

Oganometallic Pt(II) Containing Polymer as Silver Protection Against Sulfide Tarnishing

Ilaria Fratoddi,¹ Giuseppe Marghella,¹ Iole Venditti,¹ Daniela Ferro,² Maria Vittoria Russo¹

¹Department of Chemistry, University of Rome "Sapienza", P.le A. Moro, 5-00185, Rome, Italy

²Istituto per lo Studio dei Materiali Nanostrutturati, CNR, P.le A. Moro 5, 00185 Rome, Italy

Correspondence to: I. Venditti (E-mail: iole.venditti@uniroma1.it)

ABSTRACT: In this work, the use of a film of an organometallic polymer, namely Pt-DEBP, has been tested for the selective capture of sulfides with the aim of protecting silver object. Ag foils were exposed to different environmental conditions in the presence of Pt-DEBP films. Scanning electron microscopy, energy dispersive spectrometry, and colorimetric studies allowed to assess that the polymeric layer selectively captures H₂S, preventing the tarnishing of the silver substrate over a period at least of 2 months, without any manipulation of the sample. This approach open new perspectives for the prevention of aging effects on silver objects of artistic interest, for which cleaning or coating procedures should be avoid. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: silver protection; organometallic Pt(II) containing polymer; sulfide tarnishing; polymers for silver protection; new materials for cultural heritages multifunctional testing

Received 26 March 2012; accepted 10 June 2012; published online

DOI: 10.1002/app.38189

INTRODUCTION

The protection of silver objects against tarnishing, particularly those of artistic interest or coming from archeological surveys, is a multidisciplinary field of research, where science meets art, and that showed a growing interest in recent years.^{1,2} In principle, the safest way to preserve a silver object would be to put it into a sealed showcase and in an controlled atmosphere (e.g., nitrogen or a synthetic air atmosphere). However, this is not a simple solution, as it would require expensive sealed showcases and proper devices for the generation of inert atmosphere. Moreover, to avoid contaminations, a periodic regeneration of the atmosphere itself would be necessary. In some cases, this solution can not be carried out at all; in fact, silver objects are often exposed in museums showcases together with other objects or cultural heritages, which must be preserved in different environmental conditions. It is the case, for instance, of objects made of organic matter, whose preservation needs the presence of selected humidity percentages. It becomes clear that the protection of silver objects needs other methodologies.

Rare are the studies on the use of materials to absorb pollutants agents to prevent the Ag corrosion, which the literature reports several studies about the methods to detect and investigate the tarnishing and corrosion of silver precious objects, mainly based on surface specific analytical techniques, such as secondary ion mass spectrometry, scanning electron microscopy (SEM), and

SEM-EDX,³ or on statistic analytical detection of sulfide pollutants performed in a variety of environments.⁴ Up to now, the procedures proposed for the conservation of silver artifacts and to prevent aging effects are based on the capture of the sulfides and reducing their concentration in the atmosphere in which the objects are preserved, usually the museums showcases. Varnishes, volatile, and nonvolatile inhibitors, microcrystalline waxes, absorbing tissues were tested both individually and together: nevertheless, each of these products shows some drawbacks.^{1,5}

The use of new materials that actively preserve metal surfaces has been adopted,^{6,7} recently by using a self-assembled membrane of hexadecane-thiol CH₃(CH₂)₁₅SH on silver.^{8,9} Esthetic coatings for silver have been found recently by varying the formulation of ParaloidB72 by adding Al₂O₃ nanoparticles and plasma-enhanced chemical vapors deposition of SiOx thin films proved to be efficient protective materials.¹⁰

In this work, the prevention of silver tarnishing has been studied in term of realization of polymeric material able to capture the environmental pollutants responsible for the Ag tarnishing, by means of the use of polymetallaynes. Polymetallaynes are obtained when a high ethynylated organic π -conjugated spacer is σ bonded to a metal center, in our case square planar platinum (II) [Pt(II)] moiety.^{11–13} They represent an interesting class of materials that possess unique optical and electronic properties

Additional Supporting Information may be found in the online version of this article.

