INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 13, Special Issue 1, December 2022: 1603-1622 www.ijcs.ro

THE SEALING EFFECT OF CYCLODODECANE DURING THE RE-ADHESION OF FLAKING PAINT WITH METHYLCELLULOSE

Valeria-Santina MURGIA[1,*], Karolina SOPPA[1,*]

[1] Bern University of Applied Sciences – Bern University of the Arts – Fellerstrasse 11, 3027 Bern, Switzerland

Abstract

Many modern artworks exhibit flaking paint. Rarely restored, they hardly show any stains, so it is important that the absorbent canvas is not penetrated with unnecessary foreign material while re-adhering the paint layer. Such a situation was found with the painting "Cathédrale de Reims" from 1906 by the Swiss artist Annie Stebler-Hopf (1861–1918). In order to generate samples for the investigation into a temporary sealing of the canvas and re-gluing of the flaking paint, which should simulate the nature of the boundary surfaces of the original painting to be adhered as closely as possible, the artwork was first examined for the material components, solubility and absorbency. Protein residues were found on the textile support, given that proteins build up more tension while ageing, the decision was made to use the more age-resistant methylcellulose as adhesive for the samples and the following re-adhesion. With a controlled application, the penetration behaviour of the methylcellulose into the textile support was examined with admixed fluorescein-sodium. Following the positive results of the temporary sealing with Cyclododecane in isooctane, the artwork was treated in this way. This new method is simple and can be used without much equipment. It can prevent some paintings from stiffening, staining or building up tension due to adhesives penetrating the canvas.

***Keywords**: Cyclododecane; Re-adhesion; Flaking paint; Methylcellulose; Aliphatic solvents*

Introduction

The canvas painting "Cathédrale de Reims" was painted in 1906 by the Swiss artist Annie Stebler-Hopf[1] (1861–1918) and is property of the Kunstmuseum Bern[2] (Fig. 1). It was given to the Bern University of the Arts (BUA) for its conservation in 2020 due to its serious damages of the paint layers. The damages of the artwork, which are shown in Figure 2A and B, include, but are not limited to: delamination's between different paint layers; flaking paint which detaches from the ground revealing the textile support; paint losses; and concave deformed paint flakes which rise from the canvas along the edges of the detachments. To ensure an adequate conservation of the complex painting, it was important to broaden the knowledge about the artist and the artwork by doing profound research and examine the painting in all its facets. After gaining a better understanding of the artwork through some preliminary work by

* Author for correspondence: valeriasantina.murgia@students.bfh.ch; karolina.soppa@bfh.ch

[1] Annie Stebler-Hopf was born 1861 in Thun and died 1918 in Zürich (Switzerland). The Swiss artist was known for her various portraits and landscapes. Stebler-Hopf studied in Berlin under Karl Gussow (1843–1907) and later she was employed at the Royal Prussian Academy of Arts in the years between 1876 and 1881 as docent. In 1882 the artist moved to Paris where she became a member of the Académie Julian. The Académie was known to admit female artists who could benefit from the same study content as the male members (like nude painting) even though the students were divided in male and female groups.

[2] The artwork was a donation by Sylvia Y. Stebler, a relative of the artist, to the Kunstmuseum Bern in 2018.

creating a condition report and using imaging techniques (VIS, IRR and UV-fluorescence photography, X-Ray, and active thermography), some samples were taken from the different layers and examined via FTIR and SEM analysis to determine the used materials. This paper and the executed work, primarily focus on the problematic and the re-adhesion of the flaking paint which detaches completely from the canvas. Many modern and contemporary artworks on canvas exhibit flaking paint. In these rarely restored paintings, the textile support hardly shows any stains, so it is particularly important that it is not penetrated with unnecessary foreign material while re-adhering the paint layers.

Fig. 1. "Cathédrale de Reims" by Annie Stebler-Hopf, 1906, oil on canvas, 76,5 x 53,5 x 2 cm, recto, unframed, VIS

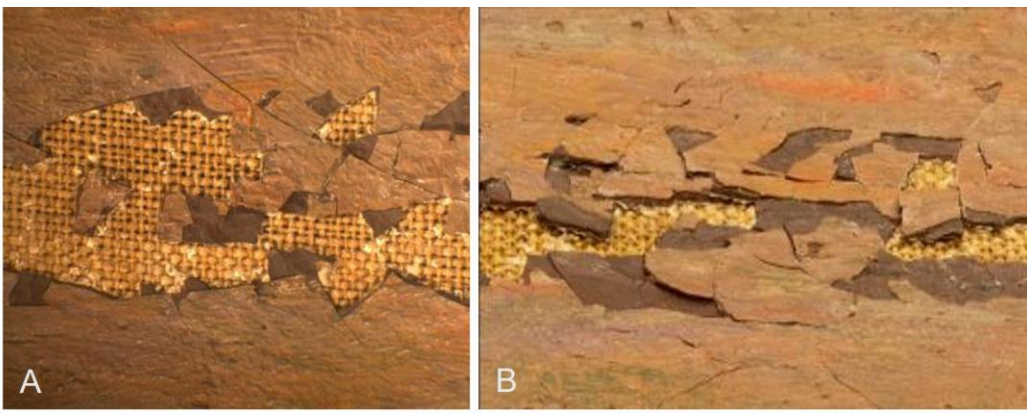


Fig. 2A. Detail of the damages: flaking paint, detachments, and paint losses; approx. 1 x 3,5 cm, frontal; **2B.** Additional details of the concave deformations; approx. 1 x 3,5 cm, photographed at approx. 45 °

The joining parts of the painting, consist of a highly absorbent canvas and the less absorbent paint flakes made of chalk ground and oil paint.

To evaluate the right adhesion agent, the joining parts must be analysed in solubility test with three solvents, also on their heath sensibility and absorbency. Solubility tests with the three most important solvents used for cleaning and as solvents for adhesives help to identify which solvents can be used safely during the re-adhesion. Following such tests on some micro-samples [1, 2] of the various components, it could be determined that none of the samples taken are soluble in deionized water, ethanol, or petroleum spirit 100–140°C. However, taking a bigger particle of a paint flake, it could be determined that the chalk ground swells lightly when coming in contact with water, while there was a slight change defined by the loss of the glossy surface when coming in contact with ethanol. However, this does not mean that adhesives dissolved in water cannot be used. Nevertheless, pure water should not be used if this swelling is to be avoided.

Through the FTIR analysis it was possible to find some protein residues on the canvas, lead white as well as wax, proteins, and carboxylates were found in the chalk ground. The paint layers showed mixtures of kaolinite, lead white, quartz, calcium carbonate and wax, it was possible to also identify traces of oxalates and carboxylates. Carboxylates are soluble in water similar to alcohols, aldehydes and ketones.

Due to the highly absorbent textile support, there is a risk that the canvas will, in case of re-adhesion of the flaking paint with consolidation agents, be impregnated with the adhesive and cause stiffening as well as staining. Using the wrong solvents and adhesives could affect the integrity of the chalk ground and the paint layer due to their advanced degradation.

The sealing of a textile painting support with aliphatic solvents and cyclododecane (CDD) solutions to prevent adhesives, like gelatine and emulsions, to penetrate in the raw unsealed textile support, has been previously demonstrated by Soppa [3, 4]. However, compared to protein glues, methylcellulose (MC) proves to be more advantageous in the following aspects: it has a very wide viscosity range, and has solution stability, transparency, less surface tension than protein glues, higher resistance to ageing and is less susceptible to mould [5-7]. In this case study it was important to re-adhere the flaking paint layers and thus create a bond between the chalk ground and the canvas.

To generate a successful result, one of the requirements for the ideal adhesive was that it has a viscosity which allows a good flow under the paint flake but, at the same time, does not get absorbed completely into the canvas. Is it possible to control the flow of a low viscose adhesive so that it does not penetrate the absorbent canvas but instead flows horizontally under the whole detached flake and forms a film between the paint layer and the textile support?

