

Diffusion of Water from a Range of Conservation Treatment Gels into Paint Films Studied by Unilateral NMR.

Part I: Acrylic Emulsion Paint

Lora V. Angelova^{a*}, Bronwyn Ormsby^b, Emma Richardson^a

^a Department of History of Art, University College London, 20 - 21 Gordon Square, London WC1H 0AG, United Kingdom

^b Conservation Department, Tate, Millbank London SW1P 4RG, United Kingdom

*Corresponding author:

Email: l.angelova@ucl.ac.uk

Tel: +44 (0)20 3108 4012

Fax: +44 (0)20 7916 5939

Abstract

Unilateral NMR was used to monitor the penetration of water into acrylic emulsion paint-outs on canvas during cleaning simulations with five thickened conservation treatment systems – agarose gels, methylcellulose paste, Pemulen-TR2, poly(vinyl alcohol)-borax gels, and Velvesil Plus - and water-moistened swabs. Studies were also carried out to measure the rate of water penetration from the different treatment methods into acrylic paints during continuous exposure. Unilateral NMR is shown to be an effective technique for comparing depth penetration of water during cleaning treatments; the volume of paint occupied by water can be extracted from these measurements. The results show that young paint films (1 month) are more prone to swelling than aged paint films (2-50 years), with light aged paints having the highest resistance to water penetration during treatments. Aged organic pigmented acrylic paint (Hansa yellow light) shows a higher propensity for swelling during cleaning than aged titanium dioxide white paint. Cleaning simulations using water-moistened swabs and agar gels deposit approximately equivalent amounts of water into the paint films, while all other

gel systems tested, with the exception of Velvesil Plus, tend to allow approximately 50% more water into the paint films. None of the aqueous thickened cleaning systems tested reduced the quantity of water which entered the paint films relative to swab cleaning.

1. Introduction

Cleaning treatments for paintings, frames, and some objects may involve the partial or complete removal of the top-most surface layer from the artwork. Historically, this would have been a protective layer of spirit or oil varnish, with more modern varnishes tending towards synthetic polymer formulations. With each type of varnish the mechanical and optical integrity is often compromised due to autoxidation and crosslinking reactions that result in embrittlement, cracking and yellowing [1-4]. Grime, dirt, and soot can also accumulate on artwork surfaces. Nicotine layers from cigarette smoke in studios and galleries, animal glue from consolidations, overpaint applied by previous restorations which may age and discolour at a different pace than the original paint, as well as drying oils rubbed into the paint surface all may need to be removed. Finally, surfactants from acrylic and other dispersion-based paints can migrate to the surface of artworks, encouraging the retention of soiling, and potentially resulting in a haze which obscures the colour, saturation and texture of the paint [5-10].

These processes can cause the stability and aesthetic quality of cultural heritage works to be compromised, necessitating conservation treatment to remove aged coatings partially or completely, or to clean the surface from accumulated pollutants and soiling, sometimes prior to the re-application of fresh protective coatings. The removal of surface materials can be mechanical through the use of specialized cloths and erasers, dusting, or simple rubbing off of the varnish in the event that it is flaked from a structurally sound paint layer. Removal can also be achieved through chemical means by the use of wet cleaning methods such as organic liquids, aqueous solutions containing enzymes, surfactants, buffers, chelators, and microemulsions, typically delivered via a gently moistened cotton swab. Alternatively, many of the same liquids can be confined into a paste or gel system. Paste-like gels from Carbopol [11], methylcellulose, laponite [12,13], Pemulen [14], or Velvesil Plus, gels from agar [15-17], gellan gum [18,19], acrylamide/bisacrylamide [20], or its interpenetrating networks with poly(vinyl pyrrolidone) [21,22], and highly viscous polymeric dispersions from poly(vinyl

alcohol) and borax [23,24] are all systems used in conservation treatments – some more commonly than others.

