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Erica I. Parisi, Nicole Bonelli, Emiliano Carretti, Rodorico Giorgi*, Gabriel M. Ingo and Piero Baglioni

Film forming PVA-based cleaning systems for the removal of corrosion products from historical bronzes

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Abstract: This paper presents an innovative poly(vinyl)alcohol-based film forming system, specifically devised for the controllable and selective cleaning of copper-based artifacts. Traditional cleaning procedures are commonly performed using mechanical and/or chemical methods. Unfortunately, both these methods present some limitations related to both the poor selectivity and invasiveness in case of the mechanical procedure, and to the scarce control over the involved reactions when dealing with a chemical approach. The innovative system proposed in this work allows combining the advantages of chemical and mechanical treatments thanks to the confinement of a complexing agent (EDTA) within a fluid, polymeric matrix, that is able to form a solid thin film upon drying. After treatment, the polymeric film can be completely removed from the artwork through a gentle peeling action. In this contribution, the film formation mechanism was investigated by means of thermal analysis and rheology; the role of plasticizers, volatile solvent fraction, and quantity of loaded EDTA is also discussed. Finally, the results of cleaning tests performed on artificially aged samples, and on a real case study, the “Fontana dei Mostri Marini” by Pietro Tacca in Florence, are presented.

Keywords: 2016 ChemCultHerit; bronze; conservation; gel; peeling; PVA.

Introduction


Within restoration processes of metallic artifacts, cleaning still represents a great challenge for conservators. In fact, this task requires a deep awareness on the intrinsic characteristics of the treated alloys and on the ongoing alteration processes, especially in case of outdoor monuments or buried artifacts. The alteration products of Cu-based alloys (e.g. bronze and brass) can form thick and adherent concretions or thin and homogeneous *patinas*, which are generally constituted by a multilayered structure that includes corrosion products of copper(I) and (II). Copper(II) oxides (carbonates and sulfates) are defacing mainly because of their intense coloration. Moreover, the presence of copper oxychlorides is generally considered as a symptom of the so-called ‘bronze disease’ [1, 2], a dangerous phenomenon induced by the exposure to air of the cuprous chloride nanotkite (CuCl). In fact, the cyclic reaction of nanotkite with air moisture and oxygen leads

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***Corresponding author: Rodorico Giorgi**, Department of Chemistry Ugo Schiff and CSGI, University of Florence, Via della Lastruccia 3, Sesto Fiorentino, 50019 Florence, Italy, e-mail: giorgi@csgi.unifi.it

Erica I. Parisi, Nicole Bonelli, Emiliano Carretti and Piero Baglioni: Department of Chemistry Ugo Schiff and CSGI, University of Florence, Via della Lastruccia 3, Sesto Fiorentino, 50019 Florence, Italy

Gabriel M. Ingo: Istituto per lo Studio dei Materiali Nanostrutturati, ISMN-CNR, Via Salaria Km 29.300-00015 Monterotondo Stazione (RM), Italy

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to formation of additional oxychlorides, which results in the progressive and irreversible deterioration of the artistic object. On the other hand, the inner part of the alteration layers, delimiting the artifacts interface, is usually constituted by cuprite (copper(I) oxide). The cuprite layer can be considered as a protective layer against further corrosion, since it acts as passivating agent. For this reason, an adequate cleaning procedure should aim to the complete removal of the defacing and harmful corrosion products (copper(II) oxides and carbonates, copper oxychlorides) while preserving the protective cuprite layer.

Cleaning is traditionally performed by mechanical (vibrating or abrasive tools, micro-peening with vegetal granulates, ultra-high-pressure water, laser) and/or chemical methods (complexing agents, bases, acids) [3]. Mechanical cleaning methods present some limitations related to scarce selectivity and control, which can lead to damage of the protective cuprite layer, to the deterioration of superficial information of the artwork, or trigger heating processes on the surface [4, 5]. Chemical treatments usually involve the use of reagents such as Rochelle salt, ethylenediaminetetraacetic acid disodium salt (Na_2EDTA), ammonia and ammonium salts, citric acid, alkaline glycerol, sodium hexametaphosphate and sodium carbonate solutions [2, 3]. However, the application of these solutions, by means of poultices, brushing and immersion, presents some important drawbacks: (i) deterioration of the protective cuprite layer, due the scarce control on the ongoing chemical reactions, especially when low selective reagents are used (e.g. citric acid and sodium hexametaphosphate); (ii) reagent residues after treatment; (iii) precipitation and re-deposition of copper salts on the surface [5]. To avoid some of the above-mentioned drawbacks, highly selective reagents such as Rochelle salt and EDTA are generally preferred. In particular, Na_2EDTA (3–12 % w/w aqueous solution) [2, 5] is the most common complexing agent used for the chemical cleaning of metal artifacts. In fact, Na_2EDTA presents several advantages including high stability of the EDTA-M^{n+} complexes (for Cu^{2+} $\log K_f = 18.8$ at 25 °C and 1 M) [6]; high selectivity (in the case of bronze artifacts it allows a selective removal of cupric salts, by negligibly affecting the protective cuprite layer) [5]; and adjustable efficacy by varying the pH value [7].

Due to the need to control the cleaning action of solvents and other cleaning fluids used in restoration, in the past decades a wide range of thickeners and confining systems for different liquid phases (i.e. solvents, micellar solutions, microemulsions, aqueous solutions of chelating agents, etc.) were developed and tested [8–16]. In particular Na_2EDTA solutions for the cleaning of metal artifacts have been applied in association with thickeners such as cellulose ethers and polyacrylic acids, and with agar-agar hydrogels [2, 5].

This paper presents a new poly(vinyl)alcohol (PVA)-based film forming system loaded with a Na_2EDTA solution for the selective surface cleaning of bronze artifacts. The Na_2EDTA -loaded polymeric system is applied as a fluid; upon drying a film is formed and the entire system can be easily removed by peeling after the cleaning action is completed. A concentrated PVA-based dispersion was chosen to act as carrier for the complexing agent since PVA presents excellent chemical stability, high biocompatibility, low toxicity and cost, and peculiar film forming properties [17–21]. In particular, partially hydrolyzed, semi-crystalline PVA, presents high water solubility and the ability to form films that are characterized by good mechanical properties thanks to the presence of both, ordered (crystalline) and amorphous domains [22]. Different plasticizers were added to the formulation in order to improve specific properties, e.g. the softness of the final dry film, allowing its gentle and easy removal by peeling after cleaning.

The combination of the complexing agent and the film forming PVA-based polymeric dispersion yields a cleaning system with enhanced performances in terms of applicability and efficacy on bronze artifacts. This innovative system represents an improvement in respect to the commonly used cleaning procedures since it permits to (i) increase chemical control thanks to high selectivity of EDTA for Cu^{2+} ions; (ii) attain highly performing cleaning results by combining chemical and mechanical action (favored by the gentle final peeling of the film); (iii) adjust the physico-mechanical properties (texture, adhesiveness, transparency, etc.) to adapt to different substrates (non-horizontal, rough and irregular surfaces).

