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Using fluorochromised gelatine to visualise the sealing effect of cyclododecane during re-adhesion of flaking paint on canvas

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When working with low viscosity adhesives on canvases without a sizing layer, it is advisable to mask the canvas prior to consolidation (for example with CDD solutions). The use of fluorochrome-labelled gelatine (type A, 180 Bloom 5% w/w in distilled water) in combination with fluorescence microscopy allows the sealing effect of various methods of cyclododecane (CDD) application to be visualised, in order to optimise the techniques for re-adhesion of flaking paint on canvas. As solvents for CDD, petroleum ether (boiling point <40 °C) and white spirit (b.p. 100–140 °C) have delivered positive results. The observed adhesion was best when using CDD in petroleum ether <40 °C. However, from a practical point of view, the handling of CDD in white spirit 100–140 °C is easier, the penetration is laterally wider and therefore the sublimation faster.

Application of solid CDD either as chips or with a spray can (both worked in using a heated spatula on the reverse of the canvas) produced irregular and poorly reproducible results. There is a significant difference between the two CDD application techniques: if the paint has no contact with the canvas, the CDD solution stops at the canvas interface, whereas melts can penetrate further, embedding the fibres entirely and even filling the joints – or they do not reach the interface. A further important practical observation is that there should be no contact with the reverse of the canvas during application of the adhesive since this contact increases capillary forces, allowing the adhesive to penetrate more easily towards the other side. An open-celled foam, which is rigid enough for placing weights on the painting after application of the adhesive, proved to work well as an underlying support.

1 Introduction

During re-adhesion of flaking paint on an absorbent canvas, it is difficult to achieve a thin, distinct bond-line, especially when the canvas is barely-sized or unsized (Figure 1). There is a high risk that the adhesive will penetrate the canvas by capillary action before the flaking paint has been re-adhered. There are numerous approaches to avoid impregnation of the canvas, for example using an adhesive with a higher viscosity, thickening a low viscosity glue (see Laaser *et al.* 2013; Soppa *et al.* 2017), masking the substrate with aliphatic solvents (Soppa 2016), sealing it with a volatile binding medium (VBM) like cyclododecane (CDD), or a combination of these methods. Using a high viscosity adhesive may prevent penetration into the canvas; however, it may also hinder penetration beneath the paint flake. Masking with aliphatic solvents is an interesting option and was discussed in (Soppa 2016). This paper concentrates on sealing the canvas with a VBM such as CDD, and presents experimental results using fluorochromised gelatine as a tracer. The gelatine can only penetrate into barely-sealed or unsealed areas and can therefore visualise the sealing effect of CDD. As stated by Rowe and Rozeik (2008), CDD has a wide range of applications on a great number of different substrates, but uncertainty with respect to health hazards, as well as undesired residues, made conservators sceptical about its use. Another goal of this study is thus to determine the minimum amount of CDD necessary to block the capillary system on an unsized canvas. Finally, this paper also explores whether it is possible to improve control of the distribution of a low viscosity glue and produce a distinct bond-line between paint flake and canvas.

The CDD was applied from the reverse of the painting to the canvas, in order to seal off most of the canvas fibres and the voids in the fabric. It is essential to control CDD penetration and make use of the penetration gradient since CDD should neither fill the bond gap, nor cover the bonding interface. To evaluate which type of CDD sealing is most suitable, different application methods were tested: the CDD was dissolved in petroleum ether <40 °C, isooctane (2,2,4-Trimethylpentane) or white spirit 100–140 °C (applied one, two or three times), or was applied as a solid, melt or spray with subse-

Figure 1 Flaking paint on canvas. Microphotograph taken with a Keyence digital microscope VHX-1000.

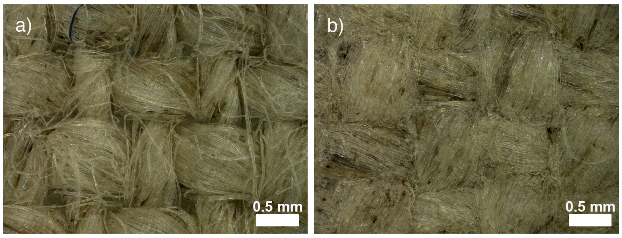

Figure 2 Canvas: a) unsized; b) sized with wheat starch. Microphotograph as before.

quent ironing. The canvas surface was modelled in 3D prior to the gelatine application with a Keyence digital microsope in multifocus mode.

Gelatine type A 180 Bloom, 5% w/w, was chosen as an adhesive because of its reproducibility (due to consistent production methods), high gelation temperature,[1] low viscosity and good adhesive tensile strength (Chiou *et al.* 2008; Nur Hanani *et al.* 2012). The gelatine was applied to the canvas at the opening of the paint–canvas interface, penetrating between the canvas and the paint flake. The distribution of the gelatine was investigated macroscopically, using UV illumination to explore the lateral distribution of the glue in the open joint and on the front and back surfaces of the canvas. To gain a deeper insight, microtome sections and cross-sections were prepared and investigated using fluorescence microscopy and scanning electron microscopy (SEM).

2 Experimental

2.1 Test samples

In order to obtain a sufficient number of samples with flaking paint, canvases and paint layers were prepared separately as follows: a washed, ironed, stretched, wetted and re-stretched linen fabric of medium quality and density served as a support. The average canvas density was 90% after Rouba (1992) and Lipinski (2006) (ø v13/h13 threads per 1 cm^2, thread size h: ø 0.45 mm, v: ø 0.6 mm, canvas thickness approximately 0.6–0.75 mm, Z-tortion, tortion angle ø 60 °). For the sized canvases, 13% wheat starch paste was used (Figure 2).

