Evaluation of Funori as adhesive for stone polychromy. The XV century Ramon Llull's sepulchre as Case Study

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Abstract

Adhesion and consolidation of pictorial layers has become one of the main challenges in conservation issues and, despite a growing availability of new resins and polymers, natural, traditional and well-known materials have been studied and improved, in order to face and solve modern issues. During the last conservation intervention on Ramon Llull's sepulchre, the original polychromy has been rediscovered. A funori solution has been evaluated as the most suitable to undertake the intervention, and a specific methodology was developed in order to fix the layers. Funori's reversibility and slight surfactant characteristics, allows that the removal of the grey overpaints could be easily carried out with water.

Keywords

Polychrome stone, Adhesive, Funori, Natural adhesive, Organic chemistry.

Introduction

The construction of the sepulchre of Blessed Ramon Llull, located inside the church of Sant Francesc in Palma de Mallorca, began in 1460, in full gothic style, but unfortunately remained unfinished in 1492 (Custurer, 1700; Sacarès, 2011, p. 62). In 2017, following the request of the Bishopric of Mallorca and the Third Order of Franciscans, studies on the history and the constitutive materials of the sepulchre were carried out, thanks to the subsidy of the Consell de Mallorca. During these investigations, traces of the original polychromy were discovered on the main sculpted elements and all over the architectural structure.

In view of the rareness and great artistic value of this finding, a thorough research on polychrome stone sculpture was undertaken as well as a scientific campaign aimed at identifying the original materials and techniques of the monument's decoration, providing essential information for its conservation. Samples of the polychromy traces and of the stone substrata were analyzed, and the results were compared with data published in the scientific literature. The investigations were performed using optical microscopy on cross-sections (OM), scan electron microscopy (SEM-EDX), X-ray diffraction (XRD), and micro investigations with chemical reagents to identify the organic binders. All these analyses were carried out at the laboratories of the Technical Scientific Service of the University of the Balearic Islands (UIB) and the company GEA Asesoría Geológica.

Figure 1 – Sepulchre of Blessed Ramon Llull.

The results showed that the main constitutive material of the structure is Santanyí stone, a local limestone[1] (tortonic oolitic calcarenite) endemic to the island. The base of the sepulchre, on the other hand, is sculpted in white marés, a different type of highly hygroscopic sedimentary stone (mix of sandstone and eolianite) which was found to play a primary role in the degradation of the monument.

The preparation layer is a plaster made of calcite and calcium sulfate as fillers and animal glue and casein as binders which suggests that the painting technique might be a tempera.

The main tones of the polychromy are black, red, crimson hues, blue and gold, and all but the latter are applied as plane colors. The pigments were identified as natural iron oxides and lead white, while the gildings are made of pure gold leaf. All these materials correspond to those that were traditionally used for painting on stone since Antiquity, and are common in medieval polychromies found and studied throughout Spain (Rivas López, 2008, p. 240-270 and Llompart Moragues, 1977, p. 118).

The Sepulchre of Ramon Llull project: conservation issues

The discovery of the original polychromy entailed the implementation of a conservation intervention, urged by the ongoing alteration of the layers caused by continued environmental changes, mainly in terms of relative humidity, with consistent crystallization of soluble salts. Conductivity tests measured maximum values as high as 1483 µS, in the lower area of the monument thanks to qualitative analysis. Moreover, the original paint traces were generally hidden under a water-soluble overpainting, made of calcite, gypsum and an organic binder (which could not be precisely identified), supposedly applied after 1619, although, this is not surely documented.[2] Through direct observation and scientific analyses, several other decaying processes were noted on the paint coat as well as on the underlying layers. These involved mainly powdering, flaking and detaching between the layers and the substratum. Given the critical structural situation of the stratigraphy, the primary concern was to evaluate an adhesive that could both consolidate the polychromy, and also allow the further removal of the overpainting. The intervention presented in this paper, in fact, only addressed the preliminary consolidation of the paint layer aimed at securing its remains, and did not consist in a full conservation treatment.

1 Despite its porous structure, Santanyí stone was extremely appreciated by local sculptors for its properties, especially its optimum resistance to humidity (Fullana, 1985, p.19-22; Mas, 2013, p. 279.)

2 The Consolation altarpiece that presides over the sepulchre chapel, was installed in 1619, covering part of two niches of the lower body of the sepulchre. It has been observed that the patina was only applied in areas with easy access, leaving the most hidden areas behind the altarpiece uncovered.

Figure 2 – Grey patina.