Preliminary tests were performed on artificially aged samples, provided by the Istituto per lo Studio dei Materiali Nanostrutturati, ISMN-CNR (Monterotondo, Rome), and on the eastern “Fontana dei Mostri Marini” by Pietro Tacca (Santissima Annunziata Square, Florence).

Materials

Poly(vinyl alcohol) [PVA] (87–89 % hydrolyzed, M_w 85,000–124,000, $DP \approx 2000$, cps 23.0–27.0, Aldrich), dipropylene glycol [DPG] (purity 99 % mixture of isomers, Aldrich), 2-methyl-1,3-propanediol [MPD] (purity 99 %, Aldrich), glycerol [GLY] (for analysis, Merck), polyethylene glycol [PEG] (average M_n 300), ethanol (purity ≥ 98 %, Fluka), ethylenediaminetetraacetic acid disodium salt dihydrate [Na_2EDTA] (purity 99.9–101.0 %, Aldrich), NH_4OH solution (30–33 % NH_3 , Sigma-Aldrich) were used as received. Water was purified by a Millipore MilliRO-6 Milli-Q gradient system (resistivity $>18 \text{ M}\Omega \cdot \text{cm}$).

Methods

Preparation of plasticized PVA-based film forming systems

A 20 % (w/w) aqueous polymeric solution was obtained by dissolving PVA powder into purified water. Complete solubilization was achieved by heating the system at 90°C for 5 h and by mixing it mechanically. After PVA solubilization, plasticizers (DPG, MPD, PEG, GLY) and EDTA aqueous stock solution (0.5 M, pH 8) were added, keeping the resulting solution at 75°C until complete homogenization. Finally, ethanol was added and the obtained system was sonicated in pulsed mode until a transparent polymeric dispersion was obtained.

Different formulations were designed by varying the amounts of each component (volatile fraction, polymer, plasticizers) in order to obtain the best performances in terms of ease of application and film formation properties (compositions are reported in Table 1). Since the complexing efficiency of EDTA is maximized when meaningful amounts of both the trianionic HY^{3-} and tetranionic Y^{4-} species are present [7], after loading the pH of the polymer dispersion was adjusted to $9\text{--}10 \pm 0.2$ (as indicated by Whatman® Indicator Paper, pH 8.0–10.0 narrow range) through the drop wise addition of an aqueous solution of NH_3 .

The final system, a viscous transparent dispersion, can be easily applied with a spatula, a hard brush or a syringe (without the needle) on the surface to be treated. After complete evaporation of the volatile fraction, a transparent film is formed, which is easily removed by tweezers with a gentle peeling action. Film formation upon drying occurs within 1–4 h, depending on the composition and thickness of the applied system, as well as on the environmental conditions (T , $\text{RH}\%$).

Physico-chemical characterization

The physico-chemical characterization of both, the polymeric dispersions and the dry films was carried out in order to study the changes in the properties of the systems during the drying process, and to

Table 1: Composition (w/w %) of selected formulations PVA_{XX} , where the subscript XX refers to the total volatiles content (water + ethanol).

	w/w %		
	PVA_{74}	PVA_{70}	PVA_{68}
H_2O	57	55	54
EtOH	17	15	14
PVA	20	20	20
DPG	2.5	3	3.5
MPD	2.5	3	3.5
GLY	0.6	2.5	3
PEG	0.4	1.5	2
Volatiles content	74	70	68
Plasticizers content	6	10	12

evaluate the influence of each component on the final properties of the system (before and after film formation).

Film formation

The evaporation process of the volatile fraction (water and ethanol) was studied by means of gravimetric measurements. To simulate the process of film formation in real conditions, same amounts (0.5 g) of different formulations were applied on a delimited area ($2.6 \times 2.5 \text{ cm}^2$) of a microscope slide. During the evaporation of the volatile fraction the systems were periodically weighted until the film could be easily removed with tweezers from the glass without breaking or leaving residues.

The evaporation kinetics are expressed as volatile fraction loss vs. time and the weight decrease was calculated as reported in eq. (1) [14]

$$W_{vf} = \frac{(W_i - W_d)}{(W_w - W_d)} \times 100 \quad (1)$$

where W_{vf} is the volatile fraction loss in function of time, W_i is the weight at the specific time i , W_d and W_w are, respectively, the final dry weight and the initial weight of the sample.

The gravimetric data were compared to those obtained in a controlled environment through isothermal thermogravimetric analysis (TGA), performed using a TA Instruments (SDT-Q600) apparatus, at 40°C under nitrogen flow (100 mL/min) in open aluminum pans. The evaporation of the volatile fraction was considered concluded when a constant weight was reached (weight loss $<1\%/10 \text{ min}$). The influence of different additives (i.e. ethanol, plasticizers, chelating agent) on the volatile fraction loss rate was also evaluated by scanning TG measurements. Fluid samples were heated from room temperature to 220°C (scan rate $10^\circ\text{C}/\text{min}$) under nitrogen flow in open aluminum pans.

Changes in viscoelastic behavior as a function of time during drying were investigated by means of rotational and oscillatory shear measurements performed both on a PVA₇₀ formulation before and after loading with 3% w/w EDTA (pH 7). Measurements were carried out on a Paar Physica (UDS200) rheometer at $25.0 \pm 0.1^\circ\text{C}$ (Peltier temperature control system) using a plate-plate geometry (25 mm diameter); the gap was adjusted in order to obtain a maximum normal force of 0.9 N. Fluid samples were continuously kept under manual stirring in order to maintain the homogeneity of the systems. Film samples were prepared by pouring 11 g of the polymeric dispersion into a Petri dish and equilibrated for 2 days at 25°C and 55% RH.

Frequency sweep measurements were carried out within the linear viscoelastic range (5% strain) determined by previous amplitude sweep tests. The storage (G') and loss (G'') moduli were measured over the frequency range 0.01–100 Hz.

Thermal analysis and evaluation of the crystallinity degree

The thermal properties of dried film samples were determined by differential scanning calorimetry (DSC) on a TA Instruments (Q1000) apparatus. To prepare dry films 1 g of polymeric dispersion was uniformly distributed on a $5 \times 2.5 \text{ cm}^2$ glass slide, dried at 60°C for 17 h and then equilibrated at 55% RH for at least 1 week. Sets of non-plasticized, mono-plasticized and four-plasticized polymer dispersions were used for the preparation of the dry films (compositions are listed in Table 2).

The polymeric films were heated up to 250°C at a scanning rate of $10^\circ\text{C}/\text{min}$, cooled to 25°C and re-heated to 250°C , under nitrogen flow (50 mL/min) [23]. Glass transition and melting temperatures (T_g and T_m , respectively) values were obtained from the thermal curves after the second heating cycle. Values of the enthalpy of fusion (ΔH_m) were obtained from the integrated area of the endothermic melting peak. The crystallization temperatures (T_c) were obtained from the crystallization exothermic peak showed by thermal curve during cooling, while the related enthalpy of crystallization (ΔH_c) was obtained from its integrated area. Each measurement was repeated twice.

