2022 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
University of Calabria, Italy, October 19-21, 2022

Experimentation on the removal of Paraloid B72® from the wooden surface of Egyptian artefacts from the National Archaeological Museum in Naples.

Altobelli Annarita[1], Cennamo Paola[1], Trojsi Giorgio[1], Barone Lumaga Maria Rosaria[2], Carpentieri Andrea[3], Fatigati Giancarlo[1]

[1] *Department of Humanities, University of Studies Suor Orsola Benincasa, Naples- Italy*
[2] *Department of Biology; University of Naples Federico II, Naples- Italy*
[3] *Department of Chemical, University of Naples Federico II, Naples- Italy*

Abstract **- This paper reports the results of experimentation about the removal of a polymeric film of aged Paraloid B72® placed to protect some wooden artifacts belonging to the Egyptian collection of the National Archaeological Museum of Naples (MANN), in particular the study was conducted on two shabties dated to the 19th Dynasty and a sculpture of Ptah-Sokar-Osiris dating to the late period. Thanks to the collaboration between the National Archaeological Museum of Naples and the Laboratory of Restoration of Wooden Artifacts of the University of Naples Suor Orsola Benincasa, it was possible to conduct an in-depth study of the artifacts, not only from an archaeological-historical point of view but also from a conservation point of view, which led to the development of the above-mentioned experimentation and the planning of a proper restoration intervention. The study and experimentation were supported by several diagnostic investigations. At first, non-invasive investigations were carried out to study the execution technique and the state of conservation of the artifacts, so it was possible to carry out the recognition of the wood species that constituted the three sculptures through optical microscopy, some investigations such as IR reflectography, and fluorescence induced by UV and X-ray radiation (XRF) were conducted for the identification of pigments and investigate their chemical nature. By analyzing the state of conservation of the artifacts, the porpoises of the restoration work were set, among which was to attempt the removal of Paraloid B72® through a methodology that would act in full respect of the wooden support of the two shabties and the statuette of Ptah-Sokar-Osiris. Therefore, a study was carried out by evaluating the pros and cons of the different methodologies that have been tested in recent decades and most used for the removal of aged Paraloid from the surfaces of the artifacts. After choosing the methodology best suited to the needs of the works under consideration, an experiment was conducted aimed at verifying the effectiveness of the selected methodology.**

Keywords - **Paraloid B72®; Hydrogel PVA-B; wood; Egyptian artefacts; Shabties; Ptah-Sokar-Osiris.**

I. INTRODUCTION

Restoration work aims to preserve the work in all its parts, opting for minimal intervention and minimal complexity of work. Degradation of materials is a physiological phenomenon, especially when it comes to organic materials such as wood [1]. The materials to be used during restoration work should be: compatible with the materials of the artifact to which they are applied, and stable from aging (since their degradation could accelerate the process of degradation of the same artifacts), but above all, these should be reversible [2], In case the previous restoration needs to be removed to perform another restoration in a different way. The concept of "reversibility," however, becomes relative when talking about consolidants. One of the procedures related to consolidation is the introduction of consolidating resins, by solution or dispersion in solvents. The action of the consolidating substance is to penetrate into the wood cavities, adhering to the walls making them more solid; the goal will be to provide the cavity walls with an auxiliary microstructure [3]. Since the second half of the 1960s, the use of polymer resins reached the highest level of popularity in the field of restoration [4], a discourse particularly valid for Paraloid B72®. The problem associated with this product, as well as with other types of polymers, is mainly related to the aging of the same resin placed inside the artifacts. The degradation process of polymer resins consists of chemical transformations due to the action of some factors such as light, temperature, interactions with the substrate and atmospheric pollution, causing phenomena of embrittlement of the film, decrease in solubility, yellowing of the resin, increase in polarity and decrease in adhesive strength. For the reasons just described, it is clear that, under these conditions, polymer films can cause irreversible damage to artworks, drastically altering the physicochemical properties of the surface to which they have been applied, becoming increasingly resistant to common solvents, thus limiting their reversibility. This is the context of the present work, which aimed at the development of a methodology for the removal of aged Paraloid B72® that would be well suited to the needs of the three wooden artifacts belonging to the Egyptian

collection of the National Archaeological Museum of Naples (MANN), in full respect of their execution technique. In particular, we discuss two wooden shabties inventoried under codes IG648 and IG655 (Fig. 1) dated to the 19th Dynasty and a small wooden sculpture of Ptah-Sokar-Osiris in the form of sarcophagus inventoried under code IG909 (Fig.2) and dated to the late period.

