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Cyclododecane as protection for water-sensitive polychromy during water bath desalination of limestone sculptures: The case study of a mid-15th-century wall-mounted memorial from the Burgundian Netherlands

Camille De Clercq*
Royal Institute for Cultural Heritage (KIK-IRPA)
Stone Conservation Studio, Monuments and monumental decoration lab
Brussels, Belgium
camille.de.clercq@kikirpa.be
www.kikirpa.be

Sebastiaan Godts
Royal Institute for Cultural Heritage (KIK-IRPA)
Stone Conservation Studio, Monuments and monumental decoration lab
Brussels, Belgium
Sebastiaan.godts@kikirpa.be

*Author for correspondence

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Abstract
This paper focuses on the protection of water-sensitive polychromy with cyclododecane (CDD) during water bath desalination treatment of limestone. For the study, several stone samples were painted with red bole, a very water-sensitive earthy clay, and then coated with CDD applied in a molten state or as a spray. Afterwards, the samples were immersed in water to simulate short-term and long-term bath desalination. CDD applied as a melt was very effective in protecting water-sensitive polychromy during the immersion stage of the experiment. Based on these results, CDD dissolved in n-heptane (C_7H_{16}) in a molten state was used as protection for the polychromy in the desalination treatment of the limestone wall-mounted memorial at Merbes-le-Château. The results of the experiments and case study show that CDD, when applied as a melt, offers considerable protection for water-sensitive polychromy during the desalination of limestone objects.

INTRODUCTION

The presence of soluble salts in stone sculptures is a problem frequently encountered by conservator-restorers. Desalination is often the only way to prevent damage and, when possible, immersion in water is the best method to remove the salts. This treatment can be problematic when the surface is covered with polychromy. In the case study described, the polychromy had to be protected to preserve its physical properties during and after a long-term water bath desalination procedure.

Cyclododecane (CDD),[1] a volatile binder with hydrophobic properties, is frequently used in conservation as a temporary consolidant, barrier or fixative for a variety of materials during treatment. CDD has also been used for the protection of water-sensitive inks during the desalination of archaeological ceramics. Not only are the hydrophobic properties of CDD useful during an aqueous treatment but its volatile nature at room temperature ensures that no manipulation is required to remove the protective layer after the treatment. The use of CDD was modified for a series of tests to examine the behaviour of the barrier and ensure the polychromy on the limestone was protected during the desalination process. The results of the tests were compared and an optimal method determined to apply CDD on the sculpted surface and remains of the polychromy of a Burgundian Netherlandish wall-mounted limestone memorial from the 15th century. The research presented can aid conservator-restorers to define the viability and application procedure of CDD for protecting polychrome limestone artefacts during bath desalination.

CASE STUDY: A MID-15TH-CENTURY WALL-MOUNTED MEMORIAL

Presentation

A sculpted limestone memorial (84 × 64 × 14 cm) of Jehan Jamet (d. 1443) in the church of Saint-Martin, Merbes-le-Château (Hainaut, Belgium), was discovered during maintenance work in December 2009 (Bedoret 2010). It was hidden behind the antependium, enshrined in the masonry of the altar dedicated to our Lady of the Rosary (Figure 1), probably to protect it from destruction or theft during war or revolution. Originally, these types of memorials were mostly mounted in walls or piers above graves to commemorate the deceased and elicit prayers for their souls (Douglas 2015).

The patrons of the work are presented with Jehan Jamet, the first known potter of Merbes-le-Château (Parmentier 2010), accompanied by his three sons and his wife and three daughters at the opposite side kneeling before the crowned Virgin and the (now headless) Child holding an open book. Jehan Jamet and his wife are presented by their patron saints, Saint John the Baptist and probably Mary Magdalene.

Figure 1. Memorial enshrined in the masonry of the altar dedicated to our Lady of the Rosary

The tablet is carved in stone from Avesnes-le-Sec (Avenderstone), a white limestone with tiny black or greenish spots – glauconite – often grouped in clouds. The northern French limestone permitted the figures to be carved almost in the round. As usually seen on similar sculptures from this period, the stone relief was entirely painted (Brine 2015). Because most of the final polychrome finish had been lost, the ground layer was mainly visible. The literature discussing the polychromy on wall-mounted memorials from the 15th century in the Low Countries (Nys 2001, Serck-Dewaide 2018) states that underlayers were generally made with earth (iron oxide-based) pigments and with little binder. Nevertheless, a thorough microscopic examination made it possible to reconstruct most of the colour palette (Figure 2).