© 2012 Wiley Periodicals, Inc.

for applications in optoelectronics and sensors fabrication.^{14–16} This class of polymers normally show good solubility, fair stability to air in the solid state, and considerable thermal stability. Moreover, polymetallaynes possess not only interesting rod-like structures due to the linearity of the carbon–carbon triple bonds but also regular arrangements of the *trans* square planar metal centers of the polymer.¹⁷ Interest has grown in the past years considering the technological potential of this class of polymers based on their exploitable properties such as luminescence and recently the possibility of obtaining them in nanostructured features.^{18,19} Polymetallaynes have been used as thin film membranes in surface acoustic wave devices showing high sensitivity toward relative humidity and sulfur-containing organic vapors.²⁰ Sensors based on Pt(II) containing polymetallaynes showed a higher sensitivity toward low relative humidity percentages, when nanostructured membranes were used.²¹ Organometallic Pt(II) containing macromolecules such as square planar Pt(II) complexes tend to coordinate sulfur-containing molecules, giving rise to pentacoordinated adducts. For example, a series of square planar Pt(II) complexes has been successfully tested as SO₂ sensors and found highly selective and particularly selective for submillimolar to molar gas quantities.²² Due to its electronic structure, hydrogen sulfide is expected to interact with Pt centers in square planar Pt(II) complexes as an electron donor (Lewis base). The interaction between H₂S and poly[1,1'-bis(ethynyl)-4,4'-biphenyl(bis-tributylphosphine)Pt(II)], named Pt-DEBP, was investigated by X-ray photoemission and X-ray absorption studies, showing a charge transfer from H₂S to the metal center, and the subsequent formation of pentacoordinated adducts that show a square-pyramidal geometry around the transition metal with H₂S in the apical position.²³ On that basis, the polymer Pt DEBP appears as a good candidate for the capture of H₂S and as silver protection against sulfide tarnishing.

In this article, Pt-DEBP has been realized in thin film to be deposited in the internal surface of glass cameras opportunely realized, containing pure Ag laminas as reference samples, exposed toward different H₂S volume. SEM, energy dispersive spectrometry (EDS), and colorimetric determinations based on CIELAB system, carried out on different samples, allowed to assess that the polymeric layer selectively captured H₂S, preventing the tarnishing of the silver substrate.

EXPERIMENTAL

Materials and Methods

Polymer Synthesis. All reactions were performed under an inert argon atmosphere. Solvents were dried on Na₂SO₄ before use. All chemicals, unless otherwise stated, were obtained from commercial sources and used as received.

The organometallic polymer Pt-DEBP [chemical structure reported in Figure 1(a)] was synthesized from equimolar amounts of dichloride square planar complex *trans*-[Pt(PBu₃)₂Cl₂] in the presence of monomer DEBP in NH₄Et₂ as solvent and base.¹² Preparative thin-layer chromatography separation was performed on 0.7 mm silica plates (Merck Kieselgel 60 GF254) and chromatographic separations were obtained with 70–230 mesh alumina (Merck), using *n*-hexane/dichloromethane mixtures, to achieve pure Pt-DEBP. Chemical–physical character-