Figure 1. Shabti IG648 (left) and Shabti IG655 (right).

Figure 2. Ptah-Sokar-Osiris IG909.

The three artifacts were stored in the collection's depository in a precarious state of preservation, mainly related to two problems: the first was caused by the gaps produced by xylophagous attack on the wood, while the second problem, related to the state of the works, was the presence of copious amounts of aged Paraloid B72®, applied during previous consolidation work carried out since the 1960s according to information obtained from interviews with former restorers. Preliminary study and analysis of the history of the MANN's Egyptian collection revealed the difficulty of keeping the state of conservation and the relative humidity level of the rooms in which the works were stored under control, justifying in a sense the need to "isolate" the artifacts by injecting copious amounts of consolidant to protect the substrate by limiting thermohygrometric exchanges. The limitation of Paraloid lies in its aging, with which the resin loses its inherent characteristics such as "reversible" behavior, transparency and flexibility. To overcome the problem related to the presence of Paraloid, a preliminary evaluation of the most widely used Paraloid removal systems in recent decades was carried out, which led to the selection of the cleaning system [5-7] best suited to the needs of our case: the high-viscosity polymer dispersion based on polyvinyl alcohol cross-linked with borax (Hydrogel PVA-B), selected for its mechanical properties such as its gentleness in solvent action, limiting the action at the interface, for its consistency that allows easy removal without leaving residue on the surface, and for its ability to retain organic solvents up to a maximum concentration of 30% [8-10]. Before using this cleaning system for the removal of Paraloid film from artifacts, an experiment was conducted to verify the effectiveness of this system and its applicability.

II. MATERIALS AND METHODS

2.1 Analyses for the study of artefacts

Some investigations were carried out on the artefacts under analysis in order to better understand their execution technique and to analyse their state of conservation. With full respect for the materials in question, it was decided not to carry out any invasive investigations, as the artefacts were already in a precarious state of preservation and were largely lacking in detail.

Wood identification

First, a taxonomic analysis was carried out to recognize the wood species used to make the artifacts. The investigation was conducted macroscopically for the two shabties (IG648 and IG655), and partly microscopically through the use of the Dino-Lite® portable microscope, which uses the coaxial illumination technique. The observation was carried out particularly at the level of the radial section at the head and feet of the artifacts and on the tangential section along the body of the ushabty. This analysis allowed us to investigate surface details using two microscopes with different lights, obtaining responses in visible light and UV-induced fluorescence; some photographs were taken and compared with some images of known woods. In the case of the Ptah-Sokar Osiris sculpture, taxonomic analysis was possible by observing the microscopic characteristics of the wood using a Zeiss Axiolab light microscope equipped with the Nikon Digital Sight DS-L1 digital photographic system; this allows morphological analysis of the specimens using different magnifications (10x and 20x), which allows observation of the microscopic structure, since a

small fragment belonging to the sculpture was found inside the box in which this artifact was stored, which unfortunately collapsed due to the fragility of the support.

UV-indued fluorescence

After obtaining information on the type of wood, we moved on to study the surface of the objects; in fact, the artifacts were analyzed to observe UV radiation-induced fluorescence in order to document the presence of protective layers present on the works. UV (UV) fluorescence analysis was performed with 2 lamps from Wood Photo Ectronics- 400W UV CURVING EQUIPMENT: single features- 400w UVA, 230Volt/50Hz, Abs. 2.5. Fluorescence recording was performed with a Canon Eos 1100D camera completely obscuring any light source other than UV, with the lamps placed at 45° to the center of the surface of the artifacts.

X-ray Fluorescence (XRF)

An X-ray fluorescence (XRF)-induced fluorescence (XRF) campaign was then carried out to investigate the chemical nature of the traces of red pigment found on the back of shabti IG655 and to look for possible traces of pigment on the other two artifacts [11]. X-ray fluorescence (XRF) analysis was performed using a portable XRF-Q Assing spectrometer, with tugsten tube, silicon PiN diode detector with beryllium window and Peltier effect cooling system, with 189 eV resolution at 5.9 KeV and operating conditions 30kV, 0.5 mA. The survey was conducted at the locations on the artifacts where traces of pigments were visible.

