Comparative approach about adhesives for the intervention of polychrome on stone: the case of Ramon Llull's Sepulchre

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Abstract

The sepulchre of the Blessed Ramon Llull is a XV century monument located in Palma (Mallorca, Spain). During the studies developed for the restoration project, remains of the original polychrome were discovered. Prolonged exposure to high levels of humidity and leaks were the main causes of the deterioration of the monument's polychromies. The plaster layers lost cohesion and adhesion from the support, so they had to be treated.

For the selection of the adhesive, the results obtained in the researches through the current scientific bibliography were analyzed. As a result of the comparative process, ammonium caseinate, Klucel H® and funori were selected, to be tested on the monument for their compatibility, stability, adhesive properties, low optical effects, re-treatability and low concentration. Finally, funori was the definitive product used, with which the desired results were obtained.

Keywords

Polychrome stone, adhesive, Funori.

Introduction

The sepulchre of Blessed Ramon Llull is located in the church of San Francisco, in Palma de Mallorca. The construction, in gothic style, began in 1460 and remained unfinished in 1492.

In 2017, at the request of the Bishopric of Mallorca and the Third Order of Franciscans, the study and diagnosis of the monument was carried out, thanks to the subsidy of the Consell de Mallorca. From them, polychromy traces were identified in the main iconographic elements and in the architectural structure.

Figure 1 – Sepulchre of Blessed Ramon Llull

The constitutive materials and polychromy traces have been studied by sampling and analyzed by optical microscopy (OM); scanning electron microscopy (SEM-EDX), X-Ray Diffraction (DRX) and chemical reagents for the organic binders. These were carried out in the laboratories of the Technical Scientific Service of the University of the Balearic Islands (UIB) and by the company GEA Asesoría Geológica.

The main constituent material of the support is the Santanyí stone, an endemic lithotype that, despite being porous, was a material extremely appreciated by the sculptors of the island for its properties and its optimum resistance to humidity (Fullana, 1985, p.19-22; Mas, 2013, p. 279).

