

# Development of an innovative film-forming cleaning system for the removal of corrosion products from copper alloy artifacts

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## ABSTRACT

The cleaning procedure for copper alloy artifacts should aim at the complete removal of the defacing and harmful corrosion products of Cu(II) (copper carbonates, sulfates, chlorides) while preserving, at the same time, the protective cuprite Cu(I) layer. Traditional procedures usually involve mechanical and/or chemical methods, which both present some limits related to scarce selectivity and control of the cleaning process. An innovative polyvinyl alcohol-based film-forming system was specifically designed to overcome these problems. The main advantages of this innovative system are related to the possibility to combine a controlled chemical action, thanks to the confinement of a complexing agent into a polymeric matrix, with a gentle mechanical peeling, which is made possible by the film-forming properties of the system. The physicochemical properties of selected systems

## INTRODUCTION

Metallic artifacts are affected by corrosion phenomena that induce the formation of a complex patina on their surface. Copper alloy artifacts suffer from alterations to the alloy components that cause the formation of overlapping structures, commonly characterized by the presence of cuprite ( $\text{Cu}_2\text{O}$ , a Cu(I) oxide) at the interface with the metal and by an external layer of Cu(II) salts (carbonates, sulfates, chlorides). Cuprite is usually considered a layer to be preserved; in fact, by slowing down further corrosion processes (Scott 2002), it acts as a protective interface between the metal surface and the environment. On the other hand, the presence of copper oxychlorides (atacamite and its polymorphs) among the corrosion products is usually considered particularly dangerous, as a symptom of the so-called “bronze disease” (Scott 1990).

The cleaning process of copper alloys should thus be addressed to the removal of the Cu(II) alteration products, which are esthetically defacing and potentially dangerous for the object, by preserving the protective cuprite layer.

Traditionally, cleaning is performed by mechanical and chemical methods chosen depending on the morphology and type of corrosion products. Mechanical cleaning is usually performed by means of vibrating or abrasive tools, micro-peening with vegetal granulates, or ultra-high-pressure water or laser (Degryny 2004). The main limitations of these methods are related to the scarce selectivity and invasiveness of the procedures, which can lead to damage of the protective cuprite layer or even delete superficial information from the artwork.

Chemical treatment generally involves the use of reagents, such as Rochelle salt (RS), ethylenediaminetetraacetic acid (EDTA), ammonium salts, citric acid, alkaline glycerol, and sodium carbonate (Scott 2002). The application of these solutions is usually performed by means of compresses, brushing, and immersion. Important drawbacks of these methods are: the scarce control over the cleaning process (i.e. attack on the cuprite layer); reagent residues left on the metal surface (which can lead to the uncontrolled progress of the chemical action); precipitation and redeposition of copper salts on the surface. To reduce the risks related to the scarce control over the process during chemical treatment, highly selective chelators for  $\text{Cu}^{2+}$  ions, such

were studied with thermal analysis (thermogravimetry, differential scanning calorimetry). After some preliminary cleaning tests on artificially aged samples, the most promising systems were used for the removal of alteration patinas from two real case studies: an ancient gilded bronze artifact and the Fontana dei Mostri Marini, by Pietro Tacca, in Florence.

as RS and EDTA, are generally preferred. In particular, EDTA disodium salt is one of the most common complexing agents used for the chemical cleaning of metal artifacts. RS is known to have a milder effect, but provides better control in complexing only the corrosion products, and preserving the cuprite layer. Usually, a combined approach between mechanical and chemical methods is adopted (Matteini et al. 2003).

In the past decades, a wide range of thickeners and gel or gel-like systems suitable for the use of different cleaning fluids have been developed and tested (Baglioni et al. 2013). These innovative confining systems were mainly devised for easel and mural painting, paper, etc., but never specifically for metal cleaning. In fact, there is a serious lack of literature concerning the application of gels or gel-like systems for cleaning procedures on metal artifacts. EDTA solutions, commonly used as chelating agents, are generally associated with thickeners, such as cellulose ethers, polyacrylic acids, and agar (Marabelli 1993), but very little data about their efficacy or applicability are available. Moreover, there are well-known issues related to the leftover residues of these gel-like systems (Stulik 2004) that require the development of appropriate clearance procedures. As an improvement with respect to traditional cleaning procedures, in this work the development of an efficient, controllable, and residue-free cleaning method for the removal of corrosion products from copper alloys is presented.