To imitate cracked, non-absorbing paint layers that are easy to handle, small 1 cm^2 paint flakes of 1 mm thickness were produced (the thickness of the dried flakes was ~0.8 mm). The 1 cm^2 test surface is estimated to be close to the average flake size found on canvas paintings. The paint ground was made of a pigment mixture using chalk, gypsum and iron oxide red (30 : 30 : 1 parts by weight) bound in gelatine type A 180 Bloom, 5% w/w. The chalk ground was coated with alkyd paint. The alkyd paint interface was imitating a non-absorbing oil ground and was therefore adhered to the mostly very absorbent non-sized canvas. For each test series, usually five (but sometime 15) paint flakes were applied to canvas strips (10 × 150 mm^2) of sized and unsized canvas.

2.2 Application of CDD in solution

CDD was diluted in various aliphatic solvents with different evaporation rates, vapour pressures and molecular weights. Films formed out of a CDD solution are less dense and less hydrophobic than films of melted CDD, but they sublime faster, require less material and the application can be contactless. As a general rule, the slower evaporating solvents transport the CDD deeper into the substrate (Riedl and Hilbert 1998; Stein *et al.* 2000; Geller and Hiby 2002). Since canvas is a thin but heterogeneous fabric (approximately 0.6–0.75 mm in this study), no aliphatic solvents with slow evaporation rates were used in this study. Furthermore, a gradient with decreasing concentration of CDD from back to front of the canvas is desirable, suggesting the use of solvents with a faster relative rate of evaporation (ether=1), DIN 53170 and a higher vapour pressure (20 °C). Petroleum ether <40 °C (evaporation rate <1, vapour pressure >350 hPa), isooctane (evaporation rate ~2.3, vapour pressure 51 hPa) and

1 T_{gel} approximately 30 °C, in comparison to 5% sturgeon glue, which is approximately 12 °C

white spirit 100–140 °C (evaporation rate ~6, vapour pressure 35 hPa) were thus prepared at ratios 5 : 3.25 (CDD : solvent; w/w) and 5 : 2.5 (CDD : solvent; w/w).[2] The CDD solutions in white spirit and isooctane were always saturated, but the solution in petroleum ether was only saturated at the higher concentration (5 : 2.5 CDD : solvent; w/w). However, the unsaturated solution in petroleum ether (5 : 3.25 CDD : solvent; w/w) was preferred to the saturated solution because its different wettability behaviour led to wider lateral impregnation. Heated solutions penetrate more deeply and were thus not taken into account.

After stirring for 1 hour, the solutions were ready for application. In general the solutions were used 24–48 hours after preparation. Application was carried out with a micropipette (Rainin XLS+LTS, 2–20 µl) with disposable polypropylene tips. 15 µl of CDD was applied to each sample, as this amount was estimated to impregnate an area of at least 1 cm^2. In theory, the CDD film does not reach maximum strength until the solvent has evaporated completely. Film strength is known to depend on various factors, such as the choice of solvent, solution concentration, depth of penetration, temperature, porosity of the substrate and air circulation (Hiby 1999; Hangleiter 2000). While Hangleiter (2000) reported a solvent evaporation time of 2 hours, Geller and Hiby (2002) stated a minimum of 2.5 hours. Krainer (2008) reported application of sturgeon glue to a canvas painting 2 hours after CDD impregnation. Considering that canvas is a thin and open system, evaporation times were expected to be at the lower end. 2 hours were thus initially regarded as sufficient time for the solvent to have evaporated.

To investigate the best mode and number of applications in order to achieve the best impregnation result without interference at the bonding surface, sequential applications and variable concentrations were tested. Only CDD in white spirit 100–140 °C was applied multiple times (up to three times) because the other solutions appeared to provide an adequate seal with just a single application. The time between each application was 2 hours (and also 4 hours in the case of white spirit because of its slower evaporation). Every parameter was tested with at least five, and a maximum of 15 samples.

Both sides of the canvas surface were imaged and modelled in 3D after application of the CDD solutions using a Keyence digital microscope VHX-1000 equipped with a VH-Z100W, RZ ×100–×1000 (real zoom lens), a VH-S50 stage with motorised z-axis (1 µm step) and software version 1.0.6.0. The maximum image resolution in multi-focus mode is 1600 × 1200 pixels.

2.3 Application of CDD in solid/melted form

Application of pure CDD in melted form produces the most compact films upon fast cooling (Rowe and Rozeik 2008; Hangleiter 2000).

Brush application was tested initially but was regarded as unable to achieve reproducible results. As an alternative solution, 1 cm^2 CDD chips of ~140–200 µm thickness were produced by shortly dipping a wetted strip of aluminium into the melt (70 °C) and sliding the CDD film off the metal strip with a rigid plastic bar upon cooling. The CDD chips were ironed into the canvas with a hot spatula (60–70 °C). To control the penetration depth, the canvas was observed on the opposite side.

2.4 Spray application of CDD

Since spray can application does not achieve penetration into porous substrates – as reported in Hangleiter (2000) and observed in a pre-test series – penetration of a sprayed film was achieved with additional ironing using a heated spatula (60–70 °C). The spray was applied six times from a distance of 5 cm. The final thickness of the film was approximately 1 mm. Similar to the melt and solid chip application above, penetration depth was irregular and difficult to control.