Fourier Transform Infrared Spectroscopy (FT-IR)

To check for the presence of the consolidant, an analysis by Fourier transform infrared spectroscopy (FT-IR) was performed on it using the Nicolet iS10 Thermo Fisher Scientific FT-IR spectrometer, with a dried and sealed optical system and optical bench, equipped with KBr windows with protective CaF2 coating. Michelson-type dynamic alignment interferometer with KBr/germanium beam splitter; interferometer scanning speed: acquisition of up to 40 independent spectra per second with a spectral resolution of 16 cm-1; spectral resolution: better than 0.4 cm-1; wavelength precision: 0.01 cm-1; spectral range: 7,800-350 cm-1, suitable for the detection of a wide class of organic compounds.

2.2 Analyses for hydrogel experimentation

The aim of the project was the removal of the Paraloid B72 layer by means of an experimental methodology, i.e. the use of a high viscosity Hydrogel based on Poly-Vinyl Alcohol (PVA) and Borax, loaded at 20% with two solvent mixtures.

Preparation of the specimens

The application phase of the methodology was preceded by a preliminary optimisation divided into two phases. firstly, the effectiveness of the methodology and the removal times were studied on slides specially prepared with Paraloid B72 and aged; subsequently, wooden specimens were prepared to simulate the characteristics of the wood of the artefacts, in order to carry out removal tests on specimens similar to the real case. For the creation: of the first specimens, simple slides measuring 5 cm x 7 cm were selected, on which a double layer of Paraloid B72 was applied in different concentrations: 5%, 10% and 15%, dissolved in different solvents and mixtures to test the effectiveness of the cleaning system for different solvents. For the second type of specimen, a wood was selected that had anatomical characteristics similar to those of the species used for the artefacts in this thesis; the choice fell on *Ficus Carica* L1753. The wood was cut to obtain approximately 60 cubes with a size of 2 cm. on which progressive consolidation was carried out with Paraloid B72® dissolved in various solvents, first at a 5% concentration and then at a 10% concentration. The specimens thus prepared were divided into three groups and subjected to different ageing cycles. The first group (Group 0) was stored in the dark, protected and away from any source of light, heat and humidity, the other two groups (Group 1 and Group 2) were subjected to two artificial ageing cycles, inside the *Angelantoni SU250* aging chamber, set to the values RH% = 50%; T = 40°C; UV = 400 nm <λ < 250 nm. Ageing was carried out for a time t=408 hours (17 days). At the end of this period, Group 1 was removed from the chamber and stored in the dark, protected and away from any source of light, heat and humidity, while Group 2 underwent a second ageing cycle, in the same chamber using the same parameters, but for a time t=264 hours (11 days) for a total of 672 hours (28 days).

Preparation of Hydrogels PVA-B

Once the ageing phase was complete, the 20% PVA-B hydrogel loaded with two different solvent mixtures could be applied to all samples: the first involved the use of a 1:1 mixture of Methyl-Ethyl-Ketone (MEK) and 1-Pentanol (1-PeOH) as described in the literature [9], while the second formulation involved the use of alternative solvents, Acetone being used to replace MEK and Ethanol replacing Pentanol.

Experimentation

For both formulations, slide tests were carried out to evaluate the time of action and the effectiveness of the method. A small amount of hydrogel was placed on the slides, which, as described earlier, had been treated with

Paraloid B72 at different concentrations and then subjected to artificial aging. The hydrogel was allowed to act for a predetermined period, starting from a time of 15 seconds up to 2 minutes. Once the hydrogel had been removed, residual swelled Paraloid was removed using a small cotton swab. The removal effect was verified by observation under grazing light and UV. In a second step, the two hydrogel formulations were then tested with a setting time of 120 seconds on the wooden samples treated with Paraloid B72 and artificially aged, in order to test their effectiveness on the substrate simulating the real case. Once the gel was lifted, the action of the cotton swab removed the aged Paraloid residue. The removal effect was verified by observation of the sample in ultraviolet light.

