EVALUATION OF COATING PERFORMANCE ON SILVER EXPOSED TO HYDROGEN SULFIDE

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Twelve coatings applied to sterling silver coupons were subjected to high levels of hydrogen sulfide to test their effectiveness in preventing tarnish in indoor environments. Silver coupons were assessed over the course of the experiment using visual observation, image analysis of digital photographs, gloss measurement, and colorimetry. Acrysol WS-24, Agateen Air Dry Lacquer No. 27, HMG Heat and Waterproof Adhesive, and PVAc AYAT generally performed best. Mowiol 28-99 performed very well on some areas but was mediocre otherwise. Butvar B-98 and Acryloid B-48N were generally less effective in retarding tarnish. Acryloid B-72 and Butvar B-76 performed less well. Aquazol 500, Aquazol 500 topped with Renaissance Wax, and Renaissance Wax were least effective. Coating thickness proved to be a significant factor in coating performance.

KEYWORDS: *silver, coatings, hydrogen sulfide, thickness, gloss, colorimetry*

1. INTRODUCTION

The common pollutant hydrogen sulfide (H_2S) is well known to be the primary cause of tarnish on silver objects, occurring at concentrations as low as 0.2 parts per billion (Franey et al. 1985). Passive methods of sulfide mitigation for storage and display environments are the goal of most museums. When these non-invasive methods are not feasible, however, conservators have applied a limited number of organic coatings to surfaces of silver artifacts. On account of excellent appearance, ease of application, and tarnish prevention, cellulose nitrate lacquers have been the most popular coatings for this purpose in the United States and United Kingdom. In particular, Agateen Air Dry Lacquer No. 27 has been used in the United States (Heller 1983; Reedy et al. 1999) and H. Marcel Guest's HMG and MacDermid's Frigilene FR65150 lacquer in the United Kingdom (Plenderleith and Werner 1971, 244; Thickett and Hockey 2003). Cellulose nitrate coatings are broken down by ultraviolet light (Selwitz 1988), however, and reapplication is necessary after 10–20 years (Luxford and Thickett 2007). The acrylic resins Paraloid (formerly Acryloid in the U.S.) B-72, B-48N, and B-44, which are so often used by conservators on other types of artifacts because of their stability, are increasingly applied on silver (Argyropoulos et al. 2007; Degrigny 2008), although two studies have shown these acrylics to be less effective in preventing tarnish from H_2S than cellulose nitrate lacquer (De Witte 1973; Reedy et al. 1999). Microcrystalline waxes have also been used for coating silver, especially when ventilation is poor, since they do not require the quantities of volatile organic solvents necessary for resin-coating formulations (Argyropoulos et al. 2007). Few scientific studies comparing the effectiveness of coatings on silver have been published.

The goal of this study was to assess the effectiveness of 12 coatings in preventing silver from tarnishing in the presence of H_2S. Five of the coatings tested are among those just described that are widely used by conservators on silver, although each is known to have drawbacks. The remaining seven materials, in use by conservators for other purposes, were selected for comparative testing as a first step in identifying possible alternatives. Preliminary data for eight of the coatings were presented at the Metal 07 conference (Grabow et al. 2007). This paper provides a more comprehensive evaluation of all 12 coatings using four assessment techniques.

2. EXPERIMENTAL

2.1 INTRODUCTION

The 12 coatings represented a range of materials from several major classes of polymers commonly used in conservation (table 1). Cellulose nitrate, acrylic resin, and Renaissance Wax coatings have

TABLE 1.   TWELVE COMMERCIAL PRODUCTS USED IN THIS STUDY AND THEIR APPLICATION CONCENTRATIONS IN ORDER BY MAIN COMPONENT

Main component	Product name	Tg°C	Solvent or diluent[a]	Conc. by wt.	In use on silver
Acrylic	Acryloid[a] B-48N (now Paraloid B-48N)	50	70% xylenes/17% acetone	13%	x
Acrylic	Acryloid[a] B-72 (now Paraloid B-72)	40	xylenes	15%	x
Acrylic dispersion	Acrysol WS-24 (Primal WS-24[b])	46	none	36%	
Cellulose nitrate	Agateen No. 27		50% Agateen thinner	–	x
Cellulose nitrate	HMG Adhesive		none	–	x
Polyvinyl acetate	PVAc AYAT	26	methanol	15%	
Polyvinyl alcohol	Mowiol 28–99		Boiling deionized water	15%	
Polyvinyl butyral	Butvar B-76	62	1-butanol	10%	
Polyvinyl butyral	Butvar B-98	72	1-butanol and acetone	12%	
Oxazoline	Aquazol 500	55	1-butanol	15%	
Oxazoline + wax, microcrystalline	Aquazol + Renaissance Wax		none	–	
Wax, microcrystalline	Renaissance Wax		none	–	x

[a]Rohm and Haas' Acryloid B-72 and B48N, now Paraloid B-72 and B-48N, were obtained in October 2004.
[b]Equivalent product outside the United States.

been commonly used on silver, while use of the remaining seven coatings has been limited to other purposes.

Coatings were prepared as listed in table 1. Acrysol WS-24, HMG Adhesive, and Renaissance wax were applied as supplied by their distributers. Since preparations of these pre-mixed solutions were identified as optimal by the manufacturers, they were not adjusted. For other coatings, the most appropriate solvent was selected for each coating based on strong solvent-solute interaction and, whenever possible, a low evaporation rate in order to improve leveling and even film formation. Fifteen percent solids were used for each coating as far as was practical, but in several cases the solutions were adjusted to achieve coatings with similar viscosities. The Butvar resins mixed at 15% were too thick for the draw-down application, for example, and were therefore thinned to 10 and 12%. The final solutions of the 12 coatings seemed to vary only slightly in viscosity.

2.2 COUPON PREPARATION

Fifty-one silver coupons were cut to measure 7.6 cm × 7.6 cm from 30-gauge (0.4-mm thick) sterling-silver sheet; the relatively large silver coupon size was chosen to avoid edge effects. Four silver coupons were coated with each of the 12 materials, and an extra three silver coupons were left uncoated as blanks. Each silver coupon was wet polished using progressively finer silicon-carbide abrasive paper and micro-mesh cushioned abrasive cloths (down to 2 μm abrasives) to match the near-mirror finish of a designated standard silver coupon. After thorough rinsing, the silver coupons were air dried at ambient conditions. This method of polishing differs from that commonly employed on historic silver in the hardness of the abrasive used, but the end result is comparable. Two glass microscope slides were coated with each material to monitor any changes in the coatings themselves, and two glass slides were left uncoated as blanks.

A random number was selected for each silver coupon and glass slide, ranging from 1 to 78. The number was scored into the lower right corner on the back of each silver coupon and on the uncoated end of each glass slide.

2.3 COATING APPLICATION

Liquid coatings were applied to the silver coupons by a draw-down method (ASTM 2001). Approximately 10 ml of the coating solution was pipetted in a line along the top edge of the silver coupon and drawn down across the surface using a glass rod elevated a fixed distance above the silver coupon. In order to maximize measurable changes in the coatings themselves, glass slides were dipped in liquid coatings to obtain thick films. Renaissance Wax was applied both by itself and over Aquazol (one day after coating)

using a Kimwipe, and it was buffed after about 20 minutes; the waxing process was repeated a second time. Coated silver coupons and glass slides were air-dried and stored in a fume hood for several months, then in the conservation laboratory. Eight months elapsed before exposure of the coated silver coupons and glass slides to H_2S. This delay, while due to a personnel change, had the advantage of ensuring that the coatings were completely dry when exposed.