### **THE FILM-FORMING SYSTEM**

The innovative polymeric film-forming system presented in this paper was specifically designed for the controlled and selective cleaning of copper alloy artifacts. The main idea was to obtain a polymeric system able to load complexing agents for the chemical cleaning of corrosion patinas. At the same time, these fluid systems should be able, upon drying, to form a soft and elastic film easily removable from the surface. In fact, the initial fluidity of the system assures intimate contact with any surface morphology, while the gentle peeling action needed for film removal after drying assists the chemical cleaning action performed by the complexing agent. This cleaning system is thus able to combine mechanical and chemical action and represents a good alternative tool for the cleaning of copper alloy artifacts.

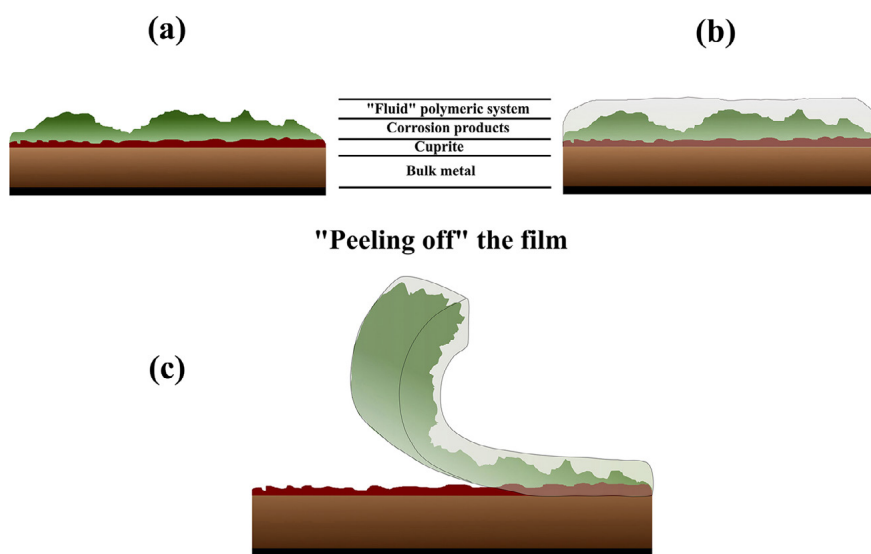
The polymeric system designed consists of a viscous transparent dispersion that can be easily applied with a spatula, a hard brush or a syringe on the surface to be treated, as schematized in Figure 1b. The fluid system perfectly follows the roughness and irregularities typical of a corroded surface (see Figure 1a), permitting at the same time good spatial control over the area of application. After complete evaporation of the volatile fraction, a transparent film is formed, which can be easily removed by a gentle peeling action (Figure 1c). The time required for film formation depends on the composition and thickness of the applied formulation, as well as on the environmental parameters – temperature (T), relative humidity (RH%).

Polyvinyl alcohol (PVA) was chosen as the most suitable polymer due to its excellent chemical stability, high biocompatibility, low toxicity, low cost,

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and peculiar film-forming properties (Ogur 2005). Partially hydrolyzed PVA (degree of hydrolysis (DH) of 87–89%,  $M_w$  85,000–124,000 g/mol) was used because, due to the presence of both ordered (crystalline) and amorphous domains, the formed films have both high water solubility and good mechanical properties.



**Figure 1.** Schematic representation of the application and removal of the film-forming systems: (a) typical stratigraphic morphology of a corroded copper alloy; (b) application of the polymeric dispersion; (c) removal of the film after the evaporation of the volatile content

The properties of the system, in terms of ease of application and final characteristics of the film, can be tuned through addition of additives such as ethanol and plasticizers. In particular, added ethanol, due to its higher vapor pressure, acts as a drying agent, influencing the evaporation rate. The ethanol content can be chosen depending on the application conditions. For example, lower temperatures and high RH% may require more ethanol to enhance evaporation. Generally, the addition of ethanol improves the texture of the polymeric solutions as a consequence of its structuring effect on water, which leads to an increase in the order of the 3D structure of the polymeric network. However, too high ethanol content would result in systems that are too fluid, reducing spatial control and the applicability of dispersion, especially on non-horizontal surfaces.