The used materials as the different methods used for the executed samples are described in the following sections. In the section “results and discussion” the findings of the different samples are described as well shown through UV photographs, then the sealing method applied in the process of sealing and re-adhering the flaking paint on the painting “Cathédrale de Reims” by Annie Stebler-Hopf is described. This last method is then presented through an illustrated step-by-step guide in the end of the paper.

Preliminary Work: Painting Technique and Materials

The preliminary work started with a condition report of the observed ageing phenomena and damages of the painting, and by analysing the artwork with non-invasive imaging techniques, such as VIS, IR-Reflectography, UV-Fluorescence, X-Ray and active thermography photography. After that, FTIR-Analysis of micro-samples and cross-sections, as well as microscopy and SEM of the embedded cross-sections, were then carried out to understand the structure and materials of the different layers. This way, the painting technique of the artist, as well as the used materials, could be defined and be understood a bit better.

Examining the verso of the painting, it could be observed that the textile support is formed by two different canvases which were sewn together in the lower part to create a new format (Fig. 3a and 3b). These textile supports differ extremely in their density, like it is shown in the Figures 3c and 3d. To create the reference samples described below, only the denser fabric was taken as example, given that the phenomena of the flaking paint which detaches from the canvas is only observed on the second textile.

Fig. 3. Details of the painting "Cathedrale de Reims": A - Verso of the painting - visible seam of the two canvases sawn together, B - Illustration of the structure of the textile supports with measurements of the single canvases, C - Close-up detail of the density of the textile support T1 in the upper part, 2 x 2 cm, Linen fabric: 13 threads/cm in vertical direction, 13 threads/cm in horizontal direction; tissue filling of 62,8% - light/sparse fabric [8], D - Close-up detail of the density of the textile support T2 in the lower part, 2 x 2 cm, Linen fabric: 30 threads/cm in vertical direction, 32 threads/cm in horizontal direction; tissue filling of 84,5% - dense fabric [8]

Painting technique

Through the imaging techniques, it was possible to observe changes in the motif, potentially made by the artist herself (Table 1). In IRR photography, it was possible to identify graphite drawings and guidelines traced by the artist for the architecture and position of the figures. What could be observed is that there were some adjustments made while painting, as some of the lines got ignored or their position changed slightly during the painting process. Even silhouettes of non-existent (not visible in VIS) figures could be identified. In the UVF images, some differences in the fluorescence are evident, the hidden figures are also visible in this case, given that they fluoresce differently from their surroundings.

Table 1. Comparison of the imaging techniques and their findings. The blue arrows in the IRR-photography show the graphite guidelines made by the artist to paint the architecture. The red arrows, present in every image, indicate the identified figures that are not visible in VIS images, these figures were overpainted in a second moment.

IRR

UVF

X-Ray

Active thermography – phase image

To have more clarity of a possible motif change, respectively an overpainting of the figures by the artist, an X-Ray examination was then carried out. On the X-Ray photograph, an overpainted group of seven people became visible on the left side, stretching its way to the lower corner and an ulterior figure was identified on the bench. The same group, on the left, could be identified with the active thermography. With this last imaging technique, more damages, like air pockets, detachments in between paint layers and paint losses, could be found.

An isolation or sealing of the canvas was not visible, however, some protein residues were found through FTIR analysis (see below: Analysis and Materials). For the ground it was possible to identify a white layer, just above the textile support, a second layer on top of it, is lightly beige-ochre coloured. After examination, it is not clear if this beige-ochre coloured one is a ground or a paint layer, it could be an underpainting to give a first base with an earthy shade to the composition. During the performed analysis, it was not possible to identify if this layer is present all over the surface of the artwork. Both layers are thick and opaque, however, the structure of the canvas remains visible on the surface of the artwork. Graphite drawings and guidelines, to sketch up the architecture and the overall composition of the artwork, seem to be located on top of these layers. The lines were probably executed with graphite. The observed paint layers are mostly brown, although, in one cross-section, which later was examined with SEM (scanning electron microscope, see below: Analysis and Materials Fig. 6), there are several diverse brown and blue layers. On the surface of the artwork, it is possible to observe the brush strokes, possibly from various smaller brushes with round pointed tips and some fan brushes to blend the colours into each other. In some parts where the artist painted with thicker paint layers, especially on the right side of the artwork, pastosities are visible (Fig. 4).

Fig. 4. Detail of the painting technique: pastosities and thick brush strokes are visible, marked with white arrows, photographed in VIS

For the colour palette, mostly dark and earthy hues were used (blue, grey, beige, and various brown tones), that dominate the artwork and represent the structure and the materiality of the cathedral. Some warm accents were given with different red, ochre and green hues, these details are mostly visible on the foreground of the painting. During the process, the artist used mixed techniques like wet-in-wet to create smooth transitions (Fig. 5a), in some parts the colours were dabbed on roughly (Fig. 5b), details were created on already dried paint and in some cases, colours were applied like glazes on top of other hues. The artist only painted to the visible edges, leaving the textile support nailed on the stretcher unpainted.

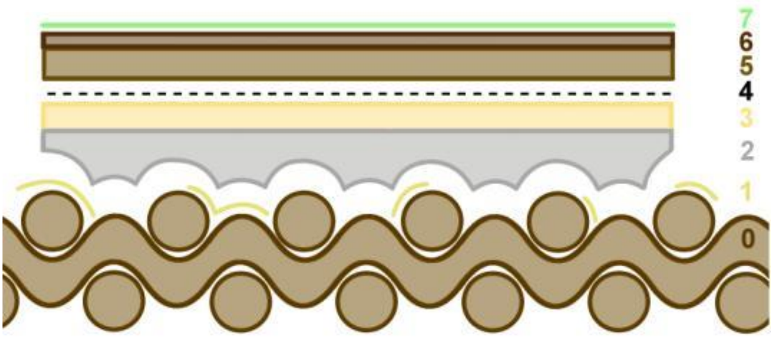
Fig. 5. Detail images of: **A.** The smooth blending of the colours inside the arched window, there are no harsh lines, which could be a hint for a wet-in-wet technique; **B.** The rough dabbing of the colours is visible in this image. It is possible that the artist also used round brushes for the dabbing, given that the shape seems to be circular.

Visually there could not be detected a varnish as top layer, however, different fluorescences were observed in the UVF photography. Some parts fluoresce bright orange under UV-light, this could be an indicator for a cadmium compound.

The signature "Annie Stebler-Hopf -1906-" was carried out in red, probably with a small round brush, near the left corner. It was possibly done, at the end, on the dried paint.

The whole layer structure of the painting technique is summarized in Table 2.

Table 2. Simplified image of the layer structure of the painting technique. In this case, it is possible to observe the examined and identified layers in a quite simple way. The layers are numbered from bottom to top, in the same way the artwork was painted by the artist. Given that it is not clear if a varnish is present, it is still represented in the image.