Table 2: Composition (w/w %) of the polymer dispersions used for the evaluation of the crystallinity degree of dry films.

	w/w						
	H ₂ O	EtOH	PVA	DPG	MPD	GLY	PEG
PVA/H ₂ O	80	–	20	–	–	–	–
PVA/H ₂ O/EtOH	65	15	20	–	–	–	–
PVA ₇₀ noEtOH	70	–	20	3	3	2.5	1.5
PVA ₇₀ /DPG	55	15	20	10	–	–	–
PVA ₇₀ /MPD	55	15	20	–	10	–	–
PVA ₇₀ /GLY	55	15	20	–	–	10	–
PVA ₇₀ /PEG	55	15	20	–	–	–	10

The final degree of crystallinity (DC%) was determined according to eq. (2) [24–29] where ΔH_m is the experimental melting enthalpy and ΔH_{100} is the melting enthalpy of a completely crystalline PVA ($\Delta H_{100} = 138.6$ J/g) [29]

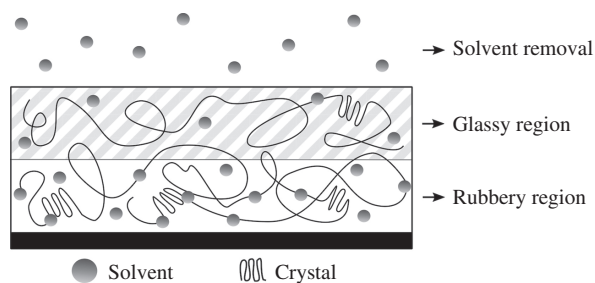
$$\text{DC}\% = (\Delta H_m / \Delta H_{100}) \times 100 \quad (2)$$

Artificially aged samples

Preliminary cleaning tests were performed on artificially aged samples. The ISMN-CNR provided bronze alloy samples (with two different compositions) produced according to an ancient procedure [30]. Artificial aging of the samples was carried out according to a procedure that involves a chemical induction of the degradation process, followed by a burial of several months in an archeological soil. This procedure permits to obtain complex corrosion *patinas* that are very similar in appearance and composition to those of naturally aged archeological bronze alloys. Alloy production and aging procedures are explained in detail in [30]. Cleaning tests were carried out on two different samples: chemical artificial aging (CAA; alloy composition w/w 92.3 % copper, 7.3 % tin, 0.2 % lead, 0.2 % CuFeS₂), and burial natural aging (BNA; alloy composition w/w 91.8 % copper, 7.5 % tin, 0.2 % lead, 0.5 % zinc, buried for 10 months after the chemical treatment).

Results and discussion

The ability of PVA to form films from a concentrated aqueous solution through the evaporation of a liquid phase is well-known from literature [20, 31–33]. As stated by Mallapragada et al. the isothermal drying process of this semi-crystalline polymer involves an overall increase in polymer chains vicinity, degree of crystallinity, and glass transition temperature [26, 34, 35]. During the evaporation process, the formation of two distinct regions occurs, as shown in Fig. 1. A glassy region forms at the polymer-air interface, where the

**Fig. 1:** Schematic representation of the glassy and rubbery region of the system during solvent evaporation.

solvent evaporation proceeds faster and the progressive immobilization of the chains hinders the formation of crystalline domains. The formation of this glassy barrier decreases the solvent evaporation rates, favoring the formation of crystalline domains in the underlying rubbery region, where the entangled polymer chains maintain a residual mobility throughout the whole drying process. The glassy-rubbery interface moves inward, as the drying process proceeds, until a glassy film (containing crystalline domains) is formed.

To be suitable to our purposes, the film forming system should satisfy following requirements: (i) the rheological properties should permit its application on both horizontal and non-horizontal surfaces; (ii) the evaporation rate of the liquid phase should be slow enough to permit the reaction of the chelating agent with the surface, but film formation should occur within a reasonable time (not more than 4 h for a single application); (iii) the final film should be soft and easy to remove in a single step, by means of a gentle peeling action; (iv) polymeric dispersions should be able to load and confine performing ligands, in order to achieve a controlled but efficient cleaning action.

To optimize the system formulation, the influence of all the additives (ethanol, plasticizers, chelating agent) on these properties was investigated.

Effect of the volatile fraction

The addition of ethanol to the polymer dispersion contributes to increase the evaporation rate, reducing the time needed for film formation. Furthermore, ethanol acts as a structuring agent on the H-bond water network, increasing the probability of H-bond formation [36], which contributes to an overall reinforcement of the three-dimensional (3D) network structure. In fact, as soon as ethanol is added into the formulation, the texture of the polymeric system is remarkably improved: it becomes easier to manipulate and to apply on a delimited area (e.g. with a spatula).

The effect of different H₂O/EtOH ratios was investigated by means of gravimetric measurements and scanning TG analysis for three different formulations, characterized by the same polymer and plasticizer content. As highlighted in Fig. 2a, ethanol content decreases the film formation rate (240 min in case of H₂O/EtOH 70/30 and 360 min for formulation H₂O/EtOH 85/15). The same trend is confirmed by the DTG curves reported in Fig. 2b, where the derivatives of the thermogravimetric curves show the temperature at which the maximum rate of volatile fraction loss occurs. By decreasing ethanol content, a shift of the peak towards higher temperatures is observed (the highest peak temperature is 111 °C for PVA₇₀ formulation, prepared without ethanol).

Moreover, the presence of ethanol influences also the crystallinity degree. As reported on Table 3, the formulations PVA/H₂O/EtOH and PVA₇₀, are characterized by lower DC% values in respect to the same formulations prepared without ethanol (PVA/H₂O and PVA₇₀ noEtOH, respectively). In fact, the higher evaporation rate of the liquid phase in presence of ethanol leads to the fast development of the glassy region, which is detrimental to the formation of ordered crystalline domains within the rubbery region.

Effect of the plasticizers

Plasticizers are added to the PVA polymeric dispersion in order to adjust the mechanical and adhesive properties of the final dry film. In fact, plasticizers act as lubricants between the polymer chains by weakening the intermolecular secondary forces and by increasing the overall free volume [31, 37]. This process causes a decrease of the thermal parameters values and of the degree of crystallinity of the final films, resulting in changes in the physico-mechanical properties (reduced adhesion and brittleness, increased flexibility and tensile strength).

Polyols (i.e. DPG, MPD, GLY and PEG) were chosen as plasticizers among the additives commonly used in similar formulations [22, 38], since they present suitable characteristics such as good solubility in both, water and ethanol, low-toxicity, low-cost and chemical affinity to PVA.