Coating thickness on the silver coupons was measured just before H_2S exposure using an Elcometer 345 thickness gauge, calibrated using a 23.7-μm standard. The 6-mm-diameter measurement head was centered over each of 20 test areas (see next paragraph) on the four coupons coated with each material. Three readings were averaged in each area.

The 20 test areas selected for measurement per coating included 15 areas (five each) on the three silver coupons that would be exposed to H_2S and five areas on the fourth silver coupon that would be the unexposed coated silver control. For each silver coupon, the five 1.0 cm² test areas were chosen randomly from 25 squares in an imaginary grid over the silver coupon, excluding a 1.3-cm border to avoid edge effects. Paper templates were custom made to mask off the outer border and other 24 squares for each test area, ensuring consistent positioning during measurement. The same 20 test areas on each set of coated silver coupons were measured for thickness before exposure to H_2S and throughout the experiment for gloss and color.

2.4 EXPOSURE TO HYDROGEN SULFIDE

While two unexposed coated controls (one silver coupon, one glass slide) for each coating were kept in the conservation lab at ambient conditions, three coated silver coupons and a glass slide for each coating set, three uncoated silver blanks, and one uncoated glass slide were placed in random order in the test chamber, a Plexiglas Fisher Scientific desiccator kept in a fume hood (fig. 1). A small fan provided air circulation in the chamber. A VWR digital hygrometer measured $61 \pm 6\%$ RH and $19 \pm 2°C$ inside the chamber during the experiment. H_2S was generated in the chamber by pipetting 10 drops of water onto 5 g of powdered barium sulfide (BaS) in a Petri dish. Both the BaS and water were renewed when silver coupons were placed back into the chamber after removal for measurements. During the first week the silver coupons were removed for measurement and returned to the chamber on a daily basis, then approximately every 3 or 4 days for a maximum of 125 days in the case of the most tarnish-resistant coated silver coupons – exclusive of the time that the coupons were removed for measurement.

FIG. 1. Hydrogen-sulfide chamber containing silver coupons in the upper half. On the bottom of the chamber are the hygrometer (left), Petri dish containing barium sulfide (center), and fan (right).

H_2S concentration in the chamber was estimated to be about 6 ppm using Dräger diffusion tubes for H_2S. During the first weeks of the experiment the Dräger tubes failed to measure any H_2S during the 24-hour periods designated for measurement. The manufacturer's scientists suggested that H_2S had preferentially tarnished uncoated backs of the silver coupons rather than registering in the Dräger tubes. This appeared to be borne out by Dräger tube measurements of 6 ppm H_2S in the chamber during 24-hour periods at the end of the experiment, both when the chamber was filled with silver coupons fully tarnished on the backs and when it was without any silver coupons.

Exposure of the silver coupons to H_2S continued until at least portions of all silver coupons showed significant tarnish. The 125 days of total exposure for the most tarnish-resistant samples was extreme. Other researchers, by comparison, exposed silver to a maximum of 7 ppm H_2S for just six days (Reedy et al. 1999). Levels of H_2S in museum environments reportedly range from about 0.05 to 0.1 ppm (Hatchfield 2002, 11).

2.5 COATING EVALUATION

Coating evaluation methods included visual observation, image analysis of digital photographs, gloss measurement, and colorimetry. The first two methods evaluated whole silver coupons, exclusive of edge regions. In contrast, gloss and color measurements were made on the five 1.0 cm² test areas on each silver coupon described above (see Section 2.3), since instrument spot sizes measured 1.0 cm or less. Two areas on each coated glass slide and coated silver

Scale	Color of silver	Scale	Amount of tarnish
1	No change	1	No tarnish
2	Iridescence	2	<3% tarnish
3	Orange-brown	3	3–10% tarnish
4	Dark brown	4	10–30% tarnish
5	Blue-black	5	>30% tarnish

control samples stored at ambient conditions were measured for color and gloss.

For visual evaluation, three to six judges rated each silver coupon four times: just before H_2S exposure and three times during the first 315 hours of exposure. Judges were "blind," i.e. judges did not know the identity of coatings on examined silver coupons. Judges gave two separate rating values, each with scores from 1 to 5, to assess color and amount of tarnish (see table 2). Assessment of color was based on the fact that when silver tarnishes, silver sulfide corrosion formed on the surface at first appears iridescent as interference colors and changes in coloration as it becomes thicker. An ASTM standard was used as an aid to determining the percent tarnish scores (ASTM 2006). A composite visual evaluation rating was obtained by multiplying the two rating components. Hence, a rating of one (1×1) indicated no change, and 25 (5×5) was the maximum. Ratings were averaged for each silver coupon.

At regular intervals photographic images were taken using a Nikon D70 digital camera. Image analysis was done using Adobe Photoshop to assess the percentage of tarnished surface. The outermost 1.3 cm edge of each silver coupon's image was cropped off, discolored areas were marked solidly in a new layer, and the dropdown histogram function under "image" provided the percentage of the discolored areas, i.e. the percent tarnish.

Average gloss measurements were obtained on each test area using a BYK-Gardner Micro-Tri-Gloss glossmeter set to 20°; the detection spot size was 1 cm² in diameter. The instrument was centered over the test area, and three readings per test area were averaged.

Average colorimetry readings were taken on each test area at the same time as gloss measurements using a Minolta CR-121 colorimeter equipped with a 0° to 45° light source; the spot size of the instrument was 8 mm in diameter. The instrument was centered over the test area, and three readings per test area were averaged.

3. Results

3.1 thickness

Thickness measurements made using the Elcometer 345 before the silver coupons were exposed to H_2S

are shown in figure 2 for each coating's 15 measurement areas and five areas on the unexposed coated silver control. Acrysol showed by far the greatest average thickness at 52 µm, and Renaissance Wax the least average thickness at 6 µm; most other coatings averaged from 10 to 22 µm. Average thicknesses for coatings and ranges of thicknesses are also reported in table 3.

Variations in average thickness measurements for each coating are reported as relative standard deviations (RSDs) in table 3. The manufacturer reports a 1% precision in measurement for the Elcometer, but actual precision for the three measurements in each area was somewhat worse (average RSD 7%), slightly expanding the margin of uncertainty. However, precision may also be tied to limit of detection. For example, thickness in Agateen was shown to have 2–9% precision for the three readings in five out of six areas where coating thickness was greater than 13 µm. Reproducibility in thickness measurement below this limit generally was 18–32% or even worse for thickness below about 5 µm. This suggests that coating thickness measurements for Agateen below about 13 µm were uncertain or that thicknesses were highly variable on account of thin areas.

Within coating sets, variation in thickness between test areas was generally more consistent on individual silver coupons (cf. data for the best coupon and average of the three coupons in table 3). Thickness measurements on individual silver coupons most thickly coated with Acrysol, Agateen, HMG, Butvar B-98, and Aquazol averaged more than twice that of coatings on other silver coupons thinly coated with the same materials.