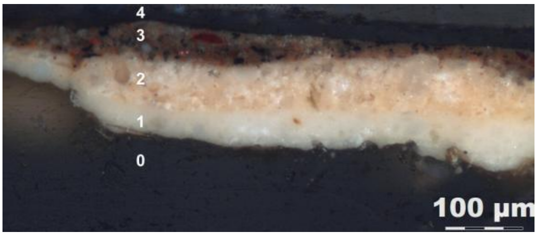
7 *Possible varnish or coating that fluoresces under UV-light (?)*
5-6 *Paint layers (can be more than two layers)*
4 *Graphite drawings and guidelines*
3 *Beige-ochre underpainting (second ground layer or paint layer)*
2 *Ground layer (whiteish in colour)*
1 *Protein residues*
0 *Canvas*

Analysis and Materials

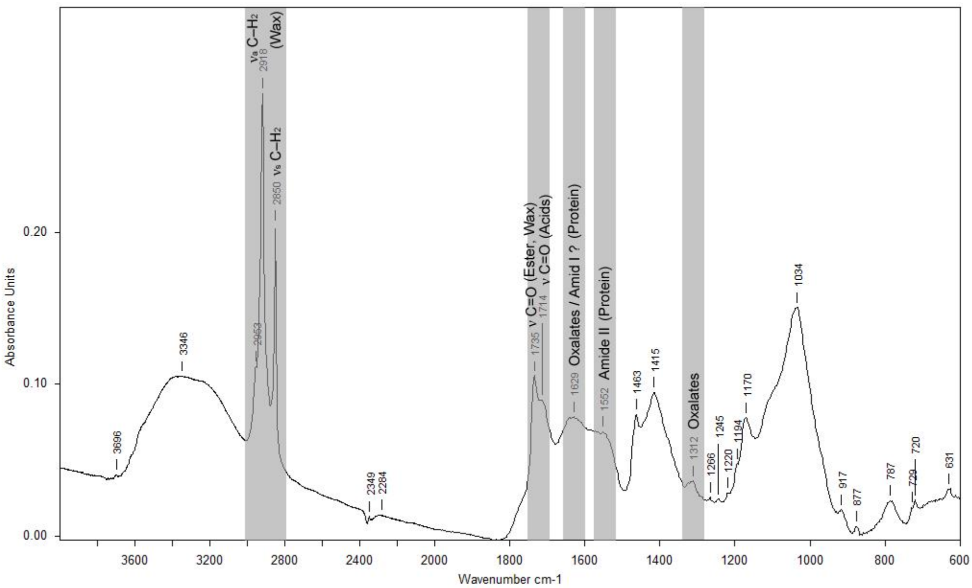
Micro-samples and cross-sections were taken from the painting to analyse them through microscopy, FTIR and SEM. Under the microscope, it was possible to see the different paint layers and the structure of the paint flake. The taken samples were then tested on their solubility in deionized water, ethanol and petroleum spirit 100–140 °C, where the paint flake swelled lightly in water (but absorbed less water than the canvas) and lost the glossy surface when coming in contact with ethanol.

The findings of the FTIR analysis are gathered in the following Table 3.

Table 3. Cross-section of a paint flake embedded into Araldite 2020 resin, photographed with a microscope[3] with 10x objective in BF mode with crossed polarizers. The FTIR[4] analysis were executed on the cross-sections, as well as micro-samples, which were taken from the different layers with a tungsten needle. The results of the FTIR analysis were interpreted by Dr. Stefan Zumbühl at the BUA.



***4** Crystalline Efflorescences (on the surface of the cross-section, not visible in the photograph, analysed through micro-samples):* Wax, esters, acids and oxalates. Protein content cannot be excluded. Partially hydrolysed wax.

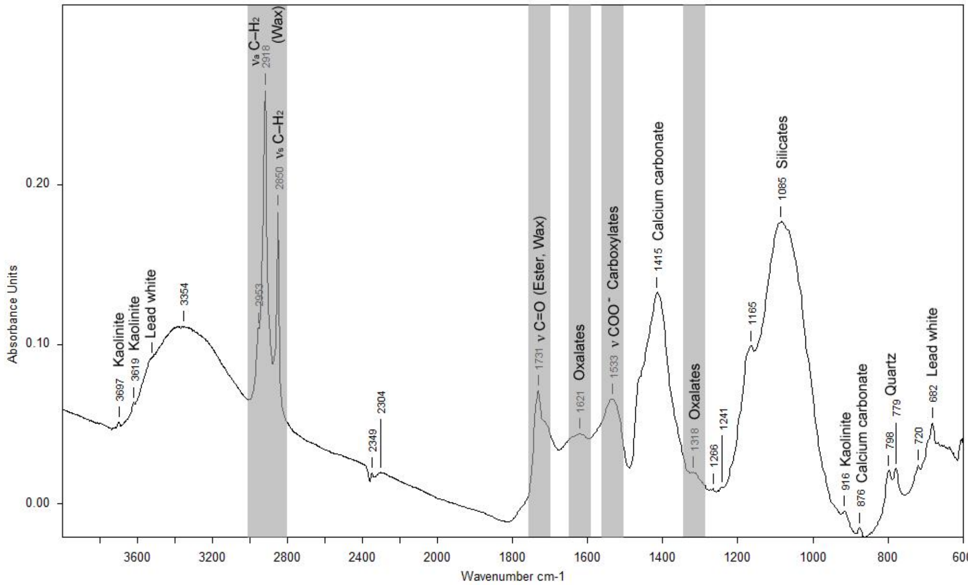


---

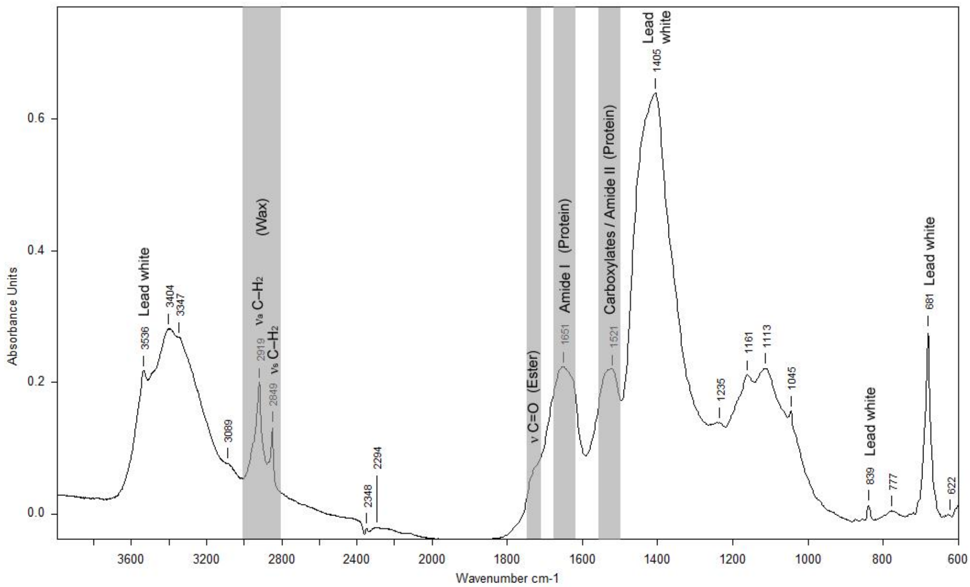
[3] Leitz DMRB, equipped with Vis and UV (CoolLED pE-300white) light and filters: DF = dark field; BF = bright field, A = UV BP340-380 LP430; I3 = blue BP450-490 LP515; BP = band-pass filter; LP = long-pass filter. Digital microscope camera: Jenoptik ProgRes Speed XT Core 3 with a resolution of 2080x1542 Pixel

[4] Bruker Lumos: - single element LN-MCT detector 10000-600cm-1 / settings: 64 scans / 4 cm-1 resolution / range 4000- 600cm-1

