

REMOVAL OF A SYNTHETIC SOILING MIXTURE ON MASTIC, SHELLAC & LAROPAL® K80 COATINGS USING TWO HYDROGELS

SCIENTIFIC PAPER

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This work investigates the effects of two hydrogels used for the selective removal of a synthetic soiling mixture on mastic, shellac and Laropal® K80 varnishes. The varnishes were spin-coated on aluminium tiles which were subjected to accelerated degradation in a xenon-arc fadeometer. A synthetic mixture, simulating urban pollution, was produced and applied on the degraded varnish films. The fabricated soil-resin film samples were further irradiated in the xenon-arc fadeometer. Subsequently, a CH₃COONa hydrogel (pH=5.5) and a C₂₃H₃₉O₂COONa hydrogel (pH=7.8) were produced using CH₃COOH and C₂₃H₃₉O₂COOH, NaOH, Triton X-100 and hydroxyl-propyl-methyl-cellulose. Both hydrogels were applied to the corresponding samples and the cleaning results were evaluated using UV-induced fluorescence imaging, FT-IR and Reflection Absorption Infrared Spectroscopy (RAIRS) and semi-quantitative data analysis. The experimental data indicated the removal of both the soiling layer as well as the partial removal of the uppermost layers of the degraded coatings. It is assumed that this phenomenon was caused by the penetration of the soiling layer into the substrates followed by partial ionisation and dissolution of the upper layers of the degraded films. A case study of surface cleaning of a 20th century panel painting from accumulated soils is also presented.

1 Introduction

Varnishes enhance colour saturation and hue and control the glossiness of painted surfaces.¹⁻³ Additionally, they protect the underlying paint layers from direct interaction with radiation, atmospheric oxygen and various polluting agents, such as particulate matter leading to soiling of surfaces.^{1,2,4,5} Owing to their direct exposure to the atmosphere, varnishes degrade mainly by the diffusion of oxygen assisted by the presence of a number of gaseous pollutants and airborne particles.^{4,7,8} In particular, the deposition of these polluting agents contributes to autoxidation and hydrolysis of resin components leading, ultimately, to the physical and optical deterioration of varnishes.^{1,4,5,9-13} Moreover, varnish discoloration, which is caused by autoxidation and condensation reactions,^{2,4,5,9-11,13,14} results in the darkening of the underlying paint layers that are further obscured by the accumulation of airborne particles on the coating surface.^{8,15} These particles adhere to varnish films by means of van der Waals and ionic forces.¹⁶ The penetration of particulate deposits into a coating depends on particle size, with particle diameters spanning across

received: 22.07.2012
accepted: 09.12.2012

key words:
resin coatings, artificial soiling, accelerated degradation, UV fluorescence, FTIR

the nano to micrometer scale,¹⁷ as well as the hardness of the varnish film, the elasticity of both particles and coatings, moisture, temperature and the contact area.^{18,19} According to these parameters and the penetration depth, the force of adhesion of a particle onto the surface of a varnish may vary. Often, adhesion is so strong that removal of soiling from a varnish becomes a laborious task.

Most of the established conservation procedures to “clean” surfaces with a deteriorated and darkened varnish, involve dissolution in a wide range of organic solvents.^{1,20,21} However, the diffusion of liquid organic solvents into varnished and painted surfaces is hardly controllable.¹ A major cause for the latter observation is the compositional heterogeneity of aged varnishes that is instigated by the recently established depth-dependent gradients in the degrees of oxidation, polarity, cross-linking and polymerisation.^{6,13,14,22} Therefore, a solvent that would marginally dissolve the highly degraded surface layers of an aged varnish, e.g. to enable removal of adhered deposits, will eventually reach the interface with the underlying paint, due to the depth-wise increasing solubility of the varnish itself.⁶ Solvent diffusion causes immediate dissolution of the soluble fraction of the incorporated resins, as well as swelling of paints^{23,24} and leaching of volatile constituents of the paint binding media.¹ Thus, even if required, there are no non-aqueous solvent-based solutions benign enough to merely unsoil varnishes. Although the low viscosity of solvents is still beneficial in the removal of unwanted aged coatings via resin dissolution, the same property is quite restraining when a varnish must be preserved. Indeed, some varnishes constitute intrinsic parts of works of art. For example, the late Russian Orthodox Icons bear yellow coatings which incorporate resins such as shellac or amber over silver alloy gildings so as to give the impression of gold.^{12,25} Amongst diverse side-effects, removal of the original coatings in the latter case results in immediate tarnishing of the silver alloy leafs, especially in polluted environments,²⁶ causing irreversible damage to the surface. Moreover, there are cases where, during removal of soiling, the removal of the original varnish would damage the historical, artistic and occasionally the monetary value of such works of art. Consequently, when the cleaning objective involves only the removal of the soiled part of varnished surfaces, safer and more selective cleaning methods must be investigated, such as the use of hydrogels.^{19,27,28}

Hydrogels, which take advantage of the physical properties of water as a solvent, such as its high polarity and dielectric constant,²⁹ are composites that incorporate hydrophilic detergent systems, buffered solutions, surfactants, resin soaps and in some cases enzymes and chelators.^{19,21,27} Naturally derived polymers such as cellulose derivatives and agar, which are commonly employed as gellants in the food industry, in catalysis, drug delivery, etc., as well as polyacrylic acid polymers (Carbopol) are used to gel the aforementioned cleaning agents and form hydrogels for art conservation.^{19,21} Recently, polyacrylamides and poly(vinyl alcohol)-borate gels have been employed as gel vehicles for aqueous micellar solutions for the conservation of works of art.³⁰⁻³² These viscous composite systems provide a number of rheological advantages over other fluid solutions,

such as precise positioning, controlled depth-wise distribution, no spilling and the means of keeping dissolved compounds in suspension. The precision and selectivity of surface cleaning using hydrogels has been well documented with case studies involving the removal of: (a) soiling layers from paint,^{19,27} (b) aged varnish from paint with diverse binding media,^{19,30-32} (c) the removal of newer varnishes on top of older ones,¹⁹ and (d) removal of polymer consolidants from paints.^{19,30-32}

This work investigates the effects of two characteristic sodium salt-based hydrogels on typical paint varnishes. These hydrogels were formulated and employed to selectively remove an artificial soiling layer applied on the respective coatings. In this context, three spirit varnishes based on mastic, shellac and polycyclohexanone Laropal® K80 resins, were produced. These coatings were subjected to accelerated degradation according to international protocols^{33,34} and soiled with an artificial urban soiling mixture, according to textile soiling protocols.^{35,36} Additional accelerated degradation cycles followed in order to assist the integration of the soiling particles within the degraded coatings. The synthesis of two hydrogels, one based on sodium acetate with a pH of 5.5 and one based on sodium deoxycholate with a pH of 7.8 is described and their cleaning efficiency aiming both at the removal of soiling and the preservation of the underlying coatings is examined. Moreover, the case study of soiling removal from the surface of a 20th century panel painting using the sodium acetate hydrogel is also described. Investigations were performed by UV fluorescence imaging, Fourier transform infrared spectroscopy (FT-IR) and Reflection Absorption Infrared Spectroscopy (RAIRS).-

2 Materials and Methods

2.1 Varnishes

Three spirit varnishes were produced: (a) 30% w/v mastic resin in xylene (Riedel & Haen), (b) 15% w/v shellac resin in ethanol (Merck) and (c) 30% w/v polycyclohexanone resin (BASF, Laropal® K80) in ethanol (Merck). Prior to dissolution each resin was ground to fine powder and weighed on an OHAUS® Scout Pro SPU202 analytical scale (± 0.01 g). Each resin/solvent blend was homogenised using a VELP SCIENTIFICA® ARE Heating Magnetic stirrer. Aluminium substrates, measuring 3 cm x 3 cm, were employed to facilitate examination according to the analytical requirements.