III. RESULTS AND DISCUSSION

3.1 Analyses for the study of artefacts

Thanks to taxonomic analysis, an affinity with the wood of *Ficus Sycomorus* was hypothesised for the shabties according to the information contained in the archival-documentary material. While for the sculpture of Ptah-Sokar-Osiris, analysis of the fragment confirmed the use of *Ficus sycomorus*, known as Sycamore. As far as the microscopic characteristics of the wood are concerned, it can be observed that the growth rings are diffused and porous; the vessels are very large and mostly solitary; when the axial parenchyma is observed in tangential section, it is characterised by large bands containing crystals; the parenchyma rays are very large and heterocellular. UV observation did not provide answers, albeit indicative, as to the type of substances present to protect the artifacts. The IR survey returned useful indication as to the type of black pigment, which was present in the form of residues on top of the artefacts (Fig.3); being very dark, it was inferred to be carbon-based. There is a good chance that the specific colour used for the decoration of the artefacts was smoke black, which was widely used in ancient Egypt for the decoration of large and small artefacts.

Figure 3. IR observation of the black pigment.

Thanks to the XRF campaign conducted on the artefacts, on the area of the back of the *shabti* IG 655, the presence of a ferrous residue attributable to the use of an iron pigment, probably red earth, was investigated. Other areas of the same artefact where also investigated with the same typology; on the back of the elbow and on the side of the foot, where residues of an ancient putty were present (Fig.4).

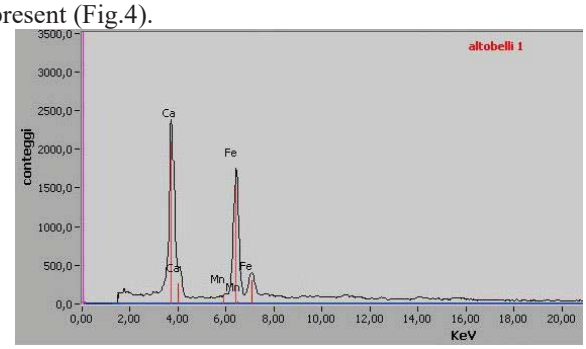

Figure 4. Shabti IG655 XRF spectrum: trace amounts of calcium (Ca) and iron (Fe) traceable to stucco residues and red pigment.

The detection of certain elements, such as calcium and sulfur, typical of the composition widely attested in the literature [11], made it possible to recognize this intervention as belonging to the artefact's original execution technique. The hypothesis was confirmed through the observation of these areas with the Dino-lite portable microscope, thanks to which the presence of a layer of pigment placed above the grout was highlighted. The same investigation carried out on the artefact IG 909 was useful for the historical- chronological framing of the piece. The front surface of the lid is characterised by a lighter colour compared to the back and the wood of the socket. The initial hypothesis of the presence of plaster on the entire surface of the lid was confirmed by the widespread presence of traces of plaster. On several areas of the lid, traces of other elements were found, such as iron, which was generally diffused over the entire 'body' of the artefact (Fig.5); at the level of the "*xSx n bik*" necklace, the presence of copper, deriving from an original green or blue pigment, was detected (Fig.6).

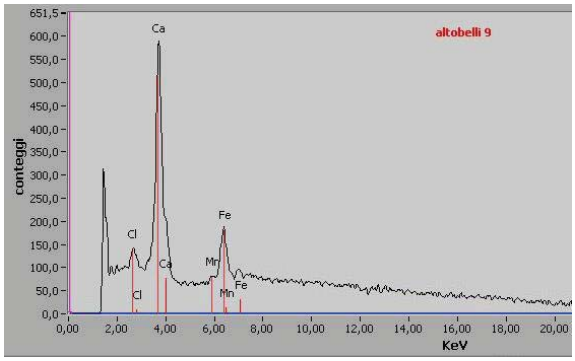

Figure 5. XRF spectrum IG909: trace amounts of calcium (Ca) and iron (Fe) traceable to stucco residues and red pigment.

