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Cleaning a Sixteenth Century Bronze Artillery Piece from the Terceira Island, Portugal. Buffering Solutions, Chelating Complexes, and Gelled Systems

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ABSTRACT

This research, developed in the *Museo de Historia Militar* (Military History Museum)*, Manuel Coelho Baptista de Lima* on the Terceira Island, proposes a system for cleaning metallic heritage using aquatic buffering solutions with a pH that is safe for the metal and controlled chelation complexes. A total of 20 solutions in liquid or gelled state were applied to a 16th century cast bronze culverin.

Based on the obtained results, it can be concluded that this chemical method of intervention enables stratigraphic and protective cleaning which can eliminate corrosion products formed on the object's metallic surfaces. This system is offered as an alternative to cleansing methods that use a simple mechanical action, which can be too invasive or ineffective. In parallel, the localized application of gelled systems replaces treatments carried out by immersion which, when performed on very large objects that are hard to manipulate, are beyond the means of institutions such as ours since we lack the technical and financial resources.

KEYWORDS

metallic heritage, conservation, chelating, gelled systems, metal conservation, cleaning metals, museum

INTRODUCTION

The *Núcleo de Historia Militar Manuel Coelho Baptista de Lima* (NHMMCBL), in Portugal, was established in an old military hospital and houses part of the *Museo de Angra do Heroísmo* (MAH) collection belonging to the Regional Government, located on one of the nine islands that constitute the Azores archipelago in the Atlantic Ocean: Terceira Island. Among its military pieces, textile collection of uniforms, accessories and weaponry, the artillery heritage stands out: it includes three 16th century portuguese cast culverins, one of which was recovered from the seabed of the city of Angra do Heroismo Bay and is signed by the portuguese smelter João Dias (Regalado, 2023, pp. 260-261).

The use of artillery as a means of warfare became essential for Portugal since the mid-fourteenth century, when the first cast-iron *bocas-de-fuego*[1] were produced. Bronze foundry dates from the end of said century (Regalado, 2020, p. 8), when this metal was obtained by alloying copper and tin. Bronze provides greater resistance than copper and has the advantage of smelting at a lower temperature (Álvarez, 2015, p. 220). Both features made it popular and led to the widespread development of artillery production: in fact, its use represents a real technological leap in the production process and the application of war tactics on the battlefield. Thus, a wide variety of *bocas-de-fuego* were developed, to be operated either on land or to arm the Portuguese ships that sailed the Atlantic.

Among the artillery pieces that were produced are the above-mentioned culverins, gunpowder-loaded *bocas-de-fuego,* which had a muzzle so long itcaused the explosive to burn inside the tube itself, to then activate the launching of the projectile or iron ball. Generally located in maritime defense forts, they are effective in reaching ships at a great distance (Matos, 1944, p. 121).

The bronze culverin selected for the present study, one of three owned by the museum, dates from the 16th century and is attributed to the smelter João Dias, presents a blackened crust formed by the accumulation of sedimented dirt particles and corrosion products. Its condition can be seen in Figures 1 and 2. Positioned outdoors in the coastal region where the *São João Baptista* Fort

[1] *Boca-de-fuego* (fire-mouth) is a generic term to designate systems of artillery weapons, regardless of their specific technical-tactical name. Eduardo Saraiva uses this term to define bronze breechloader artillery pieces from the 14th century (Saraiva, 2013, p. 12). The specific designation of *boca-de-fuego* applied to bronze artillery pieces is used in the description of the *Colegiada de Pastrana* tapestry representing the conquest of Arzila in 1471 (Araujo, 2012, p. 167). Jaime Regalado, Manager of the Arms Collection at the NHMMCBL, uses this term in his numerous publications (2020, pp. 8-11; 2023, pp. 260-263).

is located, it displays the presence of unstable forms of corrosion, cuprous oxides and chlorides, in addition to the effect of contaminants deposited by the action of wind, rain and biodegradation, the main evidence of which are avian excrements. The culverin was transferred to the NHMMCBL heavy weapons reserve in 2020. Figure 3 registers the moment this relocation took place.





FIGURES 1 and 2. Sixteenth century cast bronze culverin when it was still located at the fort of São João Baptista, on the Terceira island, Azores, Portugal (Photograph: Jaime Ferreira Regalado; courtesy of: MAH, 2022).



