ALKYLPHOSPHATES AS LOW-COST INHIBITORS IN SILVER TARNISHING

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ABSTRACT. Tarnishing is a process taking place in silver surface causing corrosion. This is due to the presence in the atmosphere, even in small amounts, of reactive species like water, sulphidric acid and carbonyl sulphide which can be physisorbed onto the silver surface thus reacting with it. We propose the use of alkylphosphates to protect the silver surface against corrosion: the polar head group should interact with the silver surface with the formation of a thin film of opportunely oriented surfactant molecules. This would shield the silver surface from the attack of reactive agents present in the atmosphere and from the adsorption of humidity water helped by the surfactant scarce hydrophilicity. The joint Raman and XPS experiments showed the protective action exerted by dibutylphosphate or bis (2-etylhexyl) phosphate according to the different sulphidizing conditions. Our discovery deserves to be tailored in cultural heritage where silver artefacts are generally precious and inimitable objects, but also in modern microelectronics where silver joints and conductors are used.

1. Introduction

Archaeological artefacts are subjected to corrosion. This is an undesirable detrimental process spontaneously taking place when the artefact is exposed to the atmosphere where humidity and reactive chemical species are usually present. Among the materials used to prepare artefacts, silver certainly plays a pivotal role: it is ductile and malleable, it shows brilliant metallic lustre and it is stable in oxygen and pure water. Due to these unique properties, silver has been used in the past to prepare jewelry, tableware, coins and medals. However, silver does not constitute an exception for corrosion: aggressive agents, usually present in small amounts in the atmosphere, like H_2S, COS and SO_2, when combined with moisture, cause quick alteration of the silver surface (Pope *et al.* 1968; Bauer 1988; Hallett *et al.* 2003; Ingo *et al.* 2006). This process, known as tarnishing, irreversibly turns a shining surface to a dark blue-brownish and uneven face made by mixed sulphide-rich corrosion products. This is a really undesirable process taking place even just after the discovery of the artefact itself. Since in the cultural heritage field every object is inimitable and any loss irreplaceable, solutions for reliable conservation are needed. Different strategies are already set up (Hughes *et al.* 2010) but the most promising are basically based on the formation, on

the artefact surface, of a thin film with protecting action (Favre-Quattropani *et al.* 2000a; Angelini *et al.* 2010; Grassini *et al.* 2011; Angelini and Grassini 2013; Faraldi *et al.* 2014a,b) Encouraged by our experience in the structural and dynamical features of surfactant-based systems we want to face the problem of tarnishing in silver artefacts exploring the possibility to use liquid surfactants to protect silver artefacts against tarnishing.

2. The tarnishing mechanism

Humidity plays a fundamental role in the corrosion of Ag as well as its common alloys (Graedel 1992; Ingo *et al.* 2015) due to the formation, on the metal surface, of a reversible physically absorbed (physisorbed) water layer whose thickness depends on the relative humidity and may be several nanometers thick (Wiesinger *et al.* 2013). This film facilitates the dissolution of metal ions and the absorption of gases from the atmosphere. In the aqueous pool, subsequently, chemical reactions can take place: H_2S and COS can generate HS^- which can diffuse reaching the silver surface, which, in presence of H_2O, can either react directly with Ag^+ or adsorb to the surface and form sulphide salt. The basic of the mechanism is shown in figure 1 left side. It has been shown that the formation of Ag_2S film follows a simple kinetics because the layer growth rate depends linearly on the H_2S and COS concentration (Lin *et al.* 2013). This final black film is mainly composed of acanthite (α-Ag_2S) if tarnishing takes place on pure silver and of mixed sulphides if on Ag–based alloy.
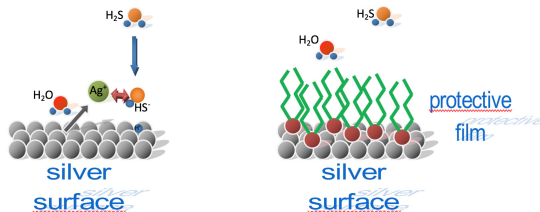

FIGURE 1. Mechanism of tarnishing on a silver surface (left panel) and the same mechanism blocked by the presence of a protective layer (right panel).