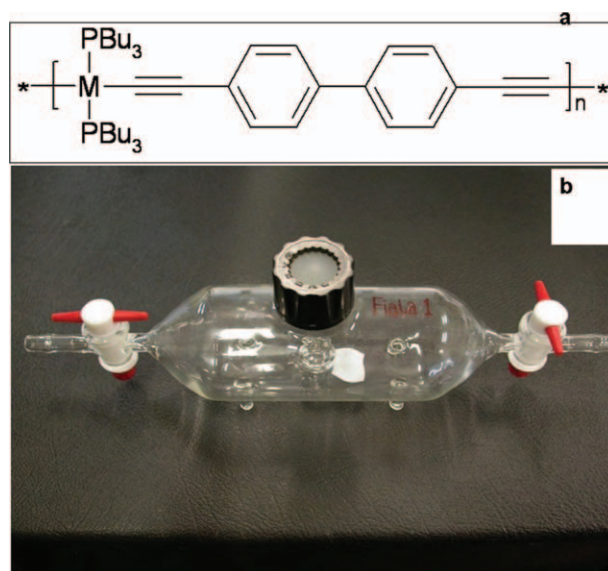


Figure 1. (a) Chemical structure of Pt-DEBP, M = Pt. (b) Reactor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

izations of organometallic polymer Pt-DEBP (see also SI1): IR (film, cm⁻¹) ν (C \equiv C): 2094; 1602, 401, 393; UV (CHCl₃): 372.2 nm; ¹H NMR (CDCl₃ δ): 7.44 (d, 4H, Ar-*H*), 7.29 (d, 4H, Ar-*H*), 2.15 (m 12H P-CH₂⁻), 1.62 (m 12H P-CH₂-CH₂⁻), 0.145 (q 12H P-CH₂-CH₂-CH₂⁻), 0.93 (t 18H -CH₃ J = 9.00 Hz); ³¹P NMR (CDCl₃ δ , (J¹⁹⁵Pt-³¹P) Hz): 3.72 (2358), 7.52 (2371); Elemental analysis (%), found (calculated for the repeating unit C₄₀H₆₂P₂Pt): C = 59.20 (60.06); H = 8.09 (7.81).

Foils of Pure Silver. Foils of pure silver up to 99.9% of Sigma-Aldrich, with dimensions of 100 × 100 mm² and thickness of 0.1 mm and a total weight of 10.4 g were preventively activated by O₃.²⁴ At microscopic scale, the surface of a pure silver foil shows the parallel lines typical of the lamination process and the elemental microanalysis put in evidence the presence of many heavy metals (see Supporting Information 2): the starting conditions are not really 99.99% pure silver, but these elements are probably relative to the extractive process and then concentration is not relevant to the aim of this research.

During the period of the experience, the sheets and the wool were kept sealed in their packages to prevent undesired alterations. The foils were cut to obtain samples of desired size directly at the time of placement in the exhibiting reactors with stainless steel dissecting scissors (Sigma-Aldrich). The silver, after being cleaned with acetone in the RPE of Carlo Erba Reagents (purity at 99.8%) to remove any oily residue left during the production of sheets from millwork machines, has been exposed without any prior surface treatment.

The cylinders containing gas mixtures (to which, eventually, other pollutants can be added) were ordered to SIAD Company (Società Italiana Acetilene & Derivati). Synthetic atmosphere was produced by a mixture of air containing about 7 mg/m³ H₂S inside the reactor (4.7 ppm) to speed up the tarnishing effect in the experiments, considering that the sulfide

atmospheric concentration is about 0.0007 mg/m^3 (0.00047 ppm). The system was maintained at constant volume for 2 months.

Instrumentation

Polymers Characterization. FTIR spectra were recorded as nujol mulls or as films deposited from CHCl_3 solutions by using KRS-5 cells, on Bruker Vertex 70 Fourier transform spectrometer. ^1H , ^{31}P NMR spectra were recorded in CDCl_3 on a Bruker AC 300 P spectrometer at 300 and 121 MHz, respectively, the chemical shifts (ppm) were referenced to Tetramethylsilane for ^1H NMR assigning the residual ^1H impurity signal in the solvent at 7.24 ppm (CDCl_3). ^{31}P NMR chemical shifts are relative to H_3PO_4 (85%). UV-Vis spectra were recorded in CHCl_3 solutions at room temperature on a Varian Cary 100 instrument. Elemental analyses were provided by the Servizio di Microanalisi at the Department of Chemistry, on an EA 1110 CHNS-O instrument.

