Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary Information

Varnish Removal from Paintings using Ionic Liquids

Maria Filipa Pacheco,[a] Ana Isabel Pereira,[a,b] Luís C. Branco[b,*] and A. Jorge Parola[b,*]

[a] *Departamento de Conservação e Restauro, FCT. Universidade Nova de Lisboa, 2829-516 Caparica, Portugal; E-mail: mariafilipa.pacheco@gmail.com, ana.pereira@campus.fct.unl.pt*

[b] *REQUIMTE, CQFB, Departamento de Química, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal; E-mail: ajp@fct.unl.pt, l.branco@fct.unl.pt*

1. Mock-ups

1.1. Description of the mock-ups

Mock-up 1: Three varnishes

This mock-up contains a white pigment (Flake white) that acts as a drying pigment and a brown pigment (Vandyke Brown) with slow drying properties.[1] Over these pigments, naturally aged for 17 years, three varnishes were applied: a dammar varnish, a varnish based on polycyclohexanone (Retouching Varnish®, Talens) and PVAc based varnish, following the scheme of Fig. S1.

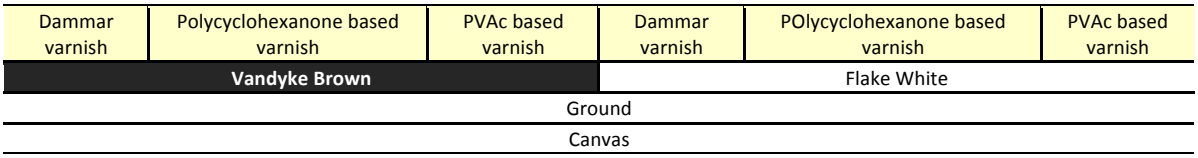


Figure S1: Cross section scheme of mock-up 1.

Mock-up 2: Dammar varnish

This mock-up was designed to represent an old painting. The binder used was linseed oil with white lead and vermillion. Lac Dye was applied on top of the vermillion red layer. Finally the mock-up was coated with dammar varnish (Fig. S2).

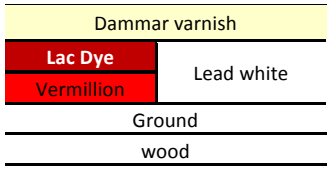


Figure S2: Cross section scheme of mock-up 2.

Mock-up 3: Acrylic varnish

To simulate a modern painting (Fig. S3), a canvas was coated with two different pigments, an organic pigment (quinacridone) and an inorganic pigment (titanium white) both in acrylic emulsion (poly(n-butyl acrylate-methyl methacrylate)). Over these layers, an acrylic varnish based on poly(iso-butyl methacrylate) was applied (Acrylic Varnish Matt®, Talens).

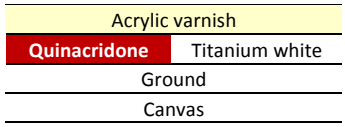


Figure S3: Cross section scheme of mock-up 3.

1.2. Preparation of the mock-ups

Mock-up 1: Three varnishes

Tis mock-up was built by applying the varnishes (dammar, PVAc based and polycyclohexanone based varnishes) over a painting that was naturally aged for 17 years. This painting was provided through the courtesy of Doctor Leslie Carlyle.[2]

Mock-up 2: Dammar varnish

In the preparation of mock-up 2, a wood board with industrial ground was used and then coated with vermillion and white lead using linseed oil as binder. Lac Dye was applied over the vermillion layer. After seven months, the dammar varnish was applied.

Mock-up 3: Acrylic varnish

In this mock-up, acrylic paints (quinacridone rose and titanium white) were applied directly from the tube (2 layers) over a canvas with industrial ground. The acrylic varnish was then applied and the canvas attached to a rigid support with the same dimensions.

Materials used in the mock-ups

Pigments

Name	Composition	Colour Index	Suppliers	Observations
Flake White	Basic lead carbonate, zinc oxide	PW1, PW4	Winton Oil Colour (#19), Winsor & Newton®	Binder: linseed oil
Vandyke Brown	Calcined natural iron oxide, bituminous earth	PBr7, NBr8	Winton Oil Colour (#41), Winsor & Newton®	
White lead	Basic lead carbonate		Kremer Pigmente	Binder: linseed oil
Vermillion	Mercuric sulphide (HgS)		Kremer Pigmente	
Lac Dye	Laccaic acid and shellac		Kremer Pigmente	
Quinacridone	Quinacridone	PV19	Rembrandt (366, series 3) Acrylic Colours, Royal Talens®	Pigments in acrylic emulsion (poly(n-butyl acrylate-methyl methacrylate)
Titanium white	Titanium dioxide	PW6	Rembrandt (105, series 1) Acrylic Colours, Royal Talens®	

Varnishes

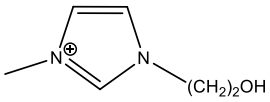
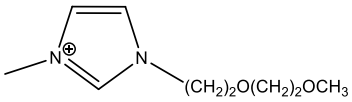
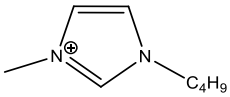
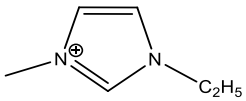
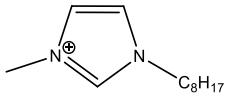
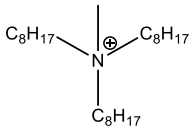
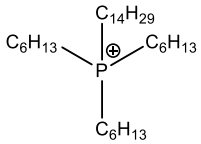
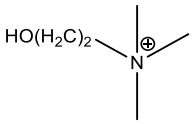
Name	Composition	Suppliers	Observations
Retouching Varnish®	Cyclohexanone resin (solution in white spirit)	Royal Talens®	
Dammar varnish	Dammar (33% (w:w) solution in turpentine)	Kremer Pigmente	prepared according to ref. [3]
PVAc varnish	AYAA:AYAC 50:50 (w:w) (9% (w:v) solution in toluene)	AYAA: PVAc, M=83000 (Aldrich) AYAC: PVAc, M=12800 (Movilith® 20, Kremer Pigmente)	prepared according to ref. [2]
Acrylic Varnish Matt®	Acrylic resin (solution in white spirit). Addition of matting agents (silica).	Acrylic Varnish Matt® (115, Series 3). Acrylic Picture, Talens®).	Acrylic resin: poly(iso-butyl methacrylate)

2. Ionic liquids

The following parameters were considered when selecting the ionic liquids to be used in varnish removal tests: i) commercial availability of the ILs; ii) miscibility of the ILs with water or with solvents of low toxicity (e.g., ethanol) to be used as clearance solvents; iii) polarity; iv) nature of the paint layers and varnishes. Particular attention was paid to the different nature of the varnishes to be removed. Dammar is a natural resin containing mainly triterpenoids[4] and is typically removed with a mixture of two solvents, one polar and more volatile, for instance acetone, which dissolves the varnish, and a more apolar and less volatile solvent, like toluene.[5] Resins based on polycyclohexanones have been used since the 50s as substitutes for natural resins; they usually require more polar solvents for removal.[4] PVAc is the most polar varnish used[4] while the acrylic varnish is rather challenging to be removed.[6] The selected ILs are presented in Table S1 and their properties shown in Table S2.

The thirteen ILs chosen comprise methylimidazolium, tetralkylammonium and tetraalkylphosphonium as cations, combined with chloride, tetrafluoroborate, triflate, trifluoroacetate, acetate, dicyanamide and alkylsulphate as anions. ILs containing cations with long alkyl chains are less polar and tend to be less soluble in water (see Table S2).

Table S1: Structure and nomenclature of the thirteen selected ILs to test as varnish removal agents.

Ionic Liquid Designation	Cation	Anion	Name (Supplier)
$[C_2OHmim][BF_4]$		BF_4^-	1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate (Solchemar)
$[C_5O_2mim][Cl]$		Cl^-	1-[2-(2-methoxyethoxy)-ethyl]-3-methylimidazolium chloride (Solchemar)
[bmim][DCA]		$N(NC)_2^-$	1-butyl-3-methylimidazolium dicyanamide (Solchemar)
$[bmim][BF_4]$		BF_4^-	1-Butyl-3-methylimidazolium tetrafluoroborate (Solchemar)
[bmim][TfO]		$CF_3SO_3^-$	1-butyl-3-methylimidazolium trifluoromethanesulfonate (Solchemar)
[bmim][TFA]		CF_3COO^-	1-butyl-3-methylimidazolium trifluoroacetate (Solchemar)
$[emim][EtSO_4]$		$EtSO_4^-$	1-ethyl-3-methylimidazolium ethylsulfate (Solchemar)
$[emim][MOEOEtSO_4]$		$MOEOEtSO_4^-$	1-ethyl-3-methylimidazolium methoxy-ethoxy-ethylsulfate (Iolitec)
[omim][Cl]		Cl^-	1-octyl-3-methylimidazolium chloride (Solchemar)
[Aliquat][DCA]		$N(NC)_2^-$	trioctylmethylammonium dicyanamide ([a])
[Aliquat][Cl]		Cl^-	trioctylmethylammonium chloride (Aldrich)
$[P_{6.6.6.14}][Cl]$		Cl^-	trihexyltetradecylphosphonium chloride (Cytec)
[Choline][Ac]		CH_3COO^-	choline acetate (Solchemar)

Prepared according to ref. [7]

Table S2: Physical properties of part of the selected ILs to test as varnish removal agents.

