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SCIENTIFIC PAPER

SILVER NANOFILM SENSORS FOR ASSESSING DAGUERREOTYPE HOUSING MATERIALS IN AN ODDY TEST SETUP

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Abstract

Daguerreotype images consist of mercury-silver or mercury-silver-gold amalgam nanoparticles on silver-coated copper substrates that are particularly sensitive to environmental pollutants such as hydrogen sulfide and chlorine-containing compounds. Typically, silver along with copper and lead foils are used in the standard Oddy test at cultural institutions to asses the suitability of materials for the display and storage of silver objects. In this study, it was observed that silver foil does not reflect the sensitivity of a daguerreotype image under the same testing conditions. Therefore, the use of vapor deposited silver films with a thickness optimized to best follow the reactivity of a daguerreotype sample in a modified Oddy test setup is proposed. Results are reported for a group of materials chosen for testing because they are either used for housing daguerreotypes at several institutions or could be good replacement options. The new procedure allows for facile visual evaluation of the silver nanofilms after the test exposure and reduces the length of the test. The Oddy test with silver nanofilm is not proposed as a replacement for the standard Oddy test but as an additional assay to be used for sensitive silver objects.

1 Introduction

The daguerreotype image consists of mercury-silver or mercury-silver-gold amalgam nanoparticles on silver-coated copper substrates.[1] Daguerreotypes are very delicate and susceptible to damage by mechanical and chemical cleaning, light, and environmental pollutants, such as hydrogen sulfide and chlorine-containing compounds.[1-3] To protect daguerreotypes from external sources of deterioration, they are stored in housings that typically consist of glass, mat board or brass, and tape.[1] If not tested properly, some housing materials themselves can be the source of corrosive compounds, especially hydrogen sulfide. For museums, the testing of materials used for display, storage and conservation has become routine practice to protect objects from harmful volatile pollutants. The most referred to method is the Oddy test which provides a visual indication of the presence of volatile pollutants that are harmful to silver, copper, and lead.[4,5] The standard Oddy test is carried out by heating a vapor-tight assembly containing the test material, metal test coupons, and water to maintain a 100 % RH environment at 60 °C for one month.

Over the last 40 years, various modifications to the Oddy test have been proposed to improve the reproducibility and reliability of the results and, in some cases, to shorten its duration. In the early 1990s, Green and Thicket reported improvements by standardizing the glassware and configuration of the test using 50 ml test tubes, hanging metal coupons with nylon monofilaments, and keeping the water to container volume ratio at 1:100.[6,7] In 1999, Bamberger reported improvements by using thin copper, silver, and lead foils and placing them in one jar with a screw top lid, termed the 3-in-1 Oddy test, which is the setup currently used at The Metropolitan Museum of Art (MMA).[8] In 2003, Robinet and Thickett reported a 3-in-1 Oddy test based on the 1995 Green publication that places the metal foils in the stopper of a 50 mL test tube.[9] In 2008, Chen and co-authors proposed using a 30 nm silver nanoparticle assembly on glass slides to increase the sensitivity of the method for detecting materials harmful to silver.[10,11] The changes in these silver nanoparticle films can be followed using a UV-Vis spectrometer. In 2011, Wang and co-authors proposed vacuum deposited silver (200 nm) and copper (1000 nm) films to increase the sensitivity of the Oddy test and to shorten its duration from one month to two weeks.[12] Wang et al. also introduced an image analysis setup and software to quantify the corrosion. A method involving metal films is promising, however these authors omit lead, which could change the final rating of the tested material.[13] The use of silver films to detect low levels of hydrogen sulfide vapors was first proposed in 1998 by Hawkins and co-workers, who report the use of Tollens colloidal silver films, prepared on PVC and on glass by dip-coating, to detect hydrogen sulfide vapors down to 0.1 ppm using UV-Vis reflectance.[14] Hawkins et al. also tested 25 nm vacuum deposited silver films, but found them to be less sensitive than the Tollens films.