3.2 visual evaluation

Figure 3 shows results for the average visual evaluation rating of coated silver coupons, made by multiplying values assigned to color and amount of tarnish by
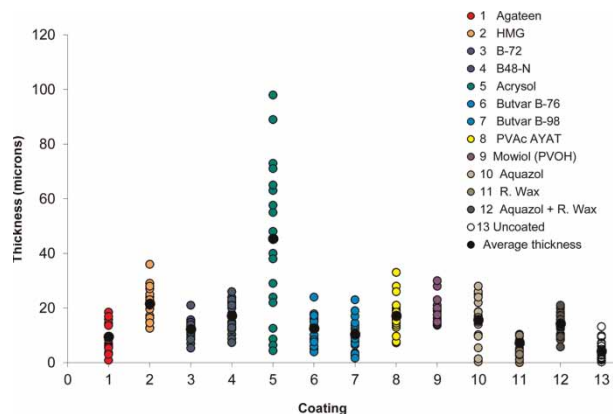

FIG. 2.   Thickness measured at 15 locations for each coating; some symbols are superimposed.

TABLE 3.   THICKNESS AND PERFORMANCE OF COATINGS USING VISUAL EVALUATION AND DIGITAL IMAGE ANALYSIS, GROUPED BY EFFECTIVENESS

Coating	Thickness		Visual evaluation color x amt. tarnish at 315 hours (RSD)	% Tarnish from image analysis		
	Avg. (RSD)	Range		At 500 hours	At 1500 hours	At 6 years
Most effective coatings						
Acrysol Control	22 μm (4%)	4–71 μm	–	–	–	0%
Best coupon #18	71 μm (3%)	63–98 μm	1 (0%)	0%	16%	
3 coupons	52 μm (4%)	4–98 μm	4 (0%)	13%	44%	
Agateen Control	7 μm (21%)	3–10 μm	–	–	–	25%
Best coupon #62	16 μm (5%)	14–19 μm	1 (0%)	3%	10%	
3 coupons	10 μm (13%)	1–19 μm	8 (2%)	49%	55%	
PVAc AYAT Control	16 μm (6%)	10–26 μm	–	–	–	0%
Best coupon #50	20 μm (9%)	7–28 μm	1 (0%)	0%	34%	
3 coupons	17 μm (10%)	7–33 μm	3 (0%)	3%	57%	
HMG Control	20 μm (9%)	15–25 μm	–	–	–	0%
Best coupon #63	27 μm (2%)	21–29 μm	1 (0%)	0%	100%	
3 coupons	22 μm (6%)	13–36 μm	6 (13%)	28%	100%	
Mowiol (PVOH) Control	18 μm (5%)	14–21 μm	–	–	–	50%
Best coupon #46	24 μm (7%)	19–30 μm	9 (0%)	24%	46%	
3 coupons	19 μm (6%)	14–30 μm	12 (17%)	50%	74%	
Less effective coatings						
B-48N Control	22 μm (2%)	20–26 μm	–	–	–	0%
Best coupon #16	18 μm (9%)	13–22 μm	4 (24%)	6%	100%	
3 coupons	16 μm (10%)	7–26 μm	8 (14%)	23%	100%	
Butvar B-98 Control	10 μm (13%)	7–14 μm	–	–	–	0%
Best coupon #65	17 μm (6%)	11–23 μm	1 (0%)	0%	100%	
3 coupons	10 μm (15%)	2–23 μm	10 (2%)	30%	100%	
B-72 Control	13 μm (5%)	5–16 μm	–	–	–	0%
Best coupon #36	11 μm (19%)	9–13 μm	8 (0%)	7%	100%	
3 coupons	12 μm (13%)	5–21 μm	13 (11%)	63%	100%	
Butvar B-76 Control	14 μm (12%)	10–16 μm	–	–	–	0%
Best coupon #45	18 μm (7%)	15–24 μm	14 (0%)	100%	100%	
3 coupons	12 μm (13%)	4–24 μm	17 (0%)	74%	100%	
Least effective coatings						
Aquazol Control	7 μm (34%)	0–15 μm	–	–	–	20%
Best coupon #75	25 μm (5%)	22–28 μm	16 (6%)	100%	100%	
3 coupons	19 μm (5%)	0–28 μm	20 (7%)	100%	100%	

Continued

TABLE 3.   CONTINUED

Coating	Thickness		Visual evaluation color x amt. tarnish at 315 hours (RSD)	% Tarnish from image analysis		
	Avg. (RSD)	Range		At 500 hours	At 1500 hours	At 6 years
Aquazol + wax Control	11 μm (3%)	13–20 μm	–	–	–	0%
Best coupon #49	18 μm (5%)	16–21 μm	20 (18%)	100%	100%	
3 coupons	14 μm (9%)	6–21 μm	23 (6%)	100%	100%	
Renaissance Wax Control	5 μm (40%)	0–10 μm	–	–	–	100%
Best coupon #66	9 μm (9%)	8–10 μm	25 (0%)	100%	100%	
3 coupons	6 μm (20%)	0–10 μm	25 (0%)	100%	100%	
Blanks (uncoated)						
3 coupons	4 μm (86%)	1–13 μm	25 (0%)	100%	100%	100%
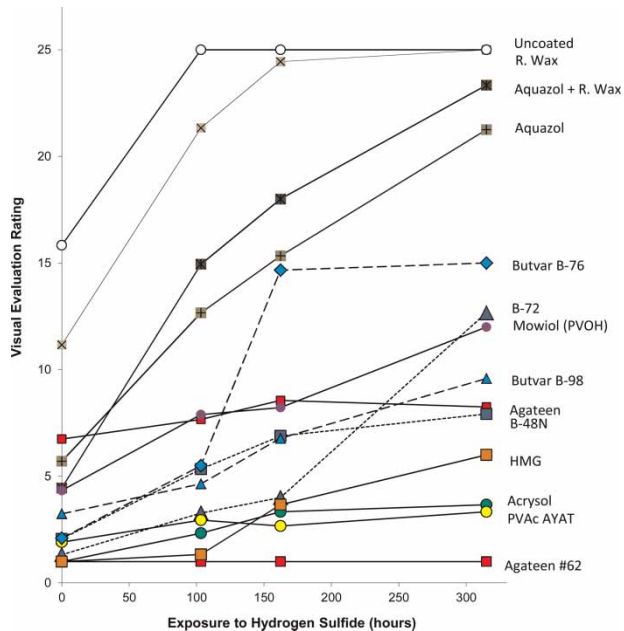
FIG. 3.   Average visual evaluation ratings for three coupons coated with each material based on color and amount of tarnish. A rating of 1 indicates no change; 25 is the maximum. The average for Agateen-coated coupon #62 is included to illustrate how much better many more thickly coated coupons performed.

four to six judges. As can be seen at 0 hours of exposure, some silver coupons exhibited tarnish even before exposure to H_2S. This phenomenon was most pronounced for uncoated controls and Renaissance Wax-coated silver coupons, but small amounts of pre-exposure tarnish were observed on at least one silver coupon in every coating set, except for those coated with Acrysol and HMG.