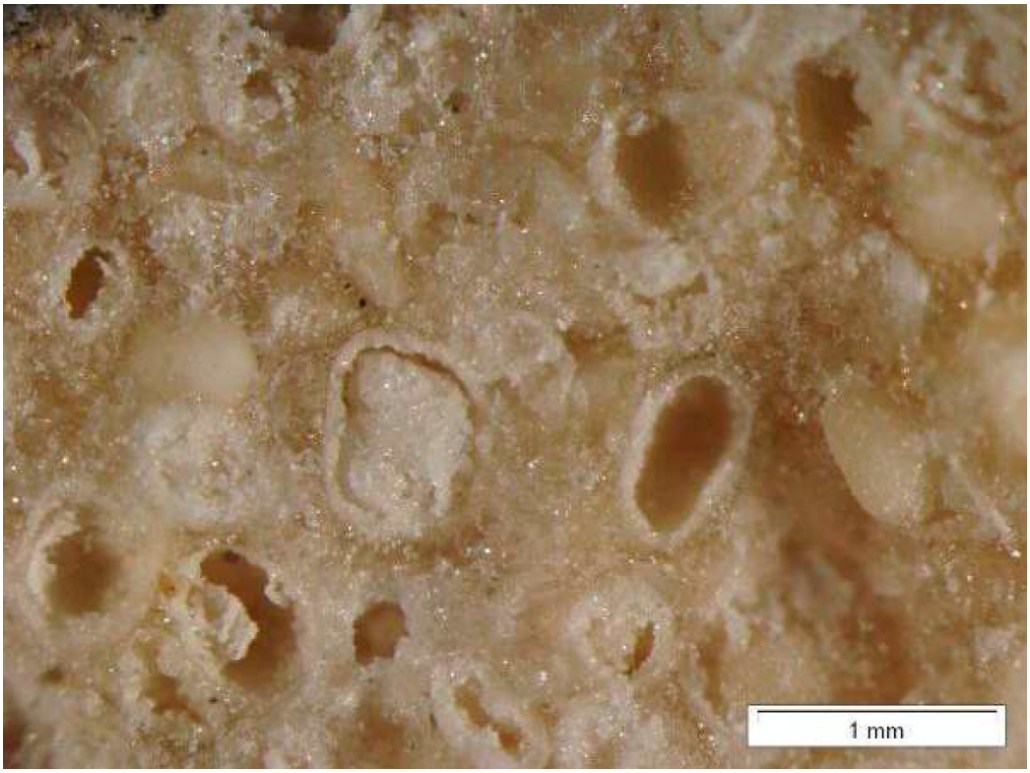

Figure 2 – View of santanyí stone and BSE of it. Images from GEA, Geological Advisory.

Even so, the base of the monument was made with white *marés*, another type of sediment highly hygroscopic, which has directly influenced the degradation of the monument.

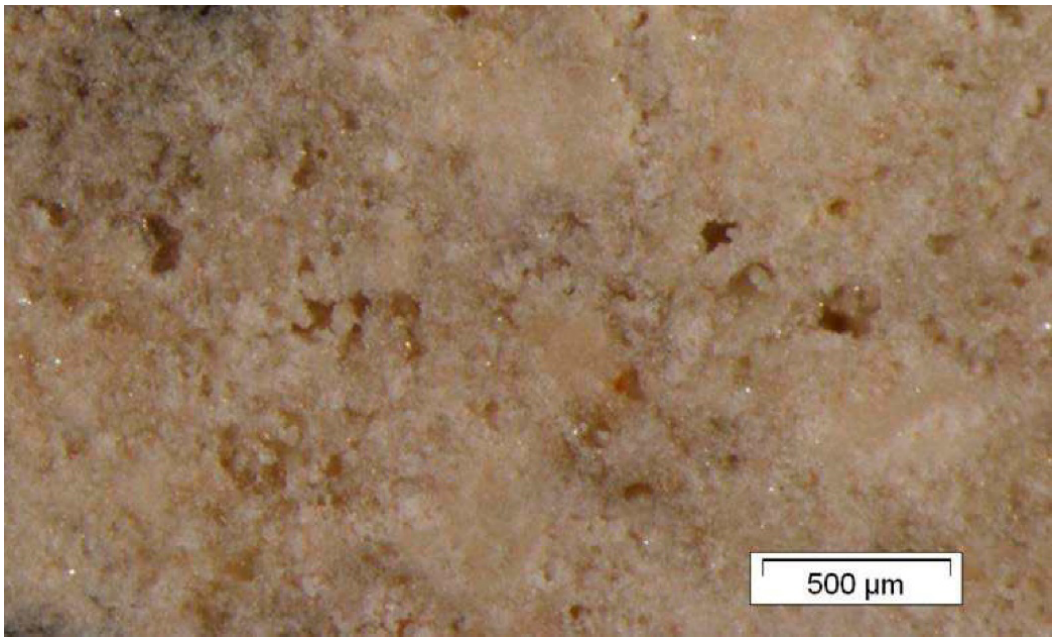

Figure 3 – View of white *marès* stone and BSE of it. Images from GEA, Geological Advisory.

The main tonalities of the polychromies identified *de visu* are black, red, crimson, blue and gold, applied with plain colors. The pigments are natural earth, lead white and iron oxide with pure gold leaf sheet for gilding. The preparation layer was a mixture of calcite and calcium sulfate inerts, while the binders are animal glue and occasionally casein, therefore the polychromy could be defined as tempera.

Figure 4 – Polychromies of de sepulcre.

These materials were used since Antiquity and common in the medieval polychromies studied throughout Spain (Rivas López, 2008, p. 240-270 and Llompart Moragues, 1977, p. 118), so it is difficult to date the polychromies, despite having historical references regarding the desire to color the sepulchre (Custurer, 1700 in Sacarés Taberner, 2014, p. 246).