Varnish films of homogeneous thickness were produced by spin-coating of the resin solutions on a custom-made low revolution spinner. The efficiency of the spinner was verified using an Avidsen SMT 700 Voltage and Ammeter and a DT2234B Digital Tachometer (range: 2.5-99.999 rpm, uncertainty: $\pm 0.05\% + 1$ significant digit) so as to provide as accurate measurements of voltage, amperage and rounds per minute (rpm) as possible. 1 ml of each resin solution was dropped on the centre of each tile and spinned at 2,780 rpm for 180 s. The same process was repeated on 7 aluminium substrates for each varnish resulting in a total of 21 samples. In particular, the tiles corresponding to each varnish were sorted out by selecting a control sample before degradation,

	Before degradation	After degradation	After degradation and soiling	After cleaning
Resin Mastic in Xylene (RMX)	A	B	C	D, E, F, G
Resin Shellac in EtOH (RSE)	A	B	C	D, E, F, G
Resin Laropal® K80 in EtOH (RLE)	A	B	C	D, E, F, G

Table 1: Classification of aluminium samples by their codenames and series.

a control sample after accelerated degradation (section 2.2) and a control sample after accelerated degradation and after soiling deposition (section 2.3). The remaining four aluminium coated tiles for each varnish were used for the cleaning tests (Table 1).

2.2 Accelerated Degradation

After coating, the samples of series B-G were placed in a SUNTEST® XLS+ xenon-arc fadeometer, equipped with an optical borosilicate filter to imitate sunlight radiation (230-800 nm), and received a total dose of 11.65 Mlux•h that is equivalent to 20 museum years according to international standards.³³ After soiling, samples C-G, received an additional dose of 582.4 klux•h that is equivalent to 1 museum year for the better incorporation of the soiling particles in the surface layers of the varnishes.

2.3 Soiling Mixture

The soiling mixture was produced according to published protocols.^{28,35,36} The dry portion of the soiling mixture consisted of: (a) Sphagnum peat moss (20.8% w/w), (b) Carbon black (1.9% w/w), (c) Iron oxide (burnt sienna pigment, 0.5% w/w), (d) Gelatine (10.4% w/w), (e) Soluble starch (10.4% w/w), (f) Portland Type I cement (18.6% w/w), (g) silica gel (1.9% w/w), (h) lime (16.7% w/w), (i) kaolin (18.6% w/w). The wet portion of the mixture consisted of (a) high grade mineral (paraffinic) oil, and (b) Chloroform (99+% pure CHCl₃, Acros Organics). The quantities were measured and prepared as follows: The peat moss was pre-treated with a 400 W blender by first weighing out a 30-35 g amount and shearing it on the highest setting for 60 s. The blender was then stopped, the sides of the vessel scraped and the whole amount was re-blended for 60 s on the highest setting again. The blended material was then sifted through a mesh screen to produce a finer, smaller and more uniform preparation in terms of size distribution. The prescribed amount of peat moss was then blended with the rest of the "dry" ingredients (that is all of the ingredients except for the mineral oil and the chloroform) at the highest setting for 60 s. The blender was then stopped, the sides of the vessel scraped and the whole mixture was re-blended for 60 s. The result was a finely divided gray/black powder in appearance. Accordingly, a 4.5% v/v solution of mineral oil in chloroform was produced. In the end, the solid and the liquid parts were mixed, thus form-

ing a 3% w/v heterogeneous 2-phase suspension. The resulting soiling solution was then applied on the aluminium samples belonging to series C-G for each resin (Table 2-1) with a soft brush.

2.4 Hydrogels

Two hydrogels were formulated. The materials used were: (a) glacial acetic acid (99.5% pure CH₃COOH, Acros Organics), (b) sodium hydroxide (1 M NaOH, Acros Organics), (c) deoxycholic acid (C₂₃H₃₉O₂COOH, Acros Organics), (d) hydroxyl-propyl-methyl-cellulose (4000 cps HPMC, Acros Organics), (e) polyoxyethylene octyl-phenyl ether (Triton X-100™, Acros Organics), (f) deionised water. The first hydrogel was based on an acetic acid/sodium hydroxide (sodium acetate) solution with a pH of 5.5 while the second hydrogel was based on a deoxycholic acid/sodium hydroxide (sodium deoxycholate) solution with a pH of 7.8.

In essence, an acetic acid/sodium acetate buffer in deionised water (0.5% v/v) was produced. The resulting solution was titrated with NaOH until the pH reached 5.5. Subsequently, 50 ml of the buffer solution were put aside to be used later for the first stage of clearance, which would involve the removal of any potential hydrogel residues.²¹ Finally, a 0.6% v/v solution of the non-ionic surfactant Triton X-100™ and the remaining 50 ml of the buffer solution were produced. The solution was then stirred and gelled using approximately 5 g of HPMC. The second hydrogel was a 0.5% w/v solution of deoxycholic acid/sodium hydroxide solution in deionised water. The solution was titrated with sodium hydroxide until the pH increased to 7.8. As was the case with the previous gel, 50 ml of the buffer solution were set aside while a 0.6% v/v solution of Triton X-100™ in the remaining 50 ml buffer was produced. Finally, the solution was gelled with the addition of approximately 5 g of HPMC.

The hydrogels were applied on the samples on designated areas with a size 00 soft brush, left for a few seconds and were immediately wiped off using a dry cotton swab. The second and final stage, which involved rinsing with mineral spirits as proposed by Wolbers,¹⁹ was skipped on purpose so as to prevent possible sample contamination and interference with results of RAIRS analysis that would follow.

2.5 Visible Light and UV Fluorescence Imaging

Photographic documentation under visible light and UV fluorescent radiation was performed with a 6.1 effective Mpixels Nikon D50 digital camera, fitted with an 18-55 mm, f/3.5-5.6G ED II (Ø52 mm) Nikkor lens. Typically, the camera was adjusted to f/5.6, at 25 s shutter speed, and a fixed sensitivity of 100 ISO, both for UV and visible photography. A linear polariser by Cinko® was employed to reduce glare and enhance picture quality. UV fluorescent imaging was carried out with a Waldmann W® Diagnosis Light TypHLL 264 portable device that incorporated two high efficacy lamps (Philips® TL 4W/08 F4T5/BLB) emitting blacklight blue radiation within a wavelength range of 315-408 nm (peak at 368 nm). Finally, UV reflections

were eliminated using a Wratten 2E, Kodak® cut-off filter.

2.6 Fourier Transform Infrared Spectroscopy

To confirm their identity, samples of each resin were collected, pulverised and mixed with a small quantity of KBr (10% w/w). The resulting mixture was then pressed into pellets using a Scac press at a pressure of 10 t/cm² and analyzed using Fourier Transform Infrared Spectroscopy in a Perkin–Elmer® GX I spectrometer. The spectra were obtained in the mid-IR range (4000–400 cm⁻¹) after 20 scans at a resolution of 4 cm⁻¹. Spectral analysis was carried out using the Spectrum® software package by Perkin-Elmer®.

2.7 Reflection Absorption Infrared Spectroscopy

Due to the nature of the aluminium substrates used, the samples were directly analyzed using Reflection Absorption Infrared Spectroscopy in a Perkin–Elmer® GX I spectrometer fitted with the Perkin-Elmer® Fixed Angle Specular Reflectance accessory. The spectra were obtained in the mid-IR range (4000–400 cm⁻¹) after 20 scans at a resolution of 4 cm⁻¹ at a fixed beam angle of 16°. Spectral analysis was again carried out using the Spectrum® software package by Perkin-Elmer®.