To drastically shorten the testing time of materials for housing and storage, Daniels and Ward suggested using the sodium azide spot test to identify easily reducible sulfur.[15,16] Results from this test can be obtained in less than a minute and can be used to quickly rule out the more harmful materials. Daniels and Ward state that the azide test can not completely replace the Oddy test as it only identifies materials that are harmful to silver. The azide test is currently one of several tests used at the Los Angeles County Museum of Art to rapidly assess potential materials for housing and storage.[17]

Special attention has been given to testing photographic materials throughout the years. In the early 1970s, Weyde reported a method to detect oxidizing vapors that were harmful to silver images in the Munich Archives.[18] Yellow films manufactured by Agfa-Gevaert, comprised of silver nanoparticles less than 30 nm in diameter, were exposed in the storage areas for up to one year. These films turned brown in the presence of oxidizing vapors due to the formation of silver sulfide. Further studies showed that the discoloration of the films occurred ten times faster than the first visible change of photographic silver.[18] In 1976, Collings and Young investigated how storage materials interacted with silver while in direct contact.[19] The test proposed by these authors consists of a piece of filter paper soaked in dilute HCl, a silver plate, a piece of the material to be tested, 2 mL of water and glass slides inside a glass petri dish that is heated at 75 °C for 8 to 24 h. The silver plate is visually examined and only after 24 h of exposure, if there is no tarnishing, the material is deemed ‘safe’. A more sophisticated and systematic method is the Photographic Activity Test (PAT, ISO 18916:2007) that sandwiches layers of detector films, filter paper, and materials of interest together and ages them at 70 °C and 86% RH for 15 days.[20] One of the detectors consists of colloidal silver dispersed in gelatin and is made by the Image Permanence Institute (IPI) specifically for the PAT.[21]

In the present work, an Oddy test enhanced with silver nanofilms is utilized for evaluating a variety of materials typically employed for housing sensitive silver images, including daguerreotypes. The silver nanofilm sensitivity is compared to silver foil used in the standard Oddy test and to daguerreotype image samples. The procedure presented allows for facile visual evaluation of the silver films after exposure and reduces the length of the test.

2 Experimental

2.1 Materials

The Oddy test materials include: silver foil (Aldrich, 0.025 mm, 99.9%), copper foil (Aldrich, 0.127 mm, 99+%), lead foil (Alfa Aesar, 0.1 mm, 99.9%), 20 mL Pyrex beaker (Corning Incorporated), 125 mL I-Chem clear short wide mouthed jar and lid (Fisher Scientific), Dow Corning high vacuum grease, and deionized water. Silver film materials include silver shots (Aldrich, 1-3 mm, 99.99%) and petrographic slides (Buehler, 27 x 46 mm). Slide cleaning supplies include Alconox (anionic powder detergent, Alconox, Inc), ethanol (HPLC grade, Fisher Scientific), acetone (HPLC grade, Fisher Scientific), hydrochloric acid (ACS Plus, Fisher Scientific), crystallizing dish (170 mm, Pyrex), shaker (Thermolyne Rotomix Type 48200), and Dust Off disposable compressed gas duster.

The materials for testing were chosen because they are either currently used at different institutions for housing daguerreotypes or could be good replacement options. The housing materials tested include: tan unbuffered barrier board (University Products), tan buffered barrier board (University Products), Alpharag Artcare black buffered mat board (Bainbridge, 4 ply), Alpharag Artcare colonial cream buffered mat board (Bainbridge, 4 ply), Photomount white unbuffered mat board (Rising, 4 ply), Museum Board antique buffered mat board (Rising, 4 ply), Filmoplast P90 paper tape, 3M Double Sided Tape, black Volara (2A, 1/8 in.), white Volara (2A, 1/8 on.), 11 year old white Volara (2A, 1/8 in.), Mylar (0.005 mm), Image Permanence Institute colloidal silver film, and Filmoplast P90 with a thin coat of Liquitex soft body mars black acrylic paint. Reference materials include wool (style 527, Testfabrics, Inc.), white braided elastic band (1 in., Dritz), and black ultrasuede (Toray Ultrasuede).