Ionic Liquids	**Viscosity** (mPa.s) (T/°C)	**Density** (g/ml) (T/°C)	**Solubility in water**	**Polarity** [(a)] E^N_T (T/°C)	**References**
$[C_2OHmim][BF_4]$	91 (25)	1.33 (25)	miscible		[8]
$[C_5O_2mim][Cl]$	613 (25)	1.14 (25)	miscible		[8]
[bmim][DCA]	32 (25)	1.06 (25)	miscible		[9]
$[bmim][BF_4]$	105 (25)	1.26 (25)	miscible	0.67 (25)	[8]
[bmim][TfO]	90-99 (20)	1.29 (20)	miscible	0.67 (25)	[10, 11]
[bmim][TFA]	73 (20)	1.21 (21)	miscible	0.63 (*ca*. 25)	[10, 11]
[omim][Cl]	33070 (25)	1.00 (25)	miscible	0.55 (25)	[8, 10]
$[emim][EtSO_4]$	123 (25)	1.24 (25)	miscible		[12]
[Aliquat][DCA]	300 (25)		immiscible		[7]
[Aliquat][Cl]	1500 (30)	0.88 (25)	immiscible		[13]
$[P_{6,6,6,14}][Cl]$	2454	0.89 (25)	immiscible		[12]

[(a)] E^N_T – *normalized solvent polarity scale* (E^N_T = 0 for TMS e E^N_T = 1.00 for water).

3. Cleaning tests

3.1. Design and methodology

The experimental procedure used in the cleaning tests is outlined in Fig. 4S. It consists in the application of the IL on the surface over which it stays during 10 minutes. After this period, the IL is removed (twice) with a dry cotton swab and the residues removed (twice) with another cotton swab embedded with the clearance solvent. This solvent was water for water-miscible ILs and water:ethanol 40:60 (v:v) for those that are immiscible with water.

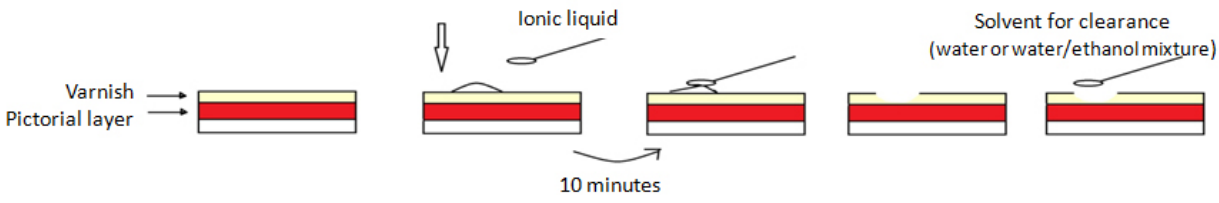
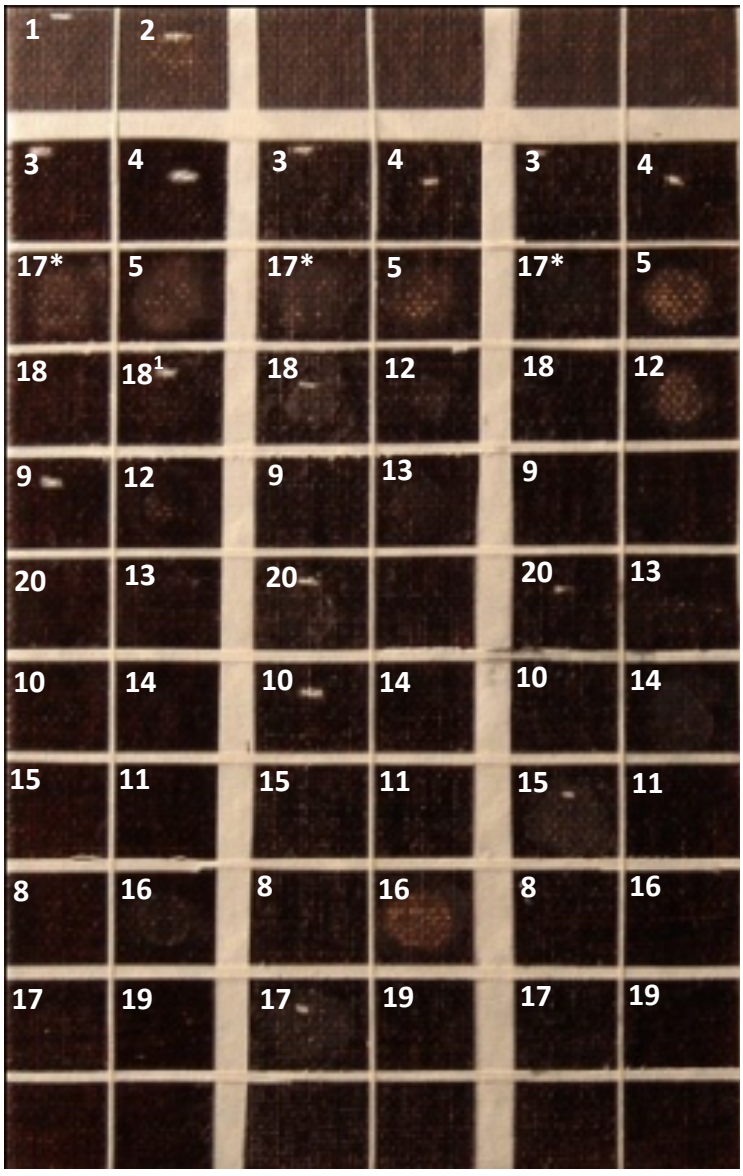


Figure 4S: Experimental procedure for the cleaning tests.

The design of the cleaning tests that were carried out in each mock-up are shown in Figs. 5S and 6S, by presenting photos of the mock-ups after cleaning.

Mock-up 1: dammar varnish, polycyclohexanone based varnish and PVAc based varnish over Vandike Brown (and Flake White).



* IL removed with a solution water:ethanol.

For the white zone (Flake white), the tests were carried out in identic order.

Control zone and solvents:

1. unvarnished (control)

2. water (unvarnished)

3. Varnish (control)

4. water

5. water : ethanol 40:60 (v:v)

6. ethanol

7. toluene: acetone 60:40 (v:v)

Ionic Liquids:

8. $[C_2OHmim][BF_4]$

9. $[C_5O_2mim][Cl]$

10. $[emim][EtSO_4]$

11. $[emim][MOEOEtSO_3]$

12. [bmim][DCA]

13. [bmim][TFA]

14. [bmim][TfO]

15. $[bmim][BF_4]$

16. [omim][cl]

17.[Aliquat][Cl]

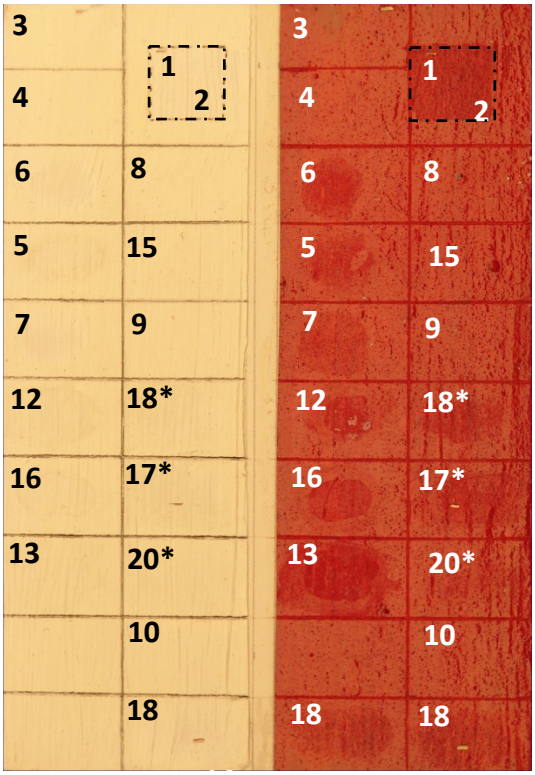
18. [Aliquat][DCA]

19. [Ch][OAc]

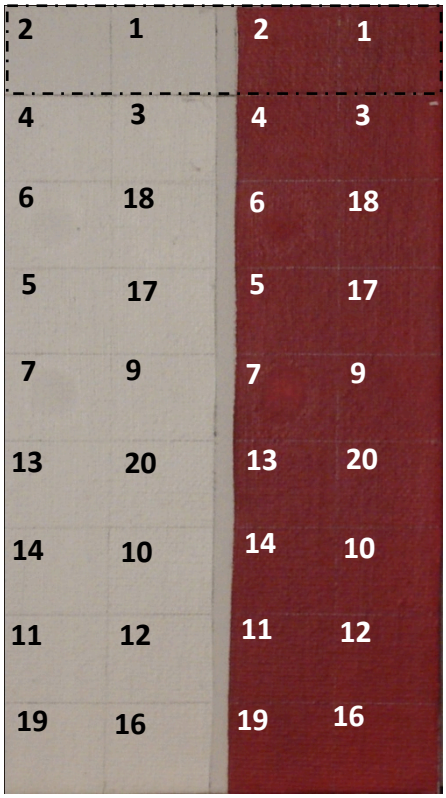
20. $[P_{6.6.6.14}][Cl]$

Figure 5S: Cleaning tests performed in mock-up 1.

Mock-up 2: dammar varnish over lead white and Lac Dye/vermillion



Mock-up 3: acrylic varnish over titanium white and quinacridone



- Unvarnished

Control zone and solvents:

1. unvarnished (control)

2. water (unvarnished)

3. Varnish (control)

4. water

5. water : ethanol 40:60 (v:v)

6. ethanol

7. toluene: acetone 60:40 (v:v)

Ionic Liquids:

8. [C_2OHmim][BF_4]

9. [C_5O_2mim][Cl]

10. [emim][$EtSO_4$]

11. [emim][MOEOEtSO_3]

12. [bmim][DCA]

13. [bmim][TFA]

14. [bmim][TfO]

15. [bmim][BF_4]

16. [omim][cl]

17.[Aliquat][Cl]

18. [Aliquat][DCA]

19. [Ch][OAc]

20. [$P_{6.6.6.14}$][Cl]

*IL removed with water:ethanol. 1:1 (v:v) solution

Figure 6S: Cleaning tests performed in mock-ups 2 and 3.

3.2. Experimental techniques

Photography with visible light and UV light

The mock-ups were photographed before and after the cleaning tests, with visible and UV light.

Stereomicroscope (SM)

The cleaning tests were made under the observation of the stereomicroscope (Olympus SZx12 with a camera Olympus DPSOFT) and photographed. The magnification used was 12,5X.