Test and Characterization of Ag Foil. To allow an exposure of the silver foils in different conditions of controlled atmosphere without contamination from the environment, an appropriate reactor has been developed [see Figure 1(b)]: a cylindrical container of transparent glass with at the end of the container two valves of small diameter for the passage of the gas flow, while on top of the cylinder is placed a screw cap with membrane in no brand Polytetrafluoroethylene where the foils are inserted. To conduct the laboratory experiments, 10 reactors of this type were built with a measured volume slightly variable around 300 cm^3 , to carry out more exposures together. Once prepared, the foils cut from the sheet of pure silver, they are located during the flow. The cylinder is opened, making the gas mixture constituting the atmosphere inside of it flow into the reactor, then the reactor output tap is closed and the cap in correspondence of the sample holder is opened. Under these conditions, the flow coming from the cylinder leak through this opening, restricting the entry of external air from outside. With tweezers, the foil of pure silver is placed on the sample holder, then the cap is closed again and the output tap is reopen: the whole operation takes a few seconds. However, a new complete washing of the reactor is completed to ensure that the concentration of external air inside does not exceed 0.01%.

The SEM instrument was a Leo 1450 VP equipped with a back-scattered electrons detector, resolution 3.5 nm and equipped with EDS INCA 300. SEM measurements were made on samples of Pt-DEBP deposited by slow evaporation from toluene solutions (1 mg/mL) on glass substrates, freshly cleaned by immersion (30 min) in KOH/EtOH solution, and accurately rinsed with H_2O , EtOH, CHCl_3 , and toluene and on Ag foils, with an without polymeric film on showcase (deposited by slow evaporation from toluene solutions 1 mg/mL at room temperature), before and after the exposition to synthetic atmosphere.²⁴

The colorimetric analysis is based on CIE LAB: CIE $L^*a^*b^*$ (CIELAB) is a color space specified by the International Commission on Illumination (French Commission internationale de l'éclairage, hence its CIE initialism). It describes all the colors visible to the human eye and was created to serve as a device independent model to be used as a reference.²⁵ The reflected

colors can be measured using a spectrophotometer. After the deflection, the light is measured at specific intervals through a set of sensors. If the custom of taking readings at 10 nm increments is followed, the visible light range of 400–700 nm will yield 31 readings. These readings are typically used to draw the spectral reflectance curve of the sample: the reflectance percentage is plotted as a function of wavelength. The colorimetric measurements were performed with a Konica Minolta CM-2600D spectrophotometer that is capable of performing simultaneous specular component included and specular component excluded measurements, and it is compliant with all the relevant standards (CIE No.15; ISO 7724/1; ASTM E1164; DIN 5033; Teil7; JIS Z8722 Condition C).

RESULTS AND DISCUSSION

The study can be undertaken in a succession of steps: (1) preparation of Pt-DEBP based on previous work¹²; (2) deposition of Pt-DEBP film on a glass probe by casting procedure from CHCl_3 solution; (3) insertion of the probes into the reactor filled with the synthetic atmosphere and characterization of the probes by means of SEM-EDS studies and colorimetric tests.

The Pt-DEBP effect on the silver tarnishing process was studied through a comparative test: a silver foil is exposed into the glass reactor under synthetic air and hydrogen sulfide (hydrogen sulfide concentration in the atmosphere was about 4.7 ppm) for 2 months, and a second foil inserted in another reactor is exposed to the same atmosphere (atmosphere composition a constant volume) but in this last case, the reactor internal surface has been covered by Pt-DEBP film; in addition, inside this reactor was insert a microscope glass slide covered by polymeric film, because it was not possible to analyze the internal reactor surface directly. After 2 months, the silver foils were investigated by nondestructive technique.

Preliminary, two silver foils and the Pt-DEBP film on the microscope slide were investigated by means of SEM-EDS to determine the blank conditions and analyzed with a colorimeter to define their starting color and the surface morphology. The surface of the Pt-DEBP film deposited on a microscope slide was characterized by SEM: it appears almost flat with some little depressions [Figure 2(a)] and thickness of the edge of about $1 \mu\text{m}$ [Figure 2(b)].