3. The idea

Amphiphiles are peculiar molecules since they are characterized by the simultaneous presence, within their molecular architecture, of both polar and apolar moieties. This allows a wide variety of interactions and the arising of complex behavior. It is well known, in fact, that the synergistic action of different types of soft interactions (such as the hydrogen bond, hydrophobic effect, Van der Waals and electrostatic interactions), strongly influences the structural and dynamic properties of nanostructured material systems (Bonaccorsi *et al.* 2009, 2013a; Lombardo 2014) and gives rise to complex self-assembly processes that regulate the colloidal stability of a wide range of material systems (Mallamace *et al.* 2001; Kiselev *et al.* 2013; Kiselev and Lombardo 2017). In these systems, the incompatibility between the different blocks causes a microphase separation and a spatial organization

in a large variety of morphologies (Lombardo *et al.* 2004b), which are characterised by complex collective behaviour (Lombardo *et al.* 2019). This can be exploited in advanced applications not only in materials science but also in biological and medicinal chemistry (Lombardo *et al.* 2004a). This trend confirms the special role of amphiphilic systems in the formation of nanostructured materials that gives rise to complex (supra-) molecular assembly processes regulating the stability and functional behavior in a wide range of (soft) material systems (Lombardo *et al.* 2016a,b, 2018). Particularly interesting is the self-assembly process involving mixed systems containing amphiphilic organophosphates compounds as they generate complex supramolecular structures, suitable for a wide range of (bio-)technology applications (Kiselev *et al.* 2008).

In this ambit, we specifically noticed, in our recent papers, that those surfactants with an acidic headgroups (phosphate, sulphosuccinate, carboxylate (Szerb *et al.* 2013; Spirache *et al.* 2018), etc.) can softly bind silver surface (Longo *et al.* 2006), or stabilize ionic (Calandra *et al.* 2009) and organic (Calandra *et al.* 2004) materials and can form, through a wide variety of mechanisms, local environment whose chemistry and self-assembly is novel (Bonaccorsi *et al.* 2013b). In addition, it has been shown that alkylphosphate can self-assemble on iron film (Guo *et al.* 2007). So, in the light of the peculiar self-assembly properties of alkylphosphates we have recently discovered, we hypothesized that alkylphosphates can efficiently form a stable film on the silver surface with specific phosphate-metal interactions for which we have already pointed out some aspects (Calandra *et al.* 2014). Since alkylphosphates are mostly hydrophobic, they are also expected to scarcely interact with water thus forming a protective layer against humidity. The protective action is expected to be exerted also against the reactive chemical species present in the atmosphere (H_2S and COS). The mechanism is shown in Figure 1(right side). Finally, the polar headgroup - metal surface interactions are not expected to be irreversible so an easy removal of the protective agent (on demand) can be foreseen (the possibility to eventually remove the protective agent is an essential requirement for practical applications (Cronyn 2003; Faraldi *et al.* 2017)).

4. Experimental Setup

Leica optical microscope with 10X, 20X, 50X and 100X objectives was used for visual inspection of the sample surface. It was used also in conjunction with a Renishaw RM 2000, equipped with a Peltier cooled charge-coupled device (CCD) camera, for micro Raman (μ-Raman) analysis. All observations were performed at room temperature. Micro-Raman measurements were carried out in backscattering geometry permitting about 1 μm information depth. A 50X objective (laser spot diameter of about $1\mu m$) and the $514.5nm$ excitation line of an Ar^+ laser were used. Two Edge filters block the Rayleigh-scattered light below $100cm^{-1}$. For this reason, the study of ultra-low wavenumber Raman spectra in the region $< 100cm^{-1}$ is overlooked (Colomban and Lucazeau 1980).

Five different points for every sample were observed to test the uniformity of the analysed layer. On the one hand Ag is not a good Raman scatterer because of its metallic character, thermal sensitivity and fluorescence (Munce *et al.* 2007) but, on the other hand, laser-induced transformation and sample degradation can take place (Ag compounds can be photosensitive to laser radiation and duration of exposure of the patina under the laser

can lead to the formation of cubic silver oxide (Ag$_2$O), due to the laser-induced expected warming at micrometer scale (Bouchard and Smith 2005)), so we kept the laser power as low as possible trying to obtain a sufficiently good signal - to -noise ratio (White 2009). We then modified the output power using the equipped density filter and with a real output of $300\mu W$. The acquisitions were carried out in dynamic mode with 30 accumulation of $1s$ for each point analysed, obtaining a good signal-to-noise ratio without any significant sample modification. The spectra were calibrated using the $520cm^{-1}$ peak of a Si crystal. The spectrometer resolution was about $2cm^{-1}$