Optical Microscopy (OM)

The optical microscope (Axioplan 2 Imaging acquired with a digital camera Nikon DXM1200F) was used to observe the cross sections and the mock-ups surface. For the last case it was always used a magnification of 50X.

Micro Fourier transform infrared spectroscopy (μ-FTIR)

Infrared spectra were acquired with a Nicolet Nexus spectrophotometer interfaced with a Continuum microscope, with a MCT-A detector cooled by liquid nitrogen. All the spectra presented were obtained in reflectance, using ATR (Attenuated Total Reflection) mode. The spectra were obtained in the range of 4000–650cm^{-1}, with a resolution of 4cm^{-1} and 128 scans. For each cleaning test were effectuated three analyses in different areas.

3.3. Results of cleaning tests

Dammar varnish

The dammar varnish was applied in mock-ups 1 (*VanDyke Brown* and *Flake White*) and 2 (lead white and *Lac Dye*). In the case of mock-up 2, the observation with an optical microscopy allowed to verify that the cleaning process using [Aliquat][Cl] and [Aliquat][DCA] partially removed the varnish, as illustrated in Fig. 7S (images 5 and 6), where the quantity of varnish is in between the quantity observed in images 1 and 2 in the same figure. However, the water:ethanol mixture which was selected as clearance solvent also removed partially the varnish (compare images 3, 5 and 6).

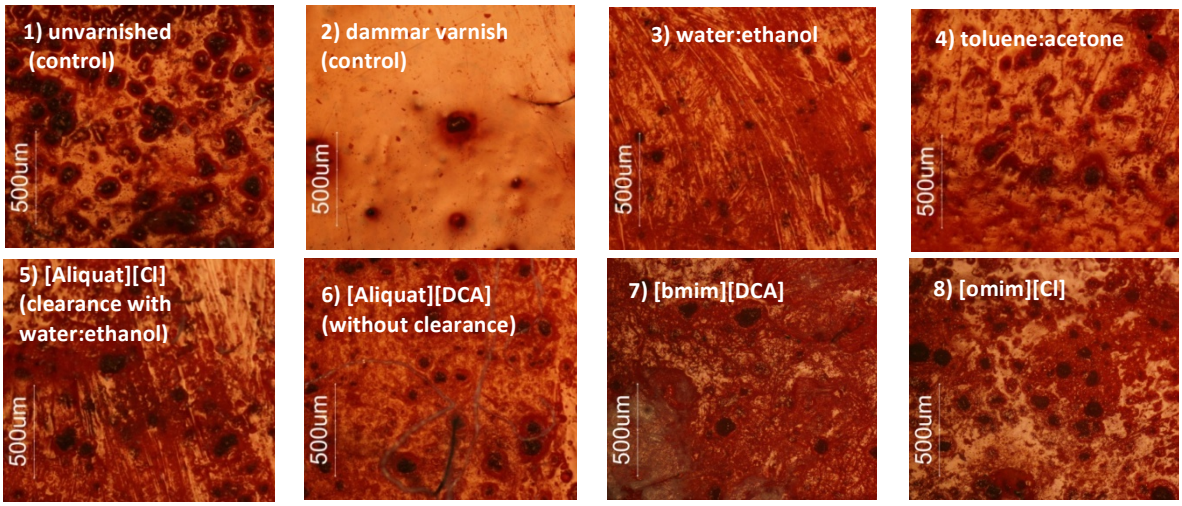


Figure 7S: Mock-up 2 surface images (red zone, dammar varnish), observed with OM, after cleaning tests. 1) unvarnished (control), 2) dammar varnish (control); 3) cleaning test with water:ethanol (control); 4) cleaning test with toluene:acetone (control); 5), 6), 7), 8) cleaning tests with the referred ILs.

The results obtained for mock-up 1 were similar, Fig. 8S. The most efficient ILs to remove the dammar varnish were [bmim][DCA] and [omim][Cl] (images c) and d)) while [Aliquat][DCA], [Aliquat][Cl] and [bmim][TFA] were less efficient, originating more heterogeneous cleaning (images e), f) e g), Fig. 8S). The ILs [Aliquat][DCA] and [Aliquat][Cl] showed some pigment (Vandike Brown) removal

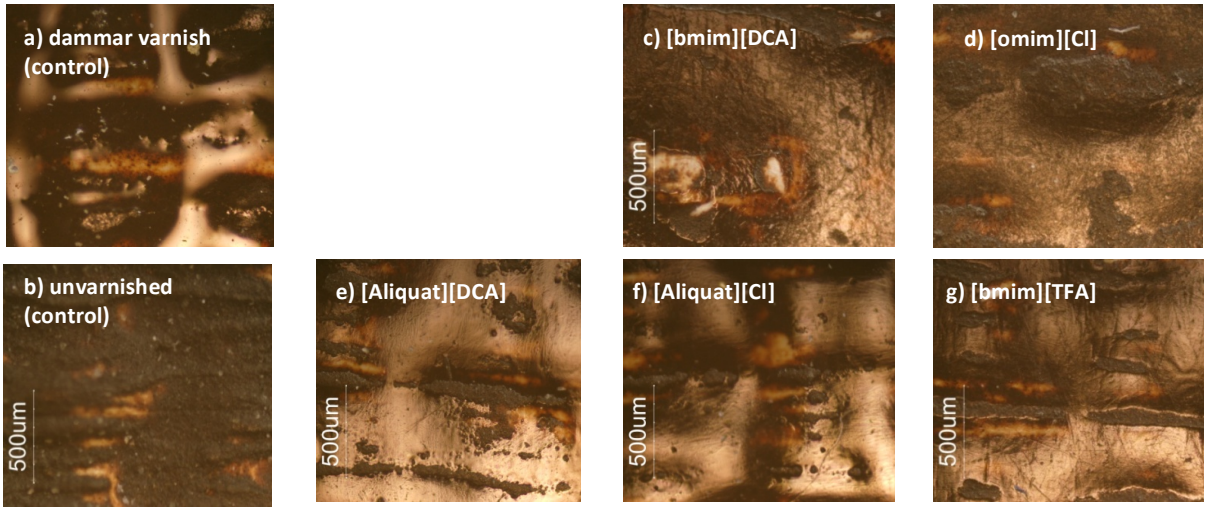


Figure 8S: Mock-up 1 surface images (brown zone, dammar varnish), observed wit OM, after cleaning tests. a) dammar varnish (control), b) unvarnished (control); c), d), e), f), g) cleaning tests with the referred ILs.

Whenever possible, depending on the position in the mock-up of the different regions defined in Figs. 5S and 6S, FTIR-ATR was used to follow the cleaning tests. Typically, three different points of analysis were chosen to run spectra. In the cleaning tests with [bmim][DCA] (characteristic CN stretching at 2160 cm^{-1}), FTIR analysis showed in one analysis point identical spectra between the unvarnished region (control) and the cleaned region, Fig. 9S, traces b) and d), respectively, while in

another analysis point varnish residues could still be detected (trace c)). In cleaning with [omim][Cl], all analysised points showed the presence of varnish traces (trace e)).

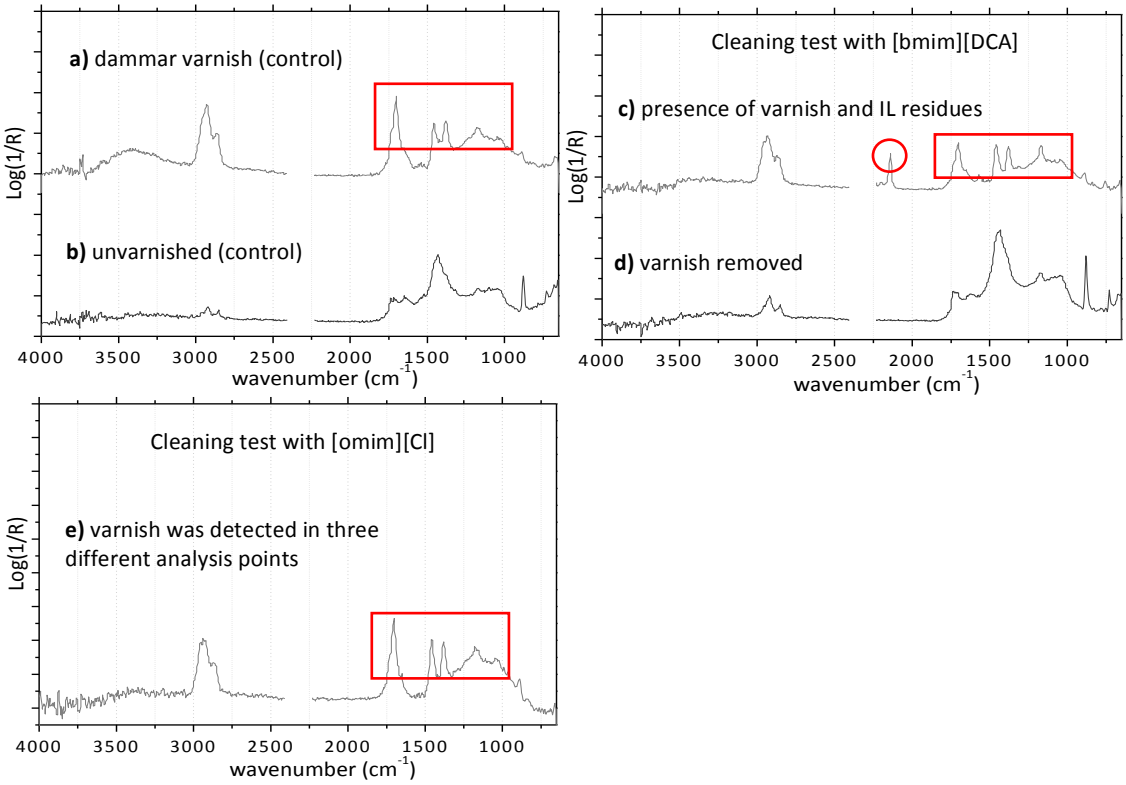


Figure 9S: FTIR-ATR Spectra after cleaning tests in mock-up 1 (brown zone, dammar varnish): a) dammar varnish (control); b) unvarnished (control); c) and d) spectra obtained on two different analysis points after the cleaning test with [bmim][DCA]; e) spectra obtained after the cleaning test with [omim][Cl]. Main varnish peaks are marked with a red square; DCA peak (CN stretching at 2160 cm^{-1}) is marked with a red circle.