Adhesives: a comparative approach

A comprehensive study on commonly used adhesives was undertaken, based on technical data sheets and scientific literature: fifty-seven conservation reports, dated between 1992 and 2018, that involved the consolidation of original polychromy on stone surfaces were consulted. This research focused on the working and performance properties of the adhesives, with a specific view to their aging characteristics. As a result, it emerged that the most widespread approach consists of using synthetic polymers such as Paraloid®, polyvinyl acetate and other acrylic or vinyl compounds. Even when non-synthetic adhesives are used, a protective top layer of Paraloid® is generally added. These materials have been preferred in view of some significant advantages in their physical characteristics, such as easy application (Martín Rey, 2017, p. 67), good adhesive properties, prompt appreciable results and, most importantly, the availability of ready-to-use products on the market.

However, these adhesives also feature a few disadvantages, especially if applied improperly. Firstly, film-forming acrylic or vinyl polymers tend to block the natural porous structure of a stone's surface by creating a hydrophobic barrier, clogging in humidity, and possible polluting substances. In a case like the sepulchre of Ramon Llull, where the stone is consistently contaminated by soluble salts, their use would have had the counterproductive effect of forcing the pollutants to crystallize inside the substratum, causing more physical damage. Moreover, the aging effects of synthetic compounds (such as depolymerization, cross-linking, formation of new functional groups (Borgioli, 2005, p. 27), and pH variations (Bonsanti, 2000, p. 34-35) can significantly alter them, converting the films into rigid and hardly removable materials, unfitting to the requirements of a conservation treatment of this kind.

Adhesive proposal

It was thus decided to seek an alternative solution among adhesives obtained from natural materials, such as casein, cellulose ethers and funori, which appeared to be more suited to the case of the sepulchre. These compounds were selected for their compatibility with the limestone substratum, as they tend to form breathable layers, which allow air and water vapor exchanges between the porous surface of the monument and its environment. Since they do not drastically alter the physical and chemical properties of the system, these materials also imply a low interference with further conservative actions, especially cleaning and overpaint removal. It is important to note that when referring to consolidation (that is the application of a substance on a surface to prevent its loss), its tendency to have an interfering effect with regard to other treatments is more relevant than reversibility in the strict sense of the term. This, as well as ageing properties and working concentration were the main aspects examined in the comparative study of the above cited adhesives.

Lastly, these materials also have encouraging advantages in terms of sustainability, as they are non-toxic natural derivatives, and in the transmission of traditional techniques and practice (especially for casein compounds and funori).

Before examining the possible interactions between the adhesives and the artwork's decorated surfaces, it is crucial to consider their respective physical characteristics.

Casein has traditionally been used as a binder in different painting techniques and as an additive in plaster formulations. In the case of the sepulchre of Ramon Llull, it is found among the components of the preparation layer of the paint coat, and is therefore compatible with the artwork's constitutive materials. Casein is a protein that can be diluted in alkaline solutions (generally ammonium or calcium hydrates) which kind determines the adhesive strength and stability of the compound, that may be adapted to different purposes. It was decided to test ammonium casein, obtained by soaking the protein in ammonium hydrate and letting the excess solvent evaporate before use, in order to prevent it from reacting with the calcium sulfate of the plaster layer. It has low hygroscopicity and creates strong bonds as a result of the evaporation process of its solvent, but dry films tend to become insoluble and therefore hardly removable. Another negative feature is its tendency to alter the optical aspect of the surface by slightly saturating the tones and increasing the gloss.

Cellulose ethers, like Klucel® H, have somewhat similar properties to those mentioned above, especially in relation to low hygroscopicity[3] and optical and chromatic alteration of the substrate. Klucel® satisfactorily maintains its solubility over time (unlike casein), and is prized for its stability, low toxicity and good adhesive properties.

The third type of materials used for testing were funori solutions. These are generally appreciated for their optical properties, as they allow to treat artworks without visible alterations in colors and texture, providing good adhesive properties as well as a light surfactant action. In recent years, its application has been extended from paper conservation to that of completely different materials with matte surfaces, especially murals paintings. Funori solutions have easy and controllable working properties, low viscosity and high solubility in water also after aging. During the tests, three different commercial types of raw product[4] were compared: a dehydrated powder, and two varieties of dry algae (one imported directly from Japan and one found via an Italian specialized supplier of conservation materials). The Japanese version turned out to offer the best quality, producing the clearest solution, whereas the others tended to become yellowish.