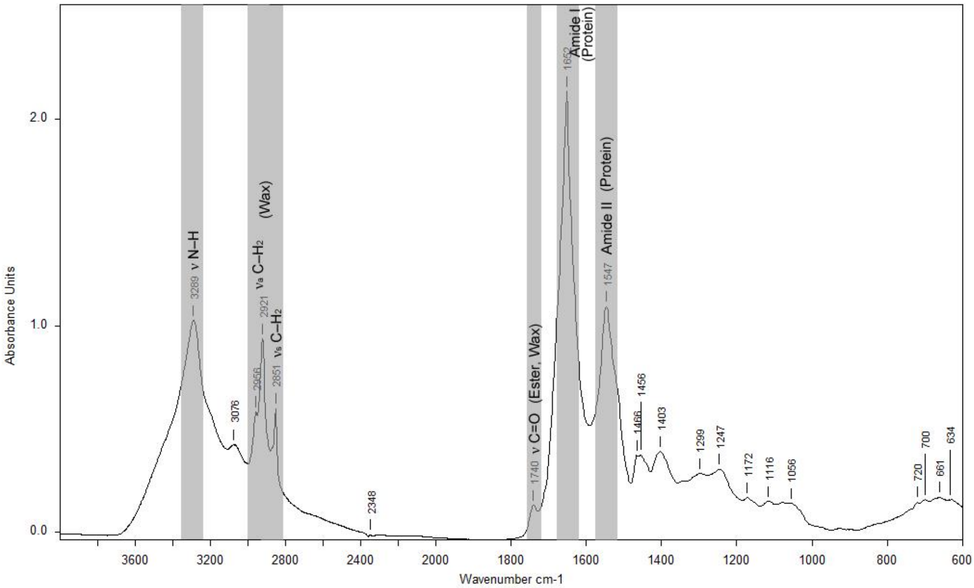
2–3 *Paint layers (or beige-ochre underpainting and brown paint layer; analysed through the embedded cross-section):* Mixtures of kaolinite, lead white, quartz, calcium carbonate, wax, esters and silicates. It was also possible to identify traces of oxalates and carboxylates, mostly in the brown layer. Protein content cannot be excluded.



1 *Ground layer (analysed through the embedded cross-section):*
Lead white, wax, esters, proteins, carboxylates.



***0** Canvas (not shown in the cross-section photograph – analysed through micro-samples):*
Protein, residues of waxes.



It was possible, with the SEM analysis of another cross-section (Fig. 6), to identify three different pigments present within the paint layers. Different particles were analysed, and the results interpreted by Dr. Nadim Scherrer at the BUA (Table 4).

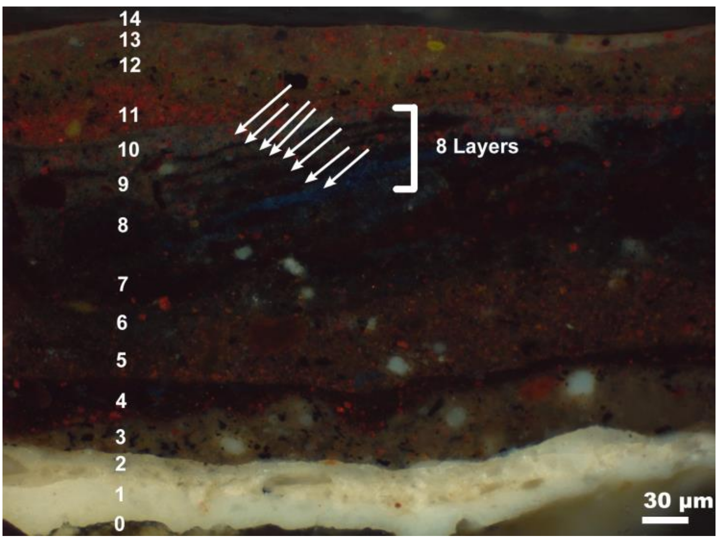
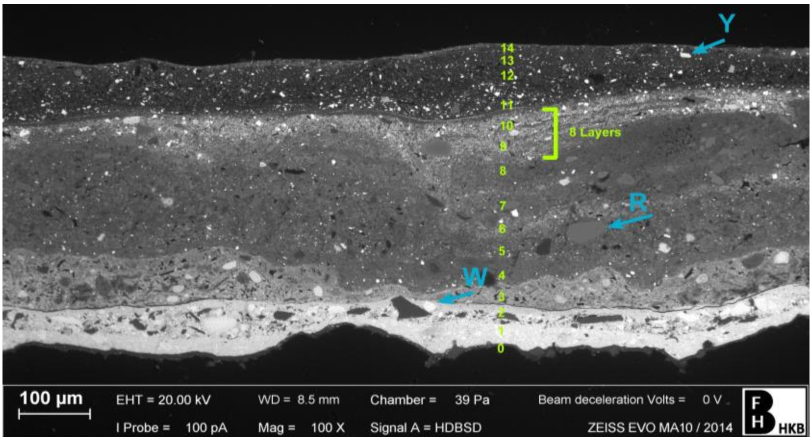


Fig. 6. Detail of a second cross-section with many paints layer, photographed with the microscope with a 20x objective in BF mode with crossed polarizers. White arrows indicate the 8 paint layers found only in this part of the sample, it possibly indicates one of the overpainted sections

Table 4. Cross-section of a paint flake embedded into Araldite 2020 resin, analysed with SEM (ZEISS EVO MA 10)[5] and interpreted by Dr. Nadim Scherrer at the BUA. The blue arrows indicate the examined particles



***Yellow particle** (in the top paint layer):* Lead red
***Red particle** (in a middle paint layer):* Vermilion
***White particle** (in the ground layer):* Lead white

Experimental

Materials

Reference Samples

As an underlaying mat, a piece of black reticulated polyurethane foam was used below the canvas, this accelerates the drying process due to the air flow and avoids capillary suction [10]. For the textile support, a previously washed (60°C) and ironed (at approx. 230°C) piece of raw unsealed canvas was used (approx. 5x1cm), which possesses similar characteristics such as the density and absorbency of the original painting[6] (linen, 30 threads/cm in vertical direction, 32 threads/cm in horizontal direction). The paint flakes used for the reference samples, were made of chalk ground with a similar absorbency and solubility. An alkyd coating to mimic oil paint and its characteristics was applied on top of the chalk ground [4].

Adhesives

As for the adhesive, methylcellulose was chosen as stated before. MC can cover a wide viscosity range of approx. 5–75’000mPa·s, varying on concentration, chain length, temperature during the preparation of the solution, and degree of polymerization (DP) [9]. The adhesive needed to be of low viscosity to be able to flow under the paint flake, but at the same time not too low for it to be completely absorbed into the canvas. In Figure 7 it can be observed how an MC A4C 2% solution has the same viscosity of 300 mPa·s as an MC A15 5% solution, however, the latter has less water in the mixture and therefore, should dry faster and bring less moisture into the textile support. After some pre-tests with various concentrations of A4C and A15 (viscosity range of 50–50’000mPa·s), it was found that a viscosity of max. 300mPa·s worked best for this kind of re-adhesion. Therefore, MC A15 5% solution in deionized water

---

[5] Zeiss EVO MA 10 (2014), W-cathode, variable pressure; High vacuum mode: < 10-5mbar VP-Mode: 10 to 400 Pa (0.1mbar – 4mbar); Detectors: SE-Detector; LM 5SBSD-Detector; Framestore max. 3072x2304 pixels Gun: W-Filament; Acceleration Voltage = 0.2 to 30kV; Probe Current: 0.5pA to 5µA Accessories: Beam deceleration kit (to put bias voltage on a single holder); Beamsleeve-1000 (to minimise skirt effect in VP); 3DSM Surface Modelling software package (with 5SBSD Detector) Motorised stage: 5-axes stage: X=80mm, Y=100mm, Z=35mm, T=-10 to 90°, R=360°, max. sample height=100mm

[6] Linen fabric; 30 threads/cm in vertical direction, 32 threads/cm in horizontal direction; tissue filling of 84,5% - dense fabric (according to Rouba and Lipinski [8])

was chosen for the samples, given that it has a shorter chain length than the A4C. Due to the reduced chain length, it needs a higher concentration to reach a viscosity of 300 mPa·s, which means less water is needed in the mixture. To ensure its accurate examination, fluorescein-sodium was added to the MC solution, allowing the visualization of the penetration behaviour of the methylcellulose under UV light and the fluorescence microscope, this is a fast and inexpensive method to track the water-based solution [10], unlike to other publications [11, 12] where attempts were made to covalently bind the fluorochrome to the methylcellulose in elaborate steps. Since the small fluorescein-sodium will penetrate the chalk ground most likely with the water in the methylcellulose solution, is possible that the MC does not completely reach all the spaces in which later a fluorescence can be lightly perceived.