Along with the difficulty of tailoring gel systems for the diverse range of materials needed to be removed from artwork surfaces (i.e. ideally, a single gelator should be capable of forming robust gels with a variety of organic solvents and aqueous cleaning agents) and the necessity of organising workshops where conservators can learn about such materials, the community has highlighted several questions which must be addressed about new gel systems before they are accepted as potential cleaning treatments. The gels should have limited adhesion toward the artwork surface so that their complete removal is ensured. If clearance steps are necessary, their potential to leach original material from the artwork must be evaluated and minimised [25]. Residues of the gel network should be limited, and their potential effects on the composition must be evaluated [12,26]. It is important to note that residues are likely to be present when using any cleaning method; their recognition will be restricted by the detection limits of the instrument(s) chosen for the study [27].

Of primary importance during a cleaning treatment is the full control of lateral and orthogonal spread of the cleaning liquid on the surface of the artwork. Thickened solvent or aqueous pastes and gels have commonly been cited as providing the conservator with superior control over the delivery of liquid to the artwork surface [28]. However, aside from anecdotal evidence, the authors are aware of only one published study comparing diffusion of liquid from a gel and from a moistened swab into paint layers [29]. As there are a variety of gels used in conservation - both physically and chemically crosslinked, rheologically weak and ‘true gels’, strain-thickening and shear-thinning - and an infinite variety of surfaces with a range of porosities to be treated, it is difficult to predict if and when a gel may limit diffusion into the surface relative to swab cleaning. Confinement of the liquid within a gel is also dependent on the gel network structure and how it may be affected by components on the surface to be cleaned – for example, some gels used in conservation are sensitive to changes in ionic strength and may undergo syneresis when in contact with the surface of some artworks [23].

Methodical studies of the capacity of different types of conservation treatment gels to reduce or ‘control’ liquid diffusion into a variety of conservation-relevant contexts are necessary. Here, we present an exploration into the ability of unilateral NMR relaxometry to aid in such experiments using a range of conservation treatment gels and two acrylic paint

substrates. This non-invasive analytical technique has already shown great potential in the heritage science field [30]. Gels have been selected from all of the commonly used categories – shear thinning paste-like methylcellulose, Pemulen and Velvesil Plus emulsion gels, strain stiffening agar gels, and PVA-borax highly viscous polymeric dispersions. Acrylic emulsion paint has been selected as a substrate due to the ease of preparation of mock-ups, the abundance of literature on water diffusion into polymer films studied by unilateral NMR, their susceptibility to accumulating surface dirt and grime, and the difficulty in finding appropriate, low risk cleaning methods for such paints [31-35].

Unilateral NMR can be used to trace how far the water has penetrated into the paint layer, monitor the rate of diffusion, and to quantitatively determine the amount of water which has swelled the paint. The acrylic paints selected are commercially available, and have been fully characterised elsewhere [36,37]. Two different pigmented acrylic paints were selected – inorganic titanium dioxide white (PW6), and organic pigment yellow 3 (2-[(4-chloro-2-nitrophenyl)diazenyl]-N-(2-chlorophenyl)-3-oxobutanamide) (PY3). Golden Heavy Body professional acrylic paints were chosen as they have used in previous swelling studies and show moderate swelling in comparison to other brands, such as Liquitex [38]. Experiments were carried out on fresh and aged paint-outs. Our results indicate that differences in water diffusion are evident not only between gel types, but also between the two different acrylic paint types, which is at least partially due to the relative increase in medium content in the PY3-based paint when compared to the PW6. Therefore, studies employing different paint binders (oil, polyvinyl acetate, alkyd resin or tempera), previously treated samples and other substrates (plaster, marble, wood) may yield different results for water ingress and will be undertaken in upcoming publications.