2.2 Daguerreotype samples

The gilded daguerreotype samples used in this study, made by contemporary artist Jerry Spagnoli, were examined by SEM-EDS before testing and were found to have image particles within the typical range of diameters and compositions of those observed in 19th century plates.[1,3]

2.3 Silver nanofilm sensors

Before silver film formation, glass slides were cleaned in a crystallizing dish to remove surface contaminants as follows: 1) washed for 15-30 min in an aqueous solution of Alconox; 2) rinsed briefly in deionized water to remove residual Alconox; 3) washed in 1% v/v HCl for 15-30 min to remove any residues; 4) rinsed in deionized water and washed for 15-30 min in water to remove HCl; 5) rinsed briefly in ethanol then washed in ethanol for 15-30 min to dehydrate; and 6) rinsed and washed with acetone for 15-30 min to finish cleaning. After cleaning, slides were submerged and stored in acetone at room temperature until use. Slides were dried immediately before use with a compressed gas duster. Silver nanofilms were made using an Edwards Vacuum Coating unit E306A comprised of an E2M8 rotary vacuum pump, E04 vapor diffusion pump, Pirani 10 vacuum gauge, Penning 8 vacuum gauge, FTM6 quartz crystal microbalance film thickness monitor, and a variable transformer. The films were formed under a vacuum of 2 x10^{-6} mbar at a deposition rate of 0.025 nm/s to a desired thickness of 7- 200 nm. The films were stored in a sealed bag with silica gel conditioned at 33% RH to prevent tarnishing when not immediately used.

2.4 Oddy test

The MMA 3-in-1 Oddy test configuration is described in detail by Bamberger et al.[8] For this method, deionized water (2 mL) is added to the I-Chem jar first. The metal foils are folded over the edges of the 20 mL beaker and the material to be tested (typically 2" x 1") is placed inside the 20 mL beaker which is then secured with grease to the bottom of the I-Chem jar. The threads of the jar are coated with grease and the jar is sealed. The test setup is placed in the oven at 60 °C for 4 weeks. After the first 5 min in the oven, the lid is tightened another eighth to a quarter turn. A subset of materials was also tested using 1 mL of deionized water for comparison.

2.5 Oddy test using daguerreotype image sample, silver foil, and wool

The standard Oddy test assembly was used for daguerreotype image sample tests. Only silver foil was used and the daguerreotype image sample was placed at the bottom of the beaker with the wool sample but not in contact. Tests were conducted for 1, 2, and 4 weeks at 60 °C.

2.6 Oddy test using silver nanofilms

The Oddy test involving the silver nanofilms used the same glassware assembly as the 3-in-1 Oddy test. The material of interest was placed at the bottom of the 20 mL beaker and the silver nanofilm slide was placed on top of the sample (Fig. 1). The test setup was placed in the oven at 60 °C for 1 or 2 weeks.

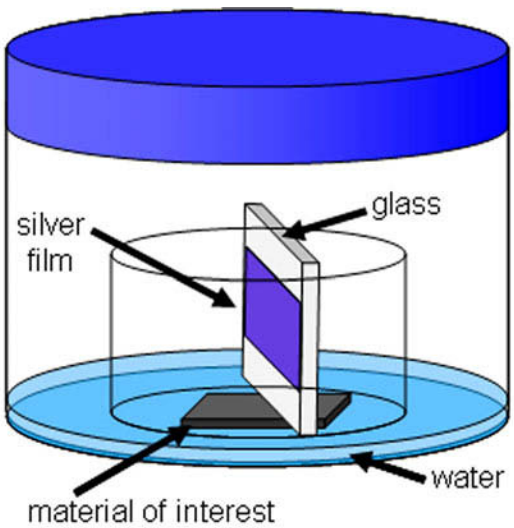

Figure 1: Oddy test with silver nanofilm setup. The material of interest is placed at the bottom of the beaker and the silver film is placed on top. Water is added to the outer jar.