By the end of the 315-hour time period for visual evaluation, sets of silver coupons ranking best on average were those coated with PVAc AYAT, Acrysol, HMG, Acryloid B-48N, Agateen, and Butvar B-98, in that order (fig. 3, table 3). Evaluators estimated that silver coupons coated with the first three materials had less than 10% tarnish at the end of the time period. In contrast, Renaissance Wax- and Aquazol-coated silver coupons had failed completely or almost completely. Remaining coated silver coupons fell in between. For these data, ranking order of coatings did not appear to correlate to average coating thickness, with the exception of Acrysol.

Better performance on individual coated silver coupons was demonstrated by two of three silver coupons coated with PVAc AYAT and Acrysol and one of three silver coupons coated with Agateen, HMG, and Butvar B-98. These better-performing silver coupons, which were more thickly coated than their cohorts, remained protective to the end of the visual evaluation period (table 3). Data for the silver coupon most thickly coated with Agateen are included in figure 3 to show how much better it performed than the average for all Agateen-coated silver coupons.

Visual evaluation was a relatively easy technique to implement, and results could be readily graphed and compared. Discrepancies occurred in a small number of evaluations and are reflected in higher RSDs for those evaluations. This might be remedied in future by a better evaluation set-up and improved evaluator training.

3.3 DIGITAL IMAGE ANALYSIS

The average percent tarnished surface on each coated silver coupon was determined by software-assisted image analysis of the digital photographs taken just before placement of the silver coupons into the H_2S chamber, 4 days after exposure to H_2S, and approximately every two weeks thereafter. Photography was
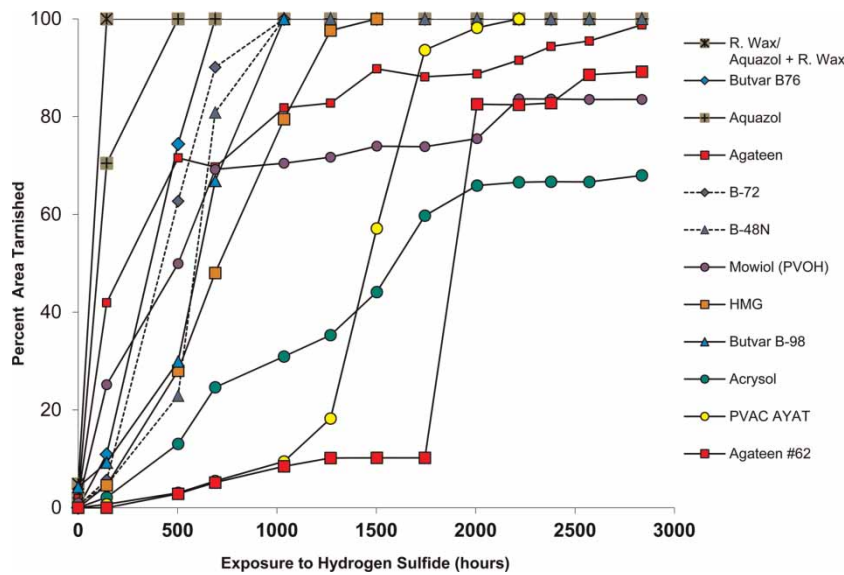
FIG. 4.   Average percent tarnished area for all coupons determined from digital photographs. The average for Agateen-coated coupon #62 is included to illustrate how much better many more thickly coated coupons performed.

stopped when a silver coupon coated with a given material became fully tarnished. During the experiment six photographs each were taken of silver coupons that were least tarnish resistant; 13 photographs were taken of the most tarnish-resistant silver coupons. Image analysis was also done on coated silver control coupons in 2012, 6 years after they were coated.

Results for the average percent tarnished surface on all three silver coupons coated with a given material are shown in figure 4 and listed at 500 and 1500 hours in Table 3. At 1500 hours exposure, silver coupons coated with 8 out of 12 coatings had completely tarnished on average, leaving only those coated with Acrysol, PVAc AYAT, Agateen, and Mowiol with average tarnished surfaces ranging from 44 to 74%. Among these four, Acrysol-coated silver coupons delayed tarnish formation best. Two of the Acrysol-coated silver coupons had only 3 and 9% tarnish, respectively, after more than 1000 hours of exposure to H_2S, and none of the Acrysol-coated silver coupons had completely tarnished after nearly 3000 hours of test exposure. The superior performance of Acrysol in
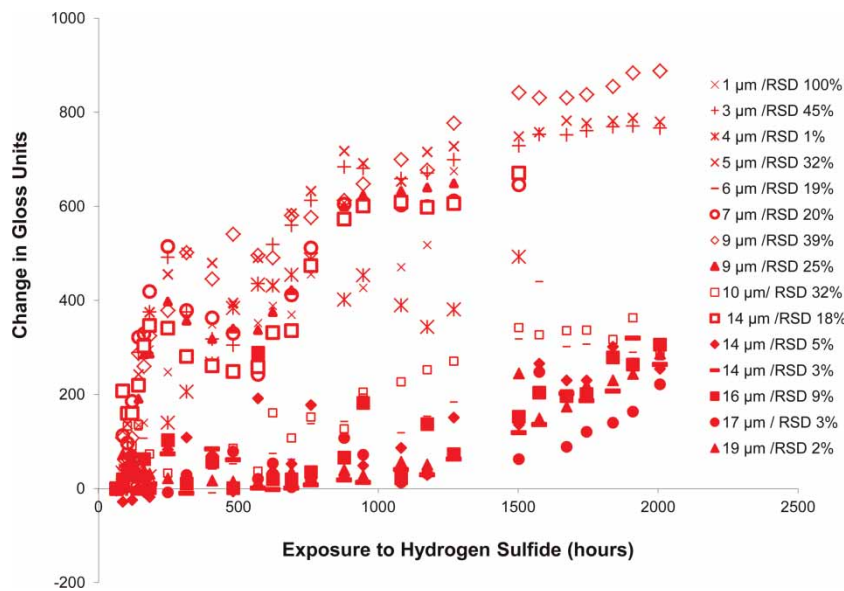

FIG. 5.   Change in gloss measurements for 15 Agateen-coated areas show wide spread of data. Solid geometric symbols reflect gloss measurements on the most thickly coated areas with least loss in gloss, outlined geometric symbols reflect less thickly coated areas, and other symbols reflect most thinly coated areas. The key at right lists the average coating thickness and its RSD for each area.
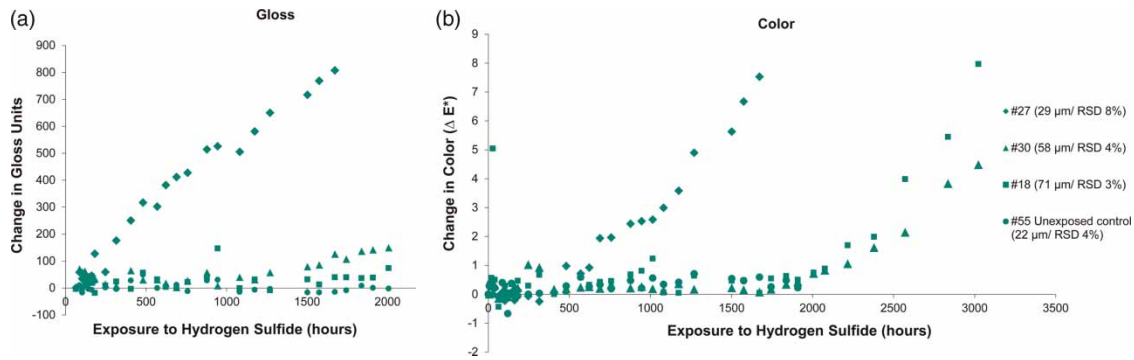
FIG. 6.   Average change in (a) gloss and (b) color measured on individual coupons coated with different average thicknesses of Acrysol listed at right. The most thinly coated coupon (#27) began to lose gloss and color after 200–400 hours. Gloss, measured through 2000 hours, did not clearly show changes on the more thickly coated coupons (#18, 30), but color, measured through 3000 hours, showed definite changes after 1900 hours.

terms of delayed surface tarnish development may in part be ascribed to its being much thicker than others tested.