2.8 Semi-Quantitative Analysis of IR Data

To further corroborate the results of the qualitative analysis and provide a quantitative measure of the reduction of the soiling layer after cleaning, a semi-quantitative analysis was performed. This essentially descriptive statistical analysis aimed at the comparison of specific absorbance bands that corresponded to the identified inorganic and organic constituents of the soiling mixture. The semi-quantitative analysis on the selected absorbance bands was performed with the spectra obtained from the samples corresponding to the states before and after implementation of both hydrogels. Analysis was enabled by integration of the areas of the IR spectra peaks of these characteristic absorbance bands, including: (a) 2775–3050 cm⁻¹, 1430–1478 cm⁻¹ and 716–732 cm⁻¹ due to asymmetrical/symmetrical stretching, bending and rocking vibrations of methylene groups, (b) 3600–3660 cm⁻¹ and 869–880 cm⁻¹ due to the presence Ca(OH)₂ and CaCO₃ respectively, and (c) 1670–1840 cm⁻¹ due to stretching vibrations of the C=O bond. These selected bands provided evidence for (a) the presence of mineral oil from the soiling mixture, (b) the reduction of the most prominent and strong absorbing inorganic particulate soils, and (c) the degree of oxidative ageing of the varnishes. The semi-quantitative analysis was carried out using OriginPro 8.1® software.

3 Results

Figure 1a shows the UV fluorescence of the varnish samples prior to accelerated degradation. The char-

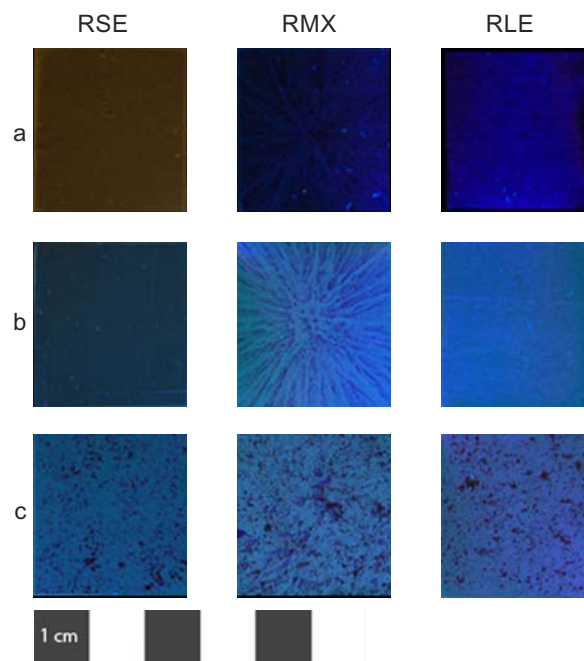


Figure 1: UV fluorescence of the varnish coatings (a) prior to degradation, (b) after degradation and (c) after degradation and soiling.

acteristic bright orange fluorescence of undegraded shellac is evident.^{38,39} In contrast, neither mastic nor ketone (Laropal® K80) coatings fluoresced to a considerable degree prior to degradation. Figure 1b shows the increase in the intensity of fluorescence after accelerated degradation where the coated samples received a total dose of 11.65 Mlux·h, which corresponded to 20 museum years.³³ The mastic samples exhibited light purple-green emission, the shellac samples exhibited green emission and the ketone resin samples exhibited blue emission. These observations are consistent with the generation of low molecular weight entities during ageing, such as saturated acids, ketones and aldehydes that absorb UV radiation and emit at longer wavelengths in the visible region of the electromagnetic spectrum.^{40,41} Soiling and successive degradation of the samples resulted in decreased fluorescence intensity in all three cases (Figure 1c), inferring the occurrence of quenching. In particular, the dispersed random-sized particulate pollutants, which are readily discriminated on the surface of the samples, hinder UV irradiation of the underlying coatings and as a consequence fluorescence emission is blocked at these particular spots.

The IR spectra of the coatings prior to and after degradation and soiling are shown in Figures 2–4 and the most characteristic frequency assignments are listed in Table 2. After degradation, all samples showed considerable increases in absorbance, especially in the fingerprint region (below 1850 cm⁻¹). The observed changes included: (a) increase in the absorbance bands between ~3200–3400 cm⁻¹ owing to bonded hydroxyl (OH) functional groups, (b) increases and shifts of the bands between ~1700–1725 cm⁻¹ that are related to the carbonyl (C=O) bond (c) increase in absorbance at ~1370–1380 cm⁻¹ owing to symmetrical bending vibrations of C–H bonds in methyl (CH₃) groups compared to the absorbance at ~1445–1485 cm⁻¹ owing to bending vibrations of C–H bonds in methylene (CH₂) groups and (d) increases in

the fingerprint region between ~ 400 and 1500 cm^{-1} that is associated with a wide range of interactions with C-C ($\sim 700\text{-}1300\text{ cm}^{-1}$), and C-O bonds in alcohols, esters, ethers and carboxylic acids ($\sim 1100\text{-}1300\text{ cm}^{-1}$).⁴²⁻⁴⁴ These changes established efficient degra-

Wavenumber (cm^{-1})	Assignment
3400–3200	O–H stretching
2949, 2929, 2921, 2867, 2855, 2853	C–H stretching of CH_3
1721, 1708, 1707	C=O stretching of aldehydes, ketones and carboxylic acids
1656, 1643, 1636	C=C stretching in vinyl groups
1467, 1457, 1449	C–H bending of CH_3 and CH_2
1385, 1377, 1376	C–H bending of CH_3 (possible gem or iso dimethyl group)
1261, 1258, 1256, 1165, 1159, 1121, 1112	C–O stretching of alcohols, carboxylic acids, esters and ethers, C–C skeletal vibrations
1056, 960 (L^*)	C–O stretching and cyclohexane ring vibrations
886, 837, 826	C–H out-of-plane bend

Table 2: Frequency assignments of the most prominent and characteristic common IR absorbance bands in Mastic, Shellac and Laropal® K80 samples. L^* = Absorption peaks specific to Laropal® K80 films.

Wavenumber (cm^{-1})	Assignment
3600-3660	Calcium hydroxide [$\text{Ca}(\text{OH})_2$]
2775-3050	C–H stretching vibrations of CH_2 (possible mineral oil participation)
1430-1478	C–H bending vibrations of CH_2 (possible mineral oil participation)
990-1127	Silicon dioxide
869-880	Calcium carbonate (CaCO_3)
716-732	C–H rocking vibrations of CH_2 (possible mineral oil participation)
445-495	Iron oxide (Fe_2O_3)

Table 3: Assignment of the observed peaks to organic and inorganic components of the soiling layer.

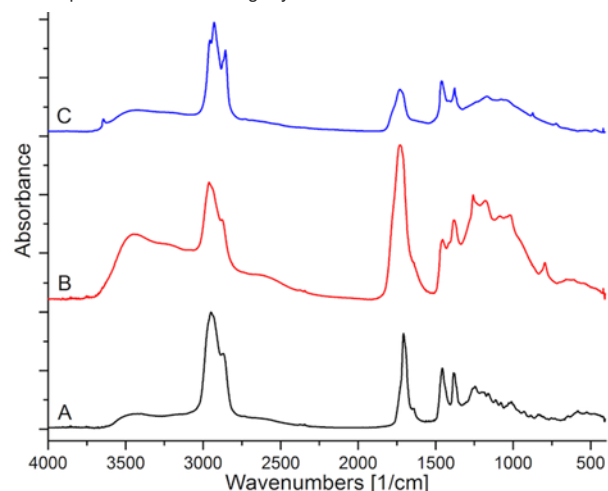


Figure 2: RAIRS spectra obtained for the mastic films prior to degradation (black), after degradation (red) and after soiling (blue). The spectra were normalised to the C–H asymmetrical/symmetrical stretch peak.

dation of the samples^{2,22} and justified the aforementioned alterations in UV fluorescence between the samples prior and post accelerated degradation (Figure 1b).