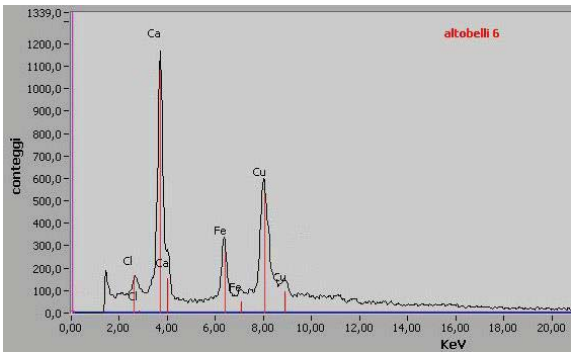

Figure 6. IG909 XRF spectrum: trace amounts of Calcium (Ca) and Copper (Cu) traceable to stucco residues and blue or green pigment.

The presence of red, green or blue pigments on the body of similar artefacts, depicting Ptah-Sokar-Osiris oriented the historical-chronological research, allowing our artefacts to be placed in a specific typology. In particular, according to Raven's classification the sculpture would fall within Type IV, i.e. artefacts characterised by a red painting body, a blue or green necklace and a gilded face. Through FT-IR investigation, it was possible to investigate the presence of Paraloid B72® (Fig.7).

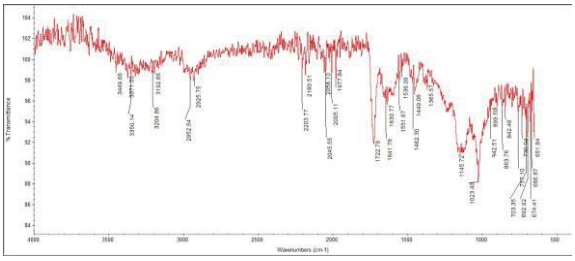
Figure 7. FT-IR spectrum in which bands attributable to Paraloid B72® are evident.

3.2 Testing for Hydrogel

Through the tests for the evaluation of the action time of the PVA-B hydrogel, it was verified that: within the first 60 seconds of contact, the hydrogel was only able to partially solubilize the aged Paraloid layer regardless of the film thickness, a complete removal of the resin was not observed in either case [10]. After the first minute of contact, the 5%-diluted Paraloid was completely swelled while the 10%-diluted Paraloid needed more insistence during the swab action to remove the Paraloid residue. After the second minute, the polymer film, both at 5% and 10%, was completely swollen, and through the gently action of the swab, any residual aged Paraloid B72 was completely removed from the glass surface. In light of the results obtained was decided to use the same formulation of Hydrogel with an application time of 120 seconds on the wooden samples treated with Paraloid B72 and subjected to artificial ageing in order to test their effectiveness on the substrate simulating the real case and possibly investigate differences between the two different formulations (Fig.8).


Figure 8. Comparison of wood specimens consolidated with Paraloid and subjected to artificial aging before and after cleaning with Hydrogel PVA-B loaded with Acetone and Ethanol in a 1:1 ratio.

Already from the first tests carried out, a similarity was found between the two gels as revealed by observation in visible an ultraviolet light of the post cleaning samples with the system tested. The choice of the formulation of Hydrogel to be used for the cleaning of the artefacts was oriented towards the formulation loaded at 20% with the 1:1 Acetone and Ethanol mixture because it was simpler in terms of complexity, availability and above all much cheaper. The efficacy of the system loaded with Acetone and Ethanol was therefore tested on a naturally aged Paraloid layer applied during an old restoration work on a polychrome wooden crucifix from the early 17th century. The application of the tested cleaning method led to the swelling of the Paraloid layer and its complete removal after only 120 seconds of application, without affecting any layer of the underlying polychromy as confirmed through observation under the handheld microscope Dino-lite® (Fig.9).


Figure 9. Detail of a portion of the leg of a polychrome crucifix covered with a layer of aged Paraloid B72 and then cleaned with Hydrogel PVA-B (Acetone and Ethanol 1:1).

IV. RESTORATION WORK

Before the cleaning operation, inconsistent residues were removed from the surface of the artefacts using a small soft-bristled brush, followed by the application phase of the tested cleaning system. A small amount of hydrogel was applied to a portion of the artefact surface, left to act for 120 seconds and then lifted off. The treated area was rubbed with a small dry cotton swab to remove

the residues of swollen consolidant (Fig.10). The cleaning operation, always controlled by means of visible and UV Dino lite observation, provided for a diversification of the intervention for the different artefacts and for the different areas of the same, reducing the contact time in the areas where the surface required a more delicate action due to the presence of traces of pigment or thinner layers of consolidating agent, and repeating the application of the hydrogel where the layer was thicker.