2.5 Testing penetration and distribution behaviour of gelatine stained with fluorochrome

Gelatine type A 180 Bloom was chosen because it exhibits a viscosity and penetration behaviour on absorbent substrates similar to sturgeon glue (Soppa *et al.* 2014). Furthermore, sturgeon glue contains less than 5% non-collagenous material, and never produces clear solutions, whereas gelatine, an industrially purified product, contains only degraded collagen, water and barely any salts (Brewing, Food and Beverage Industry Suppliers Associ-

2 Information about the evaporation rates and vapour pressures for these solvents can be found in Merck Millipore (2013, 2014, 2016); Roth (2016).

ation (BFBI) and The Brewers of Europe 2006), giving it considerable advantages over sturgeon glue (Hickman *et al.* 2000) with respect to reproducibility and clear solutions. The molecular weight distribution of sturgeon glue varies considerably (Haupt 2004), as it also does for acid-conditioned gelatine type A (Schrieber and Garies 2007). Moreover the higher T_{gel} of gelatine in comparison to sturgeon glue was also crucial, because it allows the gelatine to gel at room temperature, whereas sturgeon glue can penetrate too far into an absorbent substrate.

Fluorescence labelling of gelatine was conducted using fluorescein-isothiocyanate (FITC), according to Soppa *et al.* (2013). This produces green fluorescence when excited by visible or UV illumination.

The labelled gelatine was applied with a micropipette (Ranin XLS+LTS, 2–20 µl, poplypropylene pipette tips). 7 µl of a 5% solution was applied to the canvas at 40 °C. A single sample had 7 µl of a 1% solution applied instead, to explore the penetration behaviour of an even lower viscosity. The consolidant was always applied from the front, either directly onto the sized or unsized canvas, or placed at the accessible canvas–paint flake interface (1 cm^2). The flake had to be gently agitated repeatedly with a silicone colour shaper (taper point) in order to allow the glue to penetrate into the canvas–paint flake interface. A sheet of silicone-covered Melinex foil was placed underneath the reverse of the canvas and a layer of Hollytex was placed on top of the paint flakes. The gelatine bond was left to dry under pressure (a 75 g weight measuring 3 × 2.2 × 1.5 cm was placed on each paint sample) for at least 24 hours. After drying, the front and back surfaces and the bond-line of each sample were photographed using UV illumination (Dr Hönle UV A handlamp 250 with a black light (BL) filter 325–400nm; Camera Canon EOS 6D, EF50mm f/2.5 Compact Macro, K5000, f8, t1/60, vis: ISO 400 Vis, UV: ISO 3200). In most cases, this method clearly showed the effectiveness of the sealing effect (see Figure 3 and Table 1), but an additional view of the transverse section was made to check this using fluorescence microscopy, and the most representative sample (neither the best nor the worst, although in most cases there was hardly any difference between the five paint flakes) was cut in half and embedded in Technovit 7100 (Heraeus Kulzer) in order to produce microtome

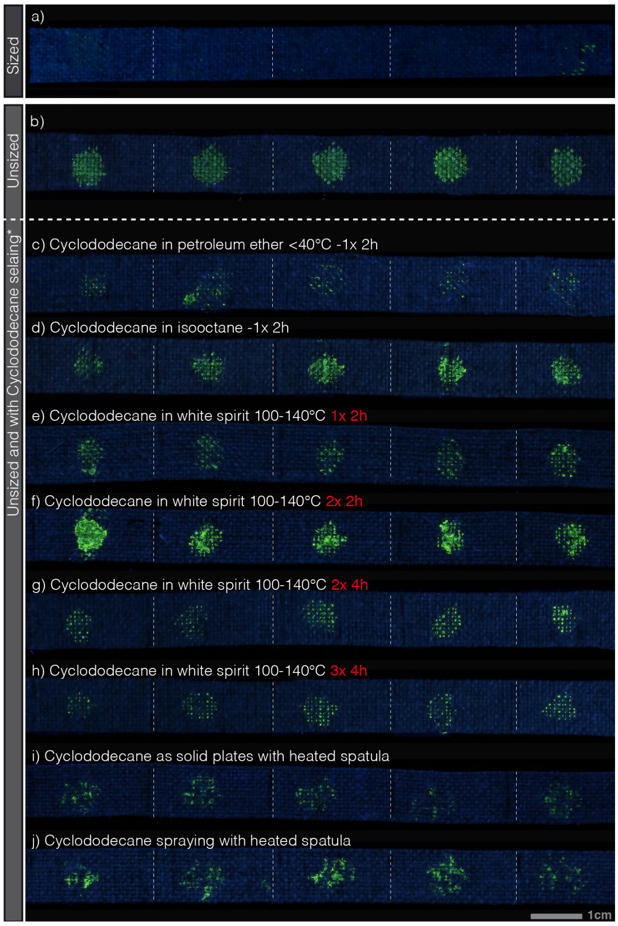

Figure 3 Overview: Penetration of gelatine type A, 180 Bloom, 5%, 40 °C, 7 µl (green) from the front to the back of the canvas. Photograph as before.

sections (8 µm) on a rotary microtome (Hyrax H55, C-knife at an angle of 8 °; refer to Soppa *et al.* (2013) for details). Documentation of the distribution of the labelled adhesive in the microtome sections was performed on a fluorescence microscope (Leitz DMRB, camera Jenoptik ProgRes Speed XT Core 3, 2080x1542 pixel), using a filter set for FITC excitation (filter BP 475–495/ beam splitter LP 510/ emission filter BP 512–542) and a halogen bulb (12 Volt, 100 W, XENOPHOT).