The addition of plasticizers usually increases the flexibility, processability, and homogeneity of the polymers. A plasticizer substance is usually liquid, non-volatile, non-mobile, inert, inexpensive, nontoxic, and compatible with the system to be plasticized. The most frequently used plasticizers for PVA are polyols. Polyols form hydrogen bonds with the hydroxyl groups of PVA decreasing the intra- and inter-molecular hydrogen bonds between neighboring PVA chains and effectively reducing the overall structural regularity of the system. Their low molecular weight allows them to penetrate easily within the 3D PVA network (Wu et al. 2012). The four polyols chosen for the characterized formulation were dipropylene glycol (DPG), 2-methyl-1,3-propanediol (MPD), glycerol (GLY), and polyethylene glycol (PEG).

The composition and macroscopic characteristics of three different formulations, selected as the best performing systems, are listed in Table 1.

The ability of the polymeric dispersions to load two different complexing agents, namely Na<sub>2</sub>EDTA and RS, and their performance in terms of removal of corrosion products from copper alloys was tested. The advantages in the use of EDTA are related to the high stability of the hexadentate complex formed with the metal ions, the high selectivity towards cupric salts (ensuring the cuprite layer is negligibly affected), and the possibility to adjust efficacy by varying the pH value. On the other hand, RS is characterized by milder complexing effectiveness, since it is a bidentate ligand characterized by a lower stability constant in respect to EDTA. However, its use is recommended in cases where very delicate cleaning action is needed (Martell and Hancock 1996). Both chelators are insoluble in ethanol and their presence can cause phase separation phenomena or other modifications to the 3D polymeric network. For this reason, the maximum amount of complexing agents loaded into the studied polymeric system was 7% w/w for Rochelle salt and 3–4% w/w for EDTA.

**Table 1.** Compositions (% w/w) of the selected formulations named as PVAXX (XX refers to the total volatile content of water + ethanol). The principal properties of each system are also reported

| Formulation | Volatile fraction (water + ethanol) | PVA | Plasticizers (DPG, MPD, GLY, PEG) | Properties   |
|-------------|-------------------------------------|-----|-----------------------------------|--|
| PVA74       | 74                                  | 20  | 6                                 | <ul style="list-style-type: none"> <li>• fluid formulation</li> <li>• applicability on horizontal surfaces</li> <li>• fast evaporation rate for high volatile fraction and low plasticizer content</li> </ul>      |
| PVA70       | 70                                  | 20  | 10                                | <ul style="list-style-type: none"> <li>• intermediate consistency and performance</li> <li>• applicability on non-horizontal surfaces</li> <li>• high evaporation rate and good spatial control</li> </ul>         |
| PVA68       | 68                                  | 20  | 12                                | <ul style="list-style-type: none"> <li>• viscous formulation</li> <li>• applicability on non-horizontal surfaces</li> <li>• low evaporation rate for high plasticizer and low volatile fraction content</li> </ul> |

## PHYSICOCHEMICAL CHARACTERIZATION

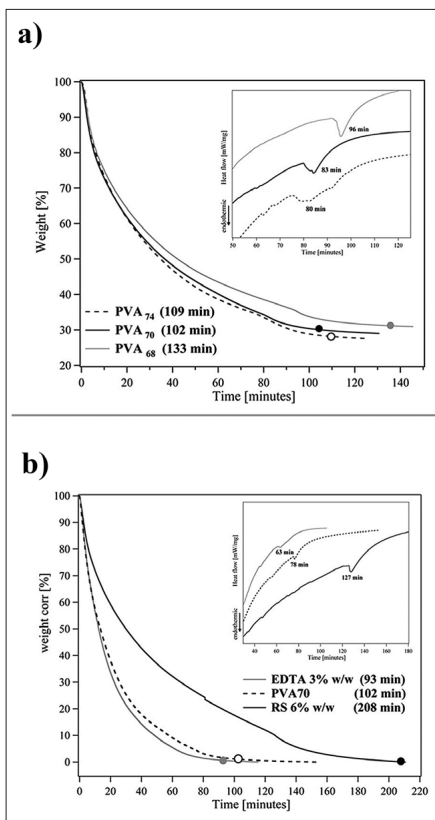
The physicochemical characterization of the polymeric formulations was performed through gravimetric, thermogravimetric analysis (TGA, both scanning and isothermal) and differential scanning calorimetry (DSC) experiments, with the aim of studying the influence of each component on the final properties of the system.