More thickly and evenly coated silver coupons performed markedly better according to percent tarnish based on digital image analysis when the best-performing silver coupons coated with Acrysol, PVAc AYAT, HMG, Butvar B-98, and Agateen were compared to their cohorts (table 3); these were exactly the same thickly coated silver coupons that performed better according to visual evaluation. For example, the silver coupon most thickly coated with Agateen (ranging from 14 to 19 µm in thickness) delayed tarnish formation much better than the average for its set (ranging from 1 to 19 µm in thickness). The most thickly Agateen-coated silver coupon was estimated to have only 10% surface tarnish after more than 1500 hours, while the average percent tarnish for all Agateen-coated silver coupons was already almost 50% by 500 hours.

Data are also included in table 3 for coated silver control coupons after 6 years exposure to ambient conditions. Silver control coupons coated with eight materials were still without tarnish, while the Renaissance Wax-coated control coupon was fully tarnished. The Agateen-coated silver control was still protective except where it was thinly coated and had turned black, while the Mowiol and Aquazol controls had begun to color slightly in some areas.

In general, once even lighting was achieved on the shiny silver surfaces, this photographic- and computer-based surface tarnish evaluation technique proved to be a useful and relatively easy method for ranking coatings. Within experimental error, results at 500 hours of exposure were generally consistent with those at the endpoint for visual evaluations at 315 hours (table 3). Regular digital photography throughout the experiment also provided invaluable documentation that assisted with interpreting and checking results of instrumental analyses. Less evaluator-dependent methods of assessing the photographs could be used, such as selecting particular color ranges in Adobe Photoshop before using the histogram function to determine the percent surface tarnish. If available, digital image analysis software could also be used as an alternative method.

3.4 GLOSS MEASUREMENT

Gloss measured on coatings applied to glass slides was constant throughout the H$_2$S test exposure; thus, change in gloss measured on silver coupons could be attributed to the change in reflectance caused by tarnish on the silver surface. At the beginning of the experiment the majority of coated silver coupons showed gloss measurements in a range between 800 and 1200 gloss units (at the 20° setting, the instrument produces values of approximately 2000 gloss units for 100% reflectance). Lower average gloss was measured
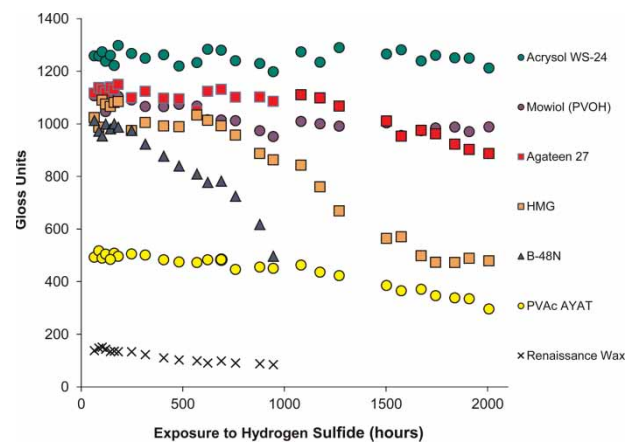

FIG. 7.   Average gloss measured on five top-performing areas for seven representative coatings. Coupons coated with Acryloid B-48N and Renaissance Wax were removed from the chamber after 1000 hours because they had completely tarnished.
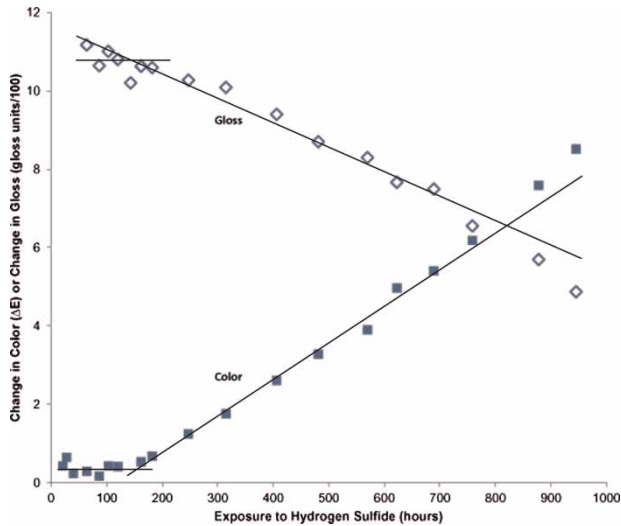
FIG. 8.   Average gloss (outlined diamonds) and change in color (solid squares) measured on five best-performing areas coated with Acryloid B-72. Flat and sloping trendlines for both color and gloss intersect at about 150 hours.

for duller coatings, notably Aquazol, PVAc AYAT, and Renaissance Wax in decreasing order of gloss.

When gloss measurements for the 15 test areas on the three silver coupons in each coating set were plotted, the spread of data was almost always large and increased over the exposure time as areas tarnished. A graph showing change in gloss for the 15 areas on Agateen-coated silver coupons, for example, showed that the average gloss at any exposure time would not adequately represent the relatively good performance

of the best-performing areas, which have thicker coatings within a relatively narrow thickness range (fig. 5). As was found by visual evaluation and digital image analysis, gloss measurements were often more consistent and showed later onset of loss in gloss on individual silver coupons that were more thickly and evenly coated than their cohorts. This is illustrated by graphs of the three silver coupons coated with Acrysol (fig. 6a).