The elemental microanalysis results, taking into account only the elements relative to the Pt-DEBP film showed the absence of sulfur and the presence of carbon and Pt are found in the same percentage ratio of the pristine material ($\text{Pt/C} = 0.5$).

The characterization of the silver foil before the deposition of Pt-DEBP was also investigated by SEM-EDS and colorimetric studies based CIELAB (see Supporting Information 2–4): SEM image of the surface exhibits the typical parallel lines of the lamination process and as concern the colorimetric measurements, it is to note that the clear and brilliant surface induces high reflectance values with no dominant wavelength in the reflectance curve.

After 2 months of exposition, the silver foils and the microscope slide were analyzed with SEM-EDS investigations with the aim

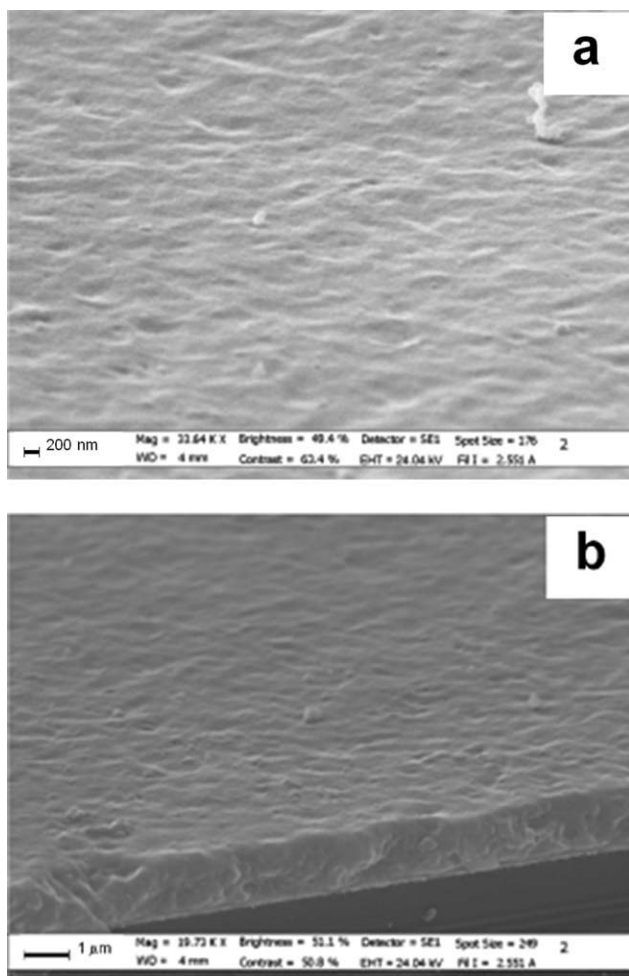


Figure 2. (a) and (b). SEM images of the sample Pt-DEBP film before exposition.

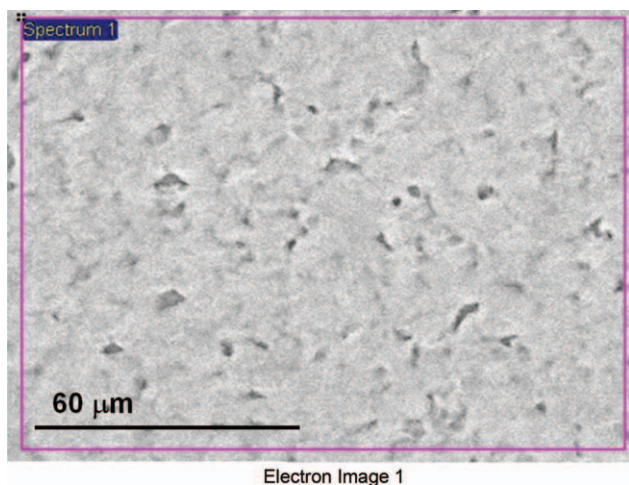


Figure 3. Pt-DEBP film after exposition to synthetic air and hydrogen sulfide for 2 months. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Elemental Microanalysis of Pt-DEBP Probe after Exposition to Synthetic Air and Hydrogen Sulfide for 2 Months