### The effect of ethanol

Three formulations with the same polymer and plasticizer content (formulation PVA 70) but increasing water/ethanol ratios (70/30, 80/20, 85/15) were investigated by means of gravimetric measurements and TGA scanning. The curves obtained from the gravimetric measurements (not reported) show that in the case of PVA70 85/15 – the formulation with the lowest ethanol content – 360 minutes are needed to obtain a film. On the other hand, PVA70 70/30 formulation, containing higher amounts of ethanol, forms a film after only 240 minutes. These data indicate that the increased

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**Figure 2.** Isothermal TG thermograms (40°C) of: a) three formulations with different volatile and plasticizer content (PVA68, PVA70, and PVA74); b) the same PVA70 formulation loaded with different amounts (3% and 6% w/w) of complexing agents (respectively EDTA and Rochelle salt)

ethanol content accelerates the evaporation process leading to a faster film formation.

**The effect of the plasticizers**

Dry films were studied through DSC experiments to evaluate the trend in thermal parameters after the addition of plasticizers into the polymer matrix.

The thermal data obtained from DSC (DC%) and isothermal TGA experiments are displayed in Table 2; the DC% values were determined as reported by Mallapragada and Peppas (1996).

The polymeric films, formed after evaporation of the volatile compounds, present both crystalline and amorphous regions which significantly affect their final properties. High crystallinity promotes the formation of more rigid and brittle films, while the amorphous regions are responsible for the elasticity and flexibility. An easy and safe film removal is possible when the film displays poor adhesiveness and great flexibility, while the mechanical stability of the film permits its residue-free removal, thus lower DC% values are preferable. The presence of small plasticizer molecules in the formulation permits both the lower adhesiveness of the film and improved mechanical features. Plasticizers act as lubricants between the polymer chains by weakening their inter-molecular secondary forces. This process causes a decrease in the thermal transition temperatures and in the overall DC% of the final films.

In fact, neat PVA films that show a higher DC (12.8%) in respect to plasticized formulations (DC% between 5.7% and 8%) are too rigid and brittle to be peeled-off from the surface: the mechanical action needed for removal from the surface is aggressive, and their adhesion is too strong for a residue-free removal.

The time required for the complete evaporation of the volatile fraction (i.e. film formation) was evaluated by means of isothermal TGA at 40°C. The data reported in Table 2 indicate that the volatile fraction loss occurs earlier for aqueous PVA solutions without the addition of plasticizers (68 and 66 minutes for formulations PVA/H<sub>2</sub>O and PVA/H<sub>2</sub>O/EtOH, respectively). When plasticizers are added, the evaporation process is hindered to different extents (depending on the molecular size and retentive power of the plasticizers) and the time required for evaporation increases (102–213 min). According to obtained data, formulations PVA74, PVA70 and PVA68 represent the most suitable candidates for the applicative tests. The isothermal TGA curves of the three formulations and their film formation rates are reported in Figure 2a.

**The effect of the complexing agent**

Increasing amounts of EDTA (1–3% w/w) at two different pH values (7 and 9) and RS (5–7% w/w) were added to a selected formulation (PVA70) to ensure that the presence of the complexing agents does not negatively affect the texture of the system, the evaporation rate, and the final mechanical properties of the film.

Gravimetric and thermogravimetric data show that with increasing EDTA concentration an increase in the evaporation rate of the volatile fraction

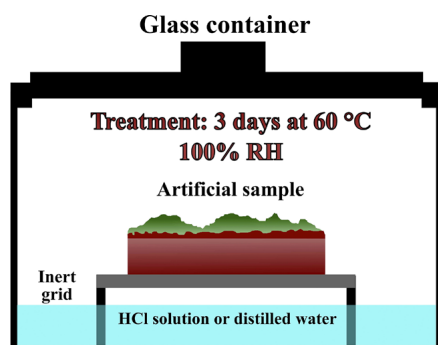


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**Table 2.** Thermal parameters obtained through DSC experiments (DC%) on dry film samples and isothermal TGA experiments (minutes required for film formation). Different samples with no plasticizers (PVA/H<sub>2</sub>O, PVA/H<sub>2</sub>O/EtOH), one plasticizer (PVA70/PEG, DPG, MPD, GLY), and four plasticizers (PVA68, PVA70, PVA74) were compared

| Formulation               | DSC  | TGA   |
|---------------------------|------|-------|
|                           | DC % | [min] |
| PVA <sub>dry</sub>        | 14.3 | /     |
| PVA/H <sub>2</sub> O      | 12.8 | 68    |
| PVA/H <sub>2</sub> O/EtOH | 11.6 | 66    |
| PVA74                     | /    | 109   |
| PVA70                     | 7.9  | 102   |
| PVA68                     | /    | 133   |
| PVA70 <sub>noEtOH</sub>   | 8.2  | 135   |
| PVA70/PEG                 | 8.3  | 164   |
| PVA70/DPG                 | 8.7  | 200   |
| PVA70/MPD                 | 8.4  | 213   |
| PVA70/GLY                 | 5.7  | 205   |