Soiling of the three varnishes resulted in the emergence of additional absorbance bands that were ascribed to the inorganic and organic components of the soiling mixture (Table 3, Figs. 2-4). Specifically, the identified inorganic constituents of the soiling mixture included: (a) calcium hydroxide $\text{Ca}(\text{OH})_2$, which exhibited strong absorbance at $3600\text{-}3660\text{ cm}^{-1}$, (b) silicon dioxide (SiO_2) with a weak absorbance at $990\text{-}1127\text{ cm}^{-1}$, (c) calcium carbonate (CaCO_3) with a strong absorbance at $869\text{-}880\text{ cm}^{-1}$ and (d) iron(III) oxide (Fe_2O_3) with weak absorbance at $445\text{-}495\text{ cm}^{-1}$.⁴⁵ The identified constituents of the organic portion of the soiling mixture mostly involved mineral oil, since the incorporated chloroform should have evaporated due to its high vapour pressure.⁴⁷ The presence of mineral oil, a mixture of long chain aliphatic

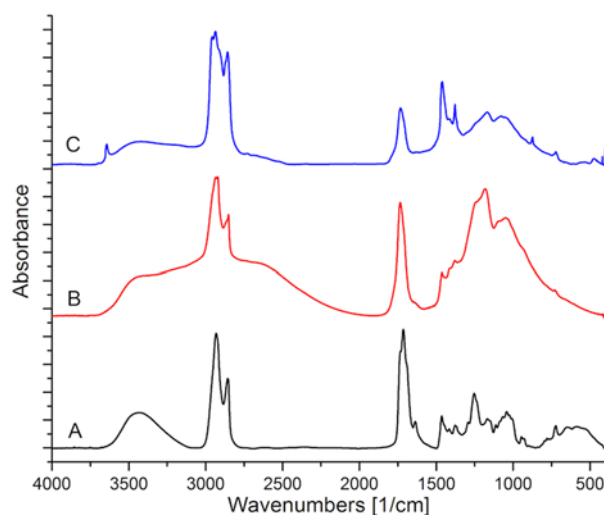


Figure 3: RAIRS spectra obtained for the shellac films prior to degradation (black), after degradation (red) and after soiling (blue). The spectra were normalised to the C–H asymmetrical/symmetrical stretch peak.

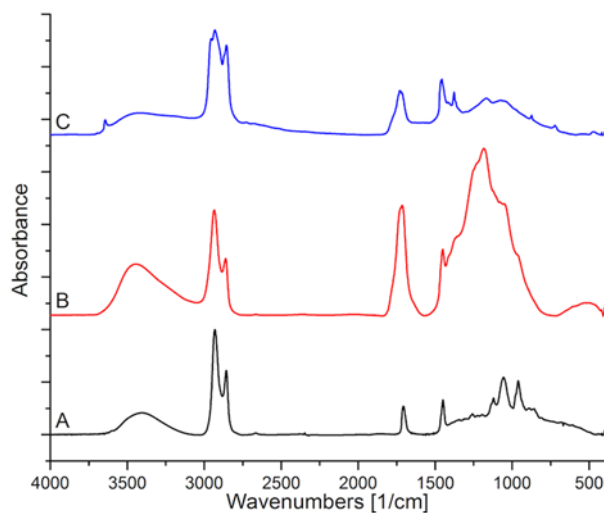


Figure 4: RAIRS spectra obtained for the Laropal® K80 films prior to degradation (black), after degradation (red) and after soiling (blue). The spectra were normalised to the C–H asymmetrical/symmetrical stretch peak.

hydrocarbons,⁴⁸ increased the absorbance of specific functional groups. In particular, major changes in absorbance were noted at 2775-3050 cm^{-1} and 1430-1478 cm^{-1} . These changes correspond to the asymmetrical/symmetrical stretching and the associated bending vibrations of methylene groups respectively.⁴²⁻⁴⁴ The newly appeared medium-intensity absorption band at 716-732 cm^{-1} , that corresponds to CH_2 rocking, also established the presence of $-(\text{CH}_2)_n-$ groups (where $n \geq 3$). These groups are pertinent to aliphatic hydrocarbons^{43,44} and constitute the backbone of mineral oils.⁴⁸ Finally, in order to exclude the possibility of the dissolution of the upper varnish layers by chloroform in the soiling mixture, the areas

corresponding to carbonyl absorbance were studied for all samples (Figs. 2-4).

After the application of the hydrogels on the surfaces of samples, UV-induced fluorescence revealed the successful removal of the soiling layer. Macroscopically, the underlying degraded varnishes appeared clean while still fluorescing to a noticeable degree. Figure 5 shows the samples prior to and after cleaning with the sodium acetate hydrogel (pH=5.5) and the sodium deoxycholate hydrogel (pH=7.8), respectively. In particular, the sodium acetate gel (pH=5.5), did not seem to affect fluorescence of the underlying mastic and shellac coatings compared to the respective controls. On the contrary, cleaning was less selective and apparently led to a partial removal of the ketone resin degraded film as indicated by the evident reduction in fluorescence (RLE, Figure 5a-c). Nevertheless, the remaining ketone resin film still fluoresced, most probably because the bulk of the resinous substrate was preserved. The sodium deoxycholate gel (pH=7.8) affected the shellac and ketone resin films to a noticeable degree -possibly the former more than the latter- as determined by the perceived reduction in fluorescence. Contrary to the observation with regards to the shellac and ketone films, the mastic samples retained their fluorescence after unsoiling with the sodium deoxycholate hydrogel, at least when compared with the corresponding controls after soiling.

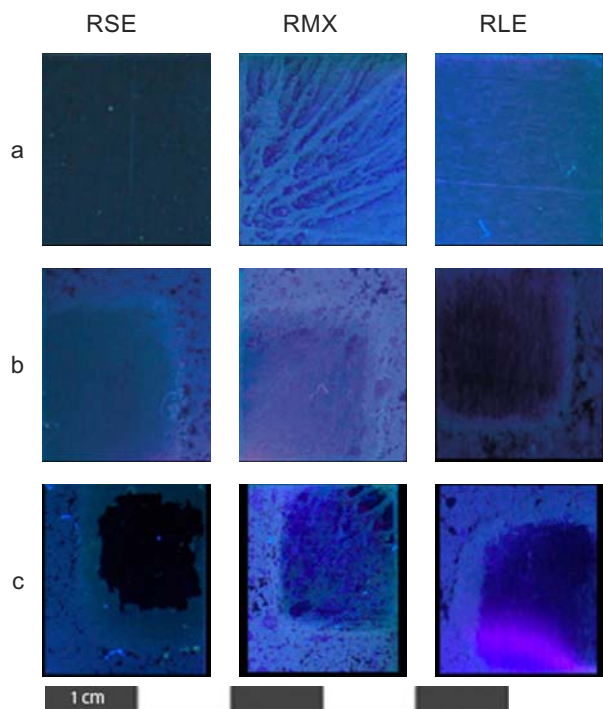


Figure 5: UV fluorescence (a) before cleaning, (b) after cleaning with the sodium acetate (pH=5.5) hydrogel and (c) the sodium deoxycholate hydrogel (pH=7.8).