Spectrum	C	P	S	Pt	Total
1	86.79	3.22	0.10	9.88	100.00

All result in weight %.

of detecting the possible presence of sulfur both on the silver foils and on the Pt-DEBP films and evaluate the color variations of the foils surface by colorimetric measure based CIELAB.

The SEM image of Pt-DEBP film surface after the exposition inside the naked reactor appear very different (Figure 3) from the original one (Figure 2); in fact, the polymeric surface appear not continuous showing evident rearrangement of matrices, forming a rough layer.

The altered microstructure probable indicates a chemical interaction between Pt-DEBP and H_2S . This is confirmed by elemental microanalysis showing the presence on the film surface of detectable amounts of sulfur, but at the instrument resolution limit (Table I).

As concern, the experiment in reactor noncovered with Pt-DEBP, after 2 months of exposition to the synthetic air and H_2S , the silver foil appears tarnished to the naked eye. EDS microanalysis, carried out on a wide surface area, reveals the presence of sulfur (Table II).

Comparing the reflectance data achieved before and after the exposition of the silver foil, the color changes are evident. The reflectance percentage is decreased strongly, in particular for lower wavelengths (see Supporting Information 5): thus, the reflected radiation is in the red area of the electromagnetic spectrum (600–700 nm), giving to the sample the red-brownish color typical of the tarnishing. It is noteworthy that even a very small amount of sulfur on the foil surface is responsible for a large change of color, and this allow to easily detect and quantify sulfur trough colorimetric measurements.

To investigate the Pt-DEBP film capability to capture H_2S from an environment, the silver foil was exposed to the synthetic air and H_2S atmosphere together with the polymer probe inside the test chamber. The silver foil showed no meaning change respect with the original sample (Figure 4). It is very interesting to observe the absence of any intergranular corrosion evidence in the BS (Backscattered electrons mode) atomic contrast observation.

The EDS analysis detects a very low percentage of sulfur, near to the instrumental limit of detection (see Table III) and as concern the color change, this is imperceptible loss by the naked-eye and also the reflective variation is negligible (see Supporting Information 6).

Table II. Elemental Microanalysis of Silver Foil after Exposition to Synthetic Air and Hydrogen Sulfide for 2 Months

Spectrum	S	Ag	Total
1	0.55	99.45	100.00

All results in weight %.

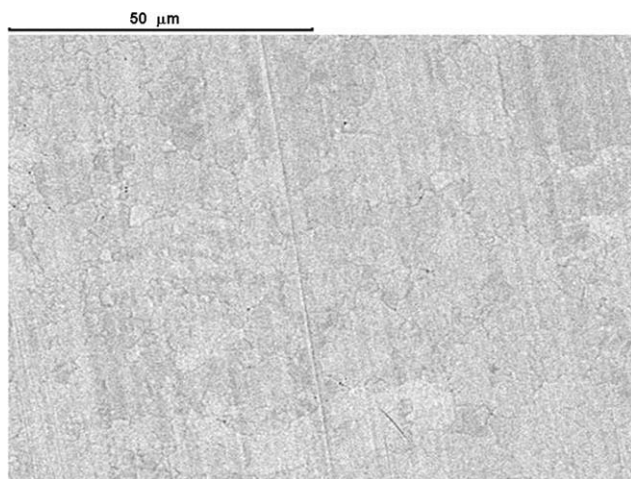


Figure 4. SEM image of silver foil after exposition to synthetic air and hydrogen sulfide for 2 months inside the reactor covered with Pt-DEBP.