The preliminary test for estimating adhesive distribution was calculation of the surface area at the front and back of the canvas after application of the labelled gelatine. This was derived using Adobe Photoshop CC 2014 for image analysis and qualified with a standard deviation and a confidence limit for all samples. It was assumed that a large surface area at the front (and a much smaller one on the back) indicated greater penetration of the gelatine, hardly any penetration of the canvas, and thus a stronger bond-line. Since the area of each paint flake was 100 mm^2, the lateral distribution was measured in

mm^2 and could be indicated as a percentage (proportional to the whole flake). Microtome sections revealed the exact remains of the gelatine within the canvas–glue–paint stratigraphy. Adhesion was observed only by opening the joints by hand for documentation and was not the main focus of this study.

2.6 Sublimation rate of CDD

To maximise sublimation, Hangleiter (2000) recommends temperatures above 30 °C. The sublimation time in the drying oven was explored for equivalent amounts of CDD deposited by various methods onto 1 cm^2 canvas dummies, using a gravimetric method (Sartorius Laboratory Balance, Practum224-1S, 0.0001 g sensitivity): CDD from a solution in white spirit (took 6 hours to sublime), in petroleum ether (10–11 hours) and sprayed and ironed (18 hours). Based on these test results, all samples were exposed to 35 °C at maximum ventilation within a Memmert drying oven for 24 hours. Afterwards, the samples were conditioned to 20 °C ±1 °C and 50% RH ±2%.[3]

2.7 Observation of the bond-line in cross-section

To gain a better insight into how the gelatine is bonded to the canvas fibres, 4 cases were observed in cross-section using SEM: canvas samples sealed with CDD in 1) petroleum ether <40 °C and 2) white spirit 100–140 °C after gelatine application and sublimation, in comparison to unsized canvas 3) before (reference sample) and 4) after gelatine application. Backscattered electron images were generated on a VP-SEM (Zeiss Evo MA10) with a W-cathode at 7 kV and 600 pA, using a 5-segment BSD detector in low vacuum (64 Pa).

3 Results and Discussion

No apparent interaction between CDD solutions and substrates was observed. For the results, see Figure 3, Figure 4, Figure 5 and Table 1.

3 For comparison, the sublimation time of CDD at room temperature took ~24 hours for solutions in white spirit, ~36.5 hours for solutions in petroleum ether, and ~168 hours (i.e. one week) for sprayed and ironed CDD.

3.1 Sized canvas

The gelatine penetrates between the paint flake and the sized canvas with no observable penetration of the canvas. The calculated lateral dispersion at the front was 75% and less than 2% at the back, representing an ideal case situation and producing a continuous adhesive bond-line. The microtome section confirms this result, showing the labelled gelatine as a distinct green line at the paint layer interface. Neither canvas nor paint exhibits any fluorescence and they are therefore invisible (black) under UV light. Because the gelatine does not penetrate the sized canvas, CDD impregnation is not necessary in this case. Experience, however, revealed two additional aspects of practical relevance, providing the isolation layer is continuous and in good condition: first, any contact between the gelatine application tool and the canvas during consolidation should be avoided. To achieve this, the use of a micropipette is ideal. Second, fast but gentle rocking movements of the flake achieve a better (lateral) distribution of the gelatine within the bonding interface so that the gelatine has no time to penetrate into the canvas.

3.2 Unsized canvas

On canvas without sizing, the gelatine moves through the stratigraphy and fully penetrates the canvas. The gelatine distribution at the front and back of the canvas is indifferent (<30%), and cannot compete with the 75% lateral distribution on sized canvas. The thin section confirms the distribution results, showing gelatine distribution throughout the canvas threads with no adhesion at all.

3.3 Application of CDD solutions on unsized canvas

After application of the CDD solutions in petroleum ether <40 °C on unsized canvas, needle-like crystals of CDD were visible at the reverse (Figure 6 (a)). The front surface exhibited slightly increased reflectivity (Figure 6 and Figure 7). There was a distinct concentration gradient in the case of petroleum ether <40 °C. Upon a second application of CDD in petroleum ether <40 °C, the CDD arrived at the bonding line, hindering any adhesion of the gelatine to the fibres. After application of the CDD solutions in isooctane and white spirit 100–140 °C,