The X-ray photoelectron spectroscopy (XPS) analyses of the samples were performed with a VG Microtech ESCA 3000 Multilab, using Al Kα source (1486.6 eV) run at 14 kV and 15 mA, and CAE analyser mode. For the individual peak energy regions, a pass energy of 20 eV set across the hemispheres was used. The constant charging of the samples was removed by referencing all the energies to the C 1s peak energy set at 285.1 eV, arising from adventitious carbon. Analysis of the peaks was performed using the CASA XPS software. The binding energy values are quoted with a precision of $\pm$ 0.15 eV and the atomic percentage with a precision of $\pm$ 10%.

5. The experiment

Commercial silver 925 platelets 2cm·2cm·2mm were polished with silicon carbide papers until 1000 grit and then carefully cleaned with ethanol to remove surface impurities. For evaluating the performances against tarnishing, three representative alkylphosphates have been chosen: two of them are protic (two alkyl tails and one acidic hydrogen) and the other one is not (three alkyl tails, the same as one of the two acidic alkylphosphates, and no acidic hydrogens). The molecular structures are reported in Figure 2. This choice provides a general and representative view of the behavior of the whole category of alkylphosphates, making the present investigation a pioneering study of the chemistry of alkylphosphates as protective agents against tarnishing in silver.

The tests were carried out following two methodologies:

(1) In a first, quick, test, two narrow ($\approx$ 1mm) stripes of adhesive tape were perpendicularly applied to the silver plate to prepare 4 sectors, as shown in Figure 4. In three sectors a small droplet (2µl) of alkylphosphate was placed, one different alkylphosphate for each sector while the fourth sector was used as reference. The alkylphosphate spanned all over the silver surface within the pertinent sector. This procedure develops, on the surface of the metal discs, a film of about μm-sized thickness. The plate was allowed to rest overnight at room temperature and then subjected to a process of artificial corrosion (Favre-Quattropani *et al.* 2000b) according to a dilute ammonium sulphide accelerated tarnishing procedure where the discs are placed inside a beaker with 200ml of distilled water and 0.08ml of ammonium sulphide solution for 2 min at room temperature.

(2) A second, more sophisticated (but longer), test implied:

(a) The deposition of the alkylphosphate by immersion of the silver platelet into a saturated aqueous solution of the alkylphosphate. In this way, the spontaneous self-assembly of the alkylphosphate onto the silver surface, generally occurring

in times of hours, was exploited. This procedure has been tested also by Zhao *et al.* (2015) and is schematically depicted in Figure 3 a

(b) The successive accelerated corrosion test involving the exposure of the (un)protected silver at H_2S saturated atmosphere (see experimental part), as shown in Figure 3 b. This would render the corrosion test more similar to that spontaneously occurring in nature with the advantage to be accelerated thanks to the higher atmospheric concentration of H_2S.

Tarnishing and protective effect of the various alkylphosphates were evaluated visually and by coupled microscopy/Raman observations. The use of Raman spectroscopy revealed to be effective in the study of tarnishing products since it is non-destructive, of fast acquisition, fit for analysis of surface because in backscattering geometry (Colomban and Truong 2004) and able to distinguish the different chemical species involved (Ag_2O, AgS, Ag) (de Caro *et al.* 2016). Chemical analysis for quantitative evaluation of the atomic abundance was then carried out by X-Ray Photoelectron Spectroscopy.

di-*n*-butyl-
phosphate

(DBP)

bis (2-etylhexyl)
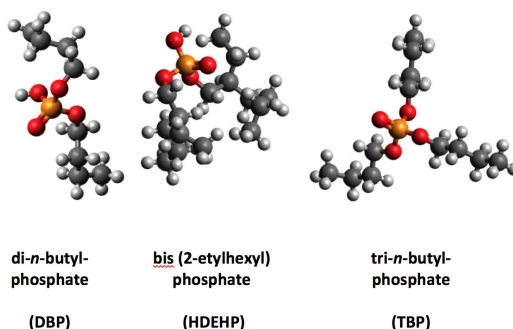phosphate

(HDEHP)

tri-*n*-butyl-
phosphate

(TBP)