In order to narrow the spread of data for comparison of coatings, the five best-performing test areas for each set of silver coupons were selected from photographs taken during the experiment based on optimal delay in tarnish over time. Plots of gloss for the average of the five areas separate with test exposure, illustrated by seven representative coatings (fig. 7). In order to rank all coatings based on such gloss plots, the "onset of tarnish" was then manually derived at the intersection of a pair of trendlines on each plot (fig. 8). The first trendline consisted of an initial slope near zero describing relatively stable unchanged gloss, and the second trendline consisted of a negative slope describing the declining gloss that followed. For most coatings, the trendlines, which roughly correspond to an induction period followed by relatively steady loss of protection, qualitatively fit data reasonably well. Results for Mowiol-coated areas were an exception in showing a slightly anomalous trend: the gloss of Mowiol-coated areas dropped around 100 gloss units in the first 600 hours before becoming stable. Tarnish onset points were generally corroborated by visual examination of photographs taken during the experiment.
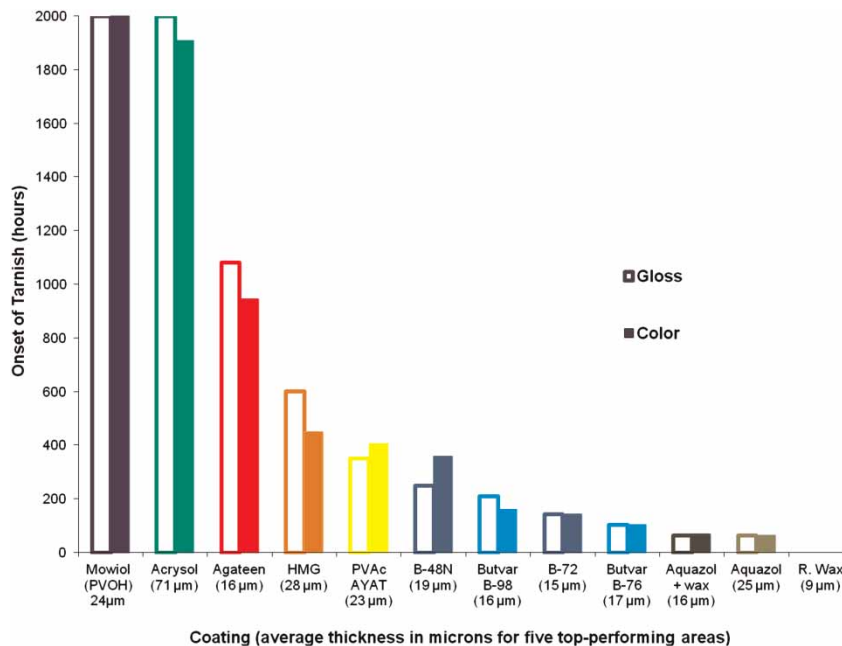

FIG. 9.   Estimated onset of tarnishing for five top-performing areas for each coating, derived from measurements of color change and gloss. Average thicknesses of coatings are noted in the legend.

Results for estimated onset of tarnish derived from average gloss for the five best-performing areas on coated silver coupons are shown in figure 9. Acrysol- and Mowiol-coated areas performed very well by this measure, with gloss measurements remaining constant through 2000 hours of test exposure (after the initial drop for Mowiol-coated areas). Results also appeared to separate out performance of Agateen and HMG from remaining coatings. Rankings for all coatings were similar to those on best-performing silver coupons evaluated visually and by image analysis with the exception of Mowiol, which performed better according to gloss results.

In general, this method of coating evaluation was found to be more labor intensive than visual evaluation or digital image analysis, and it did not allow direct ranking of coatings as the other two methods did. Rankings based on the gloss measurements were derived by determining the onset of tarnish for best-performing areas, but gradual changes in gloss as silver coupons tarnished, variability of measurements, and the anomalous behavior trend for Mowiol made interpretation difficult. Coupled with thickness measurements taken in exactly the same areas, however, gloss measurements provided precise data about the success of coatings of given thicknesses.

3.5 COLOR MEASUREMENT

Color change (E*) and the total color difference from initial pre-exposure readings (ΔE*) were calculated for all measurements in each area based on the 1976 CIE L*a*b* formula. The ΔE*s measured on coatings applied to glass slides were essentially nil throughout H_2S test exposure; thus, change in color measured on the silver coupons could be attributed to tarnish of the silver rather than the coatings themselves. Color difference generally increased as samples tarnished, first becoming iridescent, then turning orange-brown, dark brown, and finally blue black.

Spread of data for the 15 test areas was as broad as for gloss. As was found by the other three measurement techniques, ΔE*s were often more consistent and showed a later onset of color increase on individual silver coupons that were more thickly and evenly coated than their cohorts. This is illustrated by graphs of the three silver coupons coated with Acrysol (fig. 6b). Color measurement continued for more than 3000 hours of exposure for Acrysol-coated silver coupons, and results showed changes for the two more thickly coated silver coupons at about 2000 hours, as was also the case for areas more thickly coated with Mowiol. Note that colorimetry plots for the three Acrysol-coated silver coupons were similar to those for gloss (fig. 6a).

In order to narrow the spread of data for comparison of coatings, the same method of plotting data for the average of the five best-performing areas was employed. A plot for Acryloid B-72 shown in figure 8 is a near-mirror image of the coating's gloss plot, as occurred for most coatings. Using the same trendline-method for determining the onset of tarnish as was employed for gloss, colorimetry showed approximately the same onsets of tarnish on the five best-performing areas as gloss measurements, within experimental error (fig. 9). Rankings were also similar to those of better-performing silver coupons evaluated visually and by image analysis, with the exception of Mowiol. Color change was somewhat anomalous for Mowiol, as was the case for its change in gloss: ΔE* increased to nearly two units over the first 500 hours, then maintained stability up to around 2000 hours.

As was gloss measurement, colorimetry was more time-consuming than visual evaluation or digital image analysis, and ranking of coatings also had to be determined indirectly by deriving the onset of tarnish for best-performing areas. Interpretation of data also proved to be difficult because of variability in measurements, gradual change in color, and anomalous patterns such as that exhibited by Mowiol. Agreement in the onsets of tarnish determined from colorimetry or gloss, however, allowed higher confidence in the results for both techniques. They also tended to confirm that the most important evaluation factor for coating performance was the initial development of tarnish, a key moment commonly identified by visual evaluation in studies of coatings on silver (Reedy et al. 1999; Thickett and Hockey 2003; Luxford and Thickett 2007).

4. DISCUSSION

Results provided comparisons of performance between coatings on silver in an H_2S environment. Despite wide variation in data for individual coatings, mainly ascribed to variations in coating thickness, the rankings of coatings were similar using the four different evaluation methods and three selections of data: all data, data for best-performing individual silver coupons, and data for five best-performing areas. The main discrepancies in rankings were for the performances of Mowiol and Agateen. According to gloss and color measurements, Mowiol performed best of all the coatings when the five best-performing areas were compared (fig. 9), but least well among the five most effective coatings when data from other evaluation methods were considered (figs. 3 and 4, table 3). Agateen's excellent results on the most thickly coated silver coupon and five best-performing areas but mediocre performance as an average of all data clearly could be attributed to uneven, thin coatings on some coupons.

Experimental results were not correlated to expected tarnish levels or hours of exposure in normal museum

environments, as others have attempted (Luxford and Thickett 2007). Results for the five best-performing areas, however, suggested a potential for good performance when coating application was optimal. Times for the onset of tarnish derived from color and gloss measurements showed that the best-performing Mowiol- and Acrysol-coated areas lasted about twice as long as the best-performing Agateen-coated areas (fig. 9). In turn, Agateen-coated areas protected the silver almost twice as long as HMG- and PVAc-AYAT-coated areas.

Use of a relatively inexpensive thickness-measuring device based on eddy current technology (around US $500) proved to be essential for the evaluation of coatings in our experimental study. In many cases it showed that coating thickness was not even over the surface of the silver coupons and suggested that some coatings may not have achieved sufficient thickness or sufficiently even thickness for adequate protection of the metal. Based on this experience, it is essential to determine thickness of coatings and variability in coating thickness in any study that compares coatings.