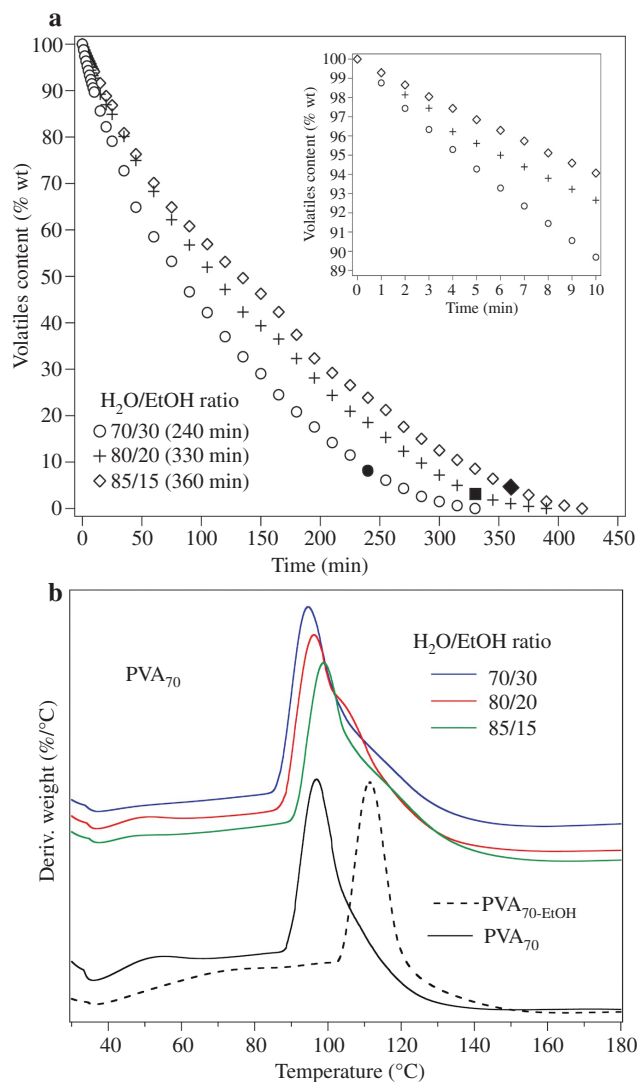


Fig. 2: (a) Gravimetric evaporation curves of PVA_{70} formulations with different $H_2O/EtOH$ ratios; solid symbols represent the time when the evaporation is complete and films can be removed from the surface; inset: initial slope of the curves. (b) DTG thermograms of PVA_{70} formulations with decreasing ethanol content; the displayed maxima of the derivatives weight loss represent the evaporation temperatures of the volatile fraction.

Table 3: Thermal parameters obtained through DSC experiments on dry film samples.

	T_m (°C)	ΔH_m (J/g)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	DC%
PVA_{powder}	157.7 ± 0.4	19.8 ± 0.7	125.6 ± 2.2	100.5 ± 1.2	12.3 ± 0.6	14.3
PVA/H_2O	161.3 ± 0.1	17.7 ± 0.1	104.0 ± 2.9	107.2 ± 1.8	12.4 ± 0.2	12.8
$PVA/H_2O/EtOH$	146.6 ± 0.8	16.1 ± 0.6	102.4 ± 2.2	89.1 ± 0.7	8.4 ± 1.0	11.6
PVA_{70}	139.3 ± 0.2	10.9 ± 0.7	86.0 ± 2.7	85.3 ± 0.5	9.4 ± 1.3	7.9
PVA_{70} noEtOH	137.3 ± 0.1	11.4 ± 1.1	74.2 ± 0.3	85.2 ± 0.8	9.5 ± 0.5	8.2
PVA_{70}/PEG	157.7 ± 1.0	11.5 ± 0.9	106.6 ± 1.3	109.9 ± 3.5	11.8 ± 0.4	8.3
PVA_{70}/DPG	150.0 ± 0.3	12.1 ± 1.5	93.8 ± 1.9	100.2 ± 0.6	9.1 ± 1.4	8.7
PVA_{70}/MPD	138.8 ± 0.5	11.7 ± 0.5	67.7 ± 4.0	85.3 ± 0.6	8.8 ± 0.3	8.4
PVA_{70}/GLY	121.0 ± 0.6	7.9 ± 0.1	79.1 ± 2.4	54.3 ± 1.3	2.8 ± 0.1	5.7

DC% was determined by using eq. 2.

Table 4: Time (min) required for the complete evaporation of the volatile fraction, evaluated through isothermal TGA experiments (40 °C).

	TGA (min)
PVA/H ₂ O	68
PVA/H ₂ O/EtOH	66
PVA ₇₄	109
PVA ₇₀	102
PVA ₆₈	133
PVA ₇₀ noEtOH	135
PVA ₇₀ /PEG	164
PVA ₇₀ /DPG	200
PVA ₇₀ /MPD	213
PVA ₇₀ /GLY	205

Thermal parameters obtained from DSC experiments on dry films are listed in Table 3. As expected [39–41], a considerable decrease of T_g , T_m and T_c values is observed for the plasticized samples (PVA₇₀, PVA₇₀ noEtOH) with respect to PVA powder (PVA_{powder}) or the dry film obtained from a neat PVA aqueous solution (PVA/H₂O). From an applicative point of view, the ease of removal of the dry films through peeling is promoted by a decrease in T_g due to the fact that resulting films are less rigid at room temperature.

Furthermore, DC% values for plasticized samples (ranging from 5.7 % to 7.9 %) are remarkably lower than DC% values for non-plasticized formulations (DC% ranging from 11.6 % to 14.3 %), indicating that the defects introduced in the crystal lattice (and/or possible cross-linking effect of the plasticizers) may inhibit the formation of crystalline domains in the film.

The decrease of DC% has important effects on the final properties of the film. The crystalline domains are responsible for the mechanical stability of dry the film, but also for his hardness, rigidity and brittleness. On the other hand, the amorphous regions promote softness and elasticity of the film, which are important properties for the easy and gentle removal of the film through peeling. In fact, removal tests performed with the different formulations revealed that an excessively aggressive peeling action is necessary for the removal of highly crystalline formulations (such as PVA/H₂O, 12.8 DC%), which are too rigid and brittle and adhere more firmly to the surface with respect to plasticized formulations (characterized by both, lower DC% and T_g).

Table 3 lists also the thermal parameters of mono-plasticized formulations (PVA₇₀/PEG; PVA₇₀/DPG; PVA₇₀/MPD; PVA₇₀/GLY), which were prepared to study how the structure of the single plasticizer affects the properties of the dry films, especially the DC%. The lowest DC% is recorded for PVA₇₀/GLY (5.7 %) indicating that, small plasticizer molecules as glycerol are the most efficient in hindering the formation of crystalline domains due to their ease insertion between the PVA polymeric chains [40, 42, 43].

The influence of plasticizers on the evaporation of the volatile fraction (i.e. on film formation) was studied by means of isothermal thermogravimetric (TGA) measurements at 40 °C.

Data reported in Table 4 indicate that film formation occurs earlier for not plasticized systems (68 min for PVA/H₂O and 66 min for PVA/H₂O/EtOH,) than for those containing plasticizers (102–213 min). Formulations PVA₇₄, PVA₇₀ and PVA₆₈, characterized by the same polymer content but different volatiles and plasticizers amounts (see Table 1), required a shorter time than for the mono-plasticized formulations (PVA₇₀/PEG; PVA₇₀/DPG; PVA₇₀/MPD; PVA₇₀/GLY) for the complete loss of the volatile fraction. According to thermal analysis, PVA₇₀ formulation was selected as the most suitable for applicative purposes: with 7.9 DC% and a T_g 86 °C, the dry film obtained from PVA₇₀ solution presents the best mechanical properties to allow the most gentle peeling off from the artwork surface.