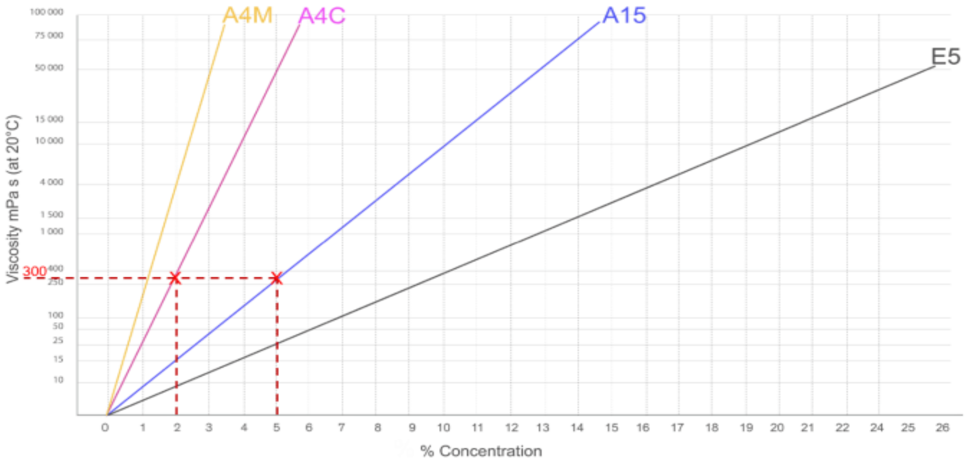


Fig. 7. Viscosity graph of methylcellulose.
Marked in red: the viscosity of 300 mPa·s for the solutions A4C 2% and A15 5%

Sealings

What was most important was that the aliphatic solvents and cyclododecane solutions did not damage the joining parts and/or the adhesive by changing or dissolving their structures, therefore, petroleum spirit 100–140°C, Shellsol T, cyclododecane in petroleum spirit 100–140°C and cyclododecane in isooctane were tested.

Sealings with Aliphatic Solvents

The solvents were chosen for their different vapour pressures. The higher the vapour pressure, the faster the solvent evaporates [2].

- Isooctane (vapour pressure 5.1 kPa at 20 °C)
- Petroleum spirit 100–140°C (vapour pressure 2 kPa at 20 °C)
- Shellsol T (vapour pressure 0.11 kPa at 20 °C)

It is also important for the solvents to be safe for conservators and restorers to use, therefore, care was taken, that the aromatic content in the chosen solvents was about 0%.

Sealings with Cyclododecane Solutions

Cyclododecane has the advantage, in contrast to aliphatic solvents, that the hydrophobisation of the textile support lasts longer due to its long sublimation time (vapour pressure of 0.003152 kPa at 20 °C). The CDD sublimates faster and can be applied contactless onto the canvas if it is in a solution, this is why the CDD was mixed with aliphatic solvents into saturated solutions. In this case, the slower the solvent evaporates, the deeper the CDD penetrates into the canvas, therefore, solvents like petroleum spirit 100–140°C and isooctane with a high vapour pressure were used to create the solutions [6, 13]. Like this it is possible to create a slight sealing near the surface of the textile painting support to favour the forming of a methylcellulose film or bond between the joining parts.

Methods

Penetration and Adhesion after Sealing with Aliphatic Solvents

Reference Sample 0 without Sealing

In the reference sample 0, the previously washed and ironed (respectively at approx. 60°C and 230°C) piece of raw canvas (about 5x1cm) was placed on top of the black reticulated polyurethane foam. 7µl of the methylcellulose A15 5% solution with fluorochrome was applied. The paint flake was then positioned on top of the adhesive drop with tweezers and lightly pressed down on it with a colour shaper.

Sealing with Petroleum Spirit 100–140°C and Sealing with Shellsol T

For the sealing with petroleum spirit 100–140°C and the sealing with Shellsol T, the used method differed from the reference sample 0 by sealing the canvas by applying 100µl of the sealing solvent with a micropipette on the textile support before applying the adhesive.

Penetration and Adhesion after Sealing with Cyclododecane

Sealing with Cyclododecane in Petroleum Spirit 100–140°C

In this reference sample with the saturated solution of CDD in petroleum spirit 100–140°C as sealing, an additional 60 minutes evaporation time between the application of the solution and the application of the methylcellulose was observed. This evaporation time is needed for the petroleum spirit to evaporate almost completely from the solution in order for a CDD coating to form between the individual threads of the canvas which, in the end, seal the textile support.

Sealing with Cyclododecane in Isooctane

With the saturated solution of CDD in isooctane sealing, only a 30 minutes evaporation time was needed, given that isooctane evaporates at a much faster rate than petroleum spirit. Afterwards the sample was treated like the previous ones.

Methylcellulose Application from the Side of the Paint Flake

For the following reference samples, the method was slightly adjusted to more accurately simulate the original situation of the painting by Annie Stebler-Hopf. The paint flakes of the artwork that need to be treated, are not completely detached from the textile support and would not be possible to be handled like the simulation in the other previous samples by positioning and pressing the paint flakes onto the adhesive. The paint flakes which need to be re-adhered to the canvas, are near losses, which means there is at best only 1–2 sides of the flake which are accessible. This caused a need to find a method to apply the adhesive evenly under the paint flake, without damaging it nor the rest of the surrounding paint layer and area. In these samples, the paint flakes were directly positioned on the canvas from the beginning. To examine the penetration of the methylcellulose into the canvas, all the following samples, with the methylcellulose application from the side of the paint flake, were photographed from recto and verso under UV light (Hönle UVAHAND LED 315–400 nm, a simple blue light can also be used as convenient alternative). Additional to the normal UV-fluorescence photographs, these samples (a–c) were cut in half, embedded in the resin Araldite 2020 and photographed with the fluorescence microscope[7]. The fluorescence of the flow and penetration of the methylcellulose, and therefore a successful sealing of the textile painting support, would be more visible in the cross-sections thanks to the vertical cut through the samples. The more complex embedding in the soft Technovit 7100 and thin sections as described in [6] were not used here, because in this case the information about where the adhesive solution mainly penetrated was sufficient. Theoretically, a cut through the samples with a new, sharp razor blade and a vertical examination of the canvas without embedding is also sufficient to locate the general disposition of the adhesive. However, these non-embedded results are more difficult to photograph.

Methylcellulose Application from the Side, Reference without Sealing

This reference sample (a), was created to show the effect of the side application of methylcellulose without previously sealing the textile support. Here, 7 µl of fluorochromed

[7] Leitz DMRB light microscope, filter A UV BP340–380 LP430 and I3 blue BP450–490 LP515 (I3 was used for the microscopic photographs), light source CoolLED PE300 white. Camera Jenoptik ProgRes Speed XT Core 3, 2080 x 1542 Pixel, software ProgRes Capture Pro.

methylcellulose A15 5% was applied from one side of the paint flake with the micropipette and the flake moved up and down with a colour shaper to spread the adhesive horizontally underneath the whole flake thanks to the motion.

Methylcellulose Application from the Side, Sealing with Cyclododecane in Isooctane

A saturated CDD in isooctane solution was then used for reference sample b. In this sample, 100µl of the CDD solution was applied on one side of the paint flake onto the textile support, then the 30 minutes evaporation time for the isooctane was observed. After the waiting period, 7µl of the methylcellulose was applied with a micropipette on the same side of the paint flake, the latter was then moved up and down with a colour shaper to again spread the adhesive underneath it.