FIGURE 3. Transfer of the piece to the heavy arms repository in the *Núcleo de História Militar Manuel Coelho Baptista de Lima* (Photograph: Jaime Ferreira Regalado, 2021; courtesy of: MAH, 2022).

Its weight, over two tons, makes manipulation difficult and reduces the range of possible cleaning treatments that could be used to remove the products of corrosion and any material foreign to the object identified as a corrosive agent. Neither the institution to which it belongs, the MAH, nor the Atlantic Region has the resources to cover the costs of the application of cleaning processes through electrochemical and electrolytical baths, which have been in use since the 1980s, because these methods require immersion of the object and the use of potentiostats (Barrio, Chamón, Pardo, & Arroyo, 2009, pp. 1767-1776; Álvarez, 2015, p. 223; Zambrano, 2014, pp. 1188-1195; Sierra, 2022, pp. 427-436). Furthermore, budgetary constraints preclude the possibility of carrying out modern treatments that have been practiced in more recent decades, such as cold plasma (Borrós & Agulló, 2006, pp. 64-73) or laser (Barrio, 2010, pp. 92-95; Medina, Muñoz & Barrio, 2022, pp. 279-287), among others.

At the same time, the possibility of cleaning based mainly on mechanical action is not foreseen; it could easily cause abrasion to the surface and, possibly, alterations to the form and composition of the original metal strata.

As senior technician in the Museum's Department of Conservation and Restoration Department, I set myself the task of developing a cleaning proposal —prior to executing any intervention treatment— that was based on the use of controlled chemical solutions which, in addition to minimizing risks, would allow for a selective and stratigraphic work. Moreover, it was decided not to use toxic solvents,[2] to protect the restorer's health and protect the environment. It includes buffering solutions based on pH control; chelating agents that can sequester the metallic ions in the compounds forming the corrosion layers to be eliminated, and, finally, gelled systems that enable the prolonged and localized action of active chemical compounds.

PURPOSES

This research aims to evaluate the interest of using buffer solutions (acidic, basic, and neutral) and gelled chelating complexes in the restoration of metals, while also contributing to a definition of its conditions of use. The proposed cleansing solutions will be applied to a 16th century cast bronze culverin in order to establish cleaning methods capable of solubilizing the extant corrosion products, surface deposits, and carbonate concretions, without damaging or altering the composition of the underlying original metallic substrate.

The study defines the main characteristics of the active principles constituting the cleaning solutions presented and the different gelling systems used, indicating out the methodology of preparation and application, for the subsequent evaluation of the results.

The method used is expected to prolong the duration of its cleaning action without having to resort to immersion treatment systems; the moistening process is controlled by applying gelled systems which can retain the action of the active principle. Furthermore, it aims to reduce the use of mechanical-abrasive cleansing actions, establishing a work method based on the power of chemical solutions capable of cleaning very large pieces that show signs of degradation due to their outdoor exposure in saline conditions.

Despite the widespread usage of gelled systems to treat pictorial works, they have been less frequently used to clean metallic objects. The combination of properties acquired through the formation of a gel, along with the use of aqueous solutions based on controlling pH, offer a novel alternative for cleaning metallic heritage hitherto unknown in our Atlantic Region.

[2] Such as organic solvents: aromatic hydrocarbons, ketones or alcohols, among others.

MATERIALS AND METHODS

Buffer solutions, chelation, and gelled systems

Buffer solutions, also simply called buffers, formed by adding moderate quantities of acids and bases to water, can maintain a constant pH (the coefficient that measures the degree of acidity or alkalinity through the concentration of hydrogen ions in aqueous solution) (Cremonesi, 2015, pp. 28-43; Wolbers, 2000, pp. 24-34). These solutions enable the cleansing of various cultural objects through a controlled, non-toxic system.

The term *chelation* comes from the Greek *chele* or *khele,* which means pincer, and describes the ability certain chemical agents have to sequester metallic ions to form water-soluble complexes. The layer of dirt or other substances to be removed is captured by the chelators, forming a chelate. Since they are made of polydent molecules, they can form more than one bond with the single metallic ion, and thus are able to solubilize in water ions that once formed insoluble salts (García, Torre, & Serrano, 2011, p. 33; Cremonesi, 2004, p. 86).