Cleaning tests for dammar varnish removal in white zones in mock-ups 1 and 2 are shown in Figs. 10S – 12S.

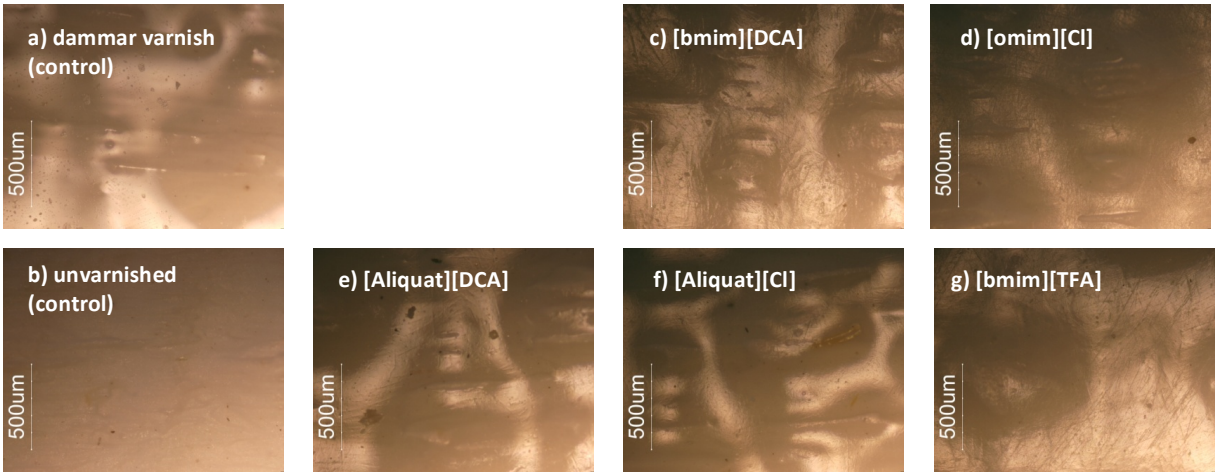


Figure 10S: Mock-up 1 surface images (white zone, dammar varnish), observed with OM, after cleaning tests. a) dammar varnish (control), b) unvarnished (control); c), d), e), f), g) cleaning tests with the referred ILs.

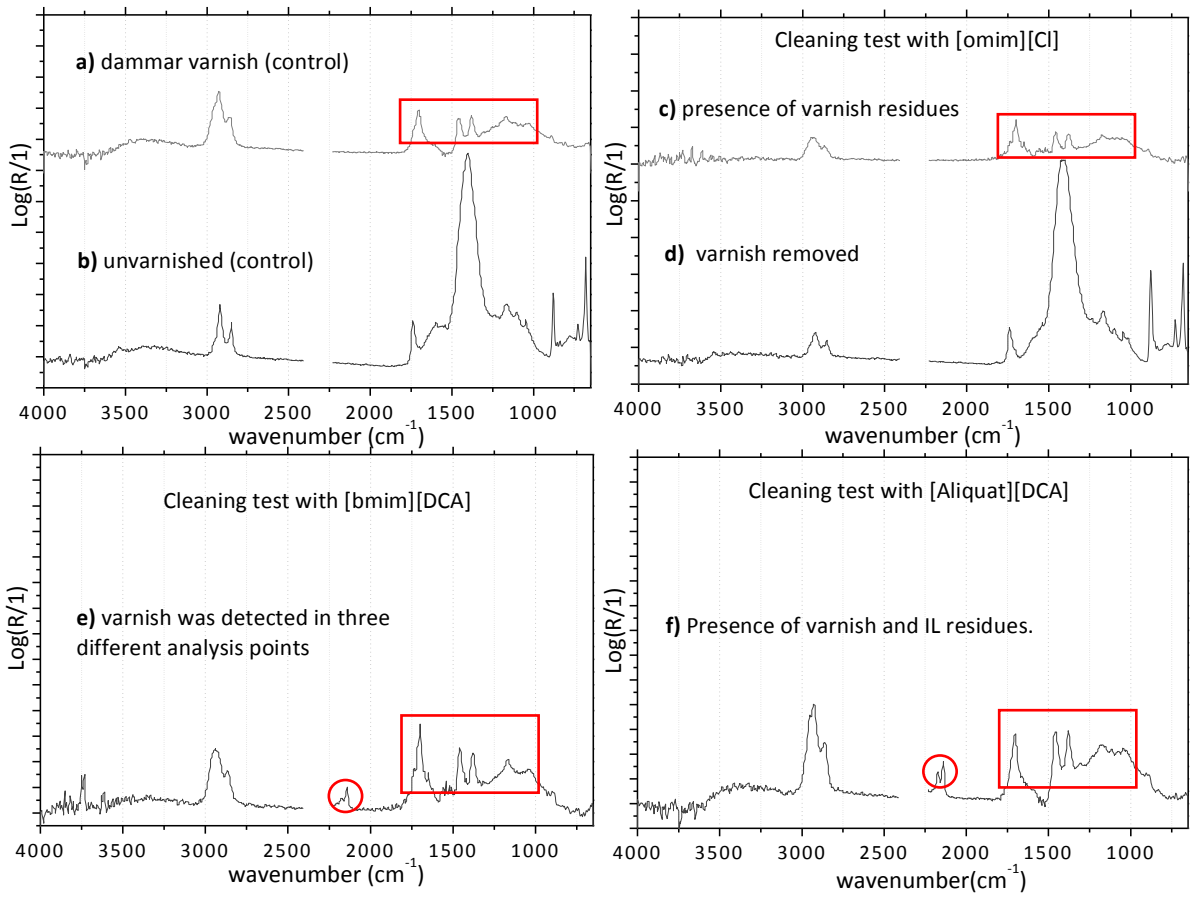


Figure 11S: FTIR-ATR Spectra after cleaning tests in the mock-up 1 (white zone, dammar varnish): a) dammar varnish (control); b) unvarnished (control); c) and d) spectra obtained for two different analysis points after the cleaning test with [omim][Cl]; e) spectra obtained for different analysis points after the cleaning test with [bmim][DCA]; f) spectra obtained for different analyse points after cleaning test with [Aliquat][DCA]. Main varnish peaks are marked with a red square; DCA peak (CN stretching at 2160 cm^{-1}) is marked with a red circle.

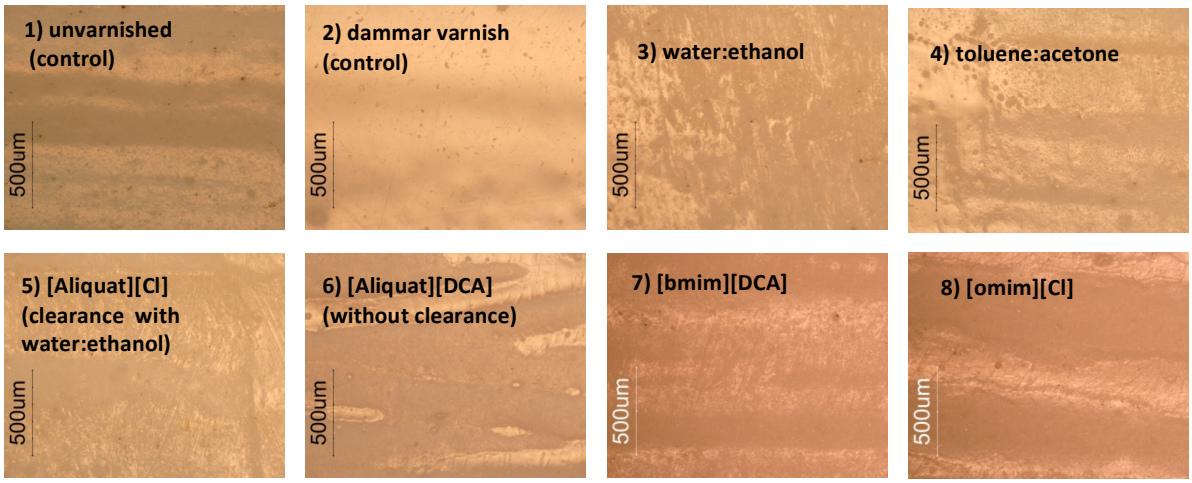


Figure 12S: Mock-up 2 surface images (white zone, dammar varnish), observed with OM, after cleaning tests. 1) unvarnished (control), 2) dammar varnish (control); 3) cleaning test with water:ethanol (control); 4) cleaning test with toluene:acetone (control); 5), 6), 7), 8) cleaning tests with the referred ILs.

Poly(vinyl acetate) based varnish

Cleaning tests for PVAc based varnish removal are shown in Fig. 13S as followed by stereomicroscopy (SM) and optical microscopy (OM). Fig. 14S shows part of the corresponding FTIR spectra. The results obtained for the white area in mock-up 1 were identical, Fig. 15S. The poly(vinyl acetate) varnish was efficiently removed using the ionic liquids [bmim][BF_4], [bmim][DCA], [bmim][TfO] and [bmim][TFA], although these last two were less efficient than the former ones.