**Figure 3.** Schematic procedure for the accelerated degradation methodology of Cu-base alloy samples

occurs, reducing the time required for film formation. This trend is probably due to an increase in polymer chain entanglements and vicinity induced by EDTA, as well as to the formation of crystalline domains. As a consequence, less molecules of the volatile fraction are linked to the PVA chains, and evaporation is facilitated. In fact, the DC% values are higher for formulations containing EDTA (about 9%) compared to the same formulations without EDTA (PVA70, 7.9 DC%).

Differences in the behavior of PVA70 formulations loaded with different complexing agents (EDTA and RS) in different concentrations (3% and 6% w/w respectively) were evaluated by means of isothermal thermogravimetric experiments (see Figure 2b). If compared to EDTA-loaded systems (93 minutes needed for film formation), the decrease in the evaporation rate induced by the presence of the complexing agent is considerably enhanced in the case of systems containing RS (208 minutes needed for film formation). In fact, RS is highly hygroscopic and loaded in higher concentrations. As a consequence, the overall hygroscopicity of the system is increased and film formation occurs at a later stage.

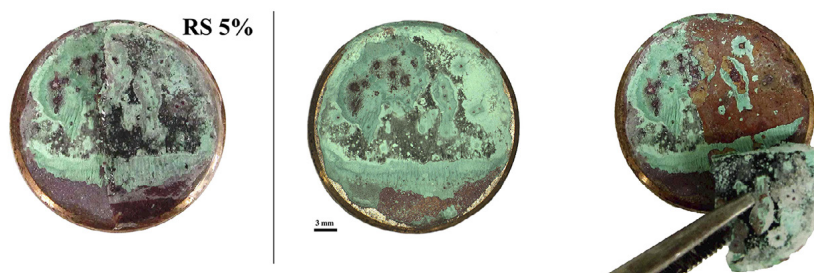
**APPLICATION TESTS**

**Cleaning tests on artificially aged samples**

Preliminary tests were performed on an artificially aged sample provided by the Institute for the Study of Nanostructured Materials – National Research Council (ISMN-CNR, Istituto per lo Studio dei Materiali Nanostrutturati, Consiglio Nazionale delle Ricerche) in Rome, Italy in order to find the best performing formulations in terms of control and selectivity of the cleaning action.

The samples reproduced typical ancient bronze alloys covered by an archeological alteration patina obtained by means of a procedure developed at the ISMN-CNR laboratories (Casaletto et al. 2006), which is outlined in Figure 3. The composition of two reference alloys (CAS4 and CAS10) subject to the artificial degradation process is reported in Table 3.

A preliminary test was performed on sample CAS4 using formulation PVA70 loaded with 5% w/w RS. The result of the cleaning test in Figure 4 shows that the removal of the green patina composed of copper oxychlorides was almost complete without affecting the underlying cuprite layer.



**Figure 4.** Cleaning test over the CAS4 sample with the PVA70 formulation loaded with 5% w/w RS

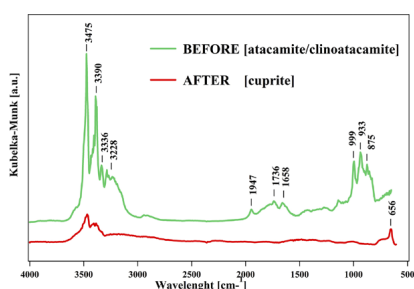
Figure 5 shows the application of PVA70 loaded with 3% w/w EDTA at pH 10 on sample CAS10. A single application resulted in a considerable

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**Table 3.** Composition in % w/w of two reference alloys used for the artificial degradation process

|              |           |           |           |                          |
|--------------|-----------|-----------|-----------|--------------------------|
| <b>CAS4</b>  | <b>Cu</b> | <b>Sn</b> | <b>Pb</b> | <b>CuFeS<sub>2</sub></b> |
|              | 92.3      | 7.5       | 0.2       | 0.2                      |
| <b>CAS10</b> | <b>Cu</b> | <b>Sn</b> | <b>Pb</b> | <b>Zn</b>                |
|              | 91.6      | 7.5       | 0.2       | 0.5                      |