Meanwhile, the gelled systems enable the replacement of the liquid cleaning medium, increasing the viscosity of the solutions by adding thickening agents which reduce evaporation and prolong the solvents' action time (Wolbers, 2000, p. 36; Cremonesi, 2010, p. 48). Researched by Paolo Cremonesi and Richard Wolbers, in recent decades gelled systems have frequently been widely used by conservation-restoration specialists throughout the world; they are predominantly applied to clean polychrome surfaces and have rarely been used to treat metallic pieces, let alone very large pieces located outdoors.

The proposal consists of preparing and applying 20 buffers made of citric acid and ethylenediaminetetraacetic acid (EDTA), to which a base known as *triethanolamine* (TEA) is added.

Citric acid is an organic acid found in a wide range of fruits and is one of the active principles most commonly used to clean copper objects and other inorganic materials, such as ceramics. It is also useful to eliminate saline efflorescence in murals (García, Torre & Serrano, 2011, p. 33; Scott, 2002, p. 366).

EDTA, another acid, has chelating properties so it can solubilize in water ions that were insoluble salts (Cremonesi, 2004, pp. 36-42), thus making it suitable to eliminate corrosions affecting copper objects (Huda, 2002, pp. 211-216). In salt form, EDTA has been used in cleaning treatments of all sorts of materials, the most commonly used salts being disodium (EDTA-Na_2) and tetrasodium (EDTA-Na_4).

The former has an acidic pH value (pH 4, 3-4, 7 in a solution of 5%) whereas the latter is alkaline (pH 11 in a solution of 5%) (García, Torre, & Serrano, 2011, p. 36). The triethanolamine or base is an organic compound derived from ammonia, in the form of hygroscopic liquid, is viscous and slightly amber, soluble in water and ethanol. It acts as a pH regulator when mixed with the acids.

The obtained solutions respond to three different pH measurements (graduated on the scale of 0 to 14): pH 5.5, pH 7, pH 9; with acidic, neutral, and basic properties respectively (Figure 4). Their effectiveness will be tested through the application of solutions in liquid and gelled state. Three types of thickeners will be used to do so: a cellulose ether, hydroxypropyl cellulose (HPC) from the commercial brand Klucel® G; polyacrylic acid Carbopol® combined with the base Ethomeen® C 25 (Cremonesi, 2004, p. 79), and agar-agar, a marine plant-based gelatin.

Number	Buffer solution	pH	Gelation systems	Additives
1	5% Nitric acid in water + TEA	5.5	Klucel® G	
2			Carbopol® + Ethomeen ® C 25	
3			Agar-agar	
4			Non-gelled	Tween® 20
5			Klucel® G	Tween® 20
6		7	Klucel® G	
7			Carbopol® + Ethomeen ® C 25	
8			Agar-agar	
9			Non-gelled	Tween® 20
10			Klucel® G	Tween® 20
11	4% EDTA in water + TEA	7	Klucel® G	
12			Carbopol® + Ethomeen ® C 25	
13			Agar-agar	
14			Non-gelled	Tween® 20
15			Klucel® G	Tween® 20
16		9	Klucel® G	
17		9	Carbopol® + Ethomeen ® C 25	
18		9	Agar-agar	
19		9	Non-gelled	Tween® 20
20		9	Klucel® G	Tween® 20

FIGURE 4. Composition of each of the 20 solutions tested to clean copper (Table: Anahí Meyer Riera, 2021).

According to the nature of the bonds within the structure of each gel, those applied here are defined as physical gels,[3] the most employed in restoration. Klucel® or HPC is a non-ionic, cellulose ether that is soluble in water and can function as an adhesive, stabilizer, protector, or thickener in the preparation of gelled systems (it helps to gel polar solvents; in the case of apolar solvents, the use of multi-cellulose is recommended, in a proportion of 6 to 10 g per 100 ml of solvent). HPC, like other cellulose derivatives, is a polysaccharide considered a weak physical gel whose three-dimensional network is based on weak hydrogen bonds (Giraud et al., 2021, p. 74).

Similarly, Carbopol® is a polyacrylic acid that works as a thickener in an alkaline medium or one previously neutralized with a base (Ethomeen®), which facilitates the formation of a gel in the form of a viscous paste. Commercialized as a white powder, an Ultrez 21 type is recommended since it does not form lumps during preparation. It is mixed with Ethomeen®, an alkaline emulsifier for gels in the form of a transparent yellow liquid. The recommended proportion to form a gel with Carbopol® is 20 ml of Ethomeen® for every 2 g of acid. In this case, the base Ethomeen® C25 was used, which is suitable to gel polar solvents such as water (if the intention is to gel apolar solvents, Ethomeen® C12 should be used).