The condition of the polychromies was clearly altered, mainly by humidity and soluble salts, whose maximum values of 1483 μs were obtained in the base zone by qualitative analysis.

In addition, they are generally hidden under an artificial grey artificial patina rich in calcite and gypsum, soluble in water, which although not documented, may have been applied later than 1619.

Finally, it was observed that polychromies were pulverulent, disintegrated and with displacement between the support and these layers.

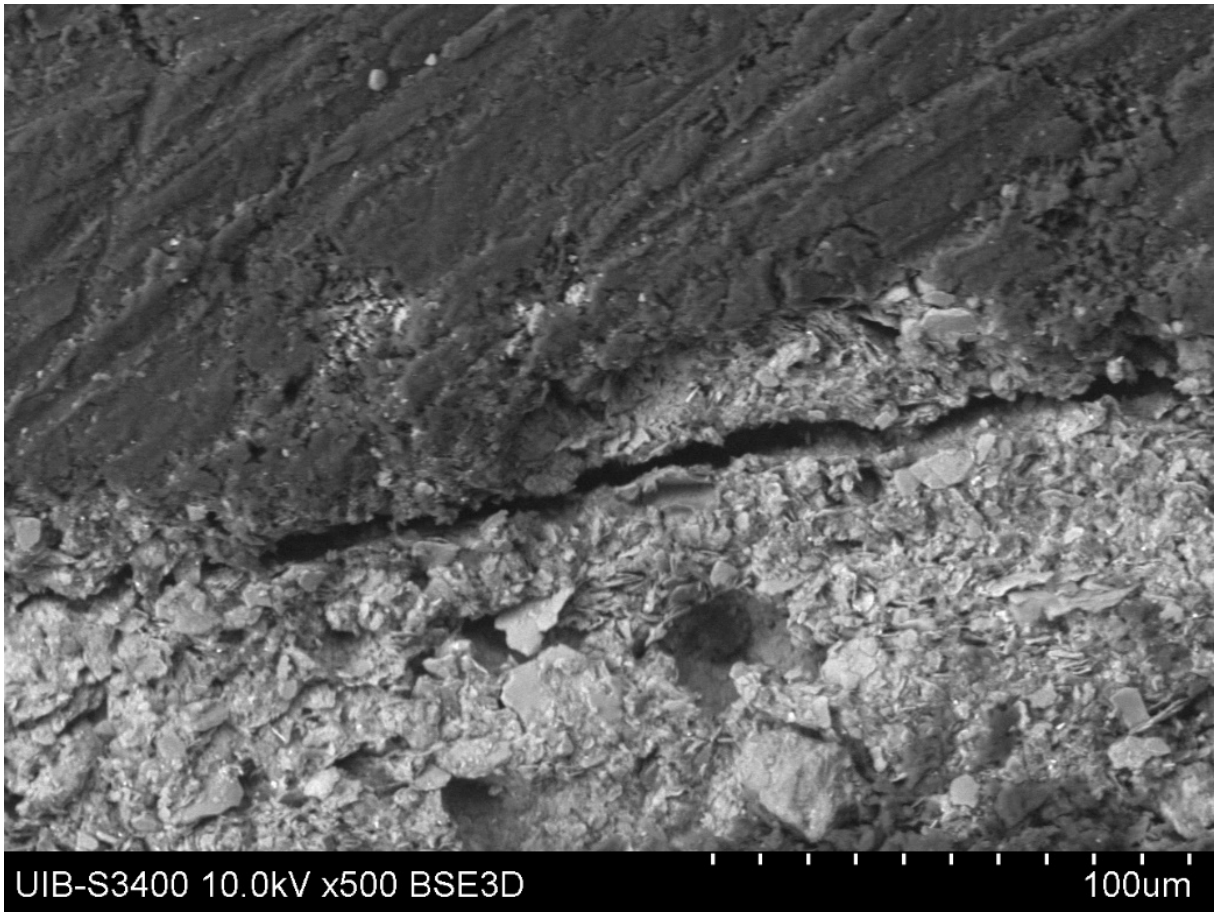

Figure 5 – BSE image of sample Llull 03/2017.