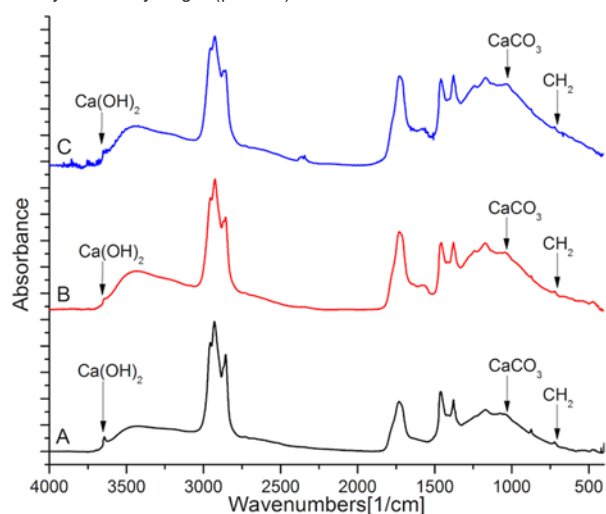


Figure 6: RAIRS spectra obtained for the mastic film (sample code: RMX30E) before cleaning (green), after cleaning with the sodium acetate hydrogel (red) and after cleaning with the sodium deoxycholate hydrogel (blue). The spectra were normalised to the C-H asymmetrical/symmetrical stretch peak.

Figures 6-8 present the IR spectra of the varnish samples before and after the cleaning procedure. After cleaning, all samples showed significant decreases in absorbance contributed by the inorganic constituents of the soiling layer, such as $\text{Ca}(\text{OH})_2$, SiO_2 , CaCO_3 and Fe_2O_3 peaking at 3600-3660 cm^{-1} , 990-1127 cm^{-1} , 869-880 cm^{-1} and 445-495 cm^{-1} respectively (Table 3), indicating that the majority of the particulates were successfully removed. In particular, Figure 6 shows how the mastic samples reacted after the cleaning trials. Both hydrogels produced similar results, first by removing the identified organic and inorganic portion of the soiling layer (Table 3-2) and then by removing part of the degraded resin mastic films. This is evident by looking at the multiplication factors, which were x3.73 and x2.45 after implementation of the sodium deoxycholate and the sodium acetate hydrogels respectively. The shellac samples seem to have reacted in a similar fashion as the ketone resin films (Figure 7). Examination of the IR spectra indicated that both gels removed most of the particulate soils and substantial amounts of the degraded shellac films. Again, the sodium acetate hydrogel removed a larger amount of the degraded films as the differences in absorbance between the unsoiled and soiled spectra show. In the case of the shellac films the multiplication factors used to normalise the IR spectra to unity were x1.86 and x4.46 after cleaning with the sodium deoxycholate and sodium acetate hydrogels respectively. Figure 8 shows the normalised IR spectra for the ketone resin samples before and after cleaning with both hydrogels. Judging by the spectral characteristics, such as the shape and intensity of the associated absorption bands, it can be deduced that both hydrogels removed a portion of the organic and inorganic parts of the soiling layer. However, they might have also removed a substantial amount of the degraded resin film. This assumption can be further corroborated by

examining the multiplication factors used to normalise the spectra. In this case, these multiplication factors were $\times 1.74$ and $\times 10.74$ after unsoiling with the sodium deoxycholate and the sodium acetate hydrogels respectively. For all, based on the IR spectra obtained, it can be assumed that both hydrogels removed greater amounts of particulate soils on mastic than on ketone and shellac coatings, which is supported by the macroscopic data of UV fluorescence (Figure 5).

In particular, the lack of fluorescence for both the shellac and ketone coatings after cleaning coincided with a reduction in absorbance noted in the IR spectra for both coatings (Figures 7 and 8), thus pointing to a case of partial removal of the degraded films. The findings of UV fluorescence and FT-IR for the mastic samples after cleaning are also in accordance showing, interestingly, a more restrained reaction to

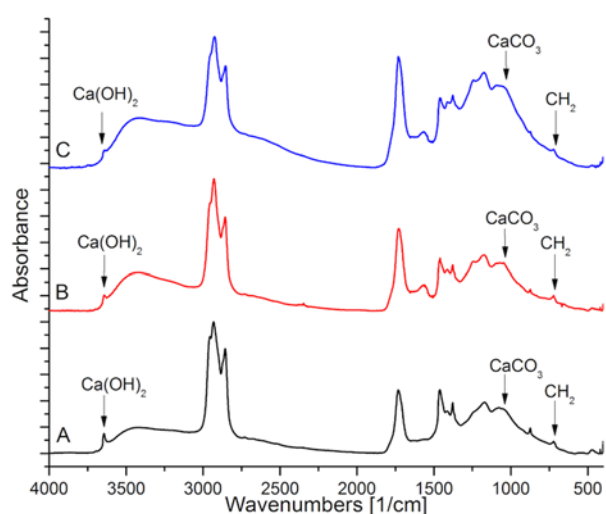


Figure 7: RAIRS spectra obtained for the shellac film (sample code: RSE15E) before cleaning (green), after cleaning with the sodium acetate hydrogel (red) and after cleaning with the sodium deoxycholate hydrogel (blue). The spectra were normalised to the C-H asymmetrical/symmetrical stretch peak.

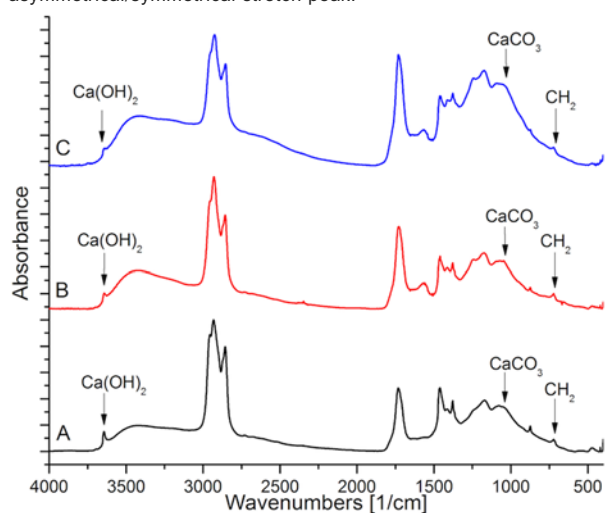


Figure 8: RAIRS spectra obtained for the Laropal® K80 film (sample code: RLE30E) before cleaning (green), after cleaning with the sodium acetate hydrogel (blue) and after cleaning with the sodium deoxycholate hydrogel (red). The spectra were normalised to the C-H asymmetrical/symmetrical stretch peak.

both hydrogels and a lesser degree of degraded film removal (Figure 6). Finally, the spectra for all coatings after interaction with the gels revealed the presence of a weak absorbance band ranging from 1530



Figure 9: Comparison of VIS images of the uncleaned area (left, marked by the black border) and the cleaned area (right).



Figure 10: Comparison of UV fluorescence images of uncleaned area (left, marked by the white border) and the cleaned area (right).