Figure 2. Left: memorial after treatment, Merbes-le-Château (1443); right: reconstruction of the polychromy

Conservation issues

Having been enshrined in the masonry, the tablet was exposed to constant rising damp and fluctuating climatic conditions. This had caused salts to accumulate at the drying front near the surface and frequent crystallisation cycles within the pore structure, leading to subsequent damage to the object. Figure 3 shows the specific distribution of the damage at the sculpted surface (Figure 3), which could be divided into three zones: the most weathered zone (red zone) where the salt damage was leading to the loss of sculpted parts; a mid-weathered zone with slightly flaky and powdery areas; and a less weathered surface with visible efflorescence.

Figure 3. The surface can be divided into three zones: the most weathered zone (red zone), where the salt damage was resulting in the loss of sculpted parts; a mid-weathered zone, with slightly flaky and powdery areas; and a less weathered zone with visible efflorescence

To identify the salts and their distribution within the stone, it was decided to take samples with a powder drill (Ø 6 mm) up to a depth of 6 cm in two discreet and damaged areas, starting at the front of the memorial. Samples were taken at every centimetre to achieve an in-depth salt profile. The ion-containing anions (Cl^-, NO_3^- and SO_4^{2-}) and cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) from the dried stone powder was determined by ion chromatography (IC, Metrohm). A mixture of up to 2 per cent by weight (wt%) of nitrate salts and some sodium chloride was detected and the content remained high at a depth of up to 6 cm. Furthermore, almost 7 wt% of calcium

Figure 4. Memorial conditioned in a closed box with a saturated solution of sodium chloride

sulfate had accumulated in the first centimetre of the sculpted surface. Details on the salt distribution and mixtures are described in Godts and De Clercq (2020).

A test in which a cotton swab soaked in water was slightly rubbed over the red underlayer largely present on the surface confirmed the suspicion that it could be considered water sensitive. To determine just how water sensitive the red underlayer was, a small flake from the original underlayer was immersed in 5 mL of deionised water over a period of two weeks. No significant changes were observed; thus, it was concluded that the red underlayer was only slightly water sensitive in deionised water.

Based on the state of preservation and the preliminary investigation, it was considered necessary to remove the memorial from the masonry and carry out a desalination treatment by immersion in water. After removing the memorial and pending testing on the samples, the object had to be stored in a stable environment to prevent crystallisation cycles from occurring. While the memorial remained in the workshop, it was conditioned in a closed box with a saturated solution of sodium chloride (Figure 4). Maintaining a relative humidity (RH) of ca. 75%, all of the salts, excluding gypsum, remained in the solution.

TESTS USING STONE SAMPLES WITH WATER-SENSITIVE POLYCHROMY

Before CDD could be used to protect the polychromy on the surface of the memorial during water bath desalination, the material was applied on painted stone samples. A red German bole (Eytzinger red poliment ‘deutsch’) was used for the paint. The paint was compared to a sample of the original underlayer found on the memorial and proved to be water sensitive.

The experiments were based on a variation of the tests conducted by Muros and Hirx (2004). Based on the results of the examinations into the working properties of CDD and earlier published successful treatments, CDD in molten and aerosol spray form were chosen as the application methods for testing.

Experiment 1

The first experiment was carried out to determine whether CDD as a melt would be effective at protecting water-sensitive polychromy and what the influence of light is during long-term immersion (two years).

Two stone samples, measuring approximately 8 × 5 × 2 cm, were partly painted with the red bole. The samples were then coated with a 0.5–1 mm melted film of CDD: the grains were applied on the surface and melted directly using a hot air blower (Leister). Samples 1 and 2 were placed under water at room temperature in a transparent and non-transparent box, respectively, before and during the actual treatment on the memorial. This method allowed the stability of CCD to be evaluated over time and to predetermine if the memorial needed to be removed from the bath.