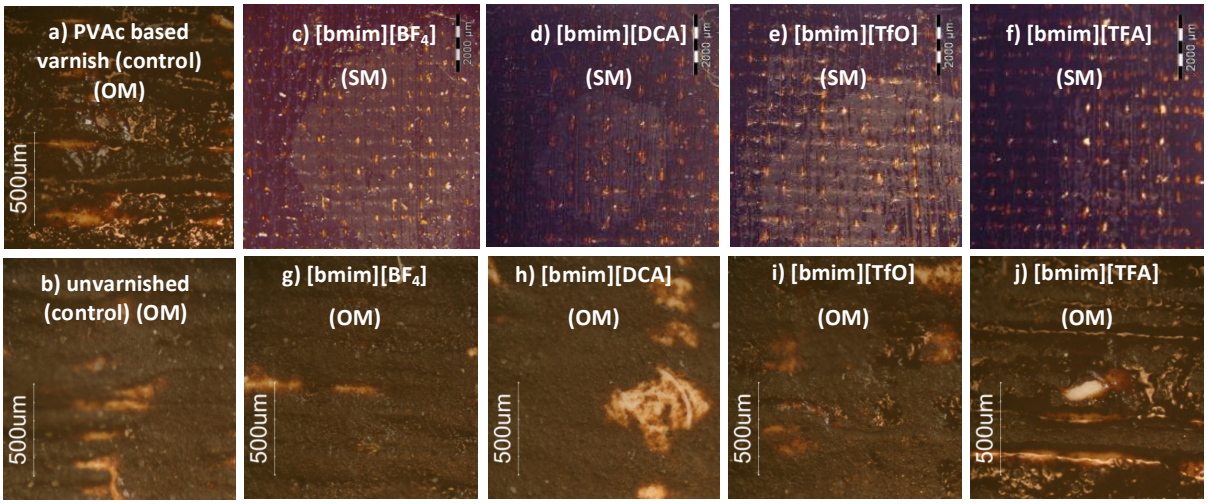


Figure 13S: Mock-up 1 surface images (brown zone, PVAc based varnish) after cleaning tests. a) PVAc based varnish (control), b) unvarnished (control) observed at OM; c), d), e), f) cleaning tests with the referred ILs, observed with a stereomicroscope (SM); g), h), i), j) cleaning tests with the referred ILs, observed with a Optical microscope (OM)

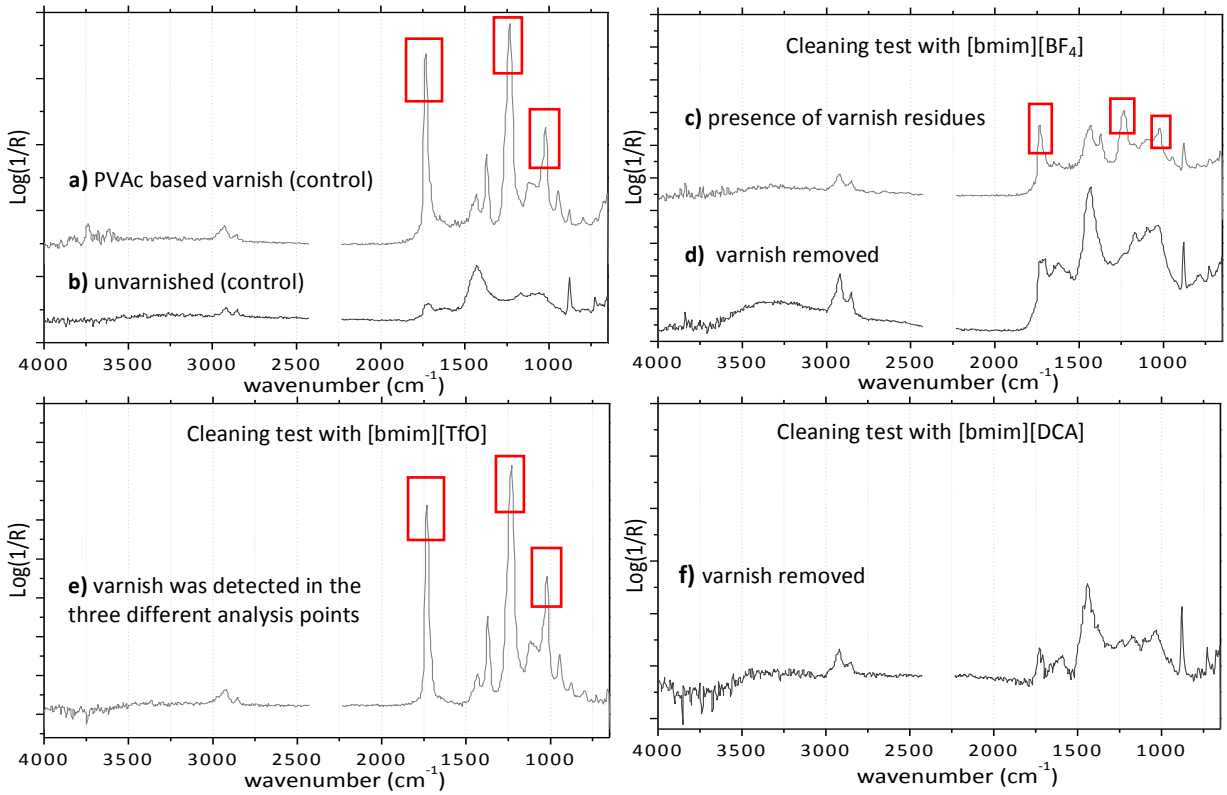


Figure 14S: FTIR-ATR Spectra after cleaning tests in the mock-up 1 (brown zone, PVAc based varnish): a) PVAc based varnish (control); b) unvarnished (control); c) and d) spectra obtained for two different analysis points after the cleaning test with [bmim][BF_4]; e) spectra obtained for different analysis points after cleaning test with [omim][TfO]; f) spectra obtained for different analyse points after cleaning test with [bmim][DCA]. Main varnish peaks are marked with a red square.

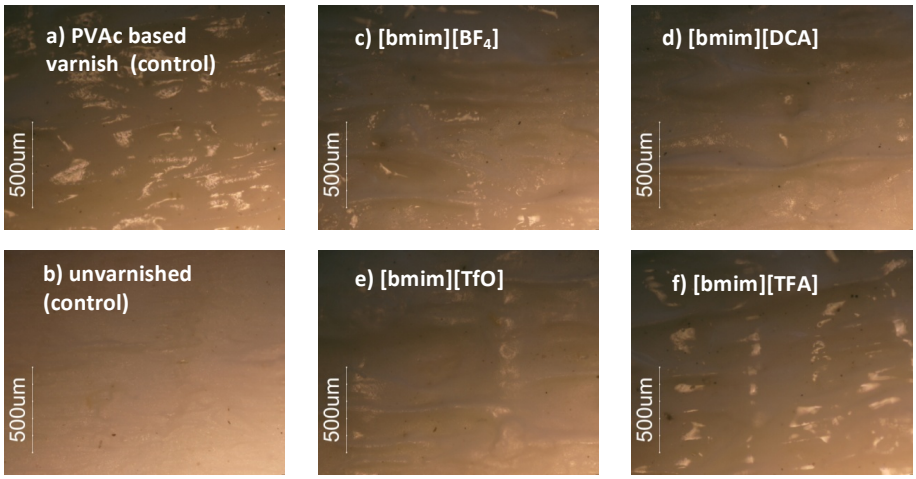


Figure 15S: Mock-up 1 surface images (white zone, PVAc based varnish), observed with OM, after cleaning tests. a) PVAc based varnish (control), b) unvarnished (control); c), d), e), f) cleaning tests with the referred ILs.

Polycyclohexanone based varnish

Cleaning tests for polycyclohexanone based varnish removal are shown in Figs. 16S – 18S, as followed by stereomicroscopy (SM) and optical microscopy (OM).

The best cleaning results were obtained with [bmim][DCA] and [omim][Cl], although [Aliquat][Cl] and [Aliquat][DCA] are able to partially remove the varnish. In cleaning with [bmim][DCA] and [omim][Cl], besides varnish removal the pigment (*VanDyke Brown)* was also partially removed. This observation has been detected for the same ILs in the cleaning tests with the dammar varnish.

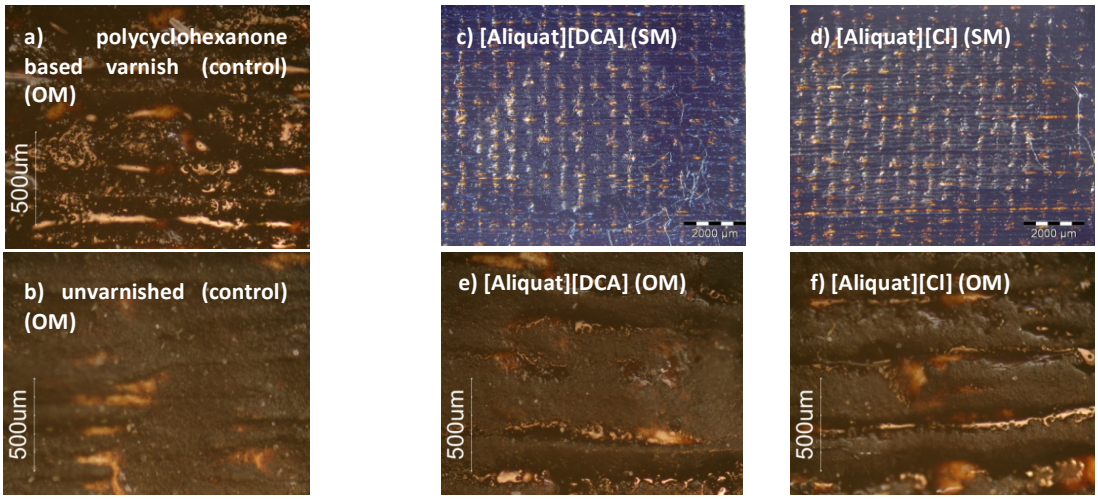


Figura 16S: Mock-up 1 surface images (brown zone, polycyclohexanone based varnish) after cleaning tests. a) polycyclohexanone based varnish (control), b) unvarnished (control) observed with OM; c), d) cleaning tests with the referred ILs, observed with a stereomicroscope (SM); e), f) cleaning tests with the referred ILs, observed with an optical microscope (OM)