Effect of the complexing agent

According to the results discussed in the section “Effect of the plasticizers”, formulation PVA₇₀ was selected as carrier for the complexing agent solution. The maximum amount of EDTA loaded in the dispersion was

4 % w/w. Increasing EDTA content above this threshold causes phase separation due to its poor solubility in ethanol. Accordingly, EDTA was loaded in different concentrations below the threshold (1–3 % w/w) and at two different pH values (pH 7 and pH 9). The behavior of the combined system was studied in order to assess on possible effects induced by the presence of the complexing agent on the initial appearance of the system, its evaporation rate, and on the mechanical properties of the final film.

Gravimetric data (Fig. 3a) show that increasing the EDTA content increases the evaporation rate of the volatile fraction, which is of advantage for applicative purposes, since the time needed for the cleaning procedure is reduced. In addition, for higher EDTA amount the DTG peak corresponding to the maximum rate of evaporation (Fig. 3b) shifts towards lower temperatures (i.e. 90 °C for 3 % w/w EDTA and 100 °C for the formulation not containing EDTA). This trend is in accordance with the fact that EDTA increases polymer chain entanglements and vicinity, resulting in the modification of the 3D structure of the polymer network and favoring the formation of crystalline domains [44]. As a consequence, the number of sites available for hydrogen-bond formation is reduced, decreasing the total amount of molecules of water and ethanol linked to the PVA chains. The evaporation is also influenced by pH, with higher maximum rate of evaporation for

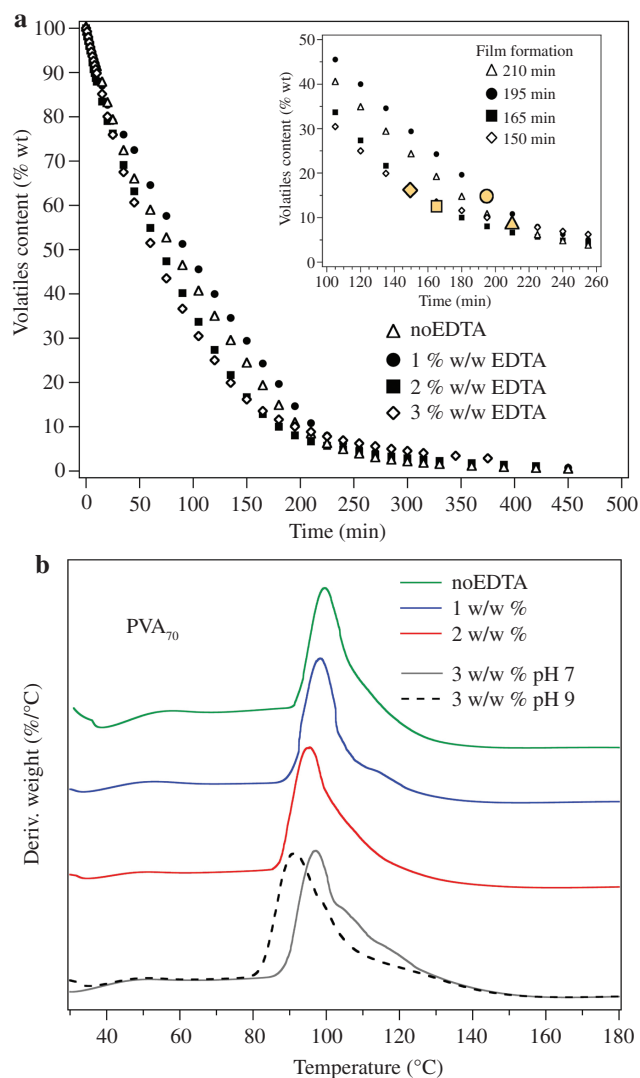


Fig. 3: (a) Gravimetric evaporation curves of PVA₇₀ formulation with increasing EDTA content; inset: complete film formation occurred in correspondence of the solid symbols. (b) DTG thermograms of PVA₇₀ formulations with increasing EDTA content and different pH; the displayed maxima of the derivatives weight loss represent the evaporation temperatures of the volatile fraction.

lower pH values and equal EDTA content (96 °C and 90 °C at pH 7 and pH 9, respectively for 3 % w/w EDTA content) (Fig. 3b).

Variation of the rheological properties during evaporation of the liquid phase

The variations of the rheological parameters as a function of time during the drying process of PVA₇₀ [before (NL) and after loading (EL) with 3 % w/w EDTA at pH 7] were investigated. Frequency sweep tests reported in Fig. 4, show a prevalent viscous behavior with $G' < G''$ over almost the entire range of explored frequencies,