Agar-agar is a marine vegetal gelatin extracted from various species of red algae, used in cooking. It is an agarose and agaropectin mixture in variable proportions, depending on the type of alga used to produce it. Considered a resistant physical gel, it forms semirigid films due to its double helix structure and is used as a thickener in conservation-restoration. Its high thickness favors the controlled humidification of the surfaces it enters into contact with, and is ideal to clean surfaces that are sensitive to the action of water. It is recommended to use laboratory-grade agar-agar, as opposed to using culinary substances, which will add unwanted residues.

Each buffer was combined with the anionic1 surfactant[4] Tween® 20, with the aim of proving whether the increased cleansing capacity derived from the performance of the hydrophobic materials is favorable. It is important to recall that both cellulose ethers and Ethomeen® C12, used as thickeners, have surfactant properties, they can diminish the surface tension on the surface to be cleaned

[3] In contrast to chemical gels, formed by polymeric chains interlinked by covalent bonds, which present good chemo-mechanical stability, such as Nanorestore Gel® (Giraud *et al.,* 2021, p. 74).

[4] *Anionic* or *non-ionic* means they do not fall apart, hence they do not change the pH of the dissolution (Llano, 2008, p. 21), thus making them suitable for the preparation of buffer solutions.

and improve humectation (Cremonesi, 2010, p. 48; García, Torre y Serrano, 2011, p. 35).

How to prepare buffer solutions

To prepare buffers it is recommended to weigh the acids in their solid-state form and place it as an aqueous solution in a magnetic stirrer. Citric acid is prepared at 4% and EDTA at 5%. Once the mixtures are obtained, the TEA base is added drop by drop, constantly measuring the solution's pH with a previously calibrated meter, until the required pH is reached in each case (pH 5.5, pH 7, pH 9). To obtain a buffer solution whose pH value responds to one of the three figures mentioned above, you must know the pKa, or strength of the acid used. The pH and pKa values must coincide for a buffer solution to form.[5] The pH value will determine the molecules' tendency to dissociate, being indicative of the cleaning solution's performance, or capacity to dissolve compounds. Thus, citric acid with a pK_2 value of 4.77, and a pK_3, of 6.39, were buffered, resulting in an acid solution of 5.5 and a neutral one of 7. The EDTA, with pK_5 6.13 and pK_6 10.37, resulted in a neutral solution of pH 7 and an alkaline one with pH 9, as shown in Figure 4.

It is essential to control the pH, based on the safety ranges stipulated for each material, since it helps to establish the degree of solubility of the metallic ions. Pourbaix determined the range of effectiveness-security necessary to eliminate corrosion from copper objects (1974, pp. 384-392): his research leads us to conclude that a pH of 9 is safe. If an overly alkaline pH were used, particularly one over 12, too many OH- (hydroxides) ions would be formed, more than the chelator could sequester (Marín, 2022, p. 83), leading to the emergence of corrosive products.

With an adequate pH control —a possibility that buffer solutions offer— the use of a chelant to clean metals becomes safe, as they have te ability to sequester metallic ions, not metallic atoms, hence they cannot sequester atoms from the nucleus (Huda, 2002, p. 213; Cremonesi, 2004, p. 40; Marín, 2022; p. 83). Once the preparation of the various buffers is complete, the amounts are divided into parts in order to be gelled.

[5] It is not mandatory that the pH and pKa values be exactly the same to form a buffer solution, a +1 to -1 margin in the pH and pKa is acceptable. Henderson & Hasselbalch's equation helps us calculate the buffer's pH: pH = pKa + log ([salt]/[acid]) (Llano, 2008, p. 19).

How to prepare gelled systems

In regards to the use of Klucel® as a thickener, the process consists of weighing the solid (4 g per 100 ml of solvent) and then adding it to the buffer solution using a magnetic stirrer.

To gel with Carbopol®, the acid must be weighed (2 g for every 100 ml of solvent) and mixed with the base Ethomeen® (20 ml). Mix with a glass rod and stir energetically in an anhydrous recipient until a homogenous mixture is obtained. Add to the buffer solution in the magnetic stirrer and add distilled water drop by drop, approximately 10 to 15 ml, which will cause the gel to form. The consistency will depend on the quantity of drops: more or less viscous.