**Figure 6.**  $\mu$ -FTIR spectrum of the areas highlighted in Figure 5, before and after the cleaning test, which confirms the complete removal of oxychloride polymorphs, by preserving the integrity of the cuprite layer

removal of the corrosion products. After a gentle mechanical action, micro-Fourier transform infrared ( $\mu$ -FTIR) spectroscopy analysis confirmed both the complete removal of the residual oxychlorides (the polymorphs atacamite and clinoatacamite), and that the cuprite layer was preserved (see Figure 6). Moreover, no detectable polymer residues were revealed by the  $\mu$ -FTIR analysis.



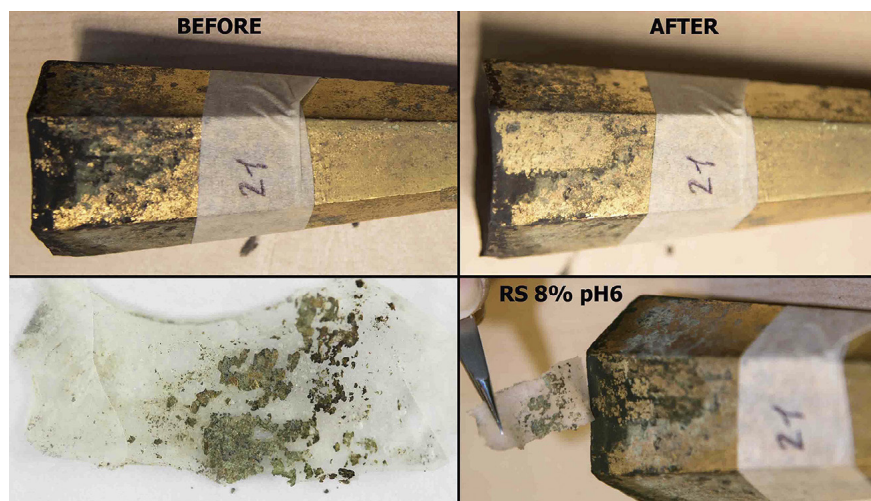
**Figure 5.** Application of the PVA70 formulation loaded with 3% w/w EDTA at pH 10 on sample CAS10

These preliminary tests revealed both the advantages and drawbacks of each chelating agent: Rochelle salt guarantees a delicate and gentle chemical action by respecting the cuprite layer, but its action might not be sufficient in the presence of highly adhering corrosion products; EDTA is more versatile as it can perform a controllable cleaning action by tuning the pH values.

**Case studies**

The new materials developed were tested on a corroded gilded metal tip and on the Fontana dei Mostri Marini monument by Pietro Tacca (17th century) in Florence.

Figure 7 shows the application of PVA70 formulation loaded with 8% w/w of RS (pH 6) on the upper part of the tip, which is covered with a dark and hardened deposit presenting the typical alteration products of an outdoor bronze (copper sulfates, brochantite and antlerite). The polymeric film was peeled off after three hours, removing some of the deposit (see Figure 7, lower panel). At this point the residual deposit was considerably softened and could be removed with a very mild mechanical action (Figure 7, upper panel), without affecting the underlying gold layer.



