitration, among other factors. The weight fraction (concentration) of the polymer in the solvent mixture, and the chemical composition of the solvent mixture, are additional variables. These factors will affect the lacquer viscosity, drying time, and adhesion to the silver surface. How much these factors

vary over time due to changes by the suppliers is generally not known to the conservator, who must accept the lacquers as they come and generally only adjusts concentration by adding more solvent to the mixture. Finally, there is the difficulty of applying a uniform coating to objects that often have multiple parts and complex shapes. Despite these caveats, the coating thicknesses we measured fall within a fairly narrow range. Perhaps most important, our measurements show that the majority of nitrocellulose coatings on silver objects at Winterthur have thicknesses well below 10  $\mu\text{m}$ . Other techniques for measuring film thickness, such as eddy current and XRF, are considerably less accurate than FORS measurements for such thin films.

Looking ahead, the authors see greater potential for FORS to assist in metals conservation with respect to coating evaluation. It is possible that FORS can provide a quantitative estimate of the amount of tarnish on silver surfaces, even in the presence of the coating, based on the differences in optical reflectivity that one observes for a tarnished compared to an untarnished silver surface (Burleigh et al. 2001; Bennett, Stanford, and Ashley 1970). This would be a useful evaluation tool, as it could help a conservator decide whether or not a coating is beginning to fail, perhaps before an unacceptable level of detectable tarnish forms beneath the coating. Such measurements will require fitting the reflectivity data to a model that includes the reflectivity contributions of the underlying silver, plus the contributions due to the lacquer coating (due to its optical reflectivity, absorption, and interference).

The next area of research for Winterthur conservators and scientists with respect to metals conservation is determining ideal coating systems for copper alloys. It is likely that FORS will be a useful tool for determining coating thickness when the base metal presents a wider range of alloy composition, surface texture, and reflectivity, and there is also coating material variability (i.e., other coatings besides nitrocellulose, such as acrylics, waxes, and natural resins), although other than the acrylic resin Paraloid B-48N coated on three objects in Table 1 we have not yet tested these possibilities. However, significantly better FORS systems than the one we used are now available, enabling the collection of FORS data over a much wider wavelength range in a single spectrum with better sensitivity and acceptable wavelength resolution. Such spectrometers will allow thicker films to be measured by FORS, and should permit spectral modeling to extract approximate optical parameters from the measurements. This should allow semi-quantitative extraction of the spectral signature due to tarnish and, in addition, simultaneous determination of the thickness of the polymer coating.

## 5. Conclusion

FORS has been used to measure the coating thickness distribution over 30 silver and silver plate objects at Winterthur, proving it to be a simple, accurate method for measuring the thickness of protective coatings on reflective historical metal objects. FORS appears to be significantly more accurate than other methods, such as XRF or eddy current techniques, and is appropriate for transparent coatings, such as nitrocellulose.

Although use of visual inspection, a conductivity tester, and dosing coatings with a UV-fluorescent dye will remain the more practical methods for evaluating coating applications within a conservation treatment workflow, FORS has proven to be a successful technique to assign quantitative values to an otherwise subjective process. Furthermore, if one wishes to conduct controlled experiments to study tarnish formation, nitrocellulose film thickness is an important variable, and we have shown that FORS measurements can be used to accurately measure film thickness.

## Sources of materials

Agateen Lacquer #27 and Agateen Thinner #1  
Agate Lacquer Tri-Nat, LLC  
824 South Ave.  
Middlesex, NJ 08846, USA  
Tel: (800) 452-4735; (732) 968-1080  
<http://www.agatelacquer.com>

Conductivity tester ET40  
Extech Instruments  
9 Townsend West  
Nashua, NH 03063, USA  
Tel: (877) 239-8324; (603) 324-7800  
<http://www.extech.com>

Coumarin 6 (CAS # 38215-36-0)  
Sigma-Aldrich, Inc.  
PO Box 14508  
St. Louis, MO 63178, USA  
Tel: (800) 325-3010  
<https://www.sigmaaldrich.com>

Paraloid B-48N  
TALAS  
330 Morgan Ave.  
Brooklyn, NY 11211, USA  
Tel: (212) 219-0770  
<https://www.talasonline.com>

## Spectroline ultraviolet handheld lamp

Model # 177-ENF-280C

Krackeler Scientific, Inc.