	Mastic									Shellac									Laropal								
	Before cleaning			After cleaning Gel 1 (pH=5.5)			After cleaning Gel 2 (pH=7.8)			Before cleaning			After cleaning Gel 1 (pH=5.5)			After cleaning Gel 2 (pH=7.8)			Before cleaning			After cleaning Gel 1 (pH=5.5)			After cleaning Gel 2 (pH=7.8)		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
C-H stretching (3050-2775 cm ⁻¹)	1.3	152	0.29	34	78	0.29	31	80	1.2	138	0.28	29	79	0.50	53	62	1.2	131	0.20	24	82	0.40	39	70			
C-H bending (1478-1430 cm ⁻¹)	0.90	10	0.19	2.1	80	0.16	4.7	54	0.80	9.2	0.19	1.9	79	0.22	2.6	72	0.71	9.4	0.15	1.5	84	0.19	2.1	78			
C-H rocking (732-716 cm ⁻¹)	0.13	80	35	50	37.5	48	50	37.5	0.17	0.20	45	80	56	74	10	95	0.11	0.14	30	60	58	48	30	79			
C=O stretching (1670-1840 cm ⁻¹)	0.55	31	0.21	12	61	0.18	10	68	0.62	28	0.27	12.4	55	0.39	21	25	0.49	26	0.11	5.4	79	0.20	10	60			
CaCO ₃ (869-880 cm ⁻¹)	0.34	0.24	75	20	92	81	20	92	0.33	0.19	91	40	79	97	30	84	0.26	0.21	57	50	76	88	20	91			
Ca(OH) ₂ (3600-3660 cm ⁻¹)	0.24	3.0	37	0.35	88.4	24	0.12	96	0.21	2.8	45	0.45	84	56	0.41	85	0.78	2.4	44	0.50	79	37	0.40	83			

Table 4: Area integrals for the respective absorbance bands measured before and after cleaning with both hydrogels, where (a) represents the maximum peak intensity of absorbance, and (b) the area integral and (c) the percentage difference of the area integrals compared to the particular bands before cleaning (when the latter is considered as 100%). The measurements for each varnish were conducted on series D-G. The values presented here are the mean values for each case and have been rounded to 2 significant digits.

to 1610 cm⁻¹ approximately. This band could possibly be attributed to the vibrational-rotational modes of carboxylates,⁴³ the presence of which may be justified by the broadening of the O-H band at approximately 3000 cm⁻¹. This observation points to the presence of trace residues of the buffering salts in the hydrogels²¹ as well as possible fragments of HPMC structures.⁴⁶

The results of semi-quantitative analysis provided further evidence on the reduction of the degraded portion of the resin films after the use of the hydrogels. In particular, they showed distinct percent reductions for both the inorganic and the organic parts of the soiling layer after the cleaning trials. Table 4 presents in detail these reductions in absorbance for the areas that corresponded to the aforementioned absorbance bands. It is, therefore, evident that the hydrogels removed a large percentage of the inorganic and organic components of the soiling mixture. At the same time, the reduction in absorbance for the C=O stretching vibrations also corroborated our assumptions about the concurrent removal of a portion of the degraded films. Interestingly, measurements on the mastic films showed even greater percent reductions at the C=O absorbance band than the shellac and ketone resins.

After the soiling removal tests, the sodium acetate hydrogel was applied on a 20th century panel painting that exhibited a distinct surface layer of accumulated soiling. The sodium acetate gel was used because of its low pH (5.5). According to Wolbers,¹⁹ such pH value should be too low to even partly ionise the underlying degraded varnish layers and thus expose the underlying binding paint surface. Soiling removal on this particular panel painting posed an even greater challenge since the underlying layers had proven to be extremely sensitive to organic solvents (painting owner, communication). Visible light and UV fluorescence images taken after cleaning are shown in Figures 9 and 10. An increase in fluores-

cence after cleaning is apparent, suggesting the successful removal of the superficial soiling layer.

4 Discussion

Although aqueous cleaning methods have been in wide use since their introduction,^{19,27,28} little information could be found in the literature on the selective removal of soiling from traditional painting varnishes with the use of hydrogels. Drawing upon similar investigations, in particular on soiling removal from paint²⁸ as well as previous research on detergents,^{35,36} the presented work focused on the effects of two aqueous gels on the removal of soiling of degraded varnishes.

The action of hydrogel systems on a coated surface is based mainly on ionisation, and subsequent deprotonation of acidic groups, which eventually leads to the breakdown and removal of unwanted material.¹⁹ The selection of buffering agents is case-specific and depends –roughly– on the molecular composition of the surface and the acidity of the targeted contaminant to be dissolved or entrapped into the hydrogel. Ideally, buffered hydrogels do not affect substrates, when the acidity of the substrates and the targeted contaminants differ.¹⁹ The ability of customised hydrogels to remove contamination layers, while keeping substrates to be preserved intact, provides a high degree of selectivity of the cleaning process. Theoretically, the hydrogel-induced removal of soiling from degraded varnishes consists of mainly two parts: (a) the efficient wetting of the surface which allows for the elimination of any types of electrical forces between the soiling particles and the surface and their subsequent separation^{16,19} and (b) the overcoming of any molecular forces that hold the smaller soiling particles to the surface of the coatings.¹⁹ The latter stage is governed by the main principles of detergency which depend upon the formation of micelles from the surfactant in the bulk of the hydro-

gels.^{19,49} These micelles should be able to “pick up” smaller particles that tend to resist the first stage of cleaning and keep them in suspension.

The selection of the three specific resins used in this research was based upon their structural and molecular diversity. We believe that the use of such structurally different materials provided a basis for (a) their characterisation after degradation and soiling and (b) the examination of the complex interactions of these varnishes with the hydrogels used in this context.

The results obtained after soiling removal were of particular interest for a number of reasons: (a) both the sodium acetate and sodium deoxycholate hydrogels seemed to have efficiently removed the soiling layer from all the three soiled varnish substrates, however, at the expense of the upper varnish layers, which were also dissolved; (b) the significantly reduced UV fluorescence emissions of both the ketone and shellac films after removal of soiling suggested that the cleaning procedure was less selective than initially anticipated, despite the macroscopic indications of soil removal; (c) the partial ionisation and dissolution of only the uppermost layers of the unsoiled coatings could owe to the strong incorporation of the components of the synthetic soiling mixture onto the degraded substrates; (d) the decrease in UV fluorescence after removal of soiling may also be associated with recent findings regarding the compositional gradients of degraded coatings.^{6,13,14,22,37} According to these findings, degradation and therefore all degradation products are exponentially reduced as a function of film depth. Moreover, the number of acid and ketone groups formed upon degradation is higher at the air/varnish interface than in the bulk of the varnish itself.^{13,22} As a result, the depth-wise reduction of such degradation products, including diverse chromophores, should account for the above phenomenon. In all, it is shown that by removing only a few microns of coatings, degraded varnishes fluoresce to a lesser degree.³⁷ Finally, (e) there is a different type of interaction between the hydrogels and the degraded ketone and shellac films compared to the degraded mastic films. While the shellac and ketone films displayed significant changes in UV fluorescence emission after removal of soiling, the respective mastic films did not display similar changes. These findings suggest that the soiling layer was successfully removed and the upper layers of the mastic films were left mostly unaltered.

Analysis carried out using reflection-absorption infrared spectroscopy corroborated the above observations. In particular, the IR spectra of the mastic films after removal of soiling showed a distinct reduction of the absorbance bands ascribed to the inorganic components of the soiling layer. Similarly, changes were noted with regards to the shape and intensity of the absorbance bands related to the organic portion of the soiling layer. Moreover, the obtained IR spectra for mastic showed minor differences in absorbance, which suggests that the degraded portion of the mastic films was successfully preserved to a notable degree after implementation of the hydrogels. On the contrary, the IR spectra corresponding to both the shellac and ketone films showed a significant reduction in absorbance after implementation. Given the direct proportionality between absorbance and concentration according to

Beer's law,^{13,22,34} it can be assumed that the top layers of the degraded films were also removed to a lesser or greater extent along with the soiling layer.

The IR spectra were further analyzed by the determination of ratios of maximum peak intensities and area integrals of the CH₂ functional group that corresponded to the organic component of the soiling mixture (mineral oil). For these purposes the identified inorganic components of the soiling layer such as Ca(OH)₂ and CaCO₃, were also analyzed. Moreover, the maximum peak intensities and area integrals of the C=O functional group were calculated. The C=O group was chosen as a point of reference, indicative of varnish degradation so as to demonstrate the percent decrease of the carbonyl group after cleaning in relation to the percent decrease of the components of the soiling layer.