Adhesion test

In addition to the intrinsic properties of the materials, another crucial factor that needed to be examined was the concentration required by each of them to achieve sufficient adhesion[5]. Selected concentrations of solutions (see Table 1) were applied to samples made of 80 g/m^2 4x1 cm paper strips, glued together as shown in Figure 3. After a 24 hour drying at room temperature, a manual tension testing was performed, including bending and contraction, to empirically observe the different flexibility, stiffness and strength of the adhesives. The results were consistent with bibliographic references (Kron Morelli, 2016 pp. 67-92; Kron Morelli 2018):

[3] At 90% R.U. Klucel® H absorbs only 12% of water vapor.
[4] Costly purified versions of funori were discarded because of their insufficient adhesion properties. For a comprehensive study on the characteristics and preparation methods of funori, see all the bibliographic reference at the end of the paper.
[5] An improper calibration in the concentration of the solution can affect both the working properties of the adhesive (by influencing its viscosity) and the future conservation of the artwork, either by under effectiveness or by excessive modification of its constitutive layers.

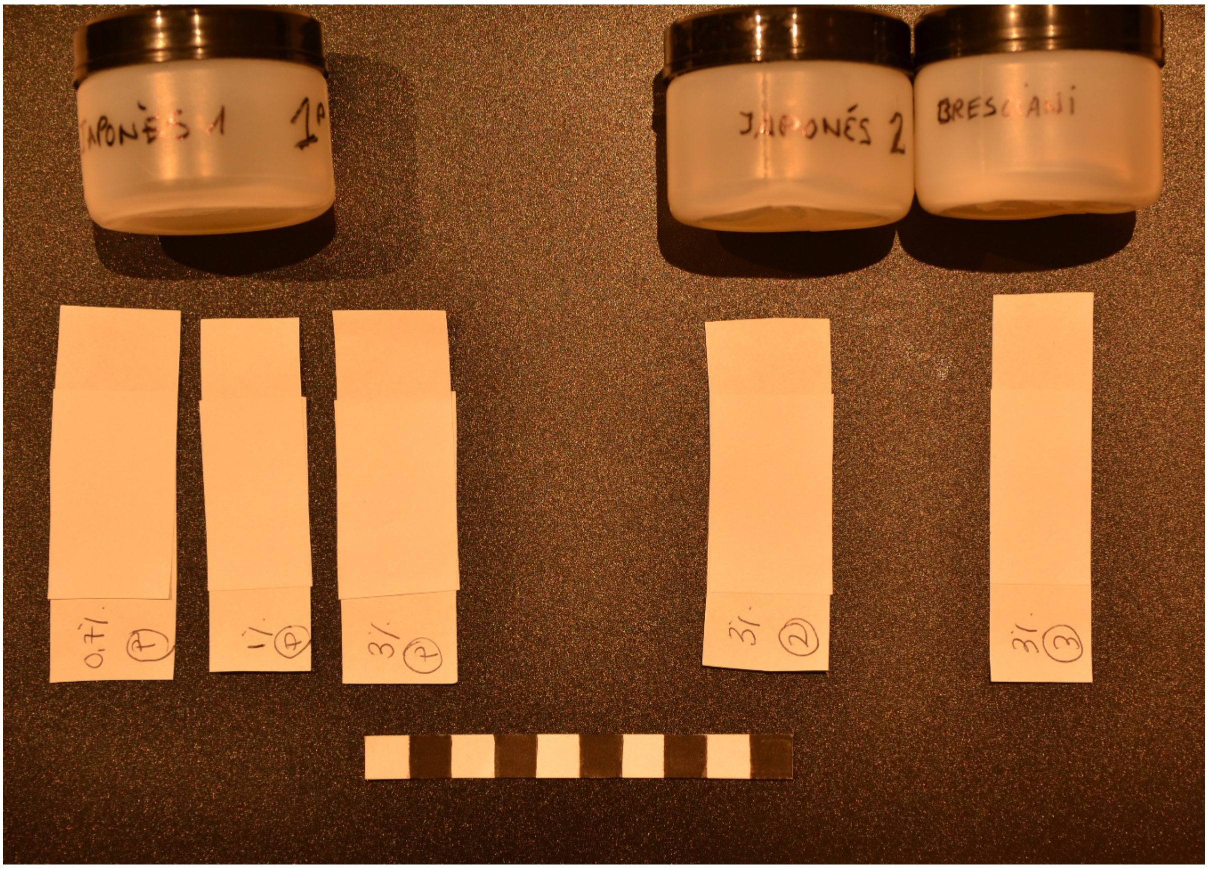

Figure 3 – Adhesive testing.