FIGURE 2. Molecular structures of the investigated molecules considered as candidates for protective agents against tarnishing in silver.
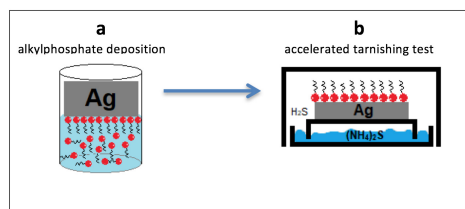

FIGURE 3. a) deposition of the alkylphosphate by immersion of the silver platelet into a saturated aqueous solution of the alkylphosphate; b) accelerated corrosion test involving the exposure of the (un)protected silver at H_2S saturated atmosphere.
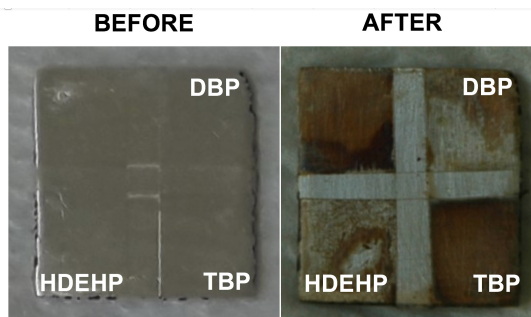
6. The findings

FIGURE 4. Left panel silver plate before accelerated sulfurization divided into four sectors: top-left, no protective agent added; top-right, DBP added; bottom-left HDEHP added and bottom-right TBP added. Right panel: the same plate of left panel after accelerated sulphurization in diluted $(NH_4)_2S$ solution.

Test 1. The first (quick) test was that where alkylphosphates were deposited by a soft paint brush on the commercial silver and the corrosion test was performed by immersion (see experimental part). This test gave already interesting results as reported in Figure 4. As it can be seen, the sector as such was subjected to intense corrosion in the accelerated tarnishing test. The sector with TBP showed no significant protection against tarnishing. The other two sectors, instead, were less corroded. This is the first evidence of the important action that protic alkylphosphates can exert. This can be rationalized in terms of a stronger polar head / metal surface interactions of DBP and HDEHP: the protic polar head, together with the alkyl chains confer stronger binding capability towards silver surface. It can be argued that intermolecular H-bonds between adjacent alhylphosphates of the surface help in the formation of a uniform and compact film on the surface. In this respect, it seems that the length of the alkyl chain, which differentiates DBP and HDEHP, has a minor role. The evident inhomogeneities of the tarnish patina are due to the manual immersion into the corrosive solution, which unavoidably leaves unpredictably small amounts of corrosive solution on the various sectors when the sample is taken out of the solution. This information deserves to be tailored for the piloted design of *ad-hoc* protective agents. Raman experiments confirm this observation.

The Raman analysis carried out in the different stages of treatment and laboratory sulphuration shows how the substances we propose are able to inhibit the tarnishing process. In Figure 5 the reference Raman spectrum (no protection – s) highlights how the tarnishing effect takes place when no protective agent is applied to Ag. In the same figure, the spectra of the Ag protected with the various substances (DBP, HDEHP and TBP) are shown. In Figure 5 are also reported the spectra acquired after the accelerated tarnishing process (DBP-s, HDEHP-s and TBP-s,) vertically shifted for clarity sake, (tarnishing test 1, see text). The abundance of sulphides has been measured by fitting the experimental data with bell-shaped curves in order to quantify the area of each contribution. The band of mixed
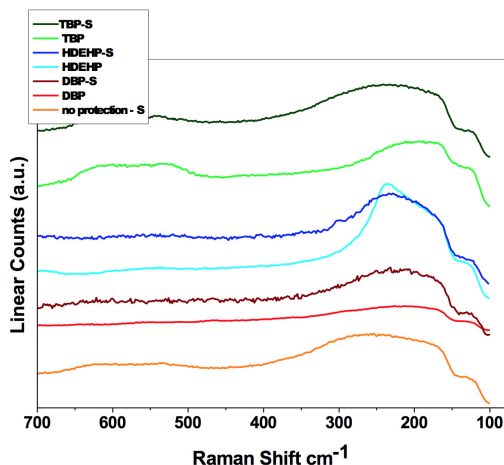
FIGURE 5. Raman Spectra of the samples under investigation. The bare Ag tarnished by the accelerated sulphurization process is reported as reference (no protection – s). The spectra of Ag protected with the various substances before (DBP, HDEHP and TBP) and after (DBP-s, HDEHP-s and TBP-s) the accelerated tarnishing process are reported vertically shifted for clarity sake.

sulphides (200-300 cm^{-1}) after the inducted corrosion turned out to be notably reduced if the protective agent is applied. In particular, DBP and HDEHP are able to severely inhibit the aggression of sulphides on the Ag which causes the tarnishing effect.