57 Broadway

Albany, NY 12202, USA

Tel: (800) 334-7725; (518) 462-4281

<https://www.krackeler.com>

## Notes

1.  $S$  is a reciprocal Henry's Law constant (DeLassus 2002). Henry's Law states that  $c = k_H P$ , where  $c$  is the concentration of a gas in a liquid,  $P$  is the partial pressure of the gas, and  $k_H$  is the Henry's Law constant for the gas-liquid combination. Thus  $(1/k_H)P = SP$ , so  $S = 1/k_H$ . The value of  $D$  depends upon temperature and is generally smaller in glassy polymers like nitrocellulose than for the same polymers at temperatures above their glass transitions ( $T_g$  nitrocellulose  $\sim 175^\circ\text{C}$  (Zhanning 1992)). If  $D$  and  $S$  are small, the permeability will also be small, and the polymer will be a good barrier to that molecule. The values of  $D$  and  $S$ , and thus the permeability  $P$ , are to a large extent determined by intrinsic properties of the polymers and the molecules, such as the polymer free volume (Zielinski and Duda 1992) and crystallinity (Waack et al. 1955; DeLassus 2002) and the relative polarities of the polymers and molecules (Sanchez and Rodgers 1990). Thus, the barrier properties of a polymer might be good for some molecules but not for others, depending upon factors such as the molecule's size and polarity. It has also been observed (Stannett and Szwarc 1955) that the ratios of permeabilities for pairs of molecules in different polymers is roughly independent of the polymer, providing a simple way to estimate an unknown permeability value for one gas (such as  $\text{H}_2\text{S}$ ) based upon a known value for a different gas (such as  $\text{N}_2$ ) in that polymer.
2. The type of light source used for illumination can affect the visibility of iridescence in thin film coatings. Light sources with well-defined peak intensities at specific wavelengths, such as typical fluorescent lamps, can enhance iridescence, while light sources that emit white light with a smooth spectral output, such as incandescent bulbs, may reveal less iridescence.
3. Although we have not found any measurements of the diffusion constant for  $\text{H}_2\text{S}$  in nitrocellulose, the diffusion constant for hydrogen sulfide through a cellulose acetate film has been reported to have a value of  $D = 0.74 \times 10^{-9} \text{ cm}^2/\text{sec}$  at  $15^\circ\text{C}$  (Heilman et al. 1956). If one assumes that the value for  $D$  is similar for nitrocellulose, diffusion through a  $d = 10 \text{ }\mu\text{m}$  thick nitrocellulose film would require times on the order of (Crank 1998)  $t \sim d^2/2D = (1 \times 10^{-3} \text{ cm})^2 / (2 \times 0.74 \times 10^{-9} \text{ cm}^2/\text{sec}) = 675.7 \text{ sec}$ , only 11.26 min!