2. Methods and Materials

2.1 Paint Mock-ups and Gel Preparation

Golden heavy bodied acrylic paints in Hansa Yellow Light PY3 (2-[(4-chloro-2-nitrophenyl)diazenyl]-N-(2-chlorophenyl)-3-oxobutanamide) and Titanium White PW6 (TiO₂) were deposited on an unprimed cotton drill canvas (25g/m², SDC enterprises Ltd., product #1205) using a draw down method through a plastic mask to create equally sized paint-outs with a dry thickness of approximately 300-500 µm. Samples were allowed to dry

for at least four weeks before treatment tests, though it is acknowledged that acrylic dispersion paints would still be coalescing at this stage of the drying process [39]. Aged paint-outs of the same two Golden paints on Fredrix 10 ounce double acrylic dispersion primed cotton duck canvas (Fredrix) were provided by Tate (Table 1). The dried paint thickness of these samples is approximately 100 μm , with an overall sample thickness (including the primed canvas substrate) of 450-500 μm . Samples of the fresh paints were the size of the sensor – 2.5 x 2.5 cm, while aged samples were 1.5 x 1.5 cm in size due to sampling limitations.

Table 1. Description of paint-outs used in this study.

<i>Sample Name</i>	<i>Paint Type</i>	<i>Age</i>	<i>Ageing Process</i>
<i>YG1</i>	Hansa Yellow Light PY3	4 weeks	Natural
<i>YG2</i>	Hansa Yellow Light PY3	2 years	Natural
<i>TG1</i>	Titanium White PW6	4 weeks	Natural
<i>TG2</i>	Titanium White PW6	2 years	Natural
<i>TG10-1</i>	Titanium White PW6	10 years	Natural
<i>TG10-2</i>	Titanium White PW6	10 years	Natural
<i>TG10-LA</i>	Titanium White PW6	10 years/~50 years ^a	Light aged ^a
<i>TG10-TA</i>	Titanium White PW6	10 years/~50 years ^b	Thermally aged ^b

^a 15,000 lux for 16 weeks under Philips TLD 58W/840 daylight fluorescent tubes with the UV component filtered out by an acrylic sheet [Perspex p(MMA)][37]

^b Fisons 185 HWC environmental oven (60. C; 55% RH) for 16 weeks[37]

An 80PVAc-borax gel (4 wt %, 5 g, pH 8) was prepared by dissolving 0.2 g of 80% hydrolyzed poly(vinyl acetate) (Poval PVA-424, Kuraray Co., Ltd.), in 3.75 g of deionized water at room temperature. Borax (0.05 g, sodium tetraborate decahydrate, Sigma, 99.5-105%) was dissolved in 1 g of deionized water, added to the polymer solution and stirred until a homogeneous gel was formed. A Pemulen TR-2 gel-emulsion (1 wt %, 10 g, pH 6) was prepared by following a recipe suggested by Stavroudis [40]. Methylcellulose (5 wt %, 0.5 g, (BDH, VWR International Ltd) was dissolved in deionized water (9.5 g water, adjusted to pH 6 with acetic acid) with gentle heating; once the mixture began to thicken, it was immediately removed from the heat and stirred manually with a spatula. Agarose (Sigma, BioReagent, low EEO) was dissolved in deionized, boiling water to form either a 1 wt % or a 4 wt % solution; the solutions had a measured pH 6. The two solutions were poured into silicone candy moulds and allowed to cool; the gels were popped-out and placed in sealed

container and refrigerated until use. Velvesil Plus (3 g, Safic-Alcan UK Ltd) was diluted with D4 (1 g, Octamethylcyclotetrasiloxane, Fluorochem Ltd) and deionized water adjusted to pH 6 with acetic acid (0.4 g, to yield 9 wt %). For treatments with a water-wetted cotton swab, 50 mL of deionized water were adjusted to pH 6 with acetic acid. The pH of the solution was checked before each treatment test, and a fresh solution was prepared daily. The studies were conducted with water and hydrogels at a pH of 6, because slightly acidic solutions have been suggested as safer for acrylic paint films [10]; PVA-borax gels which cannot form at a pH below 8 are the only exception [28].

2.2 'Reservoir' Treatment Tests

Paint-outs were attached to glass-slides with double-sided tape and placed above the NMR MOUSE sensor. An initial profile scan was obtained to locate the paint layer, then pH 6 adjusted water was spread onto the paint region above the sensor (0.4 mL for the four-week old samples, and 0.1 mL for the 2-10 year old samples due to the difference in sample dimensions, Section 2.1). Fifteen profile scans were obtained sequentially on the paint-film with the water reservoir. The same procedure was repeated for each of the five gels used in this study; the weight of gel used on the paint-surface was selected to contain 0.4 g of water (i.e. 0.42 g of 80PVAc gel was used).