Agar-agar gel is prepared by adding 2.5% to 5% of solid product to the solution to be gelled. Heat it to a temperature between 45° and 85° C using microwave, a double boiler, or the heat from the magnetic stirrer. The substance will gel once it cools and will take the consistency of a rigid gel.

Application of cleaning tests

The 20 cleaning solutions were applied to two different areas of the culverin where different types of damage had been observed (A and B). It is obvious that zone B shows greater sedimentation of corrosion and dirt particles in the form of a crust, which can be observed in Figure 5. The system of application depends on the viscosity of the cleaning solution, ranging from liquid solutions to the different gels obtained, used on cotton swabs, paintbrushes, and spatulas. The applications were renewed every 10 or 20 minutes. It is important to point out that after eliminating the gel, it will be necessary to rinse the pieces with distilled water and scrub them with a medium-hard brush in order to avoid residues being left behind. Figure 6 shows the disposition of the 20 solutions on zones A and B of the culverin.



FIGURE 5. Cleaning tests carried out by applying the 20 prepared solutions to zones A and B of the culverin (Photograph: Jaime Ferreira Regalado, 2021; courtesy of: MAH, 2022).

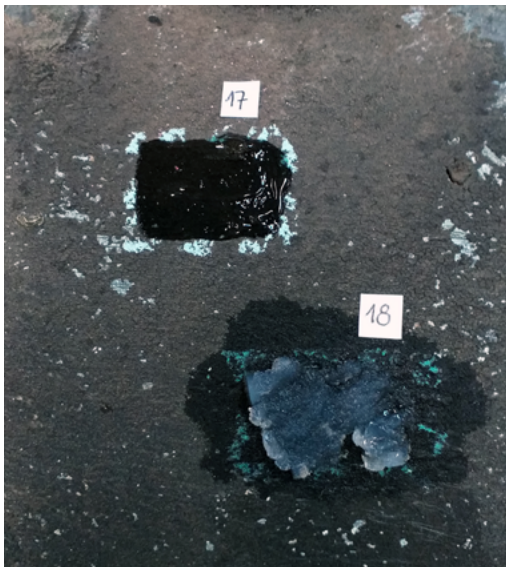


FIGURE 6. Application of solutions by means of a cotton swab, spatula or paintbrush, according to the viscosity of the mixture (Photograph: Jaime Ferreira Regalado, 2021; courtesy of: MAH, 2022).

RESULTS

From the application of the 20 solutions, it can be deduced that the most effective active principle in the study case has been chelant EDTA. In zones with a greater accumulation of dirt, the pH basic, pH 9, with a chelant is more efficient; for those with a lesser accumulation of dirt, the application of a neutral solution with pH 7, with a lower cleaning power, is recommended.

The most effective gelled systems turned out to be those prepared using Carbopol® and Ethomeen®, which offer the ideal viscosity, are easy to apply and remain on the support. The agarose rigid gel was also useful, enabling prolonged and localized cleaning action on the zones with the greatest percentage of sedimentation. The time of action depends on the work area and the thickness of the prepared gel.

As for liquid solutions (non-gelled), they are ineffective due to their limited action time and resulting runoff; they are recommended to treat objects that can be subjected to chemical immersion cleaning, not in this case.

In all situations, it was observed that the surfactant increased the cleaning's pulling power; thus, it can be added to the solution prior to gelling, in a concentration no greater than 0.5 percent.

To carry out controlled cleaning, direct contact with the undamaged metal must be avoided, regardless of the acid used as an active principle. Gradually decrease from pH basic (9) to neutral (7) to acidic (5.5), thus reducing the solutions' chelating power. This will help control unwanted cleaning effects, such as removal of the patina.

In all cases it will be necessary to rinse using deionized water and brushes to remove possible residues and gel incrustations.

To determine which of the proposed solutions was the most adequate in this case, an organoleptic exam of the surface was performed, with a magnifying glass and an optic microscope. The observation was carried out both before and after the solutions were applied, clearly evidencing the optic changes derived from eliminating harmful agents. Figure 7 shows how the colorless aspect of solution number 18 turned green following its application to the metal substrate. This hue evidences the sequestering of metallic ions generated by the corrosive process (degradation).