Test 2. This quick test was followed by a more sophisticated variant of deposition and corrosion methodology implying the deposition of the alkylphosphate by immersion of the silver platelet into a saturated aqueous solution and the successive accelerated corrosion test involving the exposure of the (un)protected silver at H_2S saturated atmosphere (see experimental part). In this case, the corrosion products were determined quantitatively by XPS. Figure 6 shows the Raman spectra of the samples exposed to accelerated corrosion and the atomic abundances derived by peak integration of the XPS signals are reported in table 1.

The data show that test 2 substantially confirms the scarce performance of TBP in silver protection. However, more interestingly, they show that in these conditions HDEHP is quite effecting in hindering tarnishing. The signal coming from S atom is almost absent in HDEHP-protected silver. The peculiar efficiency shown by HDEHP in test 2 with respect to the quick test 1 can be due to the longer and branched alkyl chains of this molecule. This actually allows the formation of a layer of opportunely oriented molecules on the silver surface, effectively protecting against H_2S aggression. These clues deserve to be tailored for use of protective agents in cultural heritage and in the piloted design of new protective chemicals.
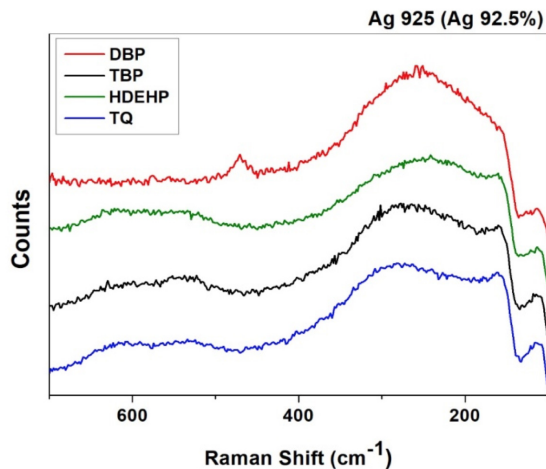
FIGURE 6. Raman spectra of the samples exposed to sulphurized atmosphere (Test 2).

	P/Ag	S/Ag
Unprotected Ag	-	
Unprotected Ag after tarnishing	-	3.2
Ag protected with DBP	1.6	-
Ag protected with DBP after tarnishing	5.8	2.3
Ag protected with TBP	0.2	-
Ag protected with TBP after tarnishing	0.7	2.5
Ag protected with HDEHP	200	-
Ag protected with HDEHP after tarnishing	150	-

TABLE 1. relative atomic abundance

7. Conclusions

We showed that alkylphosphates can be taken into account as promising liquids for Ag protection against tarnishing. Only protic ones are able to efficiently inhibit Ag corrosion as shown by our experiments of accelerated sulphurization tests. These liquids are low-cost chemicals, not polluting, hydrophobic, spanning, transparent, colorless and easily removable in case of need. We found that bis (2-etylhexyl) phosphate is the most effective in Ag protection in realistic conditions of exposure to H_2S and we ascribed this behavior to the acidic character of its polar headgroup allowing stronger bonds with the metal surface together with the long and branched alkyl tails forming an efficient barrier of a layer of opportunely oriented molecules adsorbed at the silver surface.

Acknowledgments

References

Angelini, E. and Grassini, S. (2013). *Plasma treatments for the cleaning and protection of metallic heritage artefacts*. Woodhead Publishing, Cambridge. DOI: 10.1533/9781782421573.5.552.

Angelini, E., Grassini, S., Ingo, G., Mombello, D., Fracassi, F., and Palumbo, F. (2010). "Surface analysis of SiO_2 -like high-barrier thin films for protection of silver artefacts". *Surface and Interface Analysis* **42**(6–7), 666–670. DOI: 10.1002/sia.3257.

Bauer, R. (1988). "Sulfide corrosion of silver contacts during satellite storage". *Journal of Spacecraft and Rockets* **25**(6), 439–441. DOI: 10.2514/3.26025.