The results obtained from the semi-quantitative analysis supported the UV fluorescent imaging and IR spectroscopy findings by showing a definite decrease, in absolute numbers, of the organic and inorganic portions of the soiling layer after implementation of the gels. In particular for the ketone and shellac varnishes, differences between the absorbance intensities prior to degradation and after removal of soiling were noted, suggesting that the hydrogels might have removed only part of the degraded top layers of the varnishes. These findings could be further supported by the depth-dependent exponential decreases in oxidation, polarity,^{6,13,22} cross-linking and polymerisation.¹⁴

Interestingly, the application of the sodium acetate gel gave overall similar results to the sodium deoxycholate gel. According to Wolbers,¹⁹ the more basic hydrogel should have had more or less deprotonated some of the known weakly acidic groups formed after degradation. Therefore, it would be safe to assume that at pH values of approximately one unit below the corresponding pKa values, these weakly acidic groups would be less than 50% deprotonated and the varnish layers would be preserved. On the other hand, if the pH were to be raised by one unit or more, these acidic groups would become approximately 90% deprotonated and the varnishes dissolved. However, our data showed that both hydrogels removed portions of the degraded varnishes regardless of the significant difference in the gels' acidities.

The conflicting data could be due to a number of factors, one of them being the possible solubility aspect of chloroform in the soiling solution. The soiling suspension contained chloroform, per the protocol used, a chlorinated hydrocarbon and potent organic solvent. It should be mentioned that chloroform can readily dissolve degraded ketone resins and marginally dissolve degraded mastic. Shellac, on the other hand, is not dissolvable in chloroform. In this respect the possibility of partial dissolution of the upper varnish layers, especially in the cases of Laropal K80 and mastic, should be taken into account. Arguably, the use of chloroform might have contributed to the partial dissolution of the degraded varnishes and have aided in the penetration of the soiling particles further into the resin bulk. This hypothesis, if valid, would explain the reduction in fluorescence and the subsequent varnish loss mainly in the cases of Laropal K80, but it would not account for the removal

of shellac. However, our data, before and after the application of the soiling mixture, do not show any differences in respect to the absorbance bands relative to degradation. On the contrary, the ascribed bands show a definite increase after the application of the soiling mixture and the second stage of degradation, as was initially anticipated.

The omission of clearance procedures in this research should also be examined. Clearance procedures, as described by Wolbers,¹⁹ involve mostly the use of mineral spirits to remove gel residues after cleaning. However, clearance was avoided in this investigation due to the reflection-absorption infrared spectroscopy method used, as it would inevitably lead to the contamination of the samples and ultimately provide misleading results. It is therefore proposed that a new method of producing a soiling mixture be investigated; one that does not necessarily entail the use of chloroform.

However, even at this point, removal of soiling on varnish can be carried out with minor risks when customised hydrogels are employed, given that the surface is left coated after implementation, as shown in the example of the panel painting in Figures 9 and 10.

In all, it would be interesting although quite laborious to formulate hydrogels that would target specific acidic groups formed during degradation. Therefore, we believe that further research is required to determine the pKa values of diverse acids formed in common paint varnishes after degradation.

At this point the authors would also like to add that the use of a specialised pH surface electrode would have definitely helped in the determination, or at least in the rough approximation, of the pH values on the surface of the coatings used. However, the authors could not make use of a flat surface pH probe due to technical reasons. In this respect it is proposed that flat surface pH electrodes are employed in similar investigations.

Finally, it should also be noted that the use of Triton X-100 nonionic surfactant must be avoided and that the use of alternative non-ionic surfactants is strongly encouraged.²¹

5 Conclusions

This study investigated the removal of soiling using hydrogels from typical paint varnishes and the evaluation of the outcomes using imaging, analytical and statistical methods. For these purposes a soiling mixture indicative of urban pollution was produced and applied on artificially degraded mastic, shellac and Laropal® K80 film substrates. By identifying and characterizing specific absorbance bands pertinent to the inorganic and organic components of the soiling mixture, it was shown that the soiling layer was successfully reduced and removed after the cleaning trials. UV fluorescent imaging showed a decrease in the overall fluorescence of the cleaned substrates and indicated a concurrent removal of the uppermost layers of the degraded films. These assumptions were validated by the findings from RAIRS spectroscopy, which showed a definite reduction in the overall absorbance of the produced spectra after cleaning.

This phenomenon was most prominent and evident in the cases of the shellac and Laropal® K80 resins. On the other hand, mastic films showed the least decrease both under UV-induced fluorescence as well as in absorbance. The descriptive statistical analysis that followed provided for a semi-quantitative estimate in absolute numbers and further established the above findings. In all, it was shown that, despite their difference in acidity (pH) and composition, both hydrogels behaved in an overall similar manner by removing the upper parts of the degraded and soiled resins and leaving the bulk of the degraded films intact, especially in the cases of the shellac and Laropal® K80 resins. Moreover, the correlation between the latter phenomenon and the incorporation of the soiling particulates onto the resin substrates was described. The possibility of a correlation between the depth-dependent degree of degradation of paint varnishes and the removal of the uppermost layers of the degraded films, was also presented. Finally, in the context of this work, a case study involving the successful removal of a soiling layer from the surface of a 20th century panel painting using hydrogels, was also described.

6 Acknowledgements

This is a self-funded work that was carried out in the framework of the graduate dissertation of the first author under the supervision of the co-authors in the laboratories of conservation of panel paintings and physical chemistry at the Department of Conservation of Antiquities & Works of Art at the Technological Educational Institute of Athens, Greece.

7 References

1. R. L. Feller, N. Stolow, E. H. Jones, *On Picture Varnishes and their Solvents*, 3rd Edition, National Gallery of Art, Washington, 1985, pp. 3-189.
2. R. E. De la Rie, *The Influence of Varnishes on the Appearance of Painting*, *Stud. Conserv.*, 1987, **32**, 1-13.
3. R. S. Berns, R. E. De la Rie, *Exploring the Optical Properties of Picture Varnishes Using Imaging Techniques*, *Stud. Conserv.*, 2003, **48**, 73-82.
4. G. A. Van Der Doelen, *Molecular studies of fresh and aged triterpenoid varnishes*, PhD Thesis, AMOLF Publications, Amsterdam, 1999.
5. P. Dietemann, *The Ageing of Triterpenoid Resins and Varnishes*, PhD Thesis, Swiss Federal Institute of Technology (ETH), Zürich, 2003.
6. C. Theodorakopoulos, *The Excimer Laser Ablation of Picture Varnishes. An evaluation with reference to light-induced deterioration*, PhD Thesis, AMOLF Publications, The Royal College of Art, London, 2005.
7. G. Cass, J. R. Druzik, D. Grosjean, W. W. Nazaroff, P. M. Whitmore, C. L. Wittman, *Protection of Works of Art from Atmospheric Ozone*, J. Paul Getty Trust, Los Angeles, 1989, pp. 5-23.
8. W. W. Nazaroff, M. P. Ligocki, L. G. Salmon, G. R. Cass, T. Fall, M. C. Jones, H. I. H. Liu, T. Ma, *Airborne Particles in Museums*, The J. Paul Getty Trust, Los Angeles, 1993, pp. 17-20.