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## References

- Ankersmit, Hubertus A., Norman H. Tennent, and Simon F. Watts. 2005. "Hydrogen Sulfide and Carbonyl Sulfide in the Museum Environment—Part 1." *Atmospheric Environment* 39 (4): 695–707.
- Bennett, J. M., J. L. Stanford, and E. J. Ashley. 1970. "Optical Constants of Silver Sulfide Tarnish Films." *Journal of the Optical Society of America* 60: 224–232.
- Born, M., and E. Wolf. 1999. *Principles of Optics*. 7th ed. New York: Cambridge University Press.
- Burleigh, T. D., Y. Gu, G. Donahey, M. Vida, and D. H. Waldeck. 2001. "Tarnish Protection of Silver Using a Hexadecanethiol Self-Assembled Monolayer and Descriptions of Accelerated Tarnish Tests." *Corrosion* 57 (12): 1066–1074.
- Cai, Chang-long, Xiong Han, Xiao-ling Niu, and Wei-guo Liu. 2013. "Research on Optical Properties and Micro-Processing Characteristics of Collodion Thin Film." *Defence Technology* 9 (3): 167–170. doi:10.1016/j.dt.2013.09.017.
- Costa, V. 2001. "The Deterioration of Silver Alloys and Some Aspects of Their Conservation." *Studies in Conservation* 46 (sup1): 18–34.
- Crank, J. 1998. *The Mathematics of Diffusion*. New York: Oxford University Press.
- DeLassus, Phillip. 2002. "Barrier Polymers." *Kirk-Othmer Encyclopedia of Chemical Technology* 3: 375–407.
- De Witte, E. 1973. "The Protection of Silverware with Varnishes." *Bulletin de l'Institut royal du patrimoine artistique* 14: 140–151.
- Feldman, D. 2002. "Polymer Barrier Films." *Journal of Polymers and the Environment* 9: 49–55.
- Fowles, G. R. 1989. *Introduction to Modern Optics*. New York: Dover Publications.
- Franey, J. P., G. W. Kammlott, and T. E. Graedel. 1985. "The Corrosion of Silver by Atmospheric Sulfurous Gases." *Corrosion Science* 25 (2): 133–143. doi:10.1016/0010-938X(85)90104-0.
- Graedel, T. E., J. P. Franey, G. J. Gualtieri, G. W. Kammlott, and D. L. Malm. 1985. "On the Mechanism of Silver and Copper Sulfidation by Atmospheric H<sub>2</sub>S and OCS." *Corrosion Science* 25 (12): 1163–1180. doi:10.1016/0010-938X(85)90060-5.
- Graedel, T. E., G. W. Kammlott, and J. P. Franey. 1981. "Carbonyl Sulfide: Potential Agent of Atmospheric Sulfur Corrosion." *Science* 212: 663–665.
- Grayburn, Rosie, and Ann Wagner. 2019. "A Non-Destructive Toolkit for Silver Plate Identification." In Preprints of the 9th Interim Meeting of the ICOM-CC Metals Working Group. Neuchâtel, Switzerland: ICOM.
- Grissom, C. A., N. Grabow, C. S. Riley, and A. E. Charola. 2013. "Evaluation of Coating Performance on Silver Exposed to Hydrogen Sulfide." *Journal of the American Institute for Conservation* 52: 82–96.
- Heavens, Oliver S. 1991. *Optical Properties of Thin Solid Films*. New York: Dover Publications.
- Hecht, E., and A. Zajac. 1979. *Optics*. Reading, MA: Addison-Wesley Publishing Company.
- Heginbotham, Arlen, Vincent Beltran, Briana Feston, Ruven Pillay, and Christina Simms. 2014. "An Evaluation of Protective Coatings for Brass in Indoor Environments, with an Emphasis on Boulle Marquetry." In *Furniture Finishes: Past, Present and Future of Transparent Wood Coatings*, edited by Miko Basques, 84–103. Amsterdam: Stichting Ebenist.
- Heilman, W., V. Tammela, J. A. Meyer, V. Stannett, and M. Szwarc. 1956. "Permeability of Polymer Films to Hydrogen Sulfide Gas." *Industrial & Engineering Chemistry* 48: 821.
- Heller, D. B. 1983. "The Coating of Metal Objects at Winterthur." Preprints of papers presented at the eleventh annual meeting for the American Institute for Conservation of Historic and Artistic Works, Baltimore, 11, 57–64.
- Hsieh, P. Y. 1963. "Diffusibility and Solubility of Gases in Ethylcellulose and Nitrocellulose." *Journal of Applied Polymer Science* 7: 1743–1756.
- Jiang, Y., S. Pillai, and M. A. Green. 2015. "Re-evaluation of Literature Values of Silver Optical Constants." *Optics Express* 23: 2133.
- Lilienfeld, S., and C. E. White. 1930. "A Study of the Reaction Between Hydrogen Sulfide and Silver." *Journal of the American Chemical Society* 52: 885–892.
- Neogi, P., ed. 1996. *Diffusion in Polymers*. New York: Marcel-Dekker.
- Polidori, Tia, Katelyn Rovito, and Rosie Grayburn. 2018. "Electroplated Silver during a Re-Lacquering Campaign at Winterthur Museum: Treatment and Analytical Insights." Poster, Houston, TX, June 2.
- Pope, D., H. R. Gibbens, and R. L. Moss. 1968. "The Tarnishing of Ag at Naturally-Occurring H<sub>2</sub>S and SO<sub>2</sub> Levels." *Corrosion Science* 8: 883–887.
- Porcinai, S., and M. Ferretti. 2018. "X-ray Fluorescence-Based Methods to Measure the Thickness of Protective Organic Coatings on Ancient Silver Artefacts." *Spectrochimica Acta Part B: Atomic Spectroscopy* 149: 184–189.
- Pouliot, B., C. Matsen, J. Mass, W. Donnelly, K. Andrews, and M. Bearden. 2013. "Three Decades Later: A Status Report on the Silver Lacquering Program at Winterthur." *Objects Specialty Group Postprints* 20: 32–48.
- Reedy, Chandra L., Richard A. Corbett, Deborah L. Long, Robert E. Tatnall, and Bradley D. Krantz. 1999. "Evaluation of Three Protective Coatings for Indoor Silver Objects". Objects Specialty Group Postprints, Volume Six, American Institute for Conservation of Historic and Artistic Works (AIC).
- Rice, D. W., P. Peterson, E. B. Rigby, P. B. P. Phipps, R. J. Cappell, and R. Tremoureaux. 1981. "Atmospheric Corrosion of Copper and Silver." *Journal of The Electrochemical Society* 128 (2): 275–284.
- Saleh, G., C. Xu, and S. Sanvito. 2019. "Silver Tarnishing Mechanism Revealed by Molecular Dynamics." *Angewandte Chemie International Edition* 58: 6017–6021.
- Sanchez, Isaac C., and Patrick A. Rodgers. 1990. "Solubility of Gases in Polymers." *Pure and Applied Chemistry* 62: 2107–2114.

