ALKYLPHOSPHATES AS LOW-COST INHIBITORS IN SILVER TARNISHING

PIETRO CALANDRA a, MARZIA CIONI b, VALERIA LA PAROLA c AND TILDE DE CARO a *

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-ethylhexyl) 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 H₂S, COS and SO₂, 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: $\text{H}_2\text{S}$ and $\text{COS}$ can generate $\text{HS}^-$ which can diffuse reaching the silver surface, which, in presence of $\text{H}_2\text{O}$, can either react directly with $\text{Ag}^{+}$ 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 $\text{Ag}_2\text{S}$ film follows a simple kinetics because the layer growth rate depends linearly on the $\text{H}_2\text{S}$ and $\text{COS}$ concentration (Lin et al. 2013). This final black film is mainly composed of acanthite ($\alpha$-Ag$_2$S) if tarnishing takes place on pure silver and of mixed sulphides if on Ag–based alloy.

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 (H2S 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 1µm) and the 514.5 nm excitation line of an Ar+ laser were used. Two Edge filters block the Rayleigh-scattered light below 100 cm−1. For this reason, the study of ultra-low wavenumber Raman spectra in the region < 100 cm−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 520 cm$^{-1}$ peak of a Si crystal. The spectrometer resolution was about 2 cm$^{-1}$

The X-ray photoelectron spectroscopy (XPS) analyses of the samples were performed with a VG Microtech ESCA 3000 Multilab, using Al K$\alpha$ 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 2 cm · 2 cm · 2 mm 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 ($\approx$ 1 mm) 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 (2 $\mu$l) 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 $\mu$m-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 200 ml of distilled water and 0.08 ml 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$_2$S 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$_2$S.

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$_2$O, 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.

**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$_2$S saturated atmosphere.
6. The findings

![Figure 4](image_url)

**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 (NH₄)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

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Alkylphosphates as Low-Cost Inhibitors

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 \((200-300 \text{ cm}^{-1})\) 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 \(\text{H}_2\text{S}\) 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 \(\text{H}_2\text{S}\) 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).

<table>
<thead>
<tr>
<th></th>
<th>P/Ag</th>
<th>S/Ag</th>
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<tbody>
<tr>
<td>Unprotected Ag</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Unprotected Ag after tarnishing</td>
<td>-</td>
<td>3.2</td>
</tr>
<tr>
<td>Ag protected with DBP</td>
<td>1.6</td>
<td>-</td>
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<tr>
<td>Ag protected with DBP after tarnishing</td>
<td>5.8</td>
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<tr>
<td>Ag protected with TBP</td>
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<tr>
<td>Ag protected with TBP after tarnishing</td>
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</tr>
<tr>
<td>Ag protected with HDEHP</td>
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<td>-</td>
</tr>
<tr>
<td>Ag protected with HDEHP after tarnishing</td>
<td>150</td>
<td>-</td>
</tr>
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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$_2$S 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

Financial support from the CNR-PAN bilateral project 2017-2019, allowing deep study of alkylphosphates, is acknowledged.
References


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a CNR -ISMN
Via Salaria km 29.300
Monterotondo Stazione (RM) Italy

b Università di Roma “La Sapienza”
Dipartimento di Biologia Ambientale
Via Cesare de Lollis, 21, 00185 Roma, Italy

c CNR-ISMN
Via U. La Malfa, 153
90146 Palermo, Italy

to whom correspondence should be addressed | email: tilde.decaro@cnr.it

Paper contributed to the international workshop entitled “New approaches to study complex systems”, which was held in Messina, Italy (27–28 November 2017), under the patronage of the Accademia Peloritana dei Pericolanti
Manuscript received 09 September 2018; published online 20 December 2019

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