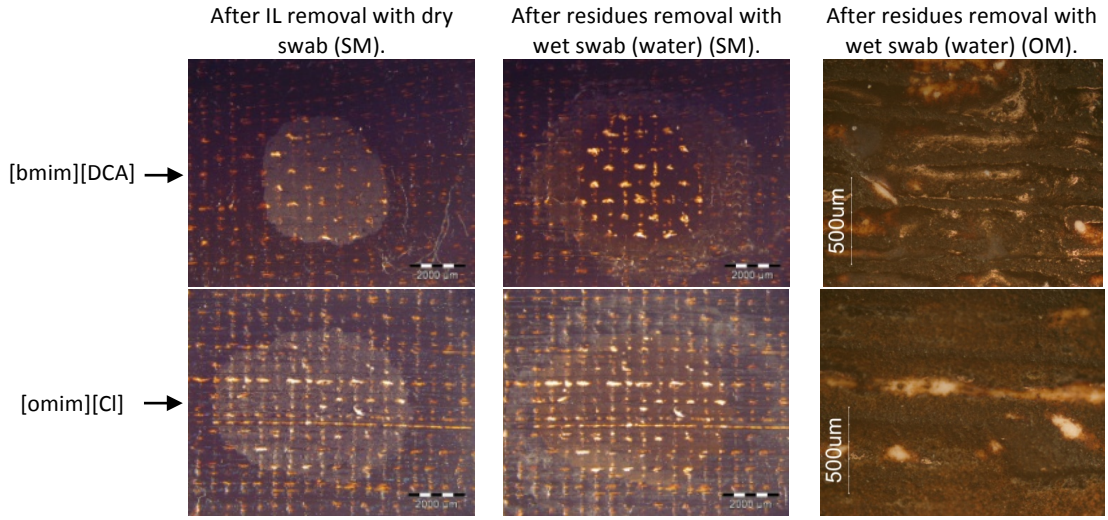


Figure 17S: Cleaning Tests with [bmim][DCA] and [omim][Cl] on mock-up 1 (brown zone, polycyclohexanone based varnish). Observation with a stereomicroscope (SM) (left and middle); observation with o OM (right).

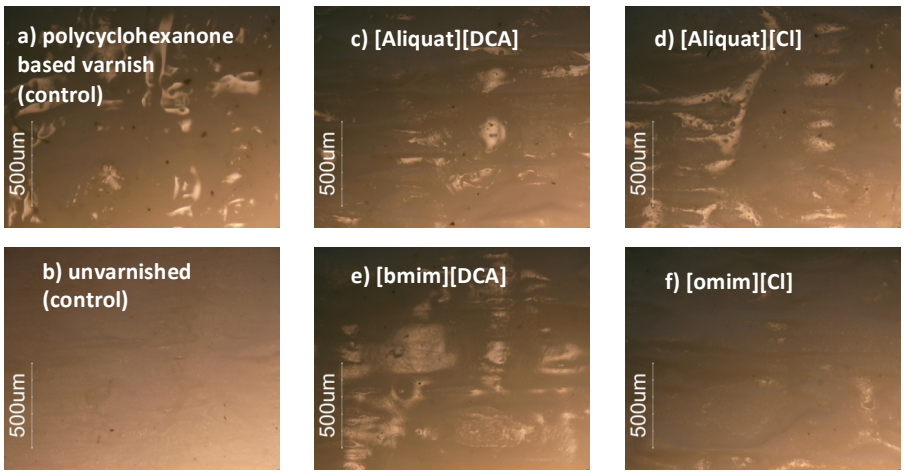


Figure 18S: Mock-up 1 surface images (white zone, polycyclohexanone based varnish), observed with OM, after cleaning tests. a) polycyclohexanone based varnish (control), b) unvarnished (control); c), d), e), f) cleaning tests with the referred ILs.

The FTIR spectra collected from the brown area (*VanDyke Brown*) with polycyclohexanone based varnish are complex due to the overlap of several peaks. The FTIR results were analysed only in the case of white area (*Flake White*), Fig. 19S.

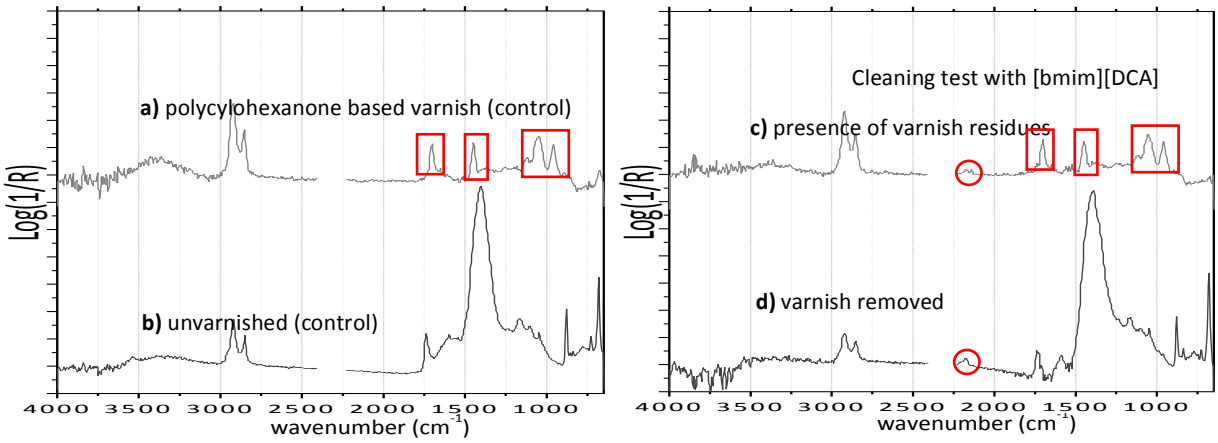


Figure 19S: FTIR-ATR Spectra after cleaning tests in the mock-up 1 (white zone, polycyclohexanone based varnish): a) polycyclohexanone based varnish (control); b) unvarnished (control); c) and d) spectra obtained for two different analysis points after the cleaning test with [bmim][DCA]. Main varnish peaks are marked with a red square; DCA peak (CN stretching at 2160 cm^{-1}) is marked with a red circle.

Acrylic varnish

Cleaning tests for acrylic varnish removal are shown in Figs. 20S and 21S, as followed by optical microscopy (OM). None of the thirteen ILs tested were efficient in the removal of the acrylic varnish by using the methodology defined for this work. These results were confirmed by cross-sections observation, Fig. 22S, and FTIR-ATR, for the case of [Aliquat][DCA].

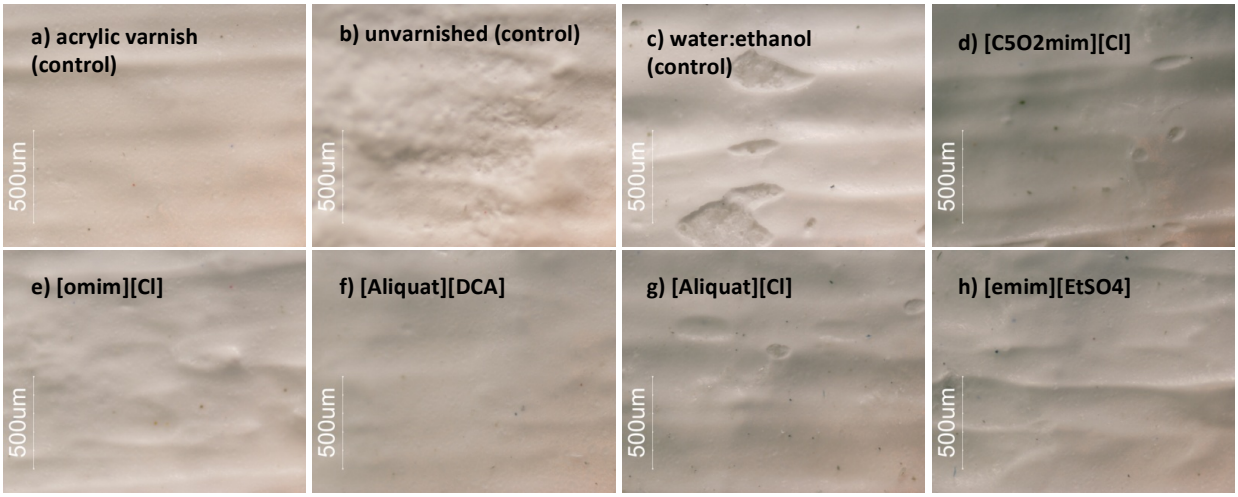


Figure 20S: Mock-up 3 surface images (white zone, acrylic varnish), observed with OM, after cleaning tests. a) acrylic varnish (control), b) unvarnished (control); c) cleaning tests with a solution of water:ethanol, d), e), f), g), h) cleaning tests with the referred ILs.

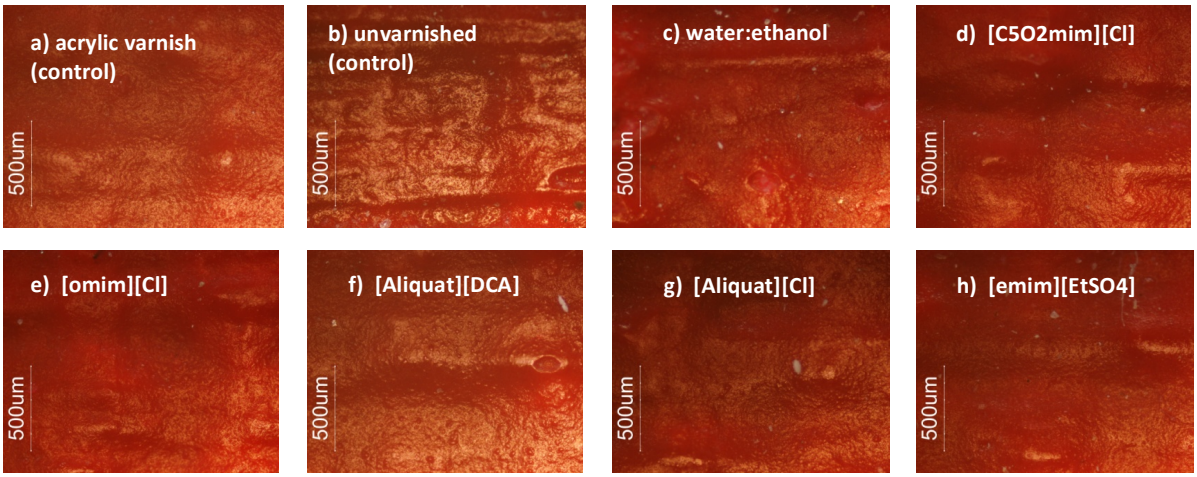


Figure 21S: Mock-up 3 surface images (red zone, quiacridone, acrylic varnish), observed with OM, after cleaning tests. a) acrylic varnish (control), b) unvarnished (control); c) cleaning tests with solution of water:ethanol, d), e), f), g), h) cleaning tests with the referred ILs.