Although the silver foil exposed to synthetic air and SH_2 showed the typical tarnishing process, the foil exposed to the same condition, but in Pt-DEBP covered reactor, shows still a brilliant surface with no tarnish, after 2 months. Reporting in a chart the colorimetric data, the difference between the two samples is clearly evidenced (Figure 5).

It is useful point up the SEM-EDS investigation carried out on the Pt-DEBP film after the exposure reveals the presence of sulfur. It is impossible to evaluate the quantitative amount of S owing to the high percentage of carbon but this can be an useful indication about the kinetic of polymer activity. This is a key point: it means that the Pt-DEBP polymer can capture the sulfur, thanks to its platinum atoms in the chemical structure, removing it from the exposition environment and avoiding the silver tarnishing.²³ The weight percent data (Table III) are relative to the following atomic concentrations: there are about 16 platinum atoms for every sulfur atom. Then, it can be supposed that the polymer film is not saturated, and many platinum atoms are still present on the surface, ready to capture sulfur, and improve the performance of Pt-DEBP for a longer period of time or for higher sulfur concentrations.

Finally, looking for the use of Pt-DEBP as silver protective non-interacting with the silver heritages, considerations must be done from the economic point of view. Platinum is a very expensive material and to be convenient the use of Pt-DEBP, the polymer should preserve its effectiveness for an adequate period of time; otherwise, the costs of a periodic renewing of the film might become counter-productive. It is noteworthy, however,

Table III. Elemental Microanalysis of Silver Foil after Exposition to Synthetic Air and Hydrogen Sulfide for 2 Months Inside the Reactor Covered with Pt-DEBP

Spectrum	S	Ag	Total
1	0.03	99.97	100.00

All results in weight %.

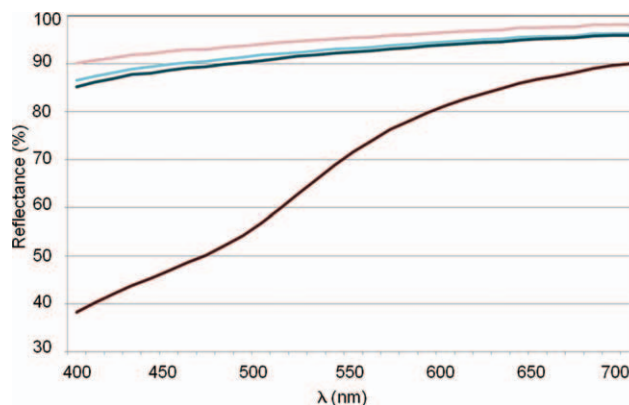


Figure 5. Chart of the reflectance variations after 2 months of hydrogen sulfide exposure: silver foil probe before exposure (first line-pink, the higher), the same silver foil probe after exposure inside uncovered reactor (fourth line-red, the lower), second silver foil probe before exposure (second line-green), second silver foil probe after exposure inside Pt-DEBP covered reactor (third line-dark green). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that only a few milligrams of Pt-DEBP in solution are capable of covering a surface of about 160 cm^2 , and that the real cost of the probe can be competitive in a cost/benefit balance.

CONCLUSIONS

The study reported in this article shows the use of nondestructive analytical methods to characterize the conservation of ancient artifacts and in particular the chance to prevent tarnish of precious silver heritages, avoiding the manipulation of the items, and the modification of the surface. The SEM-EDS investigations are supported by the colorimetric analysis: this technique gives parameterization of the object surface color, being then suitable for the determination of the tarnishing variations. The test for the innovative application of the organometallic polymer is carried out to evaluate its effectiveness in a specific field, that is, the protection of silver objects of artistic interest. The results obtained are encouraging: Pt-DEBP polymer could be effectively used for the conservation of silver objects by putting panels coated with this film inside the showcases without any additional steps.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of Progetti di Ricerca di Università 2010—prot. C26A10ZSHC.