TEST 1 Japanese Funori 1 – 0,5%	TEST 5 Bresciani Funori – 3%
TEST 2 Japanese Funori 1 - 1%	TEST 6 Klucel H® - 0,5%
TEST 3 Japanese Funori 1 - 3%	TEST 7 TEST 6 Klucel H® - 1%
TEST 4 Japanese Funori 2 - 3%	TEST 8 TEST 6 Klucel H® - 3%

Table 1 – Specification of adhesives test proportions.

- There are no significant differences in terms of adhesion and mechanical properties between the three funori commercial types. If applied at less than 1% they do not increase the rigidity of the substrate, while adhesive strength proportionate to the fixing of a pictorial layer is obtained for solutions between 0.5% and 1%.
- Klucel® H generates the strongest, but also a most rigid bond.
- Ammonium casein shows good adhesive strength, along with perceptible color changes.

After this first mock test, seven areas were selected on the monument for further comparison in relation to the peculiar material condition of the artwork. The choice of the sample surfaces and its criteria are detailed in Figure 4 and Table 2.

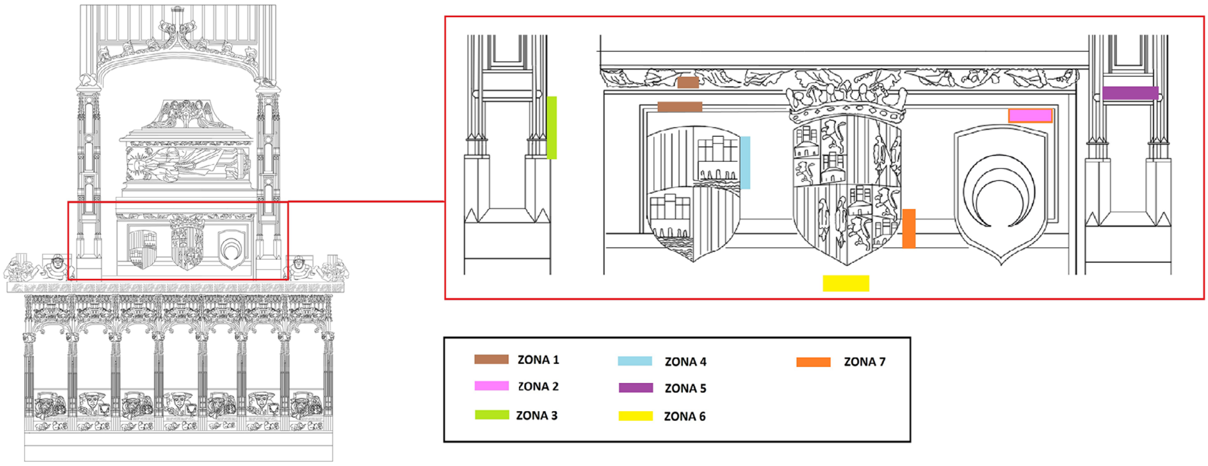

Figure 4 – Test areas.

Type of area	Layers observed	Selected area
Polychrome and patina area on stone support.	- Consolidation of the paint layer and fixation in the preparation layer. - Fixing the support and consolidation layer preparation. - Possible surface cleaning inherent to the process.	Zones 2, 3 and 7
Polycrome area on stone support, without patina.		Zones 1, 4 and 5
Area of patina directly on the stone support.	- Fixing to evaluate the solubility rear view to removing the patina in subsequent process.	Zone 6

Table 2 – Specifications of the tested areas

Each of the test areas was treated using the three following methodologies:

- Diffuse application of the adhesive solution directly on the surface using brushes.
- Diffuse application of the adhesive with brushes after interposing Japanese paper[6], then pressing the surface with a natural sponge and water in order to remove the excess and enhance the adhesion.
- Confined application behind the flaking with a syringe, followed by pressure with a natural sponge or cotton swab to secure the adhesion.

[6] Three types of Bolloré® Japanese papers were compared: 6, 9 and 12.3 g/m^2. The latter has been preferred for its easy application and removal.

Figure 5 – Application.

All the surfaces were then lightly rubbed with dry cotton to verify if the powdering persisted after the treatment. In addition, a solubility test on the overpainting was performed to verify possible variations if the firmness of the layer.

In situ tests showed that funori, and more specifically the solution obtained from the Japanese commercial raw product, was the best suited adhesive for this intervention, as it complied with all the criteria required by the condition of the sepulchre. It is effective at an extremely low concentration (possibly under 1%), allowing the original material to absorb it, thus preventing the formation of a film on the surface. It does not saturate or alter in any other way the texture of the artwork (the variations being noticeable only if measured with the colorimeter, but not to the naked eye), and does not stiffen the painted layers. Last but not least, the light surfactant properties of funori, in this case, are beneficial to the prospective cleaning treatment of the overpainting, which is not altered by the presence of the algae.