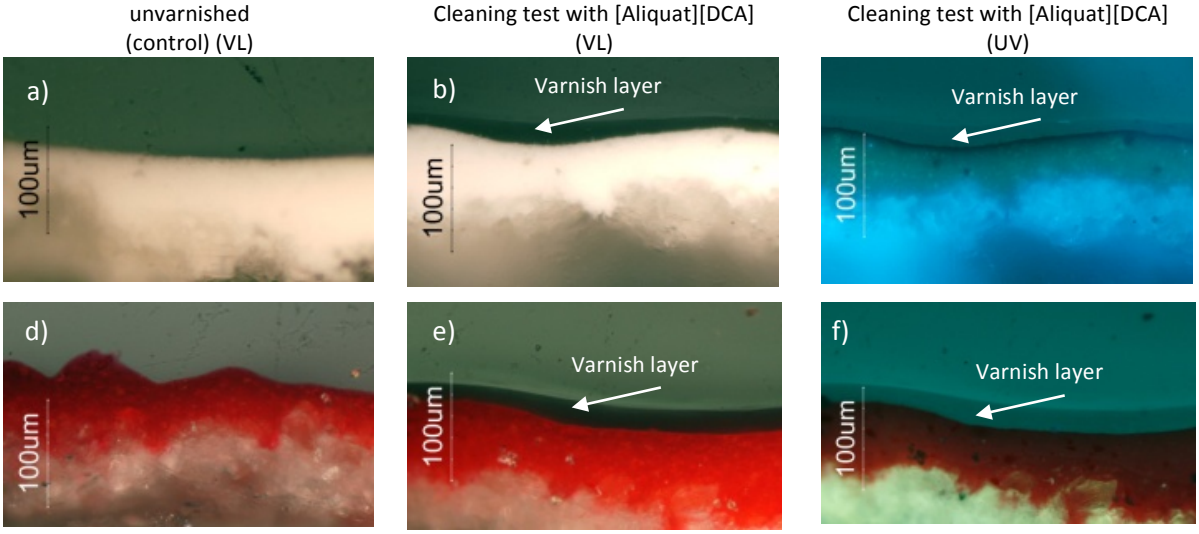


Figure 22S: Cross sections from the mock-up 3 (acrylic varnish), observed with OM under visible light (VL) and ultra-violet light (UV). a), b), c) white zone; d), e), f) red zone. a), d) unvarnished control; b), c), e), f) cleaning tests with [Aliquat][DCA].

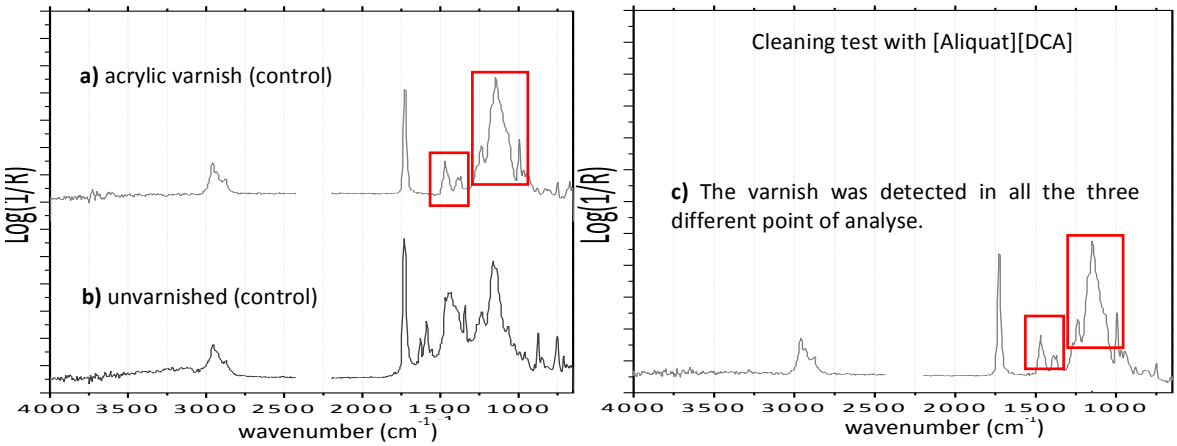


Figure 23S: FTIR-ATR Spectra after cleaning tests in the mock-up 3 (red zone, acrylic varnish): a) acrylic varnish (control); b) unvarnished (control); c) spectra obtained at different analysis points after the cleaning test with Aliquat][DCA]. Main varnish peaks are marked with a red square.

4. Assessing clearance efficiency with a fluorescent dye

In order to detect IL residues after clearance, a methodology was developed in which a strongly fluorescent dye was dissolved in the IL to be used as cleaning agent and the cleaning steps followed by fluorescence optical microscopy.

The IL with the fluorescence probe (Rhodamine B, p.a. for microscopy, Merck®, FW 479.02 g mol^{-1}) was prepared as following:

1. Dissolution of 1.00 mg of rhodamine B in ethanol (50 ml) (solution 1);
2. Dilution of 1.00 ml from solution 1 into 25 ml of ethanol (solution 2);
3. Addition of 500 µl from solution 2 to 200 µl of [bmim][BF_4] (homogeneous solution);
4. Evaporation of the ethanol under vacuum, leaving the IL with dissolved. rhodamine B.

The cleaning methodology defined in 3.1. was then applied using this [bmim][BF_4] with the Rhodamine B as fluorescent probe (4.2×10^{-6}M, 0.2% (w/v)) to remove PVAc varnish (brown area) in mock-up 1. The sample was fixed under the fluorescence optical microscope and each step of the cleaning procedure recorded photographically, keeping the same filter and lighting conditions (excitation in the visible; filter set: excitation 510-560, beam splitter 580, emission 590). The results are shown in Fig. 24S. The IL with Rhodamine B was applied to cover approximately the top left part of the image under the microscope (a); the presence of the IL is clearly seen from the Orange fluorescence of Rhodamine B. After clearance with the second dry cotton swab essentially all the ionic liquid is already removed (e), and when it proceeds to the two cotton swabs embedded with water, no perceptible residues can be observed (g). The final image under visible light (h) clearly shows the cleaning action of the IL.

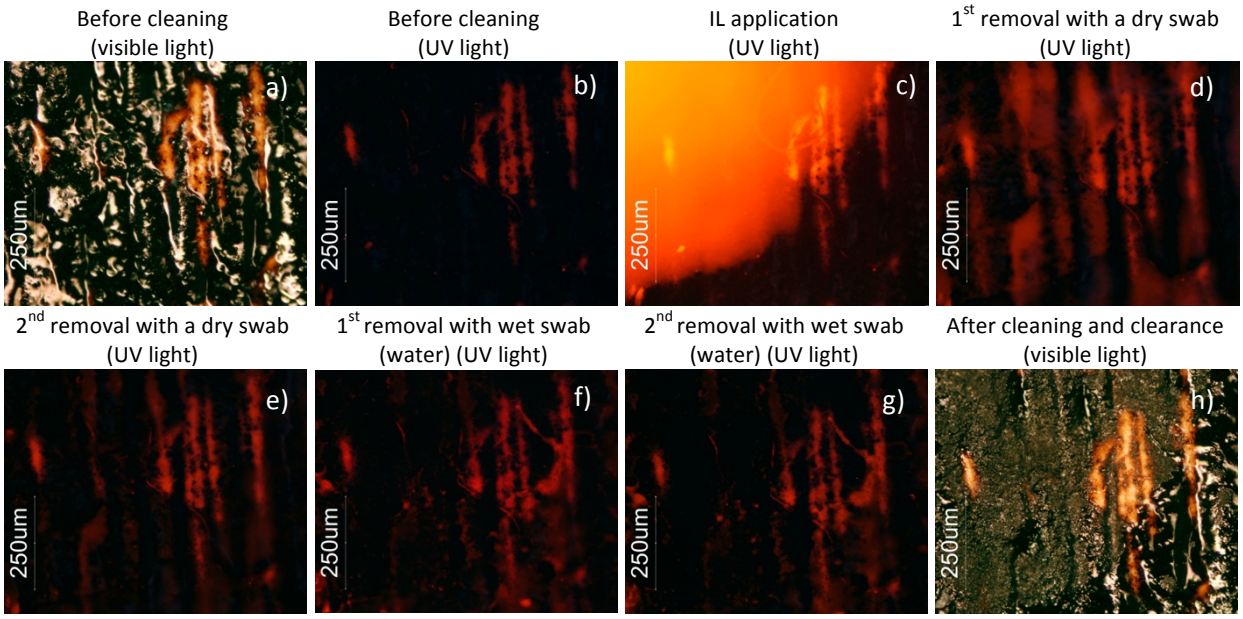


Figure 24S: Cleaning methodology using [bmim][BF_4] with Rhodamine B (0.2% w/v) as a fluorescence probe photographed under a fluorescence optical microscope upon excitation with 510-560 nm light.