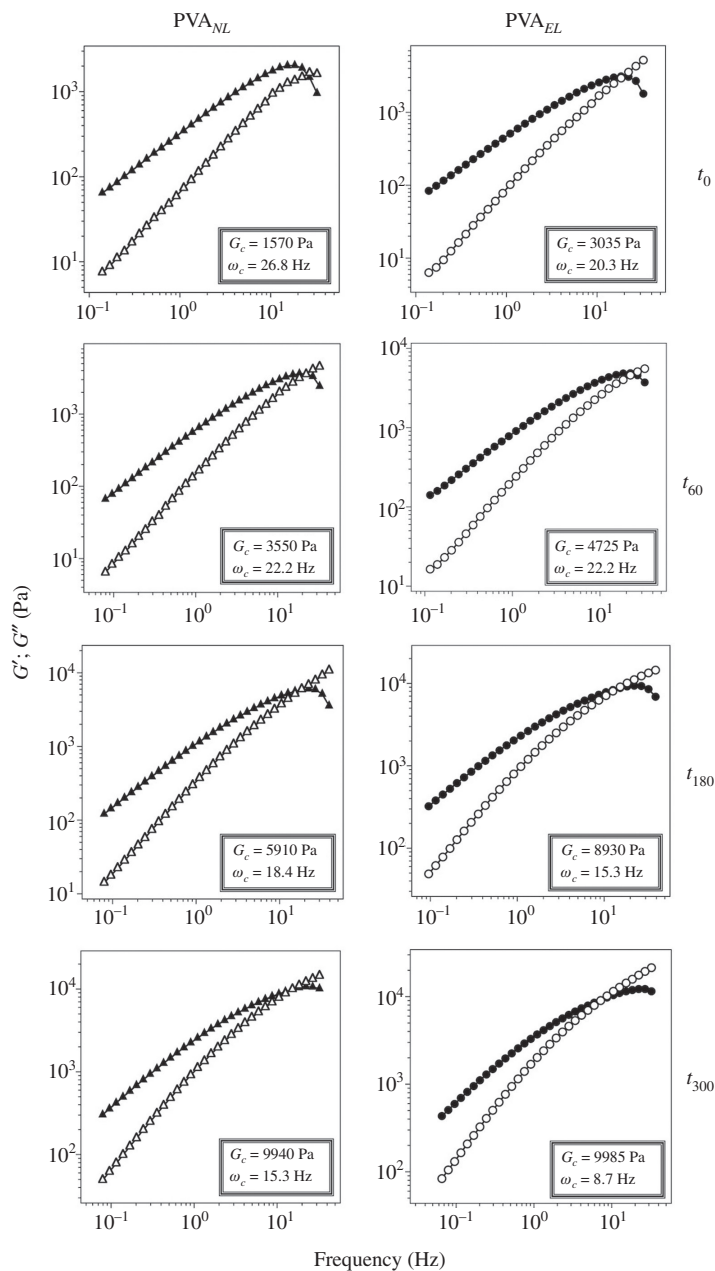


Fig. 4: Frequency sweep curves reported in function of four different times for both the NL and EL system. Solid symbols (\blacktriangle and \bullet) represent the loss modulus (G'') while empty symbols (Δ and \circ) the storage modulus (G'). Each image shows an inset with the crossover parameter; the crossover modulus G_c progressively shifts towards higher frequencies while the crossover frequency ω_c towards lower frequencies with time.

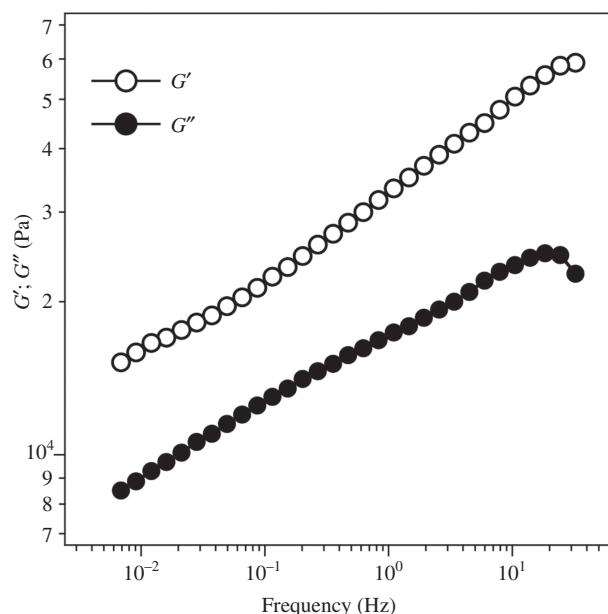


Fig. 5: *EL* system frequency sweep curves of the dry film (see Experimental section), where the storage modulus G' is always higher than the loss modulus G'' and no crossover occurs between them, thus indicating the solid-like behavior of the final film.

in a time range of 0–300 min. A crossover between G' and G'' is observed at high frequencies, as typical for polymer dispersions with low cross-linking density. As the volatile fraction evaporates, the progressive increase of G' values indicates an increase in entanglement density of the polymer chains due to the formation of inter- and intra-molecular H-bonds. Furthermore, the increase of both, the apparent relaxation time τ_c , (defined as ω_c^{-1} where ω_c is the crossover frequency between G' and G'' curves) and of the crossover modulus (G_c) indicates an enhancement of the solid-like character of the system (see Fig. 4). Figure 5 displays the frequency sweep curves of a dry PVA₇₀ *EL* film which is characterized by the absence of a crossover between G' and G'' curves: G' has higher modulus than G'' over the whole range of investigated frequencies, indicating that after drying the system is characterized by a solid-like behavior. Figure 6 reports the trend of the storage modulus G' (at 5 Hz) of PVA₇₀ *NL* and PVA₇₀ *EL* as a function of time. Upon evaporation of the liquid phase, an increase in G' is observed for both samples, indicating that a progressively stronger 3D network is formed during drying. Moreover, G'_{EL} is higher than G'_{NL} for all the considered time range. Once the films are formed, G'_{EL} is almost double (7000 Pa) in respect to G'_{NL} (4500 Pa), indicating that the presence of EDTA promotes chain entanglements, which results in a stronger network. From an applicative point of view, the higher value of G' modulus, as in case of *EL* system, guarantees an easier removal of the final film by peeling and in a single step.

Preliminary cleaning tests on artificially aged samples

Preliminary cleaning test were performed on the artificially aged samples in order to observe the cleaning performances of the selected formulations. According to the evaluation exposed in the section “Effect of the plasticizers”, PVA₇₀ was selected as the most suitable formulation to be tested. Test results of the application on the chemically aged CAA sample, are reported in Figure 7.

Cleaning tests were also performed on the naturally aged BNA sample. Natural aging (burial for several months) produced samples (BNA) with a highly adherent and inhomogeneous *patina* (Fig. 8a), very similar to those of a typical archeological object. A preliminary characterization, performed by XRD (Fig. 8b) and SEM/EDS (Fig. 8e), indicated the presence of both, copper oxychlorides (atacamite, clinoatacamite) on the surface, and of an underlying cuprite layer. The cleaning tests were performed in two steps, using PVA₇₀ loaded with

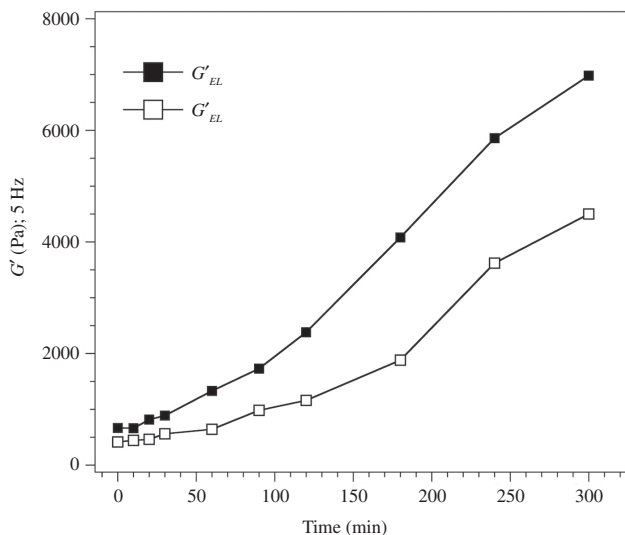


Fig. 6: G' values at 5 Hz reported in function of time for the NL and EL systems. Both the increase of the elastic modulus with the evaporation of the volatile fraction, and the EL values always higher than the NL formulation, indicate the progressive formation of a stronger 3-D network (5% calculate error).