2.7 Rating of materials

For the standard Oddy test, corrosion results were ranked on the scale from 1 to 5; 1 being no obvious change and 5 being obvious change in color with majority of the surface corroded. The ranking for all three metals are compared and a final overall rating is given for the material: pass (P), temporary (T), or unsuitable (U).[7,8] If a 4 or 5 ranking is given for one metal, the material is considered unsuitable. For the Oddy test with silver nanofilm, corrosion results are pass with no obvious discoloration, or unsuitable with brown discoloration that can be a few spots or the entire film. Daguerreotype image samples, nanofilms, and foils were photographed before and after each test using a Canon EOS 5D Mark II camera and Interfit Digilight 600 lights with Canon EOS Utility and Adobe Lightroom 3 software programs.

2.8 SEM measurements

Scanning electron microscopy (SEM) images were acquired with a Carl Zeiss Leo Ultra Scanning Electron Microscope using an accelerating voltage of 2-10 KeV, in-lens and EsB detectors. The in-lens detects the elastically backscattered electrons and the EsB detector optimizes the detection of high angle backscattered electrons carrying an energy close to the landing energy of the primary beam, and exhibits nanoscale compositional information, with contrast between the metallic (brighter) and insulating (darker) areas. EDS spectra were acquired with the Carl Zeiss Leo 1 using an accelerating voltage of 15 KeV.

3 Results and Discussion

3.1 Comparison of the Oddy test using 1 mL and 2 mL of water

During the 3-in-1 Oddy testing, corrosion spots were frequently observed on metal foils where water condensation occurred. Therefore, a set of Oddy tests were conducted with the volume of water reduced to 1 mL to determine if materials received the same rating while reducing the interference from condensation. Table 1 presents a comparison of the ratings when 1

Materials/Conditions	Oddy Results (Ag/Cu/Pb)			
	2 mL H_2O		1 mL H_2O	
Wool	4/3/1	U	5/3/1	U
Elastic band	2/1/1	P	1/1/1	P
Ultrasuede black	1/1/1	P	1/1/1	P
University Products tan unbuffered barrier board	1/2/3	T	1/1/1	P
University Products tan buffered barrier board	1/3/2	T	1/1/1	P
Rising Museum Board antique buffered mat board	1/4/1	U	1/1/1	P
Bainbridge Alpharag Artcare colonial cream buffered mat board	1/4/1	U	1/1/1	P

Table 1: Comparison of the performances of different materials in the standard Oddy test when 1 and 2 mL of water are used.

and 2 mL of water were used. In most cases, materials that received an unsuitable or temporary rating with 2 mL of water received a pass rating with 1 mL of water, since silver corrosion is facilitated by moisture.[14,22,23] The larger quantity of water guaranteed a 100% RH environment when a test material was hygroscopic and gave a more representative indication of possible corrosion. Therefore, 2 mL of water were used for both the standard Oddy test and the method that incorporates silver nanofilms.

3.2 Comparison of silver foil and daguerreotype image sample sensitivities

Silver foil and daguerreotype image samples were exposed to wool in the Oddy test setup for 1, 2, and 4 weeks to compare the sensitivity of silver foil to daguerreotype images. All daguerreotype samples had corrosion after exposure to wool, with increasing corrosion correlating to exposure time. The silver foil at 1 and 2 weeks had a small amount of tarnishing on the edges, while the silver foil at 4 weeks was almost completely tarnished and was dark black in color. The small amount of silver foil tarnishing at 1 and 2 weeks do not reflect the sensitivity of the daguerreotype image for the same exposure, therefore, a replacement silver sensor was developed.