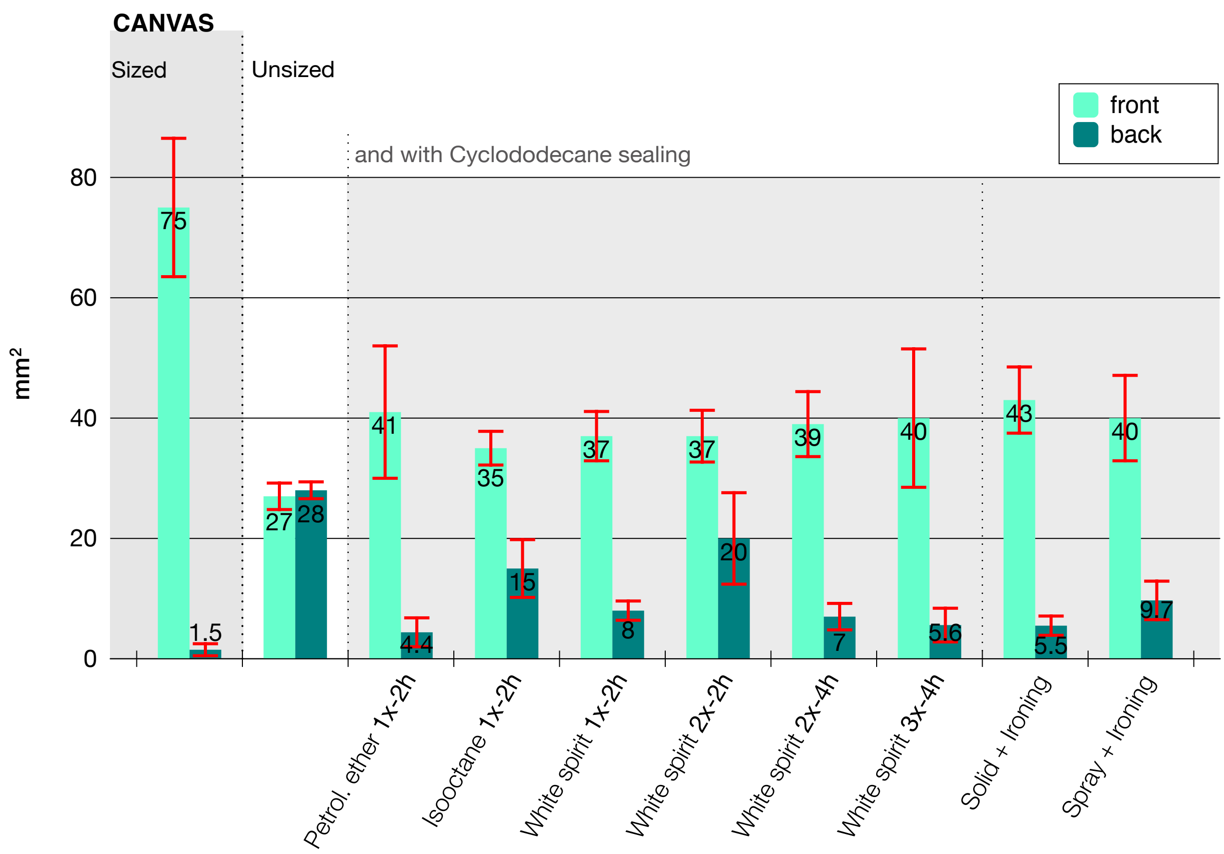

Figure 4 Lateral distribution of gelatine type A, 180 Bloom, 5%, 40 °C, 7 µl, front and back.

Cyclododecane application			Front*		Back*		Adhesion‡
Cyclododecane solution / solid format	Number and volume of applications	Evaporation time between each application in hours	Lateral gelatine distribution (mm^2) ±CI†	STD (mm^2)	Lateral gelatine distribution (mm^2) ±CI†	STD (mm^2)	
Sized canvas							
[none]	[none]	[none]	75 ± 11.5	10	1.5 ± 1.0	0.9	+++
Unsized canvas							
[none]	[none]	[none]	27 ± 2.2	1.9	28 ± 1.4	1.2	–
Petroleum ether <40 °C	1 × 15 µl	2	41 ± 11	9.5	4.4 ± 2.4	2.1	++/+++
Isooctane	1 × 15 µl	2	35 ± 2.8	2.4	15 ± 4.8	4.2	+/++
White spirit 100–140 °C	1 × 15 µl	2	37 ± 4.1	3.6	8 ± 1.6	1.4	+/++
White spirit 100–140 °C	2 × 15 µl	2	37 ± 4.3	3.7	20 ± 7.6	6.6	–/+
White spirit 100–140 °C	2 × 15 µl	4	39 ± 5.4	4.7	7 ± 2.2	1.9	+/++
White spirit 100–140 °C	3 × 15 µl	4	40 ± 11.5	10	5.6 ± 1.8	1.6	++/+++
Solid and ironing	1 × 1 cm^2	–	43 ± 5.5	4.8	5.5 ± 1.6	1.4	–/++
Spray and ironing	6 × sprays	–	40 ± 7.1	6.2	9.7 ± 3.2	2.8	+/+++

* At least five valid measurements
† Confidence interval of 95 percent
‡ Estimated adhesion scores: - poor, + sufficient, ++ good, +++ very good

Table 1 Results of the lateral distribution of gelatine (5%) on the canvas back and front with adhesion estimation.

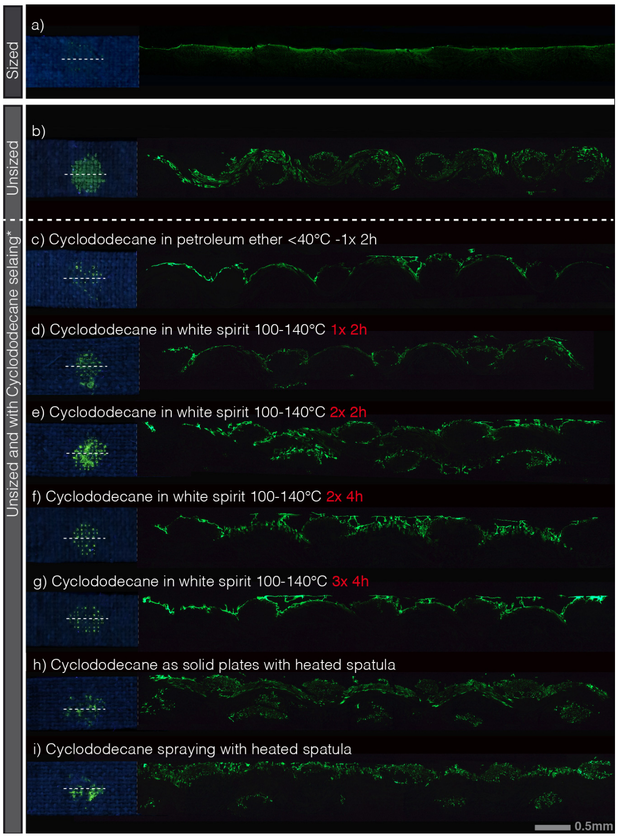

Figure 5 Overview: Penetration of gelatine type A, 180 Bloom, 5%, 40 °C, 7 µl (green) microtome sections. Photographs taken with Canon EOS 6D and Jenoptik ProgRes cameras.