Figure 5. Test

Experiment 2

The second test was carried out to determine whether different CDD application methods would be effective at protecting water-sensitive polychromy during short-term immersion (50 days).

For the following experiment, a CDD melt and CDD aerosol spray, each separately and as two layers on top of each other, were chosen to test the level of protection compared to a non-protected zone. A sculpted stone figure covered with red bole was divided into four separate zones: (A) unprotected; (B) protected with CDD aerosol spray; (C) protected with melted CDD; and (D) protected with melted CDD and aerosol spray (Figure 5).

Results of the tests

Experiment 1

Sample 1, in the non-transparent box, remained unchanged, while sample 2, in the transparent box, was covered with green algae.

After the CDD was completely sublimated, examination of the painted surface revealed a slight discolouration. The red bole appeared lighter than before immersion, especially at the edges. With magnifying glasses (10×), the painted surface appeared rougher and more porous than before immersion. It is thought the discolouration or changes in paint texture may have been due to the dissolution of soluble water-sensitive material.

Experiment 2

The bole almost completely dissolved under water where it was uncoated (zone A) or coated with CDD aerosol spray (zone B).

In zone C, the CDD melt film was very effective at protecting the bole during immersion over 50 days (Table 1). However, at the boundary between the coated and uncoated parts, the bole turned a darker colour.

Table 1. Results of tests on a limestone sample covered with red German bole (Eytzinger red poliment 'deutsch') during immersion

<table>
<tr><th>Immersion time</th><th>Zone A: Uncoated</th><th>Zone B: CDD aerosol spray</th><th>CDD melt</th><th>CDD melt + CDD aerosol spray</th></tr>
<tr><td>1 day</td><td>Bole NC</td><td>CDD aerosol spray surface crumbling slightly</td><td rowspan="7">NC</td><td rowspan="5">CDD aerosol NC</td></tr>
<tr><td>3 days</td><td>Bole crumbling on the bottom</td><td>CDD aerosol spray layer peeling off</td></tr>
<tr><td>7 days</td><td>Bole crumbling on the bottom</td><td rowspan="2">CDD aerosol spray AG</td></tr>
<tr><td>15 days</td><td>Bole PG</td></tr>
<tr><td>30 days</td><td rowspan="4">Bole almost gone</td><td rowspan="2">Bole PG</td></tr>
<tr><td>45 days</td><td>CDD aerosol spray PG</td></tr>
<tr><td>60 days</td><td rowspan="2">Bole AG</td><td>CDD aerosol spray almost gone</td></tr>
<tr><td>After sublimation</td><td>Bole slightly fade</td><td>Bole slightly faded</td></tr>
</table>

NC = No change
PO = Peeling off
PG = Partly gone
AG = Almost gone

These results concur with Muros and Hirx (2004) who found that CDD films differ in their effectiveness as a barrier and were highly dependent on the water solubility/sensitivity of the material to be protected. The aerosol spray films did not protect the bole. The melted films protected the bole but imperfectly, as the bole seemed to be extremely sensitive to water.

APPLICATION IN THE CASE STUDY ON THE BASIS OF THE TEST RESULTS

Preliminary measures

Before starting the water bath desalination procedure, the content of the soluble salts deep within the limestone was determined by ion chromatography (IC) as described earlier. It was concluded that the red underlayer on the wall-mounted memorial at Merbes-le-Château was only slightly sensitive to water, and, therefore, based on earlier test results, the melt film would provide adequate protection for the polychromy. The first step of the conservation treatment was to pre-consolidate the disintegrated stone areas (orange and red zones in Figure 5) with a single application of ethyl silicate, approximately one litre, using a wash bottle. Ledan TA1 dissolved in water (2/3) was used as a filling to hold the scales together and prevent detachment (the red zone in Figure 5). Before applying CDD on the relief surface, it was cleaned with soft brushes and a museum vacuum cleaner.

Application of the CDD

To prevent the CDD from solidifying too quickly during application, it was dissolved in n-heptane (C_7H_{16}) (90% w/v).