3.3 Evaluation of the sensitivity of silver nanofilms with different thicknesses

Silver films of five different thicknesses (7, 15, 20, 50, and 200 nm) were deposited on glass slides and their corrosion susceptibility was compared to that of a daguerreotype image sample. The films and the daguerreotype sample were placed in the Oddy setup with wool as a source of sulfur for 1 week at 60 °C and 100% RH. The colloidal silver film from IPI was also tested, but was removed from further testing after it started to melt in the oven. The films, before and after the test, are shown in Fig. 2. The top row shows the nanofilms and a daguerreotype image sample before testing. The bottom row shows the results after the test in the presence of wool. The daguerreotype sample was heavily corroded after 1 week. All five silver nanofilms had some degree of corrosion. The most drastic and visually obvious change was seen in the 7 nm film. The color of the film changed from purple/blue to brown due to the formation of silver sulfide.[11,18] Since the 7 nm thick silver film was the most sensitive and the one that more closely followed the response time of the daguerreotype image sample, it was chosen for testing the housing materials. The

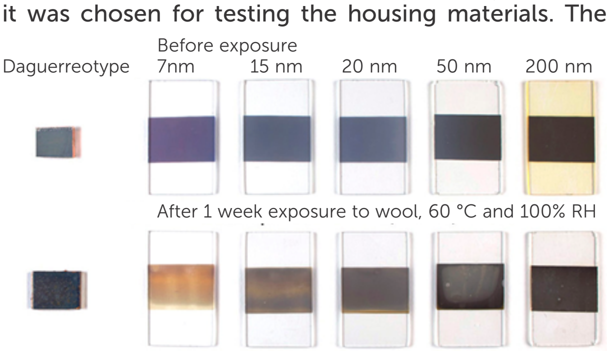

Figure 2: Daguerreotype sample and silver nanofilms before (top) and after one week exposure to wool at 60 °C and 100% RH in an Oddy test setup (bottom).

nanoisland features on the 7 nm film (Fig. 3B) are smaller than the typical daguerreotype image particle (Fig. 3A) which makes the film more sensitive toward corrosive vapors than the daguerreotype image and, therefore, a reliable sensor.[11]

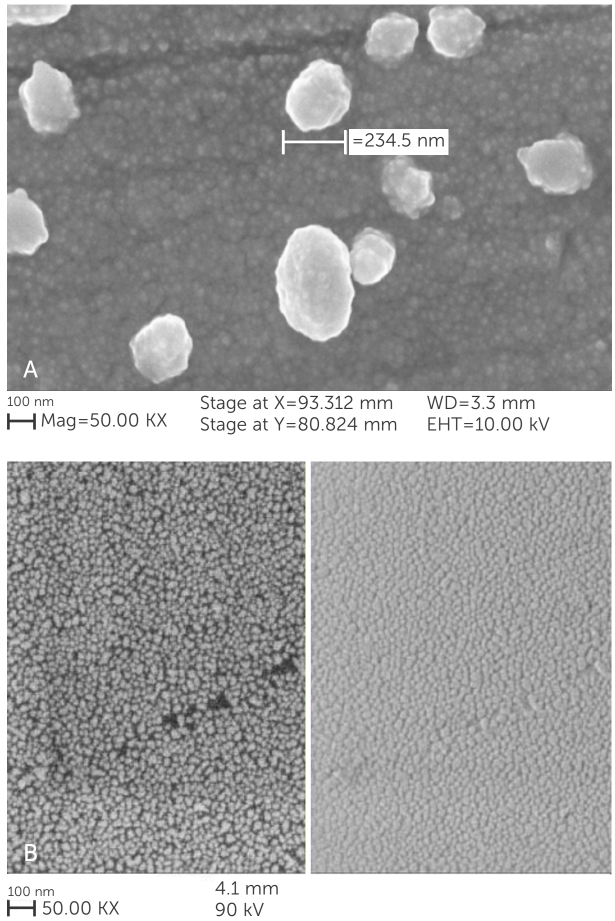

Figure 3: A - SEM image of a high image density area in a gilded daguerreotype sample, and B - SEM images of 7 nm thick silver film acquired with the EsB (left) and in-lens detectors (right), respectively.