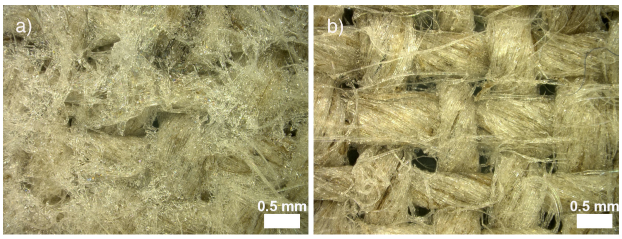

Figure 6 Cyclododecane in petroleum ether <40 °C on unsized canvas: a) back; b) front. Microphotograph as before.

a slight colour change was visible, with some local glittering (Figure 8). From a practical point of view, solutions in white spirit 100–140 °C are easier to handle because of the longer evaporation time.

Regarding the gelatine application, the wettability was worse compared with sized canvas. Apart from the impregnation, the adhesive has to cover a larger surface area, because the sizing layer is missing and the gaps between the threads are not filled, thus leading to considerable surface topography that needs to be equalised.

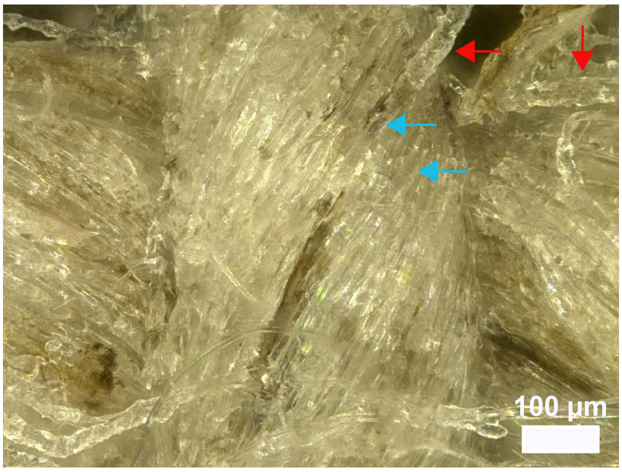

Figure 7 Detail of the front of the canvas after application of cyclododecane in petroleum ether <40 °C. The red arrows show fibres saturated with CDD, and the blue arrows show fibres where no CDD is visible. Microphotograph as before.

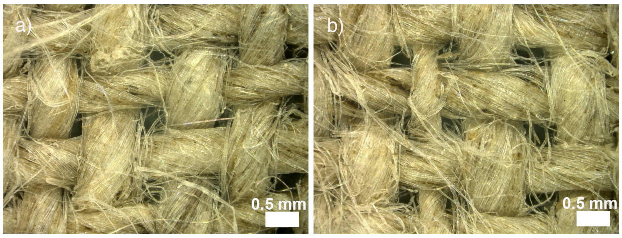

Figure 8 Cyclododecane in white spirit 100–140 °C on unsized canvas: a) back; b) front. Microphotograph as before.

3.4 CDD in petroleum ether <40 °C and gelatine penetration

For CDD in petroleum ether <40 °C the lateral distribution on the front was about 40% and on the back close to zero (Figure 9). When counting every fluorescent pixel using Adobe Photoshop, the lateral distribution on the reverse was 4.4% (Figure 4). The thin section confirms the results, showing a distinct wavy adhesion layer with minimal penetration into the canvas. Only the top fibres are coated with gelatine. In Figure 5 (c) and Figure 10, the bondline between the paint flake and the canvas, as well as the bridges and network at the paint–canvas interface is clearly visible.

3.5 CDD in isooctane

For the solution of CDD in isooctane (at a ratio of 5 : 3.25), the lateral distribution of the gelatine was 35% at the paint layer interface, yet 15% on the reverse. Although adhesion was satisfactory and a second CDD application possibly could have improved the sealing effect, no microtome section

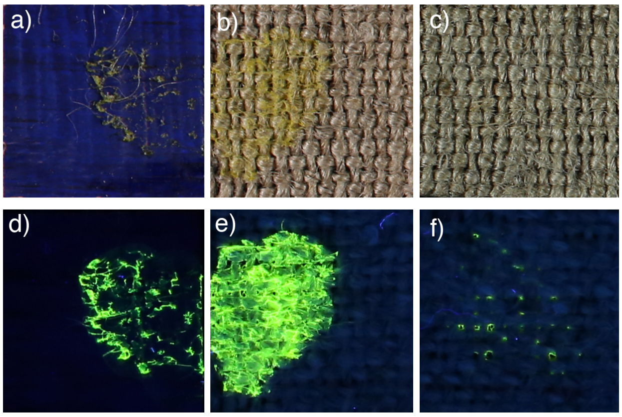

Figure 9 Canvas sealed with CDD in petroleum ether <40 °C, open joint and back in visible light (a–c) and UV light (d–f). Photograph taken with a Canon EOS 6D camera.