Bonaccorsi, L., Calandra, P., Amenitsch, H., Proverbio, E., and Lombardo, D. (2013a). "Growth of fractal aggregates during template directed SAPO-34 zeolite formation". *Microporous and Mesoporous Materials* **167**, 3–9. DOI: 10.1016/j.micromeso.2012.10.024.

Bonaccorsi, L., Calandra, P., Kiselev, M., Amenitsch, H., Proverbio, E., and Lombardo, D. (2013b). "Self-assembly in poly(dimethylsiloxane)-poly(ethylene oxide) block copolymer template directed synthesis of linde type A zeolite". **29**(23), 7079–7086. DOI: 10.1021/la400951s.

Bonaccorsi, L., Lombardo, D., Longo, A., Proverbio, E., and Triolo, A. (2009). "Dendrimer template directed self-assembly during zeolite formation". *Macromolecules* **42**(4), 1239–1243. DOI: 10.1021/ma802393e.

Bouchard, M. and Smith, D. (2005). "Database of 74 Raman Spectra of Standard Minerals of Relevance to Metal Corrosion, Stained Glass or Prehistoric Rock Art". In: *Raman Spectroscopy in Archaeology and Art History*. Cambridge: The Royal Society of Chemistry, pp. 429–464.

Calandra, P., de Caro, T., Caschera, D., Lombardo, D., Todaro, L., and Turco Liveri, V. (2014). "Spectroscopic and structural characterization of pure and FeCl<inf>3</inf>-containing tri-n-butyl phosphate". *Colloid and polymer Science* **293**(2), 597–603. DOI: 10.1007/s00396-014-3439-x.

Calandra, P., Longo, A., Ruggirello, A., and Liveri, V. (2004). "Physico-chemical investigation of the state of cyanamide confined in AOT and lecithin reversed micelles". *Journal of Physical Chemistry B* **108**(24), 8260–8268. DOI: 10.1021/jp0492422.

Calandra, P., Marco, G., Ruggirello, A., and Liveri, V. (2009). "Physico-chemical investigation of nanostructures in liquid phases: Nickel chloride ionic clusters confined in sodium bis(2-ethylhexyl) sulfosuccinate reverse micelles". *Journal of Colloid and Interface Science* **336**(1), 176–182. DOI: 10.1016/j.jcis.2009.03.066.

Colomban, P. and Truong, C. (2004). "Non-destructive Raman study of the glazing technique in lustre potteries and faience (9-14th centuries): Silver ions, nanoclusters, microstructure and processing". *Journal of Raman Spectroscopy* **35**(3), 195–207. DOI: 10.1002/jrs.1128.

Colomban, P. and Lucazeau, G. (1980). "Vibrational study of and conduction mechanism in β alumina. I. Stoichiometric β alumina". *The Journal of Chemical Physics* **72**(2), 1213–1224. DOI: 10.1063/1.439264.

Cronyn, J. (2003). *The Elements of Archaeological Conservation*. Taylor & Francis.

de Caro, T., Caschera, D., Ingo, G., and Calandra, P. (2016). "Micro-Raman innovative methodology to identify Ag–Cu mixed sulphides as tarnishing corrosion products". *Journal of Raman Spectroscopy* **47**(7), 852–859. DOI: 10.1002/jrs.4900.

Faraldi, F., Angelini, E., Caschera, D., Mezzi, A., Riccucci, C., and de Caro, T. (2014a). "Diamond-like carbon coatings for the protection of metallic artefacts: Effect on the aesthetic appearance". *Applied Physics A* **114**(3), 663–671. DOI: 10.1007/s00339-013-8171-8.

Faraldi, F., Angelini, E., Riccucci, C., Mezzi, A., Caschera, D., and Grassini, S. (2014b). "Innovative diamond-like carbon coatings for the conservation of bronzes". *Surface and Interface Analysis* **46**(10–11), 764–770. DOI: 10.1002/sia.5367.

Faraldi, F., Cortese, B., Caschera, D., Di Carlo, G., Riccucci, C., de Caro, T., and Ingo, G. (2017). "Smart conservation methodology for the preservation of copper-based objects against the hazardous corrosion". *Thin Solid Films* **622**, 130–135. DOI: 10.1016/j.tsf.2016.12.024.