2.3 Simulated Treatment Tests

A paint-out was placed above the NMR MOUSE sensor. A single profile scan was obtained of the dry paint-film. While the lift was re-adjusting for next profile scan, a cleaning treatment was carried out; 30-second or 1-minute treatments on the fresh or aged paints, respectively. Consequently, 9 profile scans were sequentially obtained of the paint film after complete removal of the treatment gel. The first of these scans was obtained immediately after the treatment was completed.

Treatments are performed as follows: swab cleaning was carried out using a cotton swab moistened with pH 6 adjusted water; residual water was wicked off the swab via filter paper. The swab was gently rolled on the surface; a filter paper was then pressed gently to the paint surface to remove any residual water. An 80PVAc-borax gel was flattened with a spatula onto a glass slide to form a thin gel film with the approximate dimensions of the paint sample. The gel was then placed in contact with the paint-film and pressed to fully cover the area above the sensor. After 30 seconds, the gel was removed and a filter paper was pressed gently to the paint surface to wick off extra moisture. Agar gels were used in the same

manner, but prior to application, excess moisture was wicked off the surface of the gel with a filter paper. Pemulen TR2, Velvesil Plus, and methylcellulose treatments were each applied via a cotton swab or paint brush rolled on the surface of the paint-film; the gel-pastes were allowed to stay on the surface undisturbed for part of the treatment time. A dry swab was used to remove the gel-paste, followed by 3 separate wet-washes carried out with gently moistened cotton swabs (extra moisture being wicked off via filter paper); the surface was finally blotted with a filter paper before the profile scan commenced. Methylcellulose and Pemulen were cleared with water adjusted to pH 6 with acetic acid, whilst Velvesil Plus was cleared with D4.

2.4 Paint Characterisation

2.4.1 DMA Testing

Dynamic Mechanical Analysis (DMA) was performed using a PerkinElmer DMA 8000 with Pyris software version 11.0. Temperature profiles were conducted in single cantilever mode at a frequency of 1.0 Hz, a temperature range of -20 °C to 50 °C and a heating rate of 3 °C/min. Samples measuring 7 x 4 x 0.4 mm were subject a displacement of 0.025 mm. The 4-week old samples were prepared from paint-outs on glass slides, as described in Section 2.1.; the paint was peeled off the slide and cut to size. The glass transition temperature (T_g) was calculated as the onset of the storage modulus curve. The T_g of the same paint-outs were measured when they were 4 months old. Unfortunately, glass transition temperatures of the aged samples could not be obtained reproducibly using this technique.

2.4.2 ATR-FTIR Characterisation of Surfactants

Relative surface surfactant amounts were measured using a Bruker Alpha Platinum FTIR with a diamond crystal ATR accessory (penetration depth at 45° and 1000 cm^{-1} = 1.65 μm). Spectra were collected from 4000-400 cm^{-1} with a resolution of 4 cm^{-1} ; 64 scans were obtained of each sample, and each paint-out was sampled in three locations. Relative surfactant abundance for each sample is reported as a ratio of the most prominent surfactant signal (1110 cm^{-1}) and the corresponding carbonyl signal (~1730 cm^{-1})[41]; standard deviation is reported from the three sampling positions on each paint-out.

2.5 NMR MOUSE Measurements

NMR spectroscopy studies were carried out on a PM-5 Profile NMR MOUSE (Magritek, Aachen, Germany), mounted on a precision lift. The sampling area was 25 mm² and a 2 mm spacer was used allowing for a sampling depth of 3250 μm. A Carr-Purcell-Meiboom-Gill (CPMG) echo radiofrequency pulse sequence [42,43] was used to obtain spin echoes at different depths through each paint-film in order to create spatially resolved profiles of the T_{2eff} (effective spin-spin relaxation time), and relative volume of water in the top layer or the paint-film after a cleaning treatment or a reservoir test. All experiments were carried out in ambient conditions, with average laboratory temperature of 21°C ± 2°C and relative humidity of 41% ± 4%.