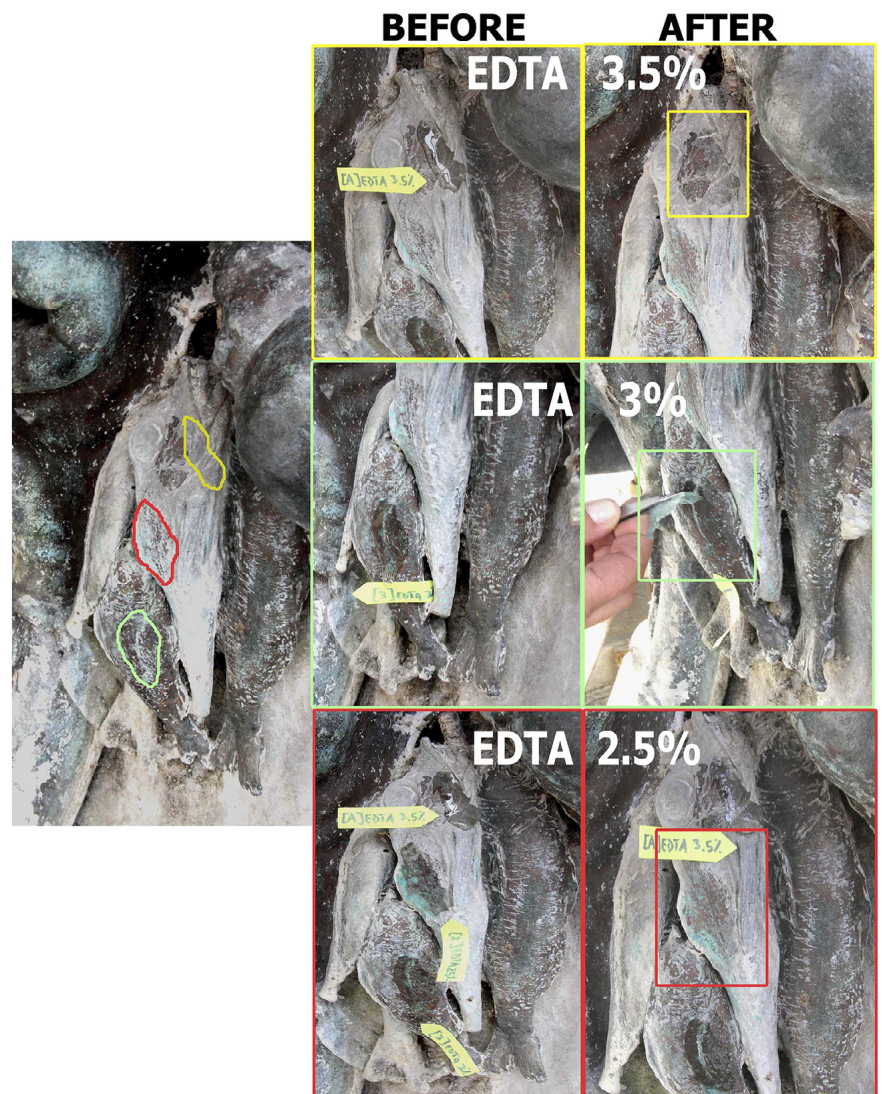
**Figure 7.** Cleaning test performed with the PVA70 formulation loaded with 8% w/w of Rochelle salt (pH 6) on the gilded surface of a bronze tip. Studio Restauri Formica (Italy) is acknowledged for the experimental tests



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The second application was performed on the eastern Fontana dei Mostri Marini by Pietro Tacca, which was subject to a conservation intervention in 2014. A preliminary diagnostic campaign was performed in order to understand the specific conservation issues, identify the alteration products, and analyze the metallurgical features of the alloy. Beyond the typical copper degradation products, the patinas to be removed from the fountain were found to be also rich in gypsum and calcite. Tests were carried out with the assistance of conservators Gabriella Tonini and Louis Dante Pierelli from Nike Restauro s.n.c. (Florence, Italy) and architect Maria Bonelli from Comune di Firenze, which contributed to the definition of the application procedure. Three different formulations (PVA76, PVA72, and PVA70), loaded with EDTA (3.5%, 3%, 2.5% w/w, respectively) were applied onto different areas, as reported in Figure 8. After the removal of the dried films by peeling, a consistent reduction of the white layer of calcite and gypsum was achieved, as well as the partial removal of the underlying corrosion products. In fact, EDTA is also an effective complexing agent for  $\text{Ca}^{2+}$  ions, thus performing a double cleaning action in a single application, preserving the cuprite layer.



**Figure 8.** Applicative tests of different formulations on a decoration on the fountain: PVA76 with 3.5% w/w EDTA (yellow), PVA72 with 3% w/w EDTA (green), and PVA70 with 2.5% w/w EDTA (red), pH 7



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## CONCLUSION

An innovative cleaning system, able to perform a combined chemical and mechanical action specifically tailored for the cleaning of copper-alloy artifacts, was developed. In particular, the system consists of a chelator, specific for Cu(II), embedded within a PVA-based polymeric matrix characterized by excellent film-forming properties. The confinement of the complexing agent ensures a highly controlled chemical action while the peeling off of the flexible and elastic film, formed after drying, provides a gentle mechanical action. The influence of several additives was studied in terms of the application features and properties of the final film. The addition of ethanol improves the texture of the polymeric dispersion and, acting as a drying agent, tunes the time required for film formation depending on the environmental conditions. The presence of plasticizers decreases the film formation rates. The final films are flexible, elastic, and less rigid and adhesive with respect to neat PVA films, and are thus more suitable for peeling off from a delicate surface.