Favre-Quattropani, L., Groening, P., Ramseyer, D., and Schlapbach, L. (2000a). "The protection of metallic archaeological objects using plasma polymer coatings". *Surface and Coatings Technology* **125**(1–3), 377–382. DOI: 10.1016/S0257-8972(99)00579-4.

Favre-Quattropani, L., Groening, P., Ramseyer, D., and Schlapbach, L. (2000b). "The protection of metallic archaeological objects using plasma polymer coatings". *Surface and Coatings Technology* **125**(1–3), 377–382. DOI: 10.1016/S0257-8972(99)00579-4.

Graedel, T. (1992). "Corrosion Mechanisms for Silver Exposed to the Atmosphere". *Journal of The Electrochemical Society* **139**(7), 1963–1970. DOI: 10.1149/1.2221162.

Grassini, S., Angelini, E., Mao, Y., Novakovic, J., and Vassiliou, P. (2011). "Aesthetic coatings for silver based alloys with improved protection efficiency". *Progress in Organic Coatings* **72**(1–2), 131–137. DOI: 10.1016/j.porgcoat.2011.04.003.

Guo, W., Chen, S., Feng, Y., and Yang, C. (2007). "Investigations of triphenyl phosphate and Bis-(2-ethylhexyl) phosphate self-assembled films on iron surface using electrochemical methods, fourier transform infrared spectroscopy, and molecular simulations". *The Journal of Physical Chemistry C* **111**(7), 3109–3115. DOI: 10.1021/jp067216t.

Hallett, K., Thickett, D., McPhail, D., and Chater, R. (2003). "Application of SIMS to silver tarnish at the British Museum". *Applied Surface Science* **203–204**, 789–792. DOI: 10.1016/S0169-4332(02)00823-1.

Hughes, A., Cole, I., Muster, T., and Varley, R. (2010). "Designing green, self-healing coatings for metal protection". *NPG Asia Materials* **2**(4), 143–151. DOI: 10.1038/asiamat.2010.136.

Ingo, G., Angelini, E., Riccucci, C., de Caro, T., Mezzi, A., Faraldi, F., Caschera, D., Giuliani, C., and Di Carlo, G. (2015). "Indoor environmental corrosion of Ag-based alloys in the Egyptian Museum (Cairo, Egypt)". *Applied Surface Science* **326**, 222–235. DOI: 10.1016/j.apsusc.2014.11.135.

Ingo, G., Balbi, S., de Caro, T., Fragalà, I., Riccucci, C., and Bultrini, G. (2006). "Microchemical investigation of Greek and Roman silver and gold plated coins: Coating techniques and corrosion mechanisms". *Applied Physics A* **83**(4), 623–629. DOI: 10.1007/s00339-006-3536-x.

Kiselev, M., Janich, M., Hildebrand, A., Strunz, P., Neubert, R., and Lombardo, D. (2013). "Structural transition in aqueous lipid/bile salt [DPPC/NaDC] supramolecular aggregates: SANS and DLS study". *Chemical Physics* **424**, 93–99. DOI: 10.1016/j.chemphys.2013.05.014.

Kiselev, M. and Lombardo, D. (2017). "Structural characterization in mixed lipid membrane systems by neutron and X-ray scattering". *Biochimica et BiophysicaActa (BBA) - General Subjects* **1861**(1), 3700–3717. DOI: 10.1016/j.bbagen.2016.04.022.

Kiselev, M., Lombardo, D., Lesieur, P., Kisselev, A., Borbely, S., Simonova, T., and Barsukov, L. (2008). "Membrane self assembly in mixed DMPC/NaC systems by SANS". *Colloids and Surfaces B: Biointerfaces* **345**(2–3), 173–180. DOI: 10.1016/j.chemphys.2007.09.034.

Lin, H., Frankel, G., Frankel, G., and Abbott, W. (2013). "Analysis of Ag Corrosion Products". *Journal of the Electrochemical Society* **160**(8), C345–C355. DOI: 10.1149/2.055308jes.

Lombardo, D. (2014). "Modeling dendrimers charge interaction in solution: Relevance in biosystems". *Biochemistry Research International* **2014**, 837651 [10 pages]. DOI: 10.1155/2014/837651.

Lombardo, D., Calandra, P., Barreca, D., Magazù, S., and Kiselev, M. (2016a). "Soft interaction in liposome nanocarriers for therapeutic drug delivery". *Nanomaterials* **6**(7), 125 [26pages]. DOI: 10.3390/nano6070125.