The CDD melt (bain-marie) was applied with brushes and afterwards to the smaller cavities with a hot-air hand tool (Leister), whose airflow and temperature were adjusted separately, as needed. The protection layer was only applied on the sculpted surface, specifically where polychromy remains are present. The sides and the back of the relief were never painted in the past and were not coated with CDD to allow the diffusion of the salts into the water bath.

Health and safety concerns

Rowe and Rozeik (2008) reported a lack of information on the human toxicity of CDD. Their report indicates that CDD is bio accumulative. The Conservation Wiki page of the AIC Objects Specialty Group (Davidson et al. 2020) recommend that fume hoods and nitrile gloves be used to protect against inhalation and skin absorption.

Positioning in the desalination tank

The stone memorial was not laid directly on the bottom of the tank but raised on a plastic tray with an open container and polystyrene foam to facilitate water circulation at the lower face of the bloc, as described by Bromblet et al. (2011). The relief was initially placed vertically in a water tank with only a few centimetres of the stone under demineralised water to allow slow capillary absorption over a period of 11 days. To prevent the sublimation of the melt coating during this period, the sculpted surface with the melted CDD was protected with an additional layer of CDD aerosol spray and covered with a black cloth. When the absorption significantly slowed down, by measuring the water table in the water tank, it was placed horizontally with the sculpture and protected surface facing upwards under water in a tank containing approximately 140 L of demineralised water. To accelerate the diffusion of the salt into the bath water, a diving pump was placed in the water to create a constant flow of water around the object.

Monitoring and finalisation of the process

The monitoring consisted of daily to weekly measurements of the ion concentration in the bath water (IC, Metrohm). After mixing the water in the bath thoroughly, 10 or 20 mL of water was removed for each measurement. The total ion content in the bath rose over time to approximately 4 g every day over a period of 111 days. On day 112, the increase slowed significantly to 1 g. The water was changed twice following the results of the IC measurements.

Desalination was completed after a total of three baths and 260 immersion days, reaching a total of 728 g of salts in the bath water. The results of the quantitative salt analysis are presented in Figure 6 as the total salt concentration in the bath (g over time, where the drops in weight represent a change of water). Details on the individual ions detected over time are described in Godts and De Clercq (2020).

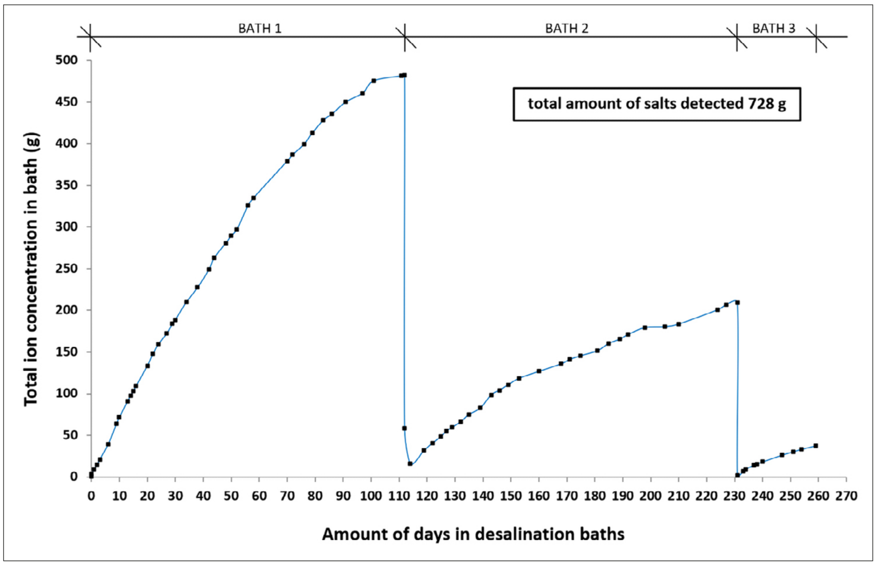

Figure 6. The total ion content in the baths over time (days) presented as the amount in weight (g)

Bio-contamination risk management

To avoid bio-contamination and the use of biocides, the bath was maintained in darkness by covering the tank with a black cloth. After each bath, the tank was cleaned with a wet sponge.