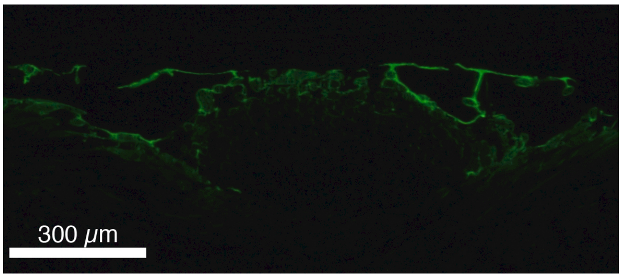

Figure 10 Microtome section c), detail: bridges of gelatine and gelatine film tightly connecting with the fibres. Photograph taken with a Jenoptik ProgRes camera.

was made. A solution of 5:2.5 CDD to isooctane, applied at 70 °C, sealed the canvas as well as CDD in petroleum ether <40 °C. The microtome sections delivered consistent results. With respect to the lateral distribution of the higher CDD concentration, a slight improvement was achieved, with 41% (front) and 9% (back).

3.6 CDD in white spirit 100–140 °C

CDD in white spirit 100–140 °C also successfully prevents the gelatine from penetrating the canvas. Here, the gelatine also produced a clear bond-line, but not as distinct as the one with CDD in petroleum ether <40 °C. The gelatine did penetrate more into the canvas. The adhesion strength observed was satisfactory, but not as strong as in the case of CDD in petroleum ether <40 °C. Since multiple applications may improve the sealing effect, a second application of CDD in white spirit 100–140 °C was tested. The result was, however, negative: the lateral distribution in the joint was reduced and the distribution on the reverse was increased substantially to ~ 20%. In order to test whether this was due to incomplete evaporation of the solvent from the CDD solution, the solvent evaporation time was doubled from 2 to 4 hours, resulting in a lateral distribution of 7% on the reverse. When observing the microtome sections it is obvious that a double application of CDD with only 2 hours evaporation time between the applications allowed gelatine to penetrate between the threads right through the canvas, and in some areas into a thread. With a 4 hour evaporation time, the gelatine produced a bond-line (although not as distinctly as in the case of CDD in petroleum ether <40 °C). Three applications produced a very distinct bond-line with a lot of gelatine–fibre bridges.

3.7 CDD as solid chips or as spray with heated spatula treatment

For CDD applied as solid chips melted into the canvas with heat, the lateral distribution was quite comparable to the solutions. However, the microtome section revealed that most of the gelatine penetrated into the canvas. The observed adhesion was weak. In the case of spraying and ironing, the microtome sections presented a better distribution image, yet the adhesive bond varied from weak to strong. Almost every paint flake had a different adhesion. Solid CDD and spray application with ironing were neither reliable nor reproducible. A further disadvantage is the longer sublimation time for a CDD layer produced by these methods.

3.8 Observed adhesion

The best adhesion was observed for CDD in petroleum ether <40 °C, followed by the solution in white spirit 100–140 °C (see Table 1). This estimation is based only on observations made during opening of the joints. For a proper evaluation of the adhesion, other tests are necessary. Another aspect that requires consideration is the longer-term behaviour of the adhesive bonds.

3.9 Attachment of gelatine to the fibres – investigation with SEM

Comparing an unsized canvas treated with gelatine without prior CDD sealing to an untreated reference, there was no visible difference. On the canvas samples sealed with CDD in petroleum ether <40 °C and with white spirit 100–140 °C, the gelatine layer on the canvas and alongside the paint layer is clearly

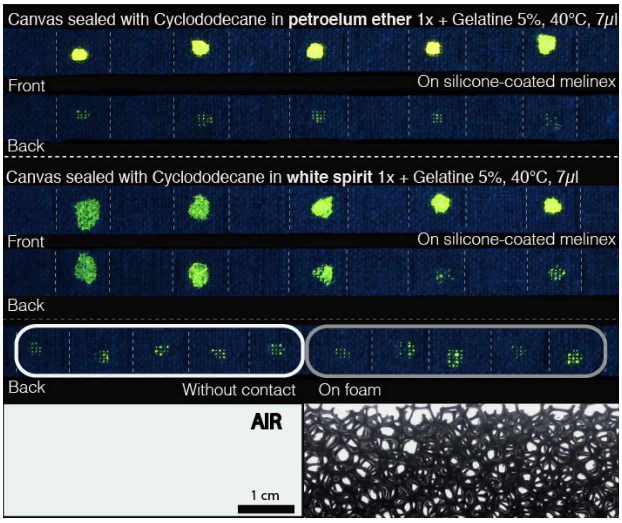

Figure 11 Gelatine drops (7 µl) on unsized canvas sealed with CDD on silicone-coated Melinex, without contact, and on foam. Photograph taken with a Canon EOS 6D camera.

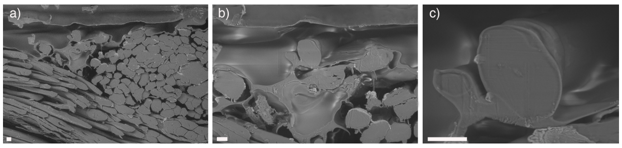

Figure 12 SEM image showing the gelatine film between the paint layer and canvas. The canvas was sealed with cyclododecane dissolved in petroleum ether <40 °C prior to gelatine application. Scale bar corresponds to 10 µm. Image: Nadim Scherrer.

visible (Figure 12). In some places the gelatine film is not in contact with the fibres. There is no clear explanation at this stage. It might have been caused during removal of the paint chip, due to cutting without using an embedding medium, or because of CDD sublimation at the bonding surface. Despite the fact that the samples were torn and cut beforehand, there are still areas where the gelatine film tightly connects with the fibres, sometimes surrounding them and producing a mechanical bond.