Lombardo, D., Calandra, P., Bellocco, E., Laganà, G., Barreca, D., Magazù, S., Wanderlingh, U., and Kiselev, M. (2016b). "Effect of anionic and cationic polyamidoamine (PAMAM) dendrimers on a model lipid membrane". *Biochimica et Biophysica Acta - Biomembranes* **1858**(11), 2769–2777. DOI: 10.1016/j.bbamem.2016.08.001.

Lombardo, D., Calandra, P., Magazù, S., Wanderlingh, U., Barreca, D., Pasqua, L., and Kiselev, M. (2018). "Soft nanoparticles charge expression within lipid membranes: The case of amino terminated dendrimers in bilayers vesicles". *Biochimica et BiophysicaActa (BBA)-Biomembrane* **170**, 609–.616. DOI: 10.1016/j.colsurfb.2018.06.031.

Lombardo, D., Longo, A., Darcy, R., and Mazzaglia, A. (2004a). "Structural Properties of Nonionic Cyclodextrin Colloids in Water". *Langmuir* **20**(4), 1057–1064. DOI: 10.1021/la035370q.

Lombardo, D., Micali, N., Villari, V., and Kiselev, M. (2004b). "Large structures in diblock copolymer micellar solution". *Physical Review E* **70**(2.1), 021402 [9 pages]. DOI: 10.1103/PhysRevE.70.021402.

Lombardo, D., Munaò, G., Calandra, P., Pasqua, L., and Caccamo, M. (2019). "Evidence of pre-micellar aggregates in aqueous solution of amphiphilic PDMS-PEO block copolymer". *Physical Chemistry Chemical Physics* **21**(22), 11983–11991. DOI: 10.1039/c9cp02195g.

Longo, A., Calandra, P., Casaletto, M., Giordano, C., Venezia, A., and Liveri, V. (2006). "Synthesis and physico-chemical characterization of gold nanoparticles softly coated by AOT". *Materials Chemistry and Physics* **96**(1), 66–72. DOI: 10.1016/j.matchemphys.2005.06.043.

Mallamace, F., Beneduci, R., Gambadauro, P., Lombardo, D., and Chen, S. (2001). "Glass and percolation transitions in dense attractive micellar system". *Physica A* **302**(1–4), 202–219. DOI: 10.1016/S0378-4371(01)00465-4.

Munce, C., Parker, G., Holt, S., and Hope, G. (2007). "A Raman spectroelectrochemical investigation of chemical bath deposited CuxS thin films and their modification". *Colloids and Surfaces A* **295**(1–3), 152–158. DOI: 10.1016/j.colsurfa.2006.08.045.

Pope, D., Gibbens, H., and Moss, R. (1968). "The tarnishing of Ag at naturally-occurring H2S and SO2 levels". *Corrosion Science* **8**(12), 883–887. DOI: 10.1016/S0010-938X(68)80141-6.

Spirache, M., Cretu, C., Cseh, L., Sasca, V., Badea, V., Tudose, R., Deveseleanu-Corici, L., Costisor, O., and Szerb, E. (2018). "Ionic salts of nicotinic acid as multifunctional materials". *Revue Roumaine de Chimie* **63**(5–6), 521–525.

Szerb, E., Pucci, D., Crispini, A., and Deda, M. (2013). "Soft luminescent materials based on Ag(I) coordination complexes". *Molecular Crystals and Liquid Crystals* **573**(1), 34–45. DOI: 10.1080/15421406.2013.763335.

White, S. (2009). "Laser Raman spectroscopy as a technique for identification of seafloor hydrothermal and cold seep minerals". *Chemical Geology* **259**(3-4), 240–252. DOI: 10.1016/j.chemgeo.2008.11.008.

Wiesinger, R., Martina, I., Kleber, C., and Schreiner, M. (2013). "Influence of relative humidity and ozone on atmospheric silver corrosion". *Corrosion Science* **77**, 69–76. DOI: 10.1016/j.corsci.2013.07.028.

Zhao, C., Gao, X., Lu, H., Yan, R., Wang, C., and Ma, H. (2015). "Spontaneous formation of mono-n-butyl phosphate and mono-n-hexyl phosphate thin films on the iron surface in aqueous solution and their corrosion protection property". *RSC Advances* **5**(67), 54420–54432. DOI: 10.1039/c5ra03899e.

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