FIGURE 7. Application of the solution that gives the best results for cleaning the culverin, EDTA buffered with base TEA at pH 9 (solution number 18 in the table above). Its chelating power is intensified by prolonging its action on the substrate thanks to gelling the mixture with agarose. The second image shows the gel is transparent when applied but turns green 30 minutes after application, which evidences the sequestering of corrosive metallic ions (Photograph: Jaime Ferreira Regalado, 2021; courtesy of: MAH, 2022).

DISCUSSION

Conservation of the patina

Regarding the preservation of cultural objects, it is essential to consider that cleaning is one of the most used processes, as well as one of the most invasive and irreversible. It aims to stabilize the metal substrate by eliminating external agents and, in other cases, to minimize the effect of the elements that cause degradation or active oxidation. Frequently, the purpose of cleansing goes beyond the conservation or permanence of the cultural object's materiality, seeking to rescue the beauty and aesthetic potential. In either case, cleansing should aim to respect the patina, defined as the superficial modification of the external part of a material caused by the environmental interaction and which possesses historic legitimacy by reflecting the passage of time.

Patina, a concept studied by art historian Cesare Brandi (1906-1988), and the difficulty of conserving it is mentioned by Ascensión Hernández in the book *Documentos para la historia de la restauración*, as:

> One of the main problems derived from the need to intervene works of art is the effect the passage of time has on them. This phenomenon equally affects paintings, sculptures, buildings, and the rest of cultural property, it is particularly evident on the objects' surface and is known as patina[6] (Santabárbara, 2019, p. 242).

On metal artefacts, patina is formed by stable corrosion and provides valuable technical and cultural information. Furthermore, it affects the metal's future behavior; eliminating it leaves the metal exposed to the environment and other external agents once again, which could cause greater corrosion and a reduction in the support's density. Systematic cleaning can result in the progressive loss of millimeters of the metallic strata.

To avoid mistaken operations or invasive cleaning, it is crucial to exhaustively study the cultural heritage destined for intervention in a range of perspectives —in an interdisciplinary manner—, performing a prior diagnosis (Díaz & García, 2011, pp. 3-45), which allows identification of the strata for removal and establishes a work methodology. In this sense, the tests performed in this case study can be used as a guide, but never as an indisputable solution, since each object and problem must be analyzed individually.

[6] Editorial translation.

Applying this methodology enables a stratified cleaning, which allows the removal of unwanted layers until the conserved original is reached, thus respecting the patina of metallic objects. However, for a better result, it is necessary to measure the piece's conductivity —the capacity that permits current to pass through it—, in addition to pH and humidification control. This will help ensure that correct parameters of solubility are obtained, and chelated stability are constant. This measurement, along with pH, will offer a pre- and post-treatment control that will enable, for example, to verify whether the surface has been properly rinsed and thus avoid uncontrolled actions related to the use of chelates with an acidic form or low pH —2 - 3— (Marín, 2022, pp. 83-84; Cremonesi, 2015, p. 52). Vigilance regarding these parameters will not only help define the buffer solution to be used in each case —linked to the selection of acidic, neutral or basic pH— but also to define application time on the substrate.

What to do after cleaning

After the intervention, certain control routines and maintenance plans, designed from the outset of the conservation work, should be followed. In most cases it is impossible to maintain standards considered "ideal" for metal preservation, since these parameters go from a relative humidity below 40% to temperature fluctuations between 18° and 20° C. This difficulty, in addition to the behavioral tendency of metallic objects to return to their original mineral state, frequently causes the corrosive process to reactivate after cleaning. Avoiding this is a more complex action, beyond the cleaning exercise itself. Therefore, the application of corrosion inhibitors and protective films are key and should be practiced regularly (Díaz & García, 2011, pp. 56-58; Álvarez, 2015, pp. 225-226).

Corrosion inhibitors are chemical substances which, diluted on the metal surface, help to maintain its stability for longer, delaying the formation of corrosive products. Among the corrosion inhibitors used on objects made of copper and its alloys, this case study proposes the application of benzotriazole (BTA), prepared between 2% and 5% in ethyl alcohol, through the creation of a vacuum chamber (Zambrano, 2014, p. 1193). It can also be applied by immersion, an operation that is possible when dealing with smaller objects or when there is the necessary infrastructure to intervene a large format piece.

Other known inhibitors include: 5-amino-2-mercapto-1, 3 ,4–thiadiazol (AMT) solution, which forms a stable compound of cu-

prous chloride, although with the drawback of being highly toxic (Cura D'Ars, De Bellis, Lins y Souza, 2007, pp. 147-153); and dimethylaminoethanol (DMAE), which is organic and recommended due to having zero toxicity (Marín, 2022, p. 83).