Figure 10. Application of Hydrogel PVA-B cleaning system (top image) and subsequent removal of swelled consolidant residue using a cotton swab (bottom image).

V. CONCLUSIONS

The hydrogel PVA-B cleaning system used for the cleaning of the artefacts under examination performed particularly well, adhering perfectly to the surface to which it was applied, guaranteeing the complete swelling of the polymer film without leaving residues that are difficult to remove. The feature that guided the choice of this cleaning system, in addition to its mechanical properties, was its ability to retain organic solvents up to a maximum concentration of 30%. The effectiveness of the system, verified through experimentation, led to the use of this method for the removal of aged Paraloid from the wooden surface of the two shabties and the sculpture of Ptah-Sokar-Osiris in the form of a sarcophagus.

REFERENCES

[1] M. MATTEINI, A. MOLES. *La chimica nel restauro. I materiali dell'arte pittorica*. Nardini Editore, 2007.

[2] C. Brandi *Teoria del restauro.* G. Einaudi, Torino, 2007.

[3] C. CASTELLI, A. SANTACESARIA *Il consolidamento* in *"Dipinti su tavola. La tecnica e la conservazione dei supporti"* M. Ciatti, C. Castelli, A. Santacesaria (a cura di). Edifir, Firenze, 2013.

[4] O. CIALLI, *Fluidi nanostrutturati per il dewetting di film polimerici da superfici di interesse per i beni culturali.* Tesi di laurea in Chimica, curriculum Scienze Chimiche, Relatrice Prof.ssa Debora Berti, Correlatore Dott. Michele Baglioni, Università degli studi di Firenze, A.A. 2015/2016.

[5] T. CIANFANELLI, F. CIANI PASSERI, C. ROSSI SCARZANELLA, "*Consolidamento dei dipinti su tavola in Problemi di restauro, riflessioni e ricerche"*, M. CIATTI (a cura di) Firenze, 1999.

[6] M. BAGLIONI, M. RAUDINO, D. BERTI, U. KEIDERLING, R. BORDES, K. HOLMBERG, P BAGLIONI "*Nanostructured fluids from degradable nonionic surfactants for the cleaning of works of art from polymer contaminants"*. Soft Matter, 2014.

[7] P. BUSCAGLIA, M. CARDINALI, T. CAVALERI, P. CROVERI, G. FERRARIS DI CELLE, A. PICCIRILLO, F. ZENUCCHINI: "*Nesimenjem and the Valley of the Queens' Coffins"* in H. Strudwick, J. Dawson (eds) *Ancient Egyptian Coffins: Past Present Future*, proceedings of the International Conference, Cambridge (United Kingdom), 07-09/04/2016. Oxbow Books. Oxford, 2018.

[8] A. GIUFFREDI, A. DEL BIANCO, M. DI FOGGIA. The removal of gypsum surface deposits using viscoelastic hydrogels of polyvinyl alcohol and borax. XVII Congresso Nazionale IGIIC-Lo Stato dell'Arte 17. Matera, October 2020;

[9] E AL-EMAM, A. G. MOTAWEA, K. JANSSENS, J. CAEN, 'Evaluation of polyvinyl alcohol borax/agarose (PVA-B/AG) blend hydrogels for removal of deteriorated consolidants from ancient Egyptian wall paintings', Heritage Science (2019);

[10]. MANFREDDA, P. BUSCAGLIA, P. GALLO, M. BORLA, S. AICARDI, G. POGGI, P. BAGUIONI, M. NERVO, D. SCALARONE, A BORGHI, A RE, L GUIDORZI, A. LO GIUDICE An Ancient Egyptian Multilayered Polychrome Wooden Sculpture Belonging to the Museo Egizio of Turin: Characterization of Painting Materials and Design of Cleaning Process by Means of Highly Retentive Hydrogels". Robert J. K. Wood, Coatings, 2021;

[11] A LUCAS, J. HARRIS, Ancient Egyptian Materials and Industries. Edward Arnold (Publishers) Ltd., London, 1962;