5. Cleaning tests on a real painting

Cleaning tests were conducted in a portrait made in oil on canvas, Figs. 25S and 26S. The surface was covered with a dark naturally aged layer. Cross section analysis (Fig. 25S and 27S) showed that the surface was composed of two layers. As identified by FTIR-ATR (Fig. 28S), the inner varnish layer contains triterpenoids and is compatible with being a natural resin such as Mastic or Dammar, while the top layer should be a wax.

Figura 25S: Painting under visible light; the white dots (top right and half bottom center) point the locals where the samples for cross section and FTIR analysis were collected.

Figura 26S: Painting under UV light.

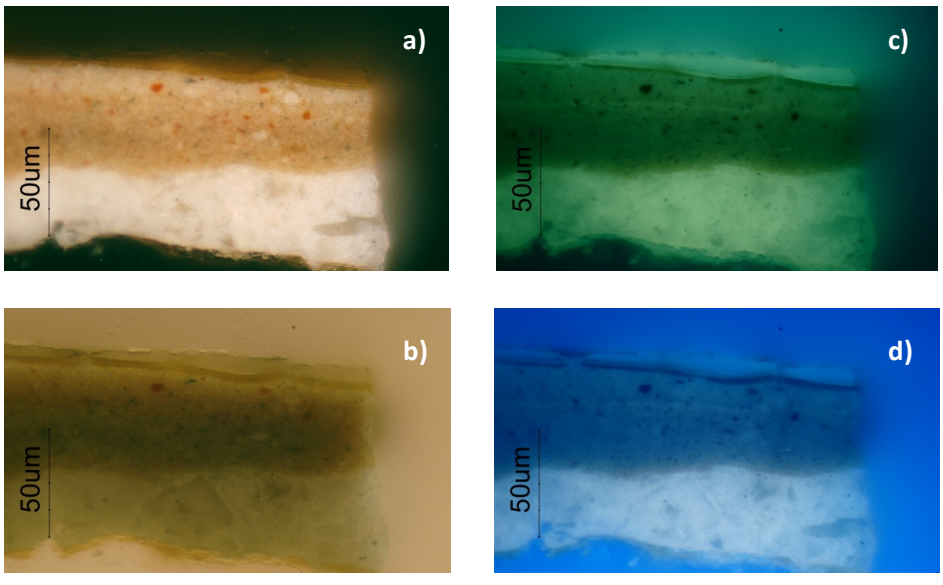


Figura 27S: Cross section from the brown paint area under reflected polarized light (a), reflected non-polarized light (b), UV light with green filter (c) and UV light with violet filter (d).

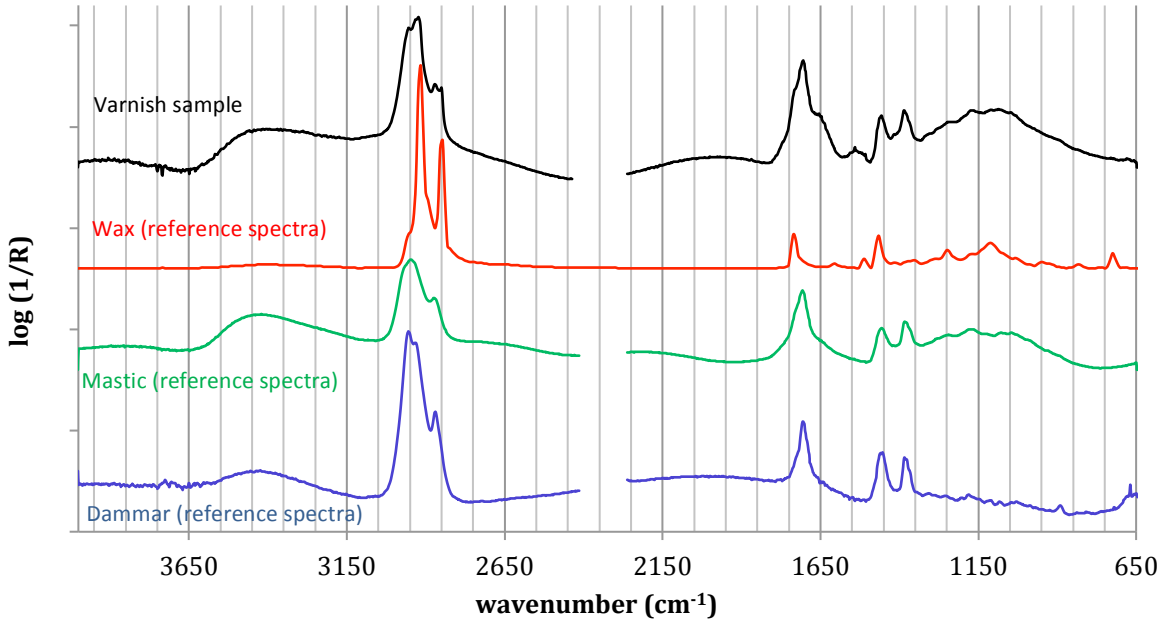


Figure 28S: FTIR Spectra of the varnish layer over the brown paint layer and reference spectra of the raw materials suspected to be contained in the varnish layers.

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Cleaning of the painting was carried out in the sampling zones (Fig. 25S), using [bmim][TFA] and [Aliquat][Cl], following the procedure with the stereomicroscope. Preliminary tests with the required clearance solvents for these ILs, respectively water and water:ethanol 40:60 (v/v), were carried out by applying a drop of each solvent during 20 min; no removal of varnish or pigment was detected. The cleaning was carried out as follows: i) a drop of each IL was applied on the surface and left for five minutes, the ILs were removed mechanically with a clean swab (twice) and finally with a swab embedded in the clearance solvent (twice). The procedure was repeated three times until no varnish was visually present in the surface. Results of the cleaning procedure are reposrted in Figs. 29S and 30S. No pigment removal could be noticed.

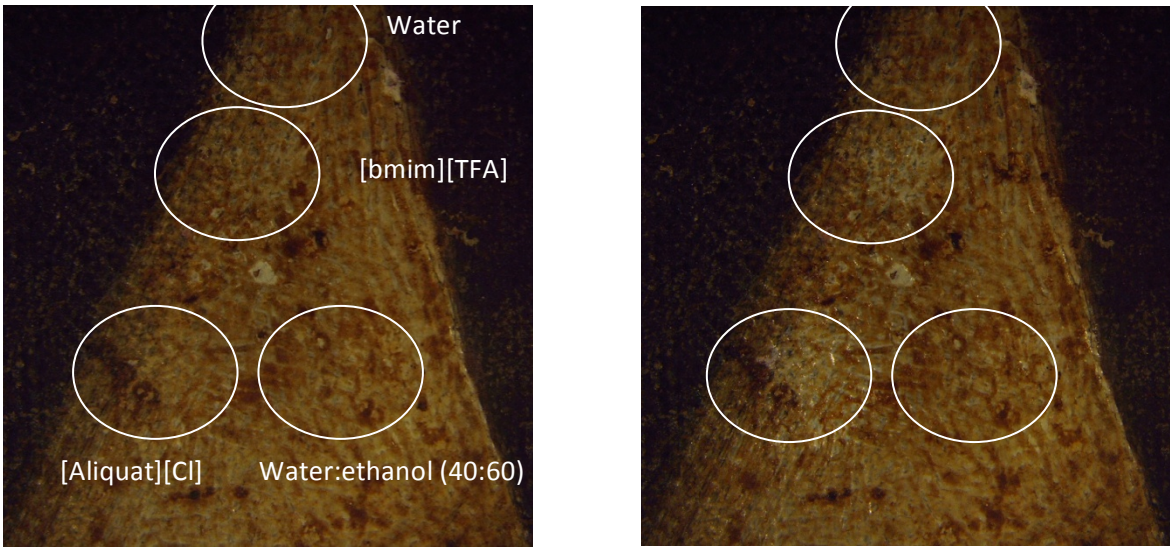

Figure 29S: Images of the test areas before (left) and after cleaning with ILs (right) taken under the stereomicroscope.

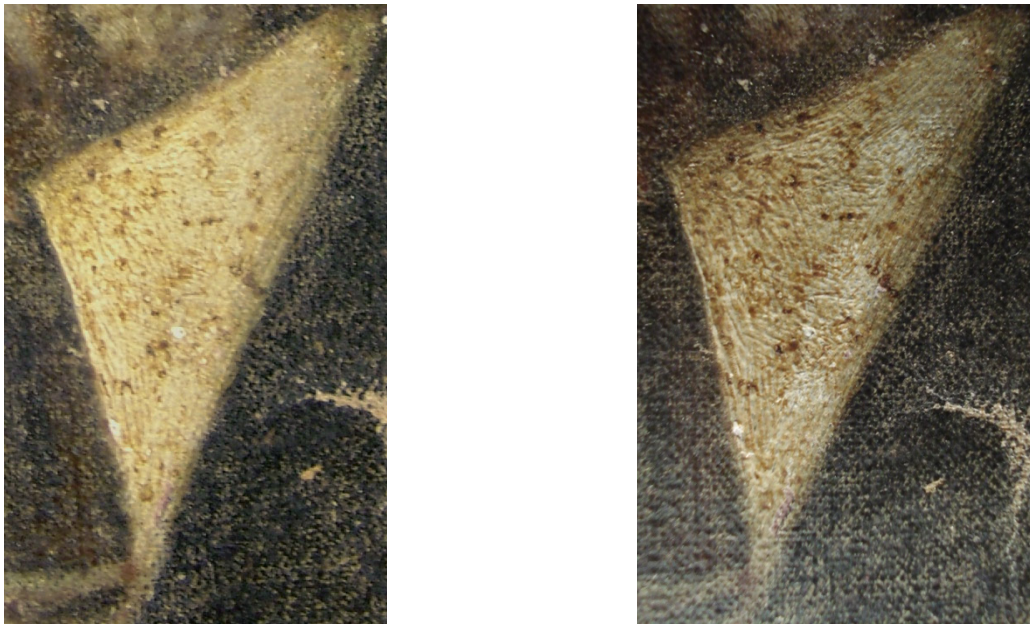

Figure 30S: Images of the test areas before (left) and after cleaning with ILs (right).

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