REFERENCES

- Costa, V. *Rev. conservat.* **2001**, 2, 18.
- Frey, T.; Kögel, M. *Surf. Coat. Technol.* **2003**, 174, 902.
- Dowsett, M. G.; Adriaens, A.; Soares, M.; Wouters, H.; Palitsin, V. V. N.; Gibbons, R.; Morris, R. J. H. *Nucl. Instrum. Methods Phys. Res. B* **2005**, 239, 51.
- Pavlogeorgatos, G. *Build. Environ.* **2003**, 38, 1457.
- Beljoudi, T.; Dugot, J.; Lacoudre, N. *In Proceedings of the International Conference on Metal Conservation*, **1998**, 265.

6. Ma, S.; Song, G.; Feng, N.; Zhao, P. *J. Appl. Polym. Sci.* **2012**, *125*, 1601.
7. Zhang, X.; Bell, J. P. *J. Appl. Polym. Sci.* **1997**, *66*, 1667.
8. Evesque, M.; Keddami, M.; Takenouti, H. *Electrochim. Acta.* **2004**, *49*, 2937.
9. Bernard, M. C.; Dauvergne, E.; Evesque, M.; Keddami, M.; Takenouti, H. *Corros. Sci.* **2005**, *47*, 663.
10. Grassini, S.; Angelini, M.; Mao, Y.; Novakovic, J.; Vassiliou, P. *Prog. Org. Coat.* **2011**, *72*, 131.
11. Long, N. J.; Williams, C. K. *Angew. Chem. Int. Ed.* **2003**, *42*, 2586.
12. Fratoddi, I.; Battocchio, C.; Groia, A.; Russo, M. V. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 3311.
13. Wong, W.-Y.; Ho, C.-L. *Coord. Chem. Rev.* **2006**, *250*, 2627.
14. Wong, W.-Y. *Dalton Trans.* **2007**, 4495.
15. Wong, W.-Y.; Zhou, G.-J.; He, Z.; Cheung, K.-Y.; Ng, A. M.-C.; Djurišić, A. B.; Chan, W.-K. *Macromol. Chem. Phys.* **2008**, *209*, 1319.
16. Caliendo, C.; Contini, G.; Fratoddi, I.; Irrera, S.; Pertici, P.; Russo, M. V.; Scavia, G. *Nanotechnology* **2007**, *18*, 125504.
17. Battocchio, C.; D'Acapito, F.; Fratoddi, I.; Groia, A.; Polzonetti, G.; Roviello, G.; Russo, M. V. *Chem. Phys.* **2006**, *328*, 269.
18. Fratoddi, I.; Gohlke, C.; Cametti, C.; Diociaiuti, M.; Russo, M. V. *Polymer* **2008**, *49*, 3211.
19. Chronopoulou, L.; Fratoddi, I.; Palocci, C.; Venditti, I.; Russo, M. V. *Langmuir* **2009**, *25*, 11940.
20. Penza, M.; Cassano, G.; Sergi, A.; Sterzo, C.; Russo, M. V. *Sens. Actuators B* **2001**, *81*, 88.
21. Caliendo, C.; Fratoddi, I.; Russo, M. V. *Appl. Phys. Lett.* **2002**, *80*, 4849.
22. Albrecht, M.; Gossage, R. A.; Lutz, M.; Spek, A. L.; Kotten, G. *Chem. Eur. J.* **2000**, *6*, 1431.
23. Battocchio, C.; Fratoddi, I.; Russo, M. V.; Polzonetti, G. *J. Phys. Chem. A* **2008**, *112*, 7365.
24. Marghella, G. PhD Dissertation, Università degli Studi di Roma "La Sapienza" Mathematical, Physical and Natural Sciences Faculty PhD course in Chemical Science – XXII cycle, **2010**.
25. Schanda, J., *Colorimetry 2007, Understanding the CIE system*. Wiley-Interscience pp 61, ISBN 9780470049044.