A critical issue was whether the experimental coating thicknesses in the study were comparable to those used by conservators. As far as can be determined, nothing has been published in this regard. Thicknesses of two types of coatings on objects in the collections of Winterthur Museum were subsequently measured using a BYK-Gardner (Byko-test 8500) thickness gauge, and those results are incorporated into discussions of individual coatings below. Unfortunately, measurements on artifact surfaces are limited when using thickness gauges based on eddy current technology: results are only accurate when measurements are made on relatively flat uncorroded surfaces, which can be difficult to find on artifacts and may not be representative. In practice, thickness measurements proved to be unreliable in recesses where coatings typically pool, at edges where they were thin, and on curved (especially concave), decorated, or tarnished surfaces. Attempts to measure thickness on artifacts using an inverted metallographic microscope proved unreliable. Successful thickness measurement using an FTIR microscope has been reported at the British Museum without including any results (Thickett and Hockey 2003).

The most promising result of our study was that Acrysol appears to have potential as a coating for silver. It has been used for dip coating brass (Dow 2012) and as a consolidant for damp plaster, bone, and ceramics, but it has not been used for coating silver as far as is known. Acrysol has a significant safety advantage during the coating process over coatings that rely on organic solvents for application, since it is delivered in an aqueous dispersion. The coating's success in our experiment, however, must be

attributed to some extent to its thickness, which averaged 71 µm in the five thickest areas. By all four evaluation methods Acrysol's performance on the most thinly coated silver coupon #27 (see fig. 6), which also had all five of the most thinly coated areas, was not as good as the average for Agateen. This was in spite of the fact that the average coating thickness on silver coupon #27 was 29 µm, higher than the average thickness for all other materials. It remains to be seen if Acrysol would be acceptable to conservators and curators if it were as thickly applied as on better-performing areas in this experiment. The coating might also be less desirable on account of a slight haze, but its appearance might be improved by application technique. Dilution with water-miscible alcohols such as isopropyl alcohol and ethanol improve its flow but increase viscosity. Additional study and experimentation are required to develop an optimal application method and evaluate Acrysol's aging properties in this use.

In this study, Mowiol, also unknown as a coating for silver, exhibited excellent performance on the five best-performing areas (also relatively thick at 25 ± 5 µm) according to gloss and color measurements. It, too, has the advantage of being applied in an aqueous solution, and its appearance was satisfactory. Its relatively mediocre rankings for visual evaluation and digital image analysis, however, raised questions. Additional work would be required before it could be considered for coating silver.

PVAc AYAT's generally good performance in this experiment confirmed De Witte's earlier study that showed the coating's low permeability to H_2S (De Witte 1973). The low gloss of the PVAc AYAT coating, however, makes it unacceptable for use on silver (fig. 7). Moreover, the low T_g (26°C) of PVAC AYAT would make it a poor choice in dusty environments, since dust would adhere to the surface.

Agateen performed relatively well in the experiment on the most thickly coated silver coupon and five best-performing areas. Thin application in one area was clearly responsible for the otherwise excellent appearance of the coated silver control coupon after 6 years at ambient conditions (table 3). Untarnished Agateen-coated objects in the collection of Winterthur Museum measured somewhat more than the 16 ± 2-µm thickness of the best-performing silver coupon and five best-performing areas measured in the experiment. A still-protective Agateen coating applied by Heller to a silver tankard (Acc. No. 1970.900) more than 30 years ago, for example, averaged 24 µm based on 200 measurements (14% RSD). Equally protective were slightly younger Agateen coatings applied to a silver bowl (Acc. No. 2004.52) and a silver sauce boat (Acc. No. 1964.51) in the museum's collection. The former measured 24 µm (RSD 29%) and the

latter 17 μm (RSD 9%), based on 50 measurements each. At the outer limit of acceptable thickness would be an Agateen coating applied to the Mace of the U.S. House of Representatives. Since the Mace is moved to the House chamber each time the body convenes, it has been intentionally coated with a thick layer of Agateen measuring 40–50 μm in thickness (RSD unknown) in order to protect the object from the regular handling (Gleason et al. 1992; Williams 2007).

In this experiment the best HMG-coated areas did not perform quite as well as the best Agateen-coated areas, despite similar coating thickness. To some extent this may attributed to the fact that Agateen is formulated with solvents to promote leveling for its use as a coating, whereas HMG is formulated as an adhesive. Like Agateen, HMG's performance correlated with thickness according to all evaluation techniques. Visual evaluation and image analysis, for example, showed no tarnishing at 350 and 500 hours, respectively, for the most thickly coated silver coupon 63 (average thickness 27 μm and RSD 2%), while the ranking was below the middle for the most thinly coated silver coupon (average thickness 15 μm and RSD 10%). Thicknesses of Frigilene, the commercial cellulose nitrate coating similar to HMG, have been successfully measured on silver objects at the British Museum but have not been reported (Thickett and Hockey 2003).

Butvar B-98 generally ranked somewhat lower than the cellulose nitrate lacquers. According to all four evaluation techniques, its performance was best when coatings averaged 17 ± 6 μm and poor when coatings averaged 7 ± 7 μm.

Despite the high quality and excellent aging properties of the Acryloid resins B-72 and B-48N, these acrylics ranked in the middle of coatings in our experiment. Difficulties in measuring thicknesses on B-72-coated silver objects prevented acquisition of relevant data about a range of objects despite a number of attempts. Measurement of the thickness of a B-72 coating was successful on only one object, the untarnished bottom of a Gorham coffee pot (Acc. No. 1983.108.21) in the collection of Winterthur Museum; it showed a coating thickness of about 19 μm based on 50 measurements (RSD 20%). This is thicker than B-72 coatings in our study, which averaged 15 μm on the five best-performing areas, and may have contributed to the relatively poor performance of B-72 in this study. Thicknesses of 23 and 7 μm on test samples coated with B-72 and B-48N are reported in the literature; not surprisingly these thicknesses correlated with "good" and "bad" results, respectively (Mourey and Czerwinski 1993). In any case, inferior test results for the acrylic coatings compared to Agateen in this experiment were consistent with those reported in another study in which B-72 was applied

according to normal treatment practice by an experienced conservator (Reedy et al. 1999).

All four evaluation techniques showed poorer performance for silver coupons coated with Butvar B-76, Aquazol (with or without wax overcoat), and Renaissance Wax exposed to H_2S. All Aquazol-coated silver coupons were blotchy and uneven in appearance and would be unacceptable to conservators for coating silver. However, Butvar B-76 and Aquazol still appeared at least somewhat protective after 6 years' exposure of coated silver control coupons stored at ambient conditions (table 3). The thinness of Renaissance Wax coatings (9 μm with RSD 9% on best-performing areas) may have contributed to its particularly poor performance, only slightly better than the performance of uncoated silver blanks exposed to H_2S. The Renaissance-Wax-coated silver control coupon was also thinly coated (5 μm with RSD 40%) and had completely tarnished after 6 years exposure at ambient conditions. In the study mentioned in the previous paragraph, by comparison, silver test samples coated with microcrystalline wax measured 17 μm in thickness, and they performed in the middle between good and bad results for acrylic resins (Mourey and Czerwinski 1993).