Moreover, the influence of the loading with two different chelators, namely EDTA and RS at different concentrations, was studied, revealing that both chelators cause an increase in the evaporation rate.

Preliminary cleaning tests were performed on artificially aged mock-ups. Tests on real samples show that the polymeric system loaded with complexing agents is efficient in removing alteration patinas, that the cuprite layer is preserved, and that no detectable residues are left on the surface after cleaning.

## ACKNOWLEDGEMENTS

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## MATERIALS LIST

2-methyl-1,3-propanediol (MPD) (purity 99%)  
Sigma-Aldrich  
[www.sigmaaldrich.com](http://www.sigmaaldrich.com)

Dipropylene glycol (DPG) (purity 99% mixture of isomers)  
Sigma-Aldrich  
[www.sigmaaldrich.com](http://www.sigmaaldrich.com)

Ethanol (purity  $\geq 98\%$ )  
[www.fluka.org/fluka.php](http://www.fluka.org/fluka.php)

Ethylenediaminetetraacetic acid disodium salt dihydrate (Na<sub>2</sub>EDTA) (purity 99.9–101.0%)  
Sigma-Aldrich  
[www.sigmaaldrich.com](http://www.sigmaaldrich.com)

Glycerol (GLY) (for analysis)  
[www.merckmillipore.com](http://www.merckmillipore.com)

Polyethylene glycol (PEG) (average M<sub>n</sub> 300)  
Sigma-Aldrich  
[www.sigmaaldrich.com](http://www.sigmaaldrich.com)

Polyvinyl alcohol (PVA)  
(87–89% hydrolyzed, M<sub>w</sub> 85,000–124,000, DP  $\approx$  2000, cps 23.0–27.0)  
Sigma-Aldrich  
[www.sigmaaldrich.com](http://www.sigmaaldrich.com)

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Potassium sodium tartrate tetrahydrate (RS) (purity 99%)  
Sigma-Aldrich  
www.sigmaaldrich.com

**REFERENCES**

- BAGLIONI P., D. CHELAZZI D. and P. O'BRIEN. 2013. *Nanoscience for the conservation of works of art*. Cambridge: Royal Society of Chemistry
- CASALETTO, M.P., T. DE CARO, G.M. INGO, and C. RICCUCCI. 2006. Production of reference "ancient" Cu-based alloys and their accelerated degradation methods. *Applied Physics A: Materials Science and Processing* 83: 617–22.
- DEGRIGNY, C. 2004. Survey of European experiences on cleaning procedures. In *Monumenti in bronzo all'aperto. Esperienze a confronto*, ed. P. Letardi, 101–108. Nardini Editore.
- MALLAPRAGADA, S.K. and N.A. PEPPAS. 1996. Dissolution mechanism of semicrystalline poly(vinyl alcohol) in water. *Journal of Polymer Science* 34: 1339–46.
- MARABELLI, M. 1993. The Monument of Marcus Aurelius: Facts and comments. In *Ancient & historic metals*, ed. D. Scott, 1–20. Los Angeles, CA: Getty Conservation Institute.
- MARTELL, A.E. and R.D. HANCOCK. 1996. *Metal complexes in aqueous solutions*. Springer Science + Business Media.
- MATTEINI, M., C. LALLI, I. TOSINI, A. GIUSTI, and S. SIANO. 2003. Laser and chemical cleaning tests for the conservation of the Porta del Paradiso by Lorenzo Ghiberti. *Journal of Cultural Heritage* 4: 147–51.
- OGUR, E. 2005. *Polyvinyl alcohol: Materials, processing and applications*. Rapra Review Report.
- SCOTT, D.A. 2002. *Copper and bronze in art*. Los Angeles, CA: Getty Conservation Institute.
- SCOTT, D.A. 1990. Bronze disease: A review of some chemical problems and the role of relative humidity. *Journal of the American Institute for Conservation* 29: 193–206.
- STULIK, D. 2004. *Solvent gels for the cleaning of works of art: The residue question*. Los Angeles, CA: Getty Conservation Institute.
- WU, W., H. TIAN, and A. XIANG. 2012. Influence of polyol plasticizers on the properties of polyvinyl alcohol films fabricated by melt processing. *Journal of Polymers and the Environment* 20(1): 63–9.

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