For all these reasons, the need to fix the polychromies was an urgent and justified measure.

Adhesive comparative approach

To decide the type of material to be used, a panoramic study was made about the different fixatives, from their technical files, specific bibliography and archives of public organisms where reports of intervention on similar monuments can be found.

From this, a comparison of qualities and properties of the fixatives commonly used and new proposals in the restoration of monuments of the same type and epoch were carried out.

From the archives, 57 reports of restoration interventions were consulted in which the fixation of polychromy on stone was necessary. The restorations, dated between 1992 and 2018, show that in 32 cases the fixative was Paraloid B-72® applied between 1-10% in acetone, toluene or xylene, with 2 applications. The same can be seen from the publication of the interventions of the Portalada de Santa María de Vitoria (Cortázar García, 2009, p. 37).

Some exceptions were found, namely, the 1988 case, where polyvinyl acetate (CRBMC 2604) was used, other cases in 1997 (CRBMC 069090) were fixed with Plextol 500®; the musicians angels from Mallorca (MC 0272) were fixed in 1985 with Synochryl 9122X® and in another case Klucel G® at 10% alcohol was used (CRBMC 12374).

Even so, in exceptional cases, a protective layer of Paraloid B-72® at 5% in acetone was subsequently applied.

It should also be noted that, in some interventions such as the one documented in 1996 in the MNAC (04356), the fixation had not been documented, but the solubility problems to remove an earlier Paraloid® application were reported; the same happens in Mallorca, as can be seen from file MC9551, which reports that it was finally removed mechanically.

The intervention of the Pórtico de la Gloria is an exceptional case, in which, according to the Pórtico Conferences[1] held at the time, the fixation with sturgeon tail was made.

Thus, it follows that the most used materials as fixatives, have been synthetic polymers, also known as synthetic resins. Specifically, for polychromy on stone fixation, the most widespread are the acrylics such as the well-known Paraloid®, Primal®, Acril® or Plextol® and the vinylics like Mowilith®, Vinavil® or Lineco®.

The advantages of its mechanical and physical properties and its easy application (Martín Rey, 2017, p. 67), good adhesive characteristics, speedy visible results, and the commercialization of the ready to use product, helped to spread and significantly increase its use.

Unfortunately, studies about the consequences of the use of polymers began when they were already widespread, and by their nature, much longer evaluation times were needed concerning other natural organic materials, thus the results came decades later, when the belief of their remaining unchanged overtime was still growing.

[1] Symposium of Pórtico de la Gloria. IPCE. November 29 - 30, 2016; and November 21-23, 2018. https://ipce.culturaydeporte.gob.es/dam/jcr:14b6fea0-3181-4003-bb55-64fee3cb7fa8/programa%20octubre-portico-5.pdf

Investigations finally certified the disadvantages and problems that these products can cause used on inorganic supports, especially in the presence of soluble salts, as in the case of the sepulchre, which forced them to crystallize as sub-florescences within the support, inducing mechanical damage. Due to the degradation of the material, which could cause its depolymerization, cross-linking, the formation of new functional groups in the structure (Borgioli, 2005, p. 27) or pH changes, converting them into rigid and practically irreversible materials, not suitable for their re-treatability (A.A.V.V., 2006, p. 47; Bonsanti, 2000, p. 34-35). Finally, and although it is currently a barely studied aspect, synthetic polymers can also suffer biological attack as organic materials (Koestler, 1988; Bloomfield, 1995, p. 73; Cappitelli, 2004, p. 399-406).

The specific bibliography provides an overview of alternatives to synthetic polymers, applied as fixed resources and that should be considered here, e.g.:

- Protein compounds and polysaccharides: funori, sturgeon glue, nopal mucilage, gelatine, ammonium caseinate.
- Synthetic compounds derived from cellulose: Tylosa MH 300P®, Klucel G® and H®, Methocel®.
- Ethyl ester: KSE 30E®.
- Derivatives of lime: Nanorestore® and lime water.