3.10 Gelatine drops on unsized canvas sealed with CDD in petroleum ether <40 °C and white spirit 100–140 °C

During practical application, it was observed that the underlying support is crucial for production of an adhesive layer: paintings on fabric need support from below so that the fabric does not sag and pressure can be applied from above to areas to be consolidated. Sometimes cold metal or stone plates are placed under the painting as a underlying support to chill and gel an animal glue more rapidly (von der Goltz *et al.* 2012). To investigate whether the observed sealing effect is also transferable to drops of gelatine that are standing on the canvas for longer than a few seconds, drops of gelatine were placed on a canvas sealed with CDD in petroleum ether <40 °C and white spirit 100–140 °C (Figure 11).

The gelatine drops (5%, 40 °C, 7 µl) on the canvas sealed with CDD in petroleum ether <40 °C did not penetrate through the canvas and the sealing effect was judged as sufficient.

With CDD in white spirit 100–140 °C, each drop showed a different distribution pattern (Figure 11). From left to right there is a decrease in extent. Looking at the reverse, the discrepancy is even greater. This variability can be explained by variable contact between the silicone-coated Melinex foil and the undulating canvas sample: the better the contact, the higher the penetration. A subsequent test was carried out to confirm this observation. Three canvas strips sealed with CDD in white spirit 100–140 °C were placed with and without contact to the Melinex foil. Another sample was place on a rigid open-celled foam. Then drops of gelatine were applied (5%, 40 °C). None of the drops penetrated through the canvas placed without contact to the foil and on the foam. For the canvas in direct contact with the Melinex, all the gelatine drops penetrated right through to the reverse. The final test with 1% gelatine showed that, while gelatine drops of 5% remained on top of a canvas sealed with petroleum ether <40 °C, a 1% solution penetrated right through to the back, suggesting that the sealing capacity is limited to a certain viscosity range.

4 Conclusion

In summary, the use of fluorochrome-labelled gelatine in combination with fluorescence microscopy, 3D surface modelling and SEM imaging successfully allows visualisation of the sealing effect of various methods cyclododecane application to optimise the techniques for re-adhesion of flaking paint on canvas. Non-absorbent flaking paint on canvas with an intact sizing layer adhered without showing any penetration of the glue into the canvas, with no need for additional CDD treatment. When working with low viscosity adhesives on canvases without a sizing layer, it is advisable to mask the canvas with a CDD solution prior to consolidation. It is important to avoid contact with the canvas and paint when applying CDD solutions. As solvents for CDD, petroleum ether <40 °C and white spirit 100–140 °C have delivered positive results. The observed adhesion was best when using CDD in petroleum ether <40 °C. However, from a practical point of view, the handling of CDD in white spirit 100–140 °C is easier, the penetration laterally wider and therefore the sublimation faster. Thickening the gelatine with methyl cellulose could help to produce a distinct bonding line.

Application of solid CDD chips and spray followed by treatment with a heated spatula on the reverse of the canvas both produced irregular and poorly reproducible results; these techniques are not recommended. There is a significant difference between the two application techniques: if the paint has no contact with the canvas, the solution stops at the canvas interface, whereas melts can penetrate further, either embedding the fibres entirely and filling the canvas–paint delamination gap, or else they do not reach the interface. A further important practical observation to note is that there should be preferably no contact between reverse and the support during application of the consolidant, since contact with a closed surface increases the capillary forces and the consolidant will penetrate more easily towards the other side. An open-celled foam which is rigid enough to support weights on the consolidated areas proved to work well as an underlying support. Furthermore, fast agitation of the paint flake improves distribution of the consolidant across the flake.

It should be kept in mind that these results refer to the application of a 5% gelatine type A, 180 Bloom. A solution of lower viscosity like 1% or 3%, or another consolidant like sturgeon glue, may not achieve the same results. Concerning possible CDD residues, one should consider the advantages and disadvantages of impregnating the canvas with a consolidant against the effects of potential residues of CDD in the canvas.

Since every art object is unique and may behave in a specific way, it is strongly recommended to evaluate carefully prior to global implementation. Tests with fluorochrome labelling have shown to be helpful to achieve a better judgement of the effectiveness.

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Biography

Karolina Soppa graduated from the Stuttgart State Academy of Art and Design (Germany) in 2006 with a diploma in Conservation and Restoration of Paintings and Painted Sculptures. After working for a year at the Doerner-Institute in Munich, she substituted for Professor Volker Schaible at the Stuttgart State Academy of Art and Design in the winter term 2009–2010. She currently works as a professor at the Berne University of Applied Sciences in Switzerland, with a focus on panel paintings and sculptures, in particular consolidation and re-adhesion.

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Material list

Test samples:

- Linen canvas, L515 Canvas 99, Kremer, www.kremer-pigmente.com
- Wheat starch, CAS number 9005-25-8, Carl Roth GmbH & Co. KG, www.carlroth.com
- Iron oxide red, chalk from Champagne, chalk from Bologna, www.kremer-pigmente.com
- Griffin alkyd paint, French ultramarine, product code 1914263, Winsor & Newton, www.winsornewton.com
- Gelatine, type A, Bloom 180, CAS number 9000-70-8, Carl Roth GmbH & Co. KG, www.carlroth.com

Sealing and adhesion:

- Cyclododecane, product code 87100, www.kremer-pigmente.com
- Cyclododecane spray can, product code 87099, www.kremer-pigmente.com
- Petroleum ether <40°C, product code 1.00915.1000, www.merck.de

- White spirit 100–140°C, product code G054, www.grogg-chemie.ch
- Isooctane, product code 59050, Fluka, www.sigmaaldrich.com
- Gelatine, type A, Bloom 180, CAS number 9000-70-8, Carl Roth GmbH & Co. KG, www.carlroth.com

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