Methylcellulose Application from the Side, Sealing with Cyclododecane in Isooctane, Heating Spatula at 55-60 °C

Reference sample c, was carried out exactly like the previous one (b), except that the drying process of the methylcellulose was modified. All the previous reference samples, with the different sealing methods, were left to dry naturally on the reticulated polyurethane foam, for this sample however, the idea came up to use a heating spatula to dry and/or gel the methylcellulose underneath the paint flake to speed up the drying process and eventually, at the same time, flatten the concave deformed paint flakes in one single step. Methylcellulose gels at approx. 55 °C [14]. To not damage the paint layer but still be able to flatten some deformed flakes, the heating spatula was used at a distance of approx. 0,5 cm from the painting, so that 55–60 °C reached the surface of the artwork. A piece of melinex foil, with one siliconized side, placed on the surface of the flake as protection and the heating spatula was used in circular motions above it to evenly heat up the whole interested area. This last method is optional but would be of great help if needed to also reduce some deformed paint layers.

Results and discussion

Penetration and Adhesion after Sealing with Aliphatic Solvents

Reference Sample 0 without Sealing

In the reference sample 0, the methylcellulose was directly applied on the textile support without sealing it in any way. What can clearly be observed is how the adhesive penetrated through almost the whole textile and found its way in and around the threads. The excessive fluorescence on the verso (Table 5, reference sample 0, verso) is a clear indication of the high absorbency of the textile support. The paint flakes did not adhere to the textile painting support given that the adhesion was not enough due to the methylcellulose penetrating through the canvas and therefore not forming a bond between the paint flake and the canvas.

Sealing with Petroleum Spirit 100–140°C

The first sealing with petroleum spirit 100–140°C shows how the methylcellulose again penetrated right through the canvas, this time, with a smaller diameter as the reference sample (Table 5, sealing with petroleum spirit 100–140°C, verso) This is an indicator that the methylcellulose stayed less time on the surface of the sealed canvas and instead, flowed vertically directly into it. After the drying process (approx. 48 hours), the adhesion was examined by manipulating the textile support. Given that the adhesive penetrated through the canvas, it did not form a strong film or bond between the chalk ground of the paint flake and the surface of the canvas. In this case with petroleum spirit 100–140°C, most of the paint flakes fell off due to the weak bond.

Sealing with Shellsol T

As second sealing, Shellsol T was used. This change was made with the thought that Shellsol T has a longer evaporation time than petroleum spirit and would remain on the surface longer causing the adhesive to spread more in the horizontal direction, however, the sealing effect was not enough to prevent the methylcellulose from penetrating directly into the canvas (Table 5, sealing with Shellsol T, verso) In this case too, after manipulation by turning the sample to take the UV photographs, some paint flakes fell off.

Penetration and Adhesion after Sealing with Cyclododecane

Sealing with Cyclododecane in Petroleum Spirit 100–140°C

In the third sealing sample, a saturated solution of cyclododecane in petroleum spirit 100–140°C was used. The cyclododecane of the solution would then sublimate spontaneously after some time from the back of the painting thanks to the reticulated polyurethane foam that permits air flow. This test series brought great results. Examining the verso of the canvas (Table 5, sealing with CDD in petroleum spirit 100–140°C, verso), it was observed that the adhesive spread horizontally but only penetrated the canvas between the gaps of the individual threads. None of the paint flakes fell off during the manipulation of the canvas, showing a strong adhesive bond.

Sealing with Cyclododecane in Isooctane

A similar method was applied in the fourth sealing sample. Here a saturated cyclododecane in isooctane solution was used instead. Since isooctane evaporates faster than petroleum spirit 100–140°C, an evaporation time of only 30 minutes was observed after the application of the solution. This test series was then carried out the same as the previous ones. These samples brought excellent results as the adhesive stayed on the surface and spread evenly under the paint flake. It slightly penetrated between the gaps of the canvas, but overall, it exceeded the set expectations, as seen from the fluorescence on the back (Table 5, sealing with CDD in isooctane, verso).

Methylcellulose Application from the Side of the Paint Flake

After the satisfactory results of the reference sample with the CDD in isooctane sealing, the test series was continued and brought to the next step. In these samples (a–c), the aim was to more accurately simulate the original situation of the painting. The paint flakes were directly positioned on the canvas from the beginning and the CDD and MC solutions were applied from one side of it onto the canvas.

Methylcellulose Application from the Side, Reference without Sealing

The reference sample (a) demonstrates again the absorbency of the unsealed textile support (Table 5, sample a, verso). The methylcellulose was applied from one side of the paint flake and moving the flake up and down with a colour shaper, the adhesive was able to be spread horizontally underneath it. In the UV-fluorescence photographs of the recto it is possible to observe that the adhesive was applied from the right side of the paint flake (Table 5, sample a, recto). To examine the flow and penetration behaviour in a clearer form and better visualize it, the sample was cut in half, embedded in resin and also photographed with the fluorescence microscope (Table 6, sample a). Beyond being able to observe on which side the methylcellulose was applied, given that it leaves a fluorescence on the side of the paint flake, it was also possible, thanks to this examination technique, to analyse the exact progress of the adhesive inside the canvas.

Methylcellulose Application from the Side, Sealing with Cyclododecane in Isooctane

For the sealing with cyclododecane in isooctane and side application of the methylcellulose (sample b), the cyclododecane solution was applied with the micropipette on one side of the paint flake, then a 30 minutes evaporation time for the isooctane was observed. After the evaporation time, the CDD coating sealed the canvas. The fluorochromed MC A15 5% solution was also applied on the same side of the paint flake. Thanks to the up and down motion of the flake with the colour shaper, the methylcellulose was able to spread horizontally under the whole paint flake. After the drying process the sample was again photographed under UV light. On the verso it is possible to see how, thanks to the sealing of the textile support, the low viscose methylcellulose did only barely penetrate through the gaps of the threads (Table 5, sample b, verso). There could not be detected a fluorescence in other parts of the threads. In the cross-section (b), a satisfactory fluorescent film of methylcellulose formed between the paint flake and the canvas, creating a good bond between the joining parts. Only a slight fluorescence can be seen inside the chalk ground, this is due to the small amount of water-bound fluorochrome that has migrated into it and can thus be ignored (Table 6, sample b).

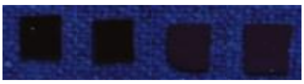
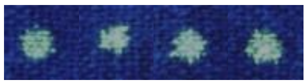
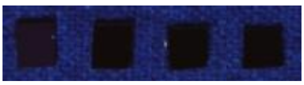
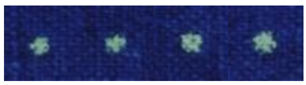
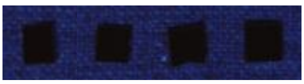
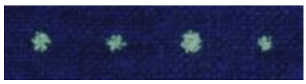
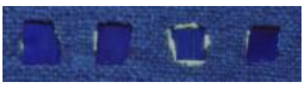
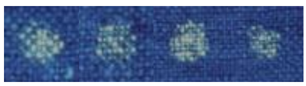
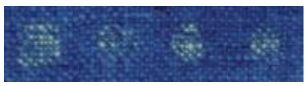
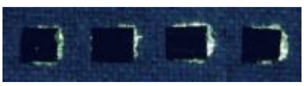
Methylcellulose Application from the Side, Sealing with Cyclododecane in Isooctane, Heating Spatula at 55-60°C

In reference sample c, the drying process of the methylcellulose was modified. All the previous samples were left to air dry on the reticulated foam, for this sample however, the methylcellulose underneath the paint flake was gelled thanks to the use of a heating spatula.