Polyacrylic resins Paraloid® B72 and B44 were used as protective films, to which Incralac can be added, that combines acrylic resin with BTA (Iglesias & Frigerio, 2013, p. 58). These varnishes can coexist with the application of a second protective layer, composed of microcrystalline wax (Álvarez, 2015, pp. 225-226; Díaz & García, 2011, pp. 58-60). However, this case study opted to apply a single layer of microcrystalline wax (Cosmolloid® 80H in White Spirit® as a vehicle), since the piece will be stored indoors in the artillery reserve and will be the object of constant conservation and maintenance processes. Hence, this protection process will have to be repeated at some point, when inevitable agieing occurs (wax darkens over time, following the evaporation of the dilutants).

CONCLUSIONS

The study demonstrates that cleaning solutions based on pH control and applied in gel form are suitable for use on metals. These help to maintain safe pH ranges for the metal of the object, protecting its integrity to the utmost. At the same time, the use of chelators enables the creation of cleaning solutions that are capable of sequestering the necessary metallic ions in each case, inducing the removal of those products derived from the corrosion phenomenon without altering the original metallic substrate.

This research confirms that gels offer possible suitable treatments which are suitable for complex objects, such as large-scale metals, whether in or outdoors, or those that combine organic and inorganic materials, by favoring contact of the cleaning solution with the surface of the piece to be treated as well as with the capacity to retain moisture and hence control the cleansing action and toxicity.

The case study analyzed concludes that the most appropriate solutions are: number 18 (EDTA at 5% in water, buffered with TEA, with pH 9 and gelled by means of agar-agar at 5%),[7] and number 12 (EDTA pH 7, gelled using Carbopol® and Ethomeen®). The former —chelated solution— will remove the sedimented dirt and harmful corrosion products visible on the metal surface whereas the latter —neutralized disodium— is used on less damaged zones; both

[7] A system successfully used in other recent interventions (Fernández, Zambrano y Bethencourt, 2023, p. 413; Giraud *et al.*, 2021, p. 78).

solutions are applied after the chelant has already visibly extracted the sedimented layers.

It is recommended to control the duration of the treatment to prevent the EDTA from altering to the object's interior layers, which would require adapting the proposed cleansing process to the conditions of the piece meant to be cleaned. Likewise, it is important to carry out the recommended flushing or rinsing with water, to avoid residues remaining and the byproducts caused by the cleaning process.

In general, the cleaning proposal presented leads to a reasoned (ethical) restoration that is based on respect for the original, meant as an alternative to invasive treatments of mechanical cleaning which are abrasive or the sometimes not viable treatment of immersion in tubs. Furthermore, the control of humidity is important for pieces which combine metal supports with other materials, such as wood. In such cases, the organic nature of cellulosic supports calls for cleansing and stabilization processes which are very different to those used for inorganic ones. The stratified methodology used here favors the selection of the layers of dirt to be removed, benefiting conservation of the patina. Other advantages lie in the non-toxic condition of the aqueous solutions, which protect the environment and restorers' health.

In juxtaposition to these advantages, there are disadvantages derived from the challenge involved in adjusting this work methodology to each specific case. An incorrect analysis could lead to the use of solutions with an overly acidic or alkaline pH, that would foster the appearance of new corrosion products. Any aqueous solution can cause electrochemical corrosions in metals, as Marín stated, even more so if the solution is charged with ionic pieces; that is to say, any destined for chemical cleaning (Marín, 2022, p. 84). Therefore, it is essential to control the solutions' pH correctly. Just as the need to buffer the solutions' pH to maintain a constant value, cleaning should be restricted to the affected or deteriorated zones, and not "healthy" metal. Such care requires carrying out a thorough diagnostic of the object.

A shortcoming in the proposal is the lack of a chemical analysis following the treatment, which could support the results contained herein, in this case, merely on organoleptic observation of visible changes subsequent to cleaning. Studies measuring gels, such as colorimetric and spectrometric evaluations of atomic absorption would enable the detection of the quantity of eliminated corrosion products present in the gel (Giraud et al., 2021, p. 77).

The above reaffirms that this type of preliminary study, performed to design a proposal of intervention, is the key to establishing appropriate methodologies for restoration work aimed to preserve metallic cultural heritage.

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Intervención

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