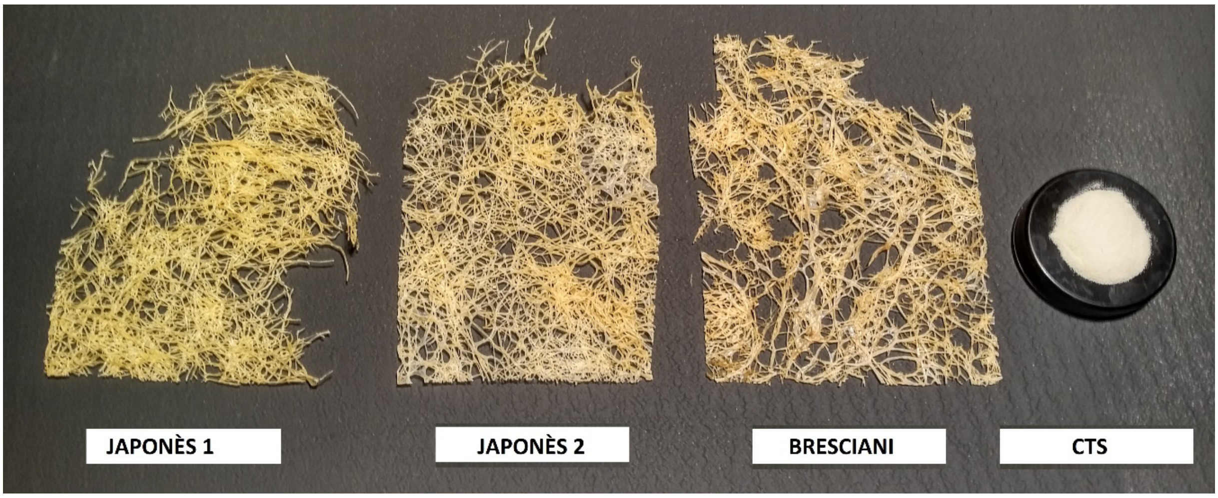

Figure 6 – Comparison between funori and caseinate.

Application methodology

The pictorial and under layer were consolidated using funori with the following methodologies:

- Confined application of 0.7% solution along the perimeter of the paint scales and injection of the same solution in the rear surfaces at the interface with the underlying layer.
- Diffuse application of 0.7% solution with a brush after the interposition of Japanese paper on the entire surface of the paint layer, sequentially pressing gently with natural sponges to remove the excess and improving the adhesion. It was observed that leaving the Japanese paper to dry (about 12 h) and removing it by wetting with a water-alcohol solution (70-30%) achieved a better result.

The applications detailed above were sometimes preceded by the administration of a 0.2% funori solution to break the surface tension. Furthermore, direct application with a brush was exceptionally performed when necessary in limited areas.

The only exception to the effectiveness of the treatment appeared to be the polychrome layer of the keystone of the arch, which was exceptionally sensitive to any fixing treatment because of its severe powdering phenomenon. During the initial removal of the Japanese paper, minor losses of pictorial and preparation layers occurred. Prior to the complete removal of the tissue, the surface was thus treated with a swab moistened with a water-alcohol (70-30%) solution to remove part of the consolidating material. Probably the most suitable option for this area would have been to preliminarily spray atomized fixative on the surface. The funori application through Japanese paper would then have been most effective.

Conclusion

Unlike ready-to-use synthetic polymers, traditional natural materials, such as funori and casein, come in numerous varieties with different physical properties depending on their preparation methods and qualities. This entails the need for a deeper theoretical and practical knowledge of their application methods in order to properly take advantage of their potentialities in solving conservation problems. On the other hand, these products allow us to achieve exceptionally high standard results in short and long terms, both for the artwork and the conservator. As for the monument, these adhesives comply with compatibility and durability requirements, whereas from the conservator's point of view they are profitable because of their low toxicity in the present and in future interventions. This is particularly true for funori, as it remains soluble in water even after aging.

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Acknowledgments

Thanks to the Bishopric of Majorca and the Franciscans of the third order, for their confidence and their wish to preserve the heritage. To the work of the Consell de Mallorca for the promotion of heritage conservation through the grants that make this project possible is appreciated. We also wish to acknowledge the Department of Serveis Científico Tècnics from University of Balearic Islands, for their availability and dedication.

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Article received on 15/02/2019
and accepted on 01/05/2020