- Sease, C., L. S. Selwyn, S. Zubiate, D. F. Bowers, and D. R. Atkins. 1997. "Problems with Coated Silver: Whisker Formation and Possible Filiform Corrosion." *Studies in Conservation* 42 (1): 1–10.
- Selwitz, Charles. 1988. "Cellulose Nitrate in Conservation." *Research in Conservation* 2. Marina del Rey, CA: Getty Conservation Institute.
- Selwyn, Lyndsie S. 1990. "Historical Silver: Storage, Display, and Tarnish Removal." *Journal of the International Institute for Conservation – Canadian Group* 15: 12–22.
- Stannett, V., and M. Szwarc. 1955. "The Permeability of Polymer Films to Gases—a Simple Relationship." *Journal of Polymer Science* 16 (81): 89–91.
- Stern, S. A., and J. R. Fried. 2007. "Permeability of Polymers to Gases and Vapors." In *Physical Properties of Polymers Handbook*, 2nd ed., Chapter 61, edited by James E. Mark, 1033–1047. New York: Springer.
- Stern, S. A., and H. L. Frisch. 1981. "The Selective Permeation of Gases Through Polymers." *Annual Review of Materials Science* 11: 523–550.
- Volpe, L., and P. J. Peterson. 1989. "The Atmospheric Sulfidation of Silver in a Tubular Corrosion Reactor." *Corrosion Science* 29 (10): 1179–1196.
- Waack, Richard, N. H. Alex, H. L. Frisch, Vivian Stannett, and Michael Szwarc. 1955. "Permeability of Polymer Films to Gases and Vapors." *Industrial and Engineering Chemistry* 47 (12): 2524–2527.
- Zhanning, J. 1992. "The Glass Transition Temperature Measurement of Nitrocellulose by Torsional Braid Analysis." *Propellants, Explosives, Pyrotechnics* 17: 34–37.
- Ziegler, J., C. Kuhn-Wawrzinek, M. Eska, and G. Eggert. 2014. "Popping Stoppers, Crumbling Coupons - Oddy Testing of Common Cellulose Nitrate Ceramic Adhesives." In ICOM-

CC 17th Triennial Conference Preprints, Melbourne, September 15–19, 2014, ed. J. Bridgland, art. 0505, 8pp. Paris: International Council of Museums (ISBN 978-92-9012-410-8).