3.4 Results of housing materials testing

Each material was assessed for suitability using both the Oddy test and the Oddy test with silver nanofilm. Initially, samples in the silver film test were heated for one week. Materials that passed the one week exposure were tested for a two week period to verify the results. In some cases corrosion was seen after two weeks, identifying weakly off-gassing corrosive materials. The results for Oddy testing, silver nanofilm testing (1 and 2 weeks), and the overall rating are presented in Table 2. Materials that passed all three tests include: Rising Photomount white unbuffered mat board, Filmoplast P90, 3M Double sided tape, black Volara, white Volara (old and new), and Mylar. There are two materials that passed the standard Oddy test and the one week silver nanofilm test, but did not pass the two week silver nanofilm test. Those materials are Bainbridge Alpahrag Artcare black buffered mat board, and Filmoplast P90 with mars black Liquitex. These materials do off-gas harmful vapors, but at very low concentrations. They could be used for temporary exhibition or storage, but are not recommended for daguerreotypes. The following materials received a temporary or unsuitable rating and should not be used for daguerreotype housing: University Products tan unbuffered barrier board, University Products tan buffered barrier board, Rising Museum Board antique buffered mat board, and Bainbridge Alpharag Artcare

Materials	Oddy test (4 weeks)	Silver film test (1 week)	Silver film test (2 weeks)	Overall rating
Mat boards				
University Products tan unbuffered barrier board	T	P	P	T
University Products tan buffered barrier board	T	U	-	U
Bainbridge Alpharag Artcare black buffered	P	P	U	U
Rising Photomount white unbuffered	P	P	P	P
Rising Museum Board antique buffered	U	P	-	U
Bainbridge Alpharag Artcare colonial cream	U	P	-	U
Tapes				
Filmoplast P90	P	P	P	P
Filmoplast P90 with Liquitex soft body mars black	P	P	U	U
3M Double Sided Tape	P	P	P	P
Other				
Black Volara	P	P	P	P
White Volara	P	P	P	P
White Volara (10 yr old)	P	P	P	P
Mylar 0.005 mm	P	P	P	P
References				
Wool	U	U	-	U
Elastic	P	U	-	U
Ultrasuede black	P	P	U	U

Table 2: Comparison of the results of the standard 3-in-1 Oddy test and the Oddy test with 7 nm silver film.

colonial cream buffered mat board.

4 Conclusions

Silver nanofilms were utilized in Oddy testing to identify materials that are suitable for daguerreotype housing and eliminate materials that are weakly off-gassing and corrosive. It was observed that a 7 nm thick silver film was the one that best followed the reactivity of a daguerreotype sample under the same conditions. Rising Photomount was the sole mat board to pass and common photographic conservation materials such as Mylar, 3M Double Sided Tape, and Filmoplast P90 were validated. Reproducible silver nanofilms were made in-house at the MMA using a vacuum deposition system. If this system is not available at a cultural institution, nanofilms could easily be made at a local university's nanofabrication laboratory. The Oddy test with silver film should not be a replacement for the standard Oddy test, but an enhancement to be used for sensitive silver objects like daguerreotypes. The standard Oddy test should be conducted first to identify if the material is unsuitable towards silver, copper, and lead. If the material receives a pass rating from the standard Oddy test, then the Oddy test with silver film should be utilized to further validate the material for use with sensitive silver objects.

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6 References

1. M. S. Barger, W. B. White, *The Daguerreotype Nineteenth-Century Technology and Modern Science*, The John Hopkins University Press, Baltimore, 1991.

2. S. A. Centeno, T. Meller, N. Kennedy, M. Wypyski, *The daguerreotype surface as a SERS substrate: characterization of image deterioration in plates from the 19th century studio of Southworth & Hawes*, J. Raman Spectrosc., 2008, **39**, 914-921.