Considerable information was gained about assessment methods during the experiment. Results were found to be easily compared for data acquired by visual observation and digital image analysis, while gloss and color measurements were relatively time consuming and more difficult to interpret and compare. Measurement of coating thickness in the same area as that used for quantitative measurement of gloss and color, however, provided data that allowed limited conclusions to be drawn regarding correlations between coating thickness and performance (protection from tarnish).

5. Conclusions

Results indicated that the relative effectiveness of 12 coatings tested on silver in a high-sulfide environment was linked to achieving even coatings of sufficient thickness, along with inherent differences in the coatings themselves. Correlation of thickness and performance on many test silver coupons underscored the importance of even and adequate coating application. Results of performance rankings were generally consistent, within experimental error, whether determined by visual evaluation, digital image analysis, gloss measurement, or colorimetry. Slight inconsistency in rankings determined by these methods was interpreted to relate primarily to variations in coatings thickness on individual silver coupons within coating sets. All four evaluation methods ranked Acrysol, Agateen, HMG, and PVAc AYAT among the five best coatings when

limited to consideration of best-performing (optimally coated) test areas on the silver coupons, and Acrysol appeared to be a promising coating for future study and development. The fifth coating, Mowiol, performed best of all in the five best-performing areas with respect to color and was equal to Acrysol in terms of gloss. It showed mediocre performance compared to the other four coatings, however, by visual evaluation and image analysis. The Acryloid and Butvar coatings showed varying ability to delay tarnish for a limited time but did not perform as well overall as the previous coatings. Aquazol and Renaissance Wax were the least effective of the twelve coatings tested by all methods on all areas. Renaissance Wax in particular performed only marginally better than uncoated controls.

ACKNOWLEDGMENTS

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SOURCE OF MATERIALS

(now a subsidiary of the Dow Chemical Company, Midland, MI)

Agateen Lacquer No. 27 and Thinner No. 1
Agate Lacquer
Tri-Nat, LLC
824 South Avenue
Middlesex, NJ 08846, USA

Aquazol 500
Talas
568 Broadway
New York, NY 10012, USA

Butvar B-76 and B-98
Solutia Inc.
PO Box 66760
St. Louis, MO 63166, USA

HMG Heat and Waterproof Adhesive
H. Marcel Guest LTD
Riverside Works
Collyhurst Road
Manchester M40 7RU, UK

Mowiol 28-29
Sigma-Aldrich
6000 N. Teutonia Avenue
Milwaukee, WI 53209-3645, USA

PVAc AYAT
Union Carbide Corporation, a subsidiary of The Dow Chemical Company

PO Box 4393
Houston, TX 77210, USA

Renaissance Wax
Picreator Enterprises LTD
44 Park View Gardens
Hendon, London NW4 2PN, UK

Sterling silver sheet
Armstrong Tool and Supply Company
31747 West Eight Mile Road
Livonia, MI 48152, USA

BYK-Gardner micro-TRI-gloss and Byko-test 8500
BYK-Gardner, USA
Rivers Park II
9104 Guilford Road
Columbia, MD 21046, USA

Dräger diffusion tube (10/a-D for H_2S)
Fisher Scientific
2000 Park Lane
Pittsburgh, PA 15275, USA

Elcometer 345 digital coating thickness gauge
Elcometer Inc.
1893 Rochester Industrial Drive
Rochester Hills, MI 48309, USA

Minolta CR-121 Colorimeter
Konica Minolta
101 Williams Drive
Ramsey, NJ 07446, USA

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Résumé – Douze revêtements appliqués à des échantillons d'argent ont été exposés à des concentrations élevées de sulfure d'hydrogène pour évaluer leur potentiel à prévenir la ternissure dans des environnements intérieurs. Lors des tests, les échantillons d'argent ont été évalués par observation visuelle, par analyse d'images numériques, par la mesure du lustre et par colorimétrie. Les meilleurs résultats ont été obtenus pour l'Acrysol WS-24, l'Agateen Air Dry Lacquer No. 27 (lacque Agateen n. 27 pour séchage à l'air), l'adhésif HMG Heat and Waterproof (HMG résistant à la chaleur et à l'eau) et le PVAc AYAT. Le Mowiol 28–99 a permis de bons résultats à quelques endroits localisés, mais s'est avéré généralement médiocre. Le Butvar B-98 et l'Acryloid B-48N se sont démontrés moins efficaces pour retarder le ternissement, quoique leurs résultats étaient un peu supérieurs à ceux pour l'Acryloid B-72 et le Butvar B-76. L'Aquazol 500, seul ou avec un revêtement de cire Renaissance, ainsi que la cire Renaissance seule, ont donné les moins bons résultats. L'épaisseur du revêtement s'est avéré un facteur déterminant dans sa performance.

Resumen – Doce barnices aplicados a cupones de plata esterlina fueron sometidos a altos niveles de sulfuro de hidrógeno (ácido sulfhídrico) para probar su efectividad al prevenir el oscurecimiento en ambientes interiores. Los cupones de plata fueron evaluados durante el transcurso del experimento utilizando observación visual, análisis de imágenes en fotografías digitales, medición de brillo, y colorimetría. En general fue mejor el desempeño de: el Acrysol WS-24, el Agateen Air Dry Lacquer No. 27, el HMG Heat and Waterproof Adhesive, y el PVAc AYAT. El Mowiol 28–99 se desempeñó muy bien en algunas áreas, pero en las demás resultó mediocre. El Butvar B-98 y el Acryloid B-48N fueron generalmente menos efectivos en retardar el oscurecimiento; y el Acryloid B-72 y el Butvar B-76 se desempeñaron menos bien. El Aquazol 500 y el Aquazol 500 cubierto con una capa de Renaissance Wax (cera Renaissance), y el Renaissance Wax resultaron ser los menos efectivos. El grosor de la capa demostró ser un factor significativo en el desempeño del recubrimiento.

Resumo – Doze revestimentos feitos em coupons (pílula) de prata de lei foram submetidos a níveis altos de sulfeto de hidrogênio, a fim de testar sua eficácia na prevenção de manchas quando em ambientes internos. Coupons (pílula) de prata foram avaliados no decorrer da experiência por meio de observação visual, análise de imagens de fotografias digitais, medição de brilho e colorimetria. Acrysol WS-24, Agateen Air Dry Lacquer No. 27 (Verniz de secagem ao ar livre Agateen nº27), Adesivo HMG Heat and Waterproof (HMG resistente ao calor e à água) e PVAc AYAT obtiveram, de modo geral, melhor desempenho. Mowiol 28–99 teve atuação muito boa em algumas áreas, mas foi medíocre em outras. Butvar B-98 e Paraloid B-48N foram geralmente menos eficazes no retardamento de manchas. Paraloid B-72 e Butvar B-76 tiveram desempenho inferior. Aquazol 500, Aquazol 500 revestido com Renaissance Wax (cera Renaissance) e a Renaissance Wax foram os menos eficazes. A espessura do revestimento provou ser um fator importante no seu desempenho.