Drying and CDD sublimation conditions

The relief was left to dry out slowly in the tank for about 6 months until a constant weight was reached. When drying was considered too fast, the tank was partially covered. The RH and temperature in the tank and within

Figure 7. White crust formed on the surface immediately after the sublimation of the CDD

Figure 8. Detail of the memorial: before treatment (left); after treatment (right)

a drilled hole (3 cm long RH and T-probe) was measured throughout the drying process.

During the CDD sublimation that started during the drying process, an unexpected phenomenon occurred: on the Gothic text below the sculpted scene and on protruding parts, such as heads and hands, a white crust formed on the surface immediately after CDD sublimation (Figure 7). The white crust was later identified by micro-Raman spectroscopy (Renishaw) as gypsum. Given the high content of calcium sulfate detected in the first centimetre of the sculpture and the long-term desalination procedure, most of the gypsum had dissolved and diffused into the bath water. However, a small amount of calcium sulfate had remained in the solution just under the surface. When the CDD evaporated, the salt solution migrated rapidly to the surface through the porous polychrome layers and crystallised as efflorescence outside the pore structure and on top of the polychromy.

Post-desalination treatments and evaluation

The white gypsum crust was found to be quite hard and, as the underlying polychromy is water sensitive, the crust was mechanically removed by scalpel and an ultrasonic scaler. After this process, the sculpted forms and their polychromy became visible again.

The content of soluble salts was quantified after the desalination and was seen to have decreased from 2 wt% down to an average value of 0.2 wt% at a depth of 6 cm, excluding calcium sulfate. The gypsum content decreased from 7 wt% down to approximately 1 wt% in the first centimetre. At a depth of 6 cm, the content decreased from 2 to 0.2 wt%.

After drying, consolidation was performed with ethyl silicate on restricted weakened areas (red zone, Figure 5) and followed by several other conservation procedures, such as filling and retouching.

Examination of the surface and polychromy showed no bleeding or fading of the layers.

The forms appeared clearer after desalination (Figure 8).

A new presentation for the memorial in the church

After treatment, the memorial was installed on a stone pedestal in the northern chapel of Saint-Martin church. The relief is protected by a glass panel and illuminated with LED lamps.

CONCLUSION

The results of the experiments and case study show that cyclododecane, when applied as a melt, offers considerable protection for water-sensitive polychromy on limestone during a long-term water bath desalination. Important findings were noted concerning the success and risks of water bath desalination, while the surface of an object, where salts mainly accumulate, is protected with a temporary hydrophobic layer. More specifically, due to the protective layer, diffusion of ions into the water bath was slow, as the salts at the surface under the hydrophobic layer needed to dissolve and the ions needed to migrate up to 14 cm through the porous structure of the limestone into the bath water. Due to long-term immersion, it was important to continue IC measurements to identify the specific ions that were diffusing into the bath. With each measurement, the equilibrium between anions and cations was checked to identify calcium, which would indicate the presence of dissolved calcium carbonate. Given that the equilibrium remained stable throughout the process, it was deemed safe to continue the desalination. The long-term immersion in a high quantity of water also allowed more gypsum to dissolve and diffuse into the bath. After CCD sublimation, this translated into an unexpected and rapid efflorescence, gypsum crust formation, on top of the stone and polychrome surface. The final removal of the crust increased the visibility of the sculpted forms significantly when compared to the memorial's condition when first discovered. The memorial has been returned to the church and stands on a stone pedestal without any specific need for conditioning, as the salt content is considered sufficiently low.

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NOTE

[1] Cyclododecane is no longer available. Menthol would be an alternative but has yet to be extensively researched (Davidson et al. 2020).

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MATERIALS LIST

Cyclododecane
Kremer Pigmente
www.kremer-pigmente.com
Cyclododecane spray
Ephemeral GMBH
Kremer Pigmente
www.kremer-pigmente.com

Ethyl Silicate
Artisil SH 75 eco from Rewah

Hot-air hand tool
Leister Hot Jet S
Leister Technologies
www.leister.be

Ledan® TA1
Tecno Edile Toscana
www.tecnoediletoscana.com

Red bole
J. G. Eytzinger GmbH
Hansastraße 15
91126 Schwabach
Germany

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