3. S. Centeno, F. Schulte, N. Kennedy, A. Schrott, *The formation of chlorine-induced alterations in daguerreotype image particles: a high resolution SEM-EDS study*, Appl. Phys. A, 2011, **105**, 55-63.

4. W. A. Oddy, *An unsuspected danger in display*, Mus. J., 1973, **73**, 27-28.

5. W. A. Oddy, *The corrosion of Metals on Display*, Conservation in Archaeology and the Applied Arts. IIC, London, 1975, pp. 235-237.

6. L. R. Green, D. Thickett, *1992/4 Re-evaluation of the Oddy test for assessment of materials for storage and display in the British Museum*, 1992.

7. L. R. Green, D. Thickett, *Testing Materials for Use in the Storage and Display of Antiquities- A Revised Methodology*, Stud. Conserv., 1995, **40**, 145-152.

8. J. A. Bamberger, E. G. Howe, G. Wheeler, *A Variant Oddy Test Procedure for Evaluating Materials Used in Storage and Display Cases*, Stud. Conserv., 1999, **44**, 86-90.

9. L. Robinet, D. Thickett, *A New Methodology for Accelerated Corrosion Testing*, Stud. Conserv., 2003, **48**, 263-268.

10. R. Chen, N. T. Nuhfer, L. Moussa, H. R. Morris, P. M. Whitmore, *Silver sulfide nanoparticle assembly obtained by reacting an assembled silver nanoparticle template with hydrogen sulfide gas*, Nanotechnology, 2008, **19**, 455604.

11. R. Chen, L. Moussa, H. Morris, P. Whitmore, *Silver nanoparticle films as sulfide gas sensors in Oddy tests*, in: P. Vandiver, B. McCarthy, R. Tykot, J. Ruvalcaba-Sil, F. Casadio (Eds.), Materials issues in art and archaeology VIII: symposium held November 26-28, 2007 Boston, Massachusetts, USA. Materials Research Symposium proceedings. Materials Research Society, 2007, pp. 287-297.

12. S. Wang, L. Kong, Z. An, J. Chen, L. Wu, X. Zhuou, *An Improved Oddy Test Using Metal Films*, Stud. Conserv., 2011, **56**, 138-153.

13. J. A. Bamberger, *Comments on an improved Oddy test using metal films,* Stud. Conserv. 2012, **57**, 187-188.

14. S. J. Hawkins, N. M. Ratcliffe, A. Sagastizabal, *The use of thin silver films for the detection of low concentrations of hydrogen sulphide*, Anal. Chim. Acta, 1998, **359**, 125-132.

15. V. Daniels, S. Ward, *A Rapid Test for the Detection of Substances Which Will Tarnish Silver*, Stud. Conserv., 1982, **27**, 58-60.

16. F. Feigl, V. Anger, *Spot Tests in Inorganic Analysis*. Elsevier Publishing Company, New York, 1972.

17. C. Eng. Conservation Center, Los Angeles County Museum of Art, Los Angeles, CA. Personal Communication, January 2013.

18. E. Weyde, *A simple test to identify gases which destroy silver images*, Photogr. Sci. Eng., 1972, **16**, 283-286.

19. T. J. Collings, F. J. Young, *Improvements in Some Tests and Techniques in Photograph Conservation*, Stud. Conserv., 1976, **21**, 79-84.

20. *Imaging materials - Processed imaging materials - Photographic activity test for enclosure materials*, ISO 18916:2007(E).

21. https://www.imagepermanenceinstitute.org/testing/pat (accessed 23/01/2012).

22. T. E. Graedel, J. P. Franey, G. J. Gualtieri, G. W. Kammlott, D. L. Malm, *On the Mechanism of Silver and Copper Sulfidation by Atmospheric H2S and OCS*, Corrosion Sci., 1985, **25**, 1163-1180.

23. S. P. Sharma, *Atmospheric Corrosion of Silver, Copper, and Nickel-Environmental Test*, J. Electrochem. Soc., 1978, **125**, 2005-2011.