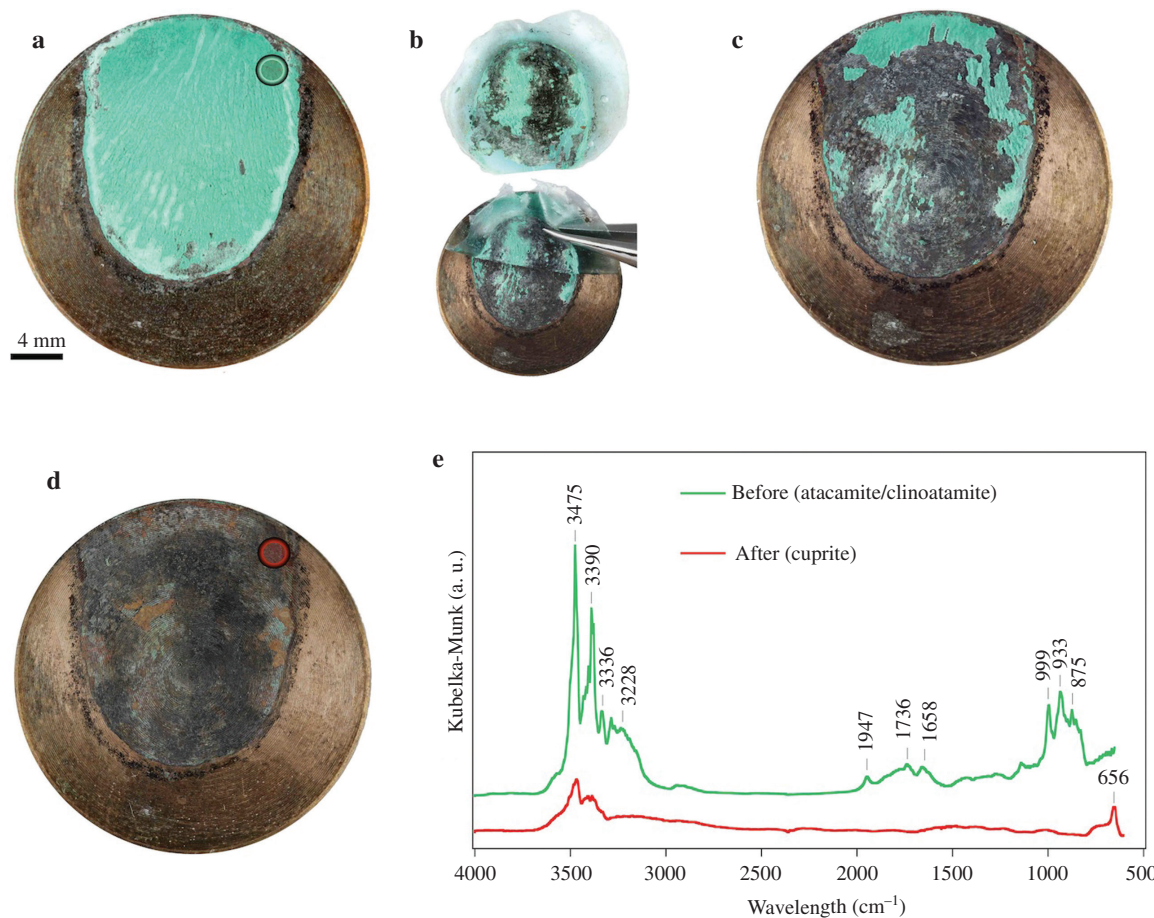


Fig. 7: Cleaning test on CAA sample with a 3% w/w EDTA (pH 10) loaded PVA₇₀ formulation; (a) sample appearance before cleaning; (b) easy removal of the dry film by peeling; (c) sample after a single application; (d) complete removal of the corrosion products after gentle mechanical action (cotton swab soaked with water); (e) micro-FTIR spectra collected before and after the cleaning test.

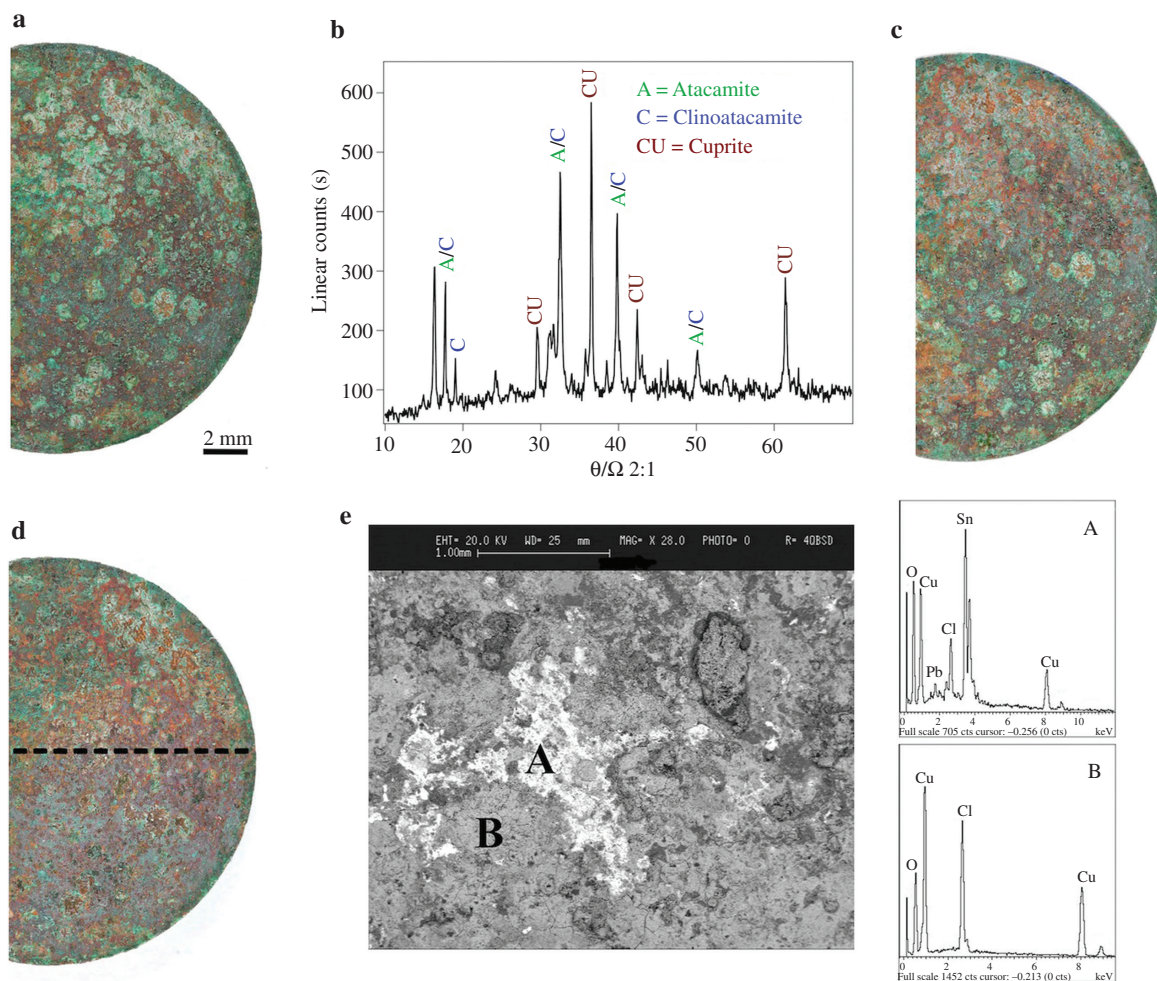


Fig. 8: Cleaning tests on the BNA sample; (a) sample before cleaning; (b) XRD spectrum of the surface before cleaning; (c) cleaning result after a single application; (d) cleaning result after a further application (lower part of the sample); (e) SEM image and relative EDS spectra of the sample surface before cleaning.