9. J. S. Mills, R. White, *The Organic Chemistry of Museum Objects*, Butterworth-Heinemann, Oxford, 1987, pp. 95-122.
10. R. E. De la Rie, *Photochemical and Thermal Degradation of Films of Dammar Resin*, *Stud. Conserv.*, 1988, **33**, 53-70.
11. G. Scott, *Autoxidation and antioxidants: historical perspective*, in: G. Scott, Ed., *Atmospheric oxidation and antioxidants*, vol. 1, Elsevier Science Publishers B.V., Amsterdam, 1993, pp. 1-44.
12. N. Umney, S. Rivers, *Conservation of Furniture*, Butterworth-Heinemann, Oxford, 2003, pp. 146-147, 260-266, 539-552.
13. C. Theodorakopoulos, J. J. Boon, V. Zafirooulos, *Direct-temperature mass spectrometric study on the depth-dependent compositional gradients of aged triterpenoid varnishes*, *Int. J. Mass Spectrom.*, 2009, **284**, 98-107.
14. C. Theodorakopoulos, J. J. Boon, *A high performance size exclusion chromatographic study on the depth-dependent gradient in the molecular weight of aged triterpenoid varnish films*, *Prog. Org. Coat.*, 2011, **72**, 778-783.
15. N. S. Baer, P. N. Banks, *Indoor Air Pollution: Effects on Cultural and Historical Materials*, in: S. Knell, Ed., *Care of Collections*, Leicester Readers in Museum Studies, Routledge, London, 1994, pp. 150-163.
16. A. Zimon, *Adhesion of Dust and Powders*, Plenum Press, New York, 1969, 14, pp. 115, 157-170.
17. C. E. Lapple, *Characteristics of Particles and Particle Dispersoids*, *Stanf. Res. Inst. J.*, 1961, **5**, 95.
18. M. R. Schilling, *The Glass Transition of Materials Used in Conservation*, *Stud. Conserv.*, 1989, **34**, 110-116.
19. R. Wolbers, *Cleaning Painted Surfaces. Aqueous Methods*, Archetype Publications, London, 2000, pp. 1-191.
20. G. Hedley, *Measured opinions: The collected papers on the conservation of paintings*, Institute for Conservation, London, 1993, pp. 8-13.
21. D. Stulik, D. Miller, M. Khanjian, N. Khandekar, R. Wolbers, J. Carlson, C. Petersen, *Solvent Gels for the Cleaning of Works of Art. The Residue Question*, Getty Publications, Los Angeles, 2004.
22. C. Theodorakopoulos, V. Zafirooulos, J. J. Boon, S. Boyatzis, *Spectroscopic Investigations on the Depth-Dependent Degradation Gradients of Aged Triterpenoid Varnishes*, *Appl. Spectrosc.*, 2007, **61**, 1045-1051.
23. A. Phenix, *The Swelling of Artist's Paints in Organic Solvents. Part 1, a Simple Method for Measuring the in-Plane Swelling of Unsupported Paint Films*, *J. Am. Inst. Conserv.*, 2002, **41**, 43-60.
24. A. Phenix, *The Swelling of Artist's Paints in Organic Solvents. Part 2, Comparative swelling powers of selected organic solvents and solvent mixtures*, *J. Am. Inst. Conserv.*, 2002, **41**, 61-90.
25. V. B. B. Espinola, *Russian Icons: Spiritual and Material aspects*, *J. Am. Inst. Conserv.*, 1992, **31**, 17-22.
26. R. J. Gettens, *The corrosion products of metal antiquities*, Annual Report to the Board of Trustees of the Smithsonian Institution, 1964, pp. 547-568.
27. R. Wolbers, N. Serman, C. Stavroudis, *Notes for Workshop on New Methods for the Cleaning of Works of Art*. The Getty Conservation Institute, 1988.
28. R. Wolbers, *The Use of a Synthetic Soiling Mixture as a means for evaluating the efficacy of aqueous cleaning materials on painted surfaces*, *Conservation-Restauration des Biens Culturels*, 1992, **4**, 22-29.
29. N. A. Campbell, B. Williamson, R. J. Heyden, *Biology: Exploring Life*, Pearson Prentice Hall, Boston, Massachusetts, 2006.
30. M. Bonini, S. Lenz, R. Giorgi, P. Baglioni, *Nanomagnetic Sponges for the Cleaning of Works of Art*, *Langmuir*, 2007, **23**, 8681-8685.
31. E. Carretti, S. Grassi, M. Cossalter, I. Natali, G. Caminati, R. G. Weiss, P. Baglioni, L. Dei, *Poly(vinyl-alcohol)-Borate Hydro/Cosolvent Gels: Viscoelastic properties, Solubilising Power, and Application to Art Conservation*, *Langmuir*, 2009, **25**, 8656-8662.
32. E. Carretti, M. Bonini, L. Dei, B. H. Berrie, L. V. Angelova, P. Baglioni, R. G. Weiss, *New Frontiers in Material Science for Art Conservation: Responsive Gels and Beyond*, *Acc. Chem. Res.*, 2010, **43**, 751-760.
33. G. Thomson, *The Museum Environment*, Butterworth, London, 1986, pp. 2-61.
34. R. L. Feller, *Accelerated Ageing. Photochemical and Thermal Aspects*, The Getty Conservation Institute, Los Angeles, 1994, pp. 45-62, 187-196.
35. P. A. Florio, E. P. Mersereau, *Control of Appearance Changes due to Soiling. The Mechanism, Measurement and Reduction of Soiling Changes in Carpet During Use*, *Text. Res. J.*, 1955, **25**, 641-649.
36. N. F. Getchell, *Cotton Quality Study III: Resistance to Soiling*, *Text. Res. J.*, 1955, **25**, 150-194.
37. C. Theodorakopoulos, V. Zafirooulos, *Uncovering of scalar oxidation within naturally aged varnish layers*, *J. Cult. Her.*, 2003, **4**, 216-222.
38. A. Pelagotti, L. Pezzati, N. Bevilacqua, V. Vascotto, V. Reillon, C. Daffara, *A Study of UV Fluorescence Emission of Painting Material*, *Proc. of Art'05, 8th Int. Conf. on "Non-Destructive Testing and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage"*, 2005.
39. N. Petronella, *A preliminary investigation into the identification of adhesives on archaeological pottery*, *AICCM Bull.*, 2006, **30**, 27-37.
40. R. E. De la Rie, *Fluorescence of paint and varnish layers (Part I)*, *Stud. Conserv.*, 1982, **27**, 1-7.
41. R. E. De la Rie, *Old Master Paintings. A Study of the Varnish Problem*, *Anal. Chem.*, 1989, **61**, 1228A-1240A.
42. B. H. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, J. Wiley & Sons Ltd, 2004.
43. M. R. Derrick, D. Stulik, J. M. Landry, *Infrared Spectroscopy in Conservation Science*, The Getty Conservation Institute, Los Angeles, 1999, pp. 1-129.
44. J. Coates, *Interpretation of Infrared Spectra, A Practical Approach*, in: R.A. Meyers, Ed., *Encyclopaedia of Analytical Chemistry*, John Wiley & Sons Ltd, Chichester, 2000, pp. 10815-10837.
45. Fiveash Data Management Inc., *FDM Reference Spectra Databases*, Fiveash Data Management, Inc., <http://www.fdm spectra.com/> (accessed 22-07-2012).
46. Infrared and Raman Users Group, *IRUG Spectral Database Edition 2000*, IRUG, <http://www.irug.org> (accessed 22-07-2012).
47. World Health Organisation, *Chloroform: Health and Safety Guide*, IPCS, Geneva, 1994.

48. M. Freund, S. Csikos, S. Keszthelyi, G. Y. Mozes, *Paraffin Products: Properties, Technologies, Applications*, in: GY. Mozes, Ed., *Developments in Petroleum Science*, Elsevier, Budapest, Hungary, 1982.
49. E. Kissa, *Wetting and Detergency*, *Pure Appl. Chem.*, 1981, **53**, 2255-2268.