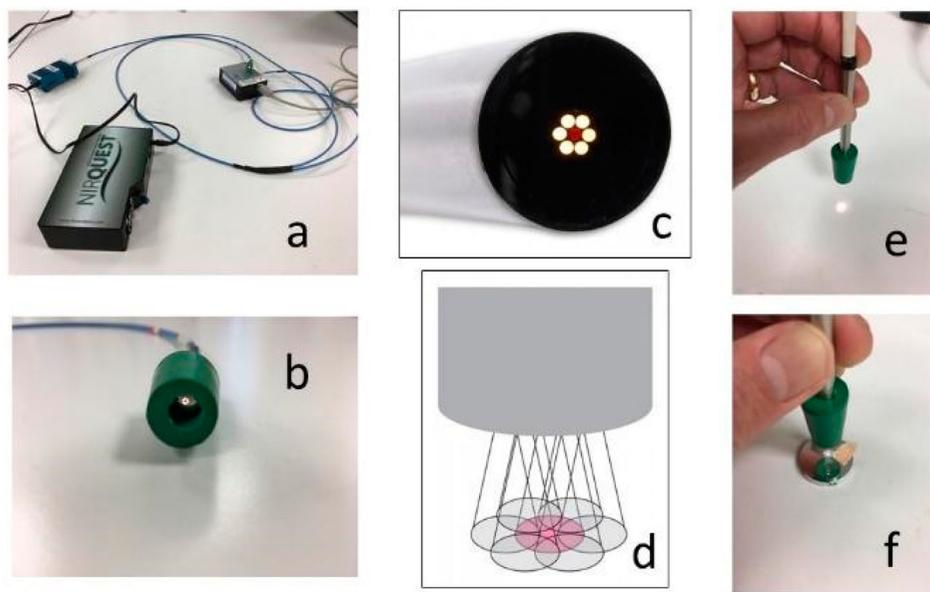
- Zielinski, John M., and J. L. Duda. 1992. "Predicting Polymer/Solvent Diffusion Coefficients Using Free-Volume Theory." *AIChE Journal* 38 (3): 405–415.

## Appendix

### 1. Additional FORS instrument specifications

Data were primarily collected using a portable Ocean Optics USB2000 spectrometer, but in several cases an Ocean Optics NIRQuest spectrometer was used (Table 1). These instruments were suitable for FORS measurements of nitrocellulose film thicknesses, although their spectral resolutions and wavelength ranges limited the range of film thicknesses that could be measured. The USB2000 covers the UV-visible spectral region (200–860 nm), and the NIRQuest covers the near-infrared spectral region (960–2200 nm). There are also two light sources: a tungsten lamp for the visible and near-IR regions and a UV lamp for the 200–400 nm region. The USB2000 spectrometer was equipped with a 600 line/mm diffraction grating blazed at 400 nm. The detector was a UV2/OFLV-4 (Sony ILX511 1 × 2048 pixel) with a 25 μm slit size. Spectral resolution is approximately 1.1 nm and the spectral response extends from 200–860 nm (400–860 nm with the quartz halogen lamp).

We have made measurements primarily in the visible (400–860 nm), although some measurements were made in the near-IR. No measurements have been attempted in the UV. Some photos of the instrument and examples of its operation are shown in Figure A1.



**Figure A1.** Ocean Optics spectrometer components. (a) UV-vis (upper right) and near-IR (lower left) spectrometers, tungsten lamp (upper left) and fiber optic cables and probe; (b) Fiber optic probe with rubber stopper to control sample-probe distance; (c) Fiber optic tip showing six illumination fibers and single central collection fiber; (d) Fiber optic illumination pattern (gray) and light collection region (purple); (e) Fiber optic illumination spot is 1–2 mm in diameter near end of rubber stopper; (f) Measuring the reflectance of the silver reference mirror. This setup requires gentle contact of the stopper to the object to control sample-probe distance, although any setup which allows the probe to be at fixed distance to the surface would suffice.