The compatibility between the original materials and the fixative, reveals that the most similar would be protein fixatives, secondly the ammonium caseinate for its compatibility with the organic and inorganic parts of the pictorial technique; and finally, the polysaccharides for their similar physical-mechanical behavior (Mora, 2001, p. 241).

Regarding the adhesive property, all of them present suitable fixative properties, certified by the manufacturers and abundant bibliography, although Acril 33® would present insufficient properties attributable to its low penetration (Mora, 2001, p. 252).

The mechanical behavior of protein and polysaccharide fixatives, is based on the adaptable humidity absorption movement through swelling and subsequent release thereof, which doesn't cause rigidity of the medium while remaining unchanged, but varying somewhat the behavior of the stratum, maintaining its elongation capacity and allowing low deformation loads which are absorbed by the polychromy without modifying the porous structure or surface morphology.

Secondly, there are cellulose derivatives which, although they do not behave in the same way as the organic original binder of polychromies, maintain the flexibility of the stratum at low concentrations.

The rest of fixatives present instability and rigidity as superimposed films formers, which directly affect properties such porosity, and do not allow the balanced passage of a flow of

aqueous vapor present in the environment between the inside and the outside, which must be respected (Bandini, 2000, p. 13-47). In this sense, synthetic polymers form a barrier within the pores of the support due to their macromolecular structure and impermeable character, which force the salts to crystallize inside the structure (Matteini, 2001, p. 35).

Regarding solubility, it has been determined that when a fixative has a solvent that also can dissolve the original, it could create some complications during its application; but even this, and for its long-term preservation, the incompatibility between solvents of fixative and the original pictorial layer, could be more problematic by the creation of a final dispersion. Conversely, fixatives that, like the original, are soluble in water, can create a heterogeneous solution that would favor the re-treatability. For this reason, the water-soluble proteinaceous compounds, polysaccharides and cellulose derivatives would be the most suitable for their re-treatability, being also those of lower toxicity (Robles Andreu, 2014, p. 97-110).

In reference to the pH, it has also been observed after the aging of fixatives, that only funori and Acril 33® would maintain a stable or slightly alkaline pH (pH 9), although some specific bibliographic data are missing, From the rest of the data obtained, it can be seen that even though initially the majority presents a pH close to neutral, with time they tend to acidify (Down, 1996, p. 19-44), which creates an incompatible medium with the original.

The concentration of products in the applications oscillates enormously as recommended by the manufacturer of each fixative and most of them recommend two applications, those of lower concentration would be the proteinics (0.5-10%), the funori (0.5-3%), cellulose derivatives (1-4%) and Paraloid® (2-5%).

Finally, with respect to the optical behavior, the fixatives that present an initial color are: funori, the animal and sturgeon glues, which are slightly yellow, as well as the derivatives of lime which are whitish. Even so, the funori and the sturgeon glue do not modify the color or intensity of the polychromy to be treated, unlike the nopal mucilage or ammonium caseinate. Paraloid B-72®, is presented as a fixative that would modify the saturation of the color and its own color (Botticelli, 2008, p. 127). This problem is also present in the inorganic fixatives, which bleach the polychromy.

In reference to the brightness, considering the original surface is matt, the fixatives that present this property are: funori, the ammonium caseinate, the Klucel® and the other derivatives of the cellulose. Unlike these, the Tylosa® would be satiny and the others fixatives satin or shiny.

Conclusion

The fixative used will act as a new binder replacing part of the original and being in total contact with the material of the sepulchre, solving the problems of decohesion and pulverulence. Considering the impossibility of reversibility, the priority has been to warrant the best aging and compatibility qualities with the original as well as its re-treatability.

In relation to compatibility, adhesive characteristics, mechanical behavior, re-treatability, lower contribution of material to the original and optical properties, the most suitable fixative are funori, ammonium caseinate and cellulose derivatives; so they have been tested as a methodology for the intervention of the sepulchre.

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