The heating spatula was set in the manner that approx. 55–60°C reached the surface of the paint flake. With this optional method it was possible to dry and/or gel the MC within one minute and reduce the deformed paint flakes at the same moment. The UV photographs do not show great deviations from the results of sample b (Table 5, sample c, recto and verso), however, thanks to the accelerated drying process, it is possible to see a slight change of the fluorescence inside the chalk ground by observing the cross-section (Table 6, sample c). This is probably due to the shortened drying period, the water inside the methylcellulose mixture did, presumably, not have enough time to spread and find its way into the chalk ground. Overall, this sample too, brought great results by forming a uniform methylcellulose film between textile painting support and flaking paint thanks to the sealing with a CDD in isooctane solution. This sealed the canvas efficiently and, therefore, hydrophobized it.

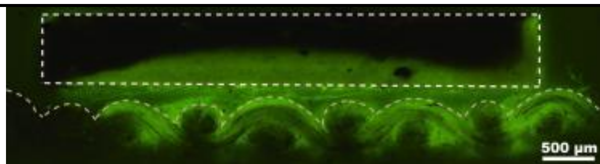
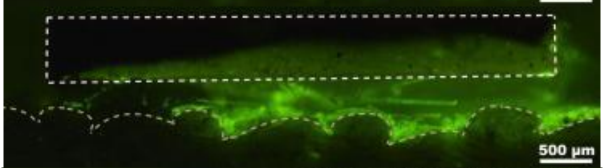
All the reference samples were collected in Table 5 to compare the different sealing methods of the textile painting support and the flow of the methylcellulose thanks to the UV photographs.

Table 5. Comparison of the reference samples, recto and verso of the different sealing methods. The bigger the fluorescent surface, the better, because this shows that the adhesive formed a horizontal film between the chalk ground of the paint flake and the surface of the textile painting support ensuring a good adhesion between the joining parts

Sample/Sealing	Recto	Verso
Reference sample 0, without sealing		
Sealing with petroleum spirit 100–140°C		
Sealing with Shellsol T		
Sealing with CDD in petroleum spirit 100–140°C		
Sealing with CDD in isooctane		
(a) MC side application, reference without sealing		
(b) MC side application, sealing with CDD in isooctane		
(c) MC side application, sealing with CDD in isooctane, heating spatula at 55–60 °C		

In Table 6, it is possible to observe the cross-sections photographed with the fluorescence microscope of the reference samples where the methylcellulose was applied from the side of the paint flakes (a–c). Here it is possible to compare the penetration of the methylcellulose and the forming of a film (or bond) between the joining parts.

Table 6. Comparison of samples 5a–5c, UV-fluorescence microscopic photographs of the cross-sections 2,5x lens

Sample	Sealing	Cross-sections
a	MC side application, reference without sealing	
b	MC side application, sealing with CDD in isooctane	
c	MC side application, sealing with CDD in isooctane, heating spatula at 55–60 °C	

The Re-Adhesion of Flaking Paint of the Artwork by Annie Stebler-Hopf

After the very satisfactory results of the reference samples with a CDD in isooctane sealing, this sealing method was used to hydrophobized the canvas of the painting “Cathédrale de Reims” by Annie Stebler-Hopf. The artwork was raised from the ground by approx. 15 cm thanks to wooden bars that were positioned under the stretcher of the painting. To document the sealing and re-adhesion process of the backside of the painting, a smartphone (due to the zooming and resolution capacities) was placed underneath it and the process was filmed and photographed from underneath. Like in the various samples, the black reticulated foam was placed underneath the canvas (starting point, Fig. 8A), then the saturated CDD in isooctane solution was applied with a micropipette on the textile support through a gap of a paint loss until the surrounding canvas was completely saturated with the solution. Due to the application of the sealing solution, the canvas temporarily darkened because of the isooctane (Fig. 8B), then, a 30 minutes evaporation time was observed. Once the 30 minutes passed, the canvas possessed still a slight discoloration and darkening from the isooctane. On the backside of the painting, thanks to the documentation with the smartphone, it could be observed that some CDD settled between the threads of the canvas (Fig. 8C). Afterwards, the MC A15 5% solution (this time without adding fluorescein-sodium) was applied on the side of the flaking paint. The affected paint flakes were then moved up and down with a colour shaper, in this case, some movement could be observed from the verso of the canvas (Fig. 8C). A melinex foil, with the siliconized side turned towards the paint layer, was placed on top of the area and the methylcellulose underneath the paint flakes was then dried/gelled with the heating spatula at approx. 55–60°C. At the end, after the complete drying process, no differences or modifications of the canvas were seen in comparison to the starting point. It was possible to execute the sealing and the re-adhesion onto the original artwork in the exact same way as in the samples. The method did not need to be modified while advancing in the procedure and could be performed like planned. The sealing with the saturated cyclododecane solution and the re-adhesion of the flaking paint with methylcellulose did not leave any stains on the reverse side of the painting.

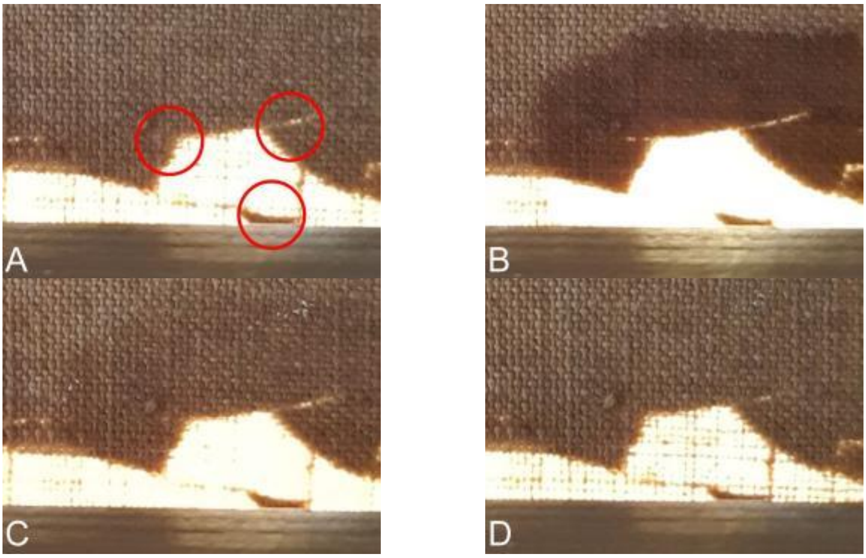


Fig. 8. Sealing and re-adhesion process on the original artwork seen from the verso of the painting by Annie Stebler-Hopf, approx. 7 x 5 cm, photographed with the Samsung Galaxy S10 smartphone front camera (10MP dual pixel auto focus). Part of the stretcher can be seen in the lower part of the images, the paint flakes that need to be re-adhered and/or flattened are marked in red:
A. Starting point before the sealing. The raw unsealed canvas can be observed.
B. During the sealing. The saturated CDD in isooctane solution was applied with a micropipette, the saturated area of the canvas darkened because of the impregnation.
C. After the 30 minutes evaporation time. It is possible to still see a slight darkening of the textile support because of the sealing solution, in this state the methylcellulose A15 5% was applied and afterwards dried/gelled with the heating spatula.
D. This shows the final stage of the process in which the methylcellulose dried completely, and the sealing solution evaporated from the textile support.

Conclusions

Thanks to the reference samples tailored to the original, it was possible to find a method which can efficiently seal a textile painting support with a saturated cyclododecane in isooctane solution to be able to re-adhere flaking paint with a low viscose methylcellulose. An MC A15 5% was found to be better, in this case, than the A4C 2% solution, given that it needed less water for the same viscosity of 300mPa·s. The visualization, and thus the examination, of the flow and penetration behaviour of the methylcellulose into the textile support was improved thanks to adding fluorochrome-sodium into the adhesive. This made it possible to use UV-fluorescence lamps and a fluorescence microscope to analyse the samples.

In the following illustration (Fig. 9), one can see the re-adhesion of the paint flake without the previous sealing of the textile painting support. In this case, the fluorochromed methylcellulose would penetrate right through the joining parts. This was the condition which needed to be improved.