3% and 4% w/w EDTA at (pH 10). After each application, a SEM/EDS analysis was performed in order to evaluate the cleaning efficacy of the system. The results show a progressive reduction of the soil-related elements (Na, Si, P), as well as of the chlorine species (Cl); and a reduction in tin content, due to the removal of tin corrosion products on the surface [probably cassiterite (SnO_2)]. In fact, after the first application the EDS analysis shows a partial removal ($\sim 59\%$ w/w) of the typical elements coming from the burial soil (Na, Si, P, Cl) (Table 5). After an additional application (Fig. 8d, bottom part of the disk), more than 90% w/w of the

Table 5: % w/w variation of the elemental composition of the BNA surface, after a two-step cleaning, performed with EDTA loaded PVA₇₀ formulations.

	Not cleaned	1 st application	2 nd application
Na, Si, P, Cl	11.9	-59	-92
Cu	20.3	+21	+69
Sn	12.5	-27	-92

Data were obtained through EDS semi-quantitative analysis. Other elements were detected (C, O, Ca) but not reported in the table.

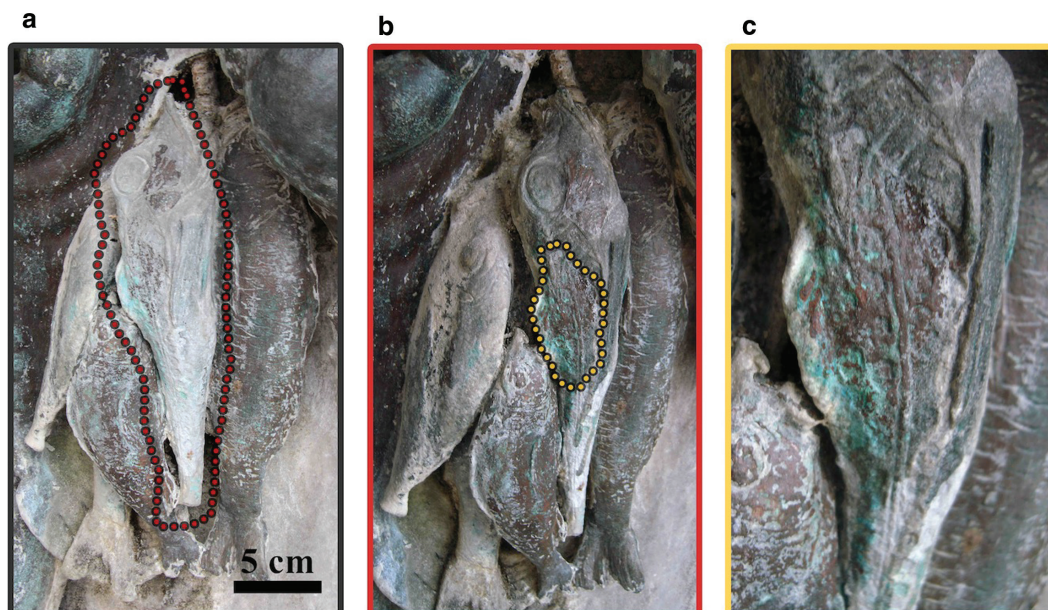


Fig. 9: Cleaning test on a fish of a decorative group located at the base of the fountain; (a) area chosen for the cleaning test with a white layer of calcium carbonate/sulfate and an underlying layer of copper corrosion products; (b) partial removal of the calcium carbonate/sulfate layer after one application of the 3.5 % w/w EDTA (pH 7) loaded PVA₇₀ formulation; (c) enlargement showing the partial removal of the Cu-based corrosion products after the same application.

soil-related elements is removed (see Table 5). At the same time, the increasing Cu amount after two applications (+69 % w/w) indicates the preservation of the cuprite layer and of the underlying metal alloy.

Cleaning test results evidenced that the action of the complexing agent loaded in the polymeric dispersion is fully controllable, permitting a gradual layer-by-layer removal of the corrosion products.

Cleaning tests on the “Fontana dei Mostri Marini”

The cleaning tests on the bronze fountain “Fontana dei Mostri Marini” of P. Tacca in Florence were performed during its recent restoration, occurred in 2014. Preliminary analysis performed on samples taken from several alteration patinas of the fountain showed the presence of copper carbonates (malachite $\text{CuCO}_3(\text{OH})_2$), sulfates (antlerite $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$, brochantite $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$), nitrates and chlorides (atacamite $\text{Cu}_2\text{Cl}(\text{OH})_3$ and its polymorph clinoatacamite). Moreover, calcium carbonate (calcite) and sulfate (gypsum), were also found on the investigated surface as white or dark-gray concretions.

The cleaning tests were performed by applying a 3.5 % w/w EDTA (pH 7) loaded PVA₇₀ formulation on a fish of a decorative group at the base of the fountain (Fig. 9a). Since EDTA is an effective complexing agent also for Ca^{2+} ions, after a single application both, the white calcium carbonate/sulfate as well as the copper corrosion layers were removed (see details in Fig. 9b and c, respectively). Moreover, the cleaning process is fully controllable, since the complexing reaction cannot further occur after loss of the volatile fraction and the formation of the polymeric film.

Conclusions

A novel method, based on the combination of complexing agents with PVA-based polymeric film forming systems, was formulated and tested for the removal of corrosion products from Cu-based alloys (bronzes).

PVA₇₀, formulation, with a H₂O/EtOH ratio of 70/30 (ca. 15 % w/w of ethanol) and a plasticizers content of 10 % w/w displayed the most suitable characteristics for application in respect to the other investigated formulations. Loading of the polymeric dispersion with a 3 % w/w EDTA chelating agent solution improves the mechanical and film forming properties granting a fully controllable chemical reaction. This selected composition allows to obtain: (i) a viscous system with suitable properties also for application on non-horizontal surfaces, able to adapt to the roughness and discontinuities of a non-homogeneous surface (as in the case-study of “Fontana dei Mostri Marini”); (ii) high cleaning efficacy with low ligand concentration, as confirmed by the 92 % w/w removal of the species unrelated to the alloy after a two-step application; (iii) safe chemical reactions thanks to the selectivity of EDTA.

Supporting information

Supporting video of the cleaning test on the artificially aged samples (CAA and BNA).

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Graphical abstract

Erica I. Parisi, Nicole Bonelli, Emiliano Carretti, Rodorico Giorgi, Gabriel M. Ingo and Piero Baglioni

Film forming PVA-based cleaning systems for the removal of corrosion products from historical bronzes

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Conference paper:

Complete removal of corrosion products is achieved by peeling away the solid film formed upon drying. The cleaning system is based on the complexing reaction of copper ions with EDTA solution loaded into the viscous PVA paste.

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