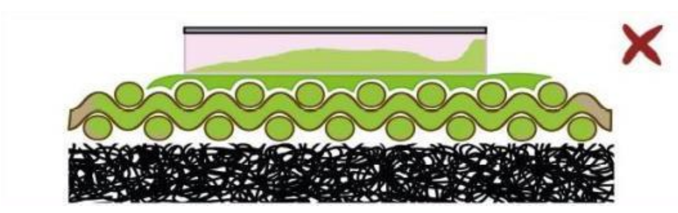
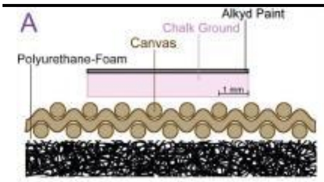


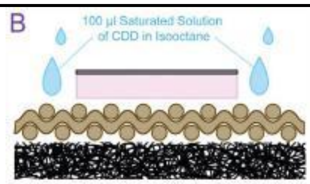
Fig. 9. Re-adhesion without sealing, the fluorochromed MC penetrated through the joining parts.

During the work, following step-by-step instruction was illustrated, for the sealing and re-adhesion procedure to achieve a successful result:

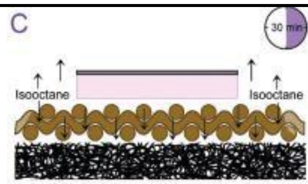
Table 7. Step-by-step illustration of the method of re-adhesion of flaking paint with CDD in isooctane sealing, with the optional step of drying/gelling the methylcellulose solution with a heating spatula



Starting point and used materials

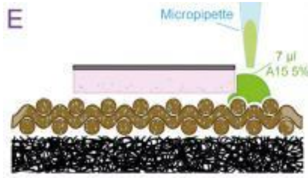


100 µl of saturated CDD solution in isooctane were applied from the accessible side on the raw canvas

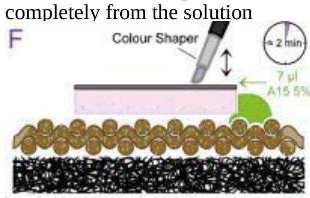


Before applying the adhesive, an evaporation time of approx. 30 minutes was observed allowing the isooctane to evaporate almost completely from the solution

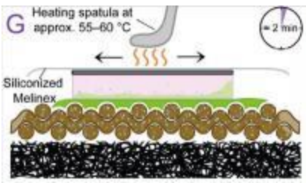
The evaporation of the isooctane left CDD behind that formed in between the individual threads and sealed the canvas



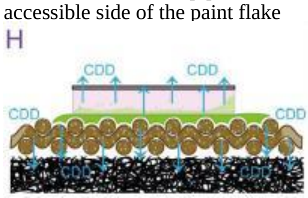
7 µl of a 5% solution of MC A15, in deionized water mixed with fluorescein, was applied to the canvas with a micropipette on the accessible side of the paint flake



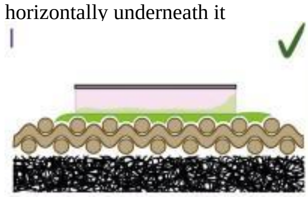
After applying the adhesive, the paint flake was moved up and down with a colour shaper for approx. 2 minutes to distribute the MC horizontally underneath it



The following step is optional. It is possible with a heated spatula at approx. 55–60 °C to dry/gel the MC underneath the paint flake, allowing the faster formation of a solid film. This step can be used, if needed, to flatten and re-adhere the flaking paint in one single step



The CDD sublimates from the canvas through the back thanks to the air-permeable polyurethane foam



Final stage of the process with a successful re-adhesion

The results clearly show an achievement of a temporary sealing using the cyclododecane in isooctane solution. This method could now be applied to an artwork. The modern canvas painting by Annie Stebler-Hopf from the Kunstmuseum Bern was treated in this way.

Thanks to the previous sealing with the CDD in isooctane solution, the low viscose methylcellulose did not leave any stains on the verso of the textile support. The use of a heating spatula during the re-adhesion process, helped reduce the concave deformations and uneven edges of the flaking paint. This new method is simple and can be applied by any conservator and restorer without any specific equipment. It could prevent canvas paintings from staining, becoming rigid or build up tension due to consolidation agents.

Acknowledgments

The authors are grateful to the Kunstmuseum Bern and especially to Nathalie Bäschlin for the opportunity to work on the painting by Annie Stebler-Hopf. To the Bern University of the Arts, we thank Katja Friese for the organization and the support during the preliminary work, Cornelius Palmbach for the active thermography photographs, Thomas Becker for the X-Ray examination of the painting, Stefan Zumbühl and Nadim Scherrer respectively for the interpretation and assistance of the FTIR and SEM analysis.

References

[1] S. Zumbühl, *"Wie geht das?" - Die Löslichkeit von Materialien: Teil III: Lösemittelevaluation und Löslichkeitstests*, **Zeitschrift für Kunsttechnologie und Konservierung, 31**(2), 2017, pp. 273–275.

[2] S. Zumbühl, **Solvents, Solvation, Solubilization and Solution: The Solubility of Materials**, HDW Publications, Bern, 2019.

[3] K. Soppa, *Wegweisende apolare Lösungsmittel? Teil I: Vorabsperrung textile Bildträger und Kreidegrundierung durch apolare Lösungsmittel zur Malschichtklebung mit Gelatine*, **Zeitschrift für Kunsttechnologie und Konservierung 30**(2), 2016, pp. 363–378.

[4] K. Soppa, *Pre-Wetting and Masking with Aliphatic, Non-Aromatic Solvents during Re-adhesion of Chalk Ground Flakes and Alkyd Paint Flakes with Acrylic Dispersions: New Insights into an Old Technique*, **AIC Paintings Speciality Group Postprints 32**, 2019, pp. 195–206.

[5] S. Zumbühl, *Proteinische Leime - Ein vertrauter Werkstoff? Aspekte zum feuchtephysikalischen Verhalten von Gelatine*, **Zeitschrift für Kunsttechnologie und Konservierung 17**(1), 2003, pp. 95–104.

[6] K. Soppa, **Die Klebung von Malschicht und textilem Bildträger**, Dissertation, Stastliche Akademie der Bildenden Künste Stuttgart, 2018.

[7] S. Steger, G. Eggert, W. Horn, C. Krekel, *Are cellulose ethers safe for the conservation of artwork? New insights in their VOC activity by means of Oddy testing*, **Heritage Science 10 (1)**, 2022, pp. 1–12

[8] B. Rouba, *Die Leinwandstrukturanalyse und ihre Anwendung für die Gemäldekonservierung*, **Restauratorenblätter 13**, Mayer & Comp., 1992.

[9] * * *, **METHOCEL Cellulose Ethers Technical Handbook,** Dow Chemical Company, USA, 2002.

[10] K. Soppa, *Basic Steps for Adhesion of Flaking Paint and Canvas. With a focus on absorbent substrates bonded with collagen-based adhesives*, **Structural Treatments on Double-Sided Paintings,** Centro Conservazione e Restauro La Venaria Reale, Genova, 2022.

[11] E. Hummert, U. Henniges, A. Potthast, *Fluorescence labeling of gelatin and methylcellulose: monitoring their penetration behavior into paper*, **Cellulose 20**(2), 2013, pp. 919–931.

[12] K. Soppa, *Using fluorochromised gelatine to visualize the sealing effect of cyclododecane during re-adhesion of flaking paint on canvas*, **Subliming Surfaces: Volatile Binding Media in Heritage Conservation**, 2018, pp. 53–64.

[13] C. Rozeik, **Subliming Surfaces: Volatile Binding Media in Heritage Conservation,** University of Cambridge Museums, 2018.

[14] R.L. Feller, M. Wilt, **Evaluation of Cellulose Ethers for Conservation**, Getty Publications, 1990.

Received: August 12, 2022
Accepted: December 20, 2022