A ‘Profile’ collection method was used [44], which allows for the following parameters to be set (Table 2): repetition time, number of echoes in the CPMG train, the number of scans to be carried out at each step through the film depth, and the resolution (50 μm in all cases – this was also the step size of the lift movement through the sample depth). In the Profile mode, a CPMG echo train is obtained in each step as the lift moves the sensitive volume through the paint-film. This macro also allows for the amplitude of different parts of the echo train to be averaged in order to obtain T_2 -weighing of the signal intensity. Thus, if the paint-film magnetization has relaxed fully after 32 echoes, while at least 2000 echoes are necessary for the full relaxation of water in the paint-film, two weight signal profiles can be obtained – an addition of the 1st through 32nd echoes which is representative of the location of the paint-film, and an addition of the 33rd through 512th echoes which is representative of the location of the water in the paint-film. This method eliminates the need to subtract a dry paint background from the echo train profiles of the treated paint samples.

Table 2. Experimental parameters for ‘profile’ tests used in different experiments in this study.

<i>Treatment test</i>	<i>Repetition time (ms)</i>	<i>Scans</i>	<i>Echoes</i>
<i>Simulated treatments</i>	650	16	256
<i>Reservoir studies on 4-week paint-outs</i>	1300	4	512
<i>Reservoir studies on 2-10 year-old paint-outs</i>	500	8	128

3.5 Data Processing

Data were acquired using a Prospa spectrometer and accompanying software (Magritek, Aachen, Germany). Data were processed using OriginPro 2015 Software. Contour

colour maps were created for each paint-out from Profile scans obtained before the sample was treated, immediately after treatments, and then sequentially 2-5 more iterations after the treatment. Solvent-front movement could be graphically represented by plotting the average echo amplitude at each depth for each of the scans – before treatment, immediately after treatment, and during the drying process.

To extract information on the relative volume of water in the paint-film after treatment, the echo train from each affected depth-slice was extracted. The first 32 echoes (representative of the paint film relaxation) were masked, the y-axis was converted to a natural logarithmic scale, and the scatter points were fitted linearly. The y-intercept ($\tau = 0$) corresponding to the maximum signal amplitude of water in the sample was compared to the y-intercept ($\tau = 0$) of signal of water obtained under the same experimental parameters (i.e. a bulk water sample with the same dimensions, covering the same sensitive volume) [31,45].

3. Theory

3.1 Water Diffusion into Acrylic Paint Films

The diffusion of liquids into polymeric films, coatings, and paints has been extensively studied in industry. The swelling of polymer films and gels has also received much attention recently, as diffusion into, within, and out of gels is of great interest in the biomedical community. In this study, the amount of water diffusing from gels into pigmented acrylic emulsion films is of primary interest. Therefore, a brief summary of liquid diffusion into acrylic films will be covered; van der Wel's review [34] of diffusion into polymer coatings provides an accessible and extensive look into this topic, while Ormsby and Learner have covered the research pertaining to wet cleaning of acrylic emulsion paints in detail [46].

Numerous variables affect diffusion in polymer films; these include, but are not limited to, film thickness, glass transition temperature (T_g), the type of pigment particles (and their loading in the binder, *PVC* – pigment volume concentration) [47], the polymer type, and the presence of surfactants and a myriad of other additives in the case of paint-films. The situation becomes even more complex when considering the multi-layer structure, ageing processes, and experimental methods often found in works of art. Classic Fickian diffusion is heavily dependent on concentration, which in polymer films can occur only in an ideal case under the assumption that polymer chain rearrangement (so called, structural relaxation), does not interfere with penetrant diffusion [34,48]. The three most common non-Fickian

diffusion kinetic models observed in polymer films are ‘two-stage sorption’, ‘sigmoidal sorption’, and ‘case II sorption’. Two-stage sorption is characterised by an initial period of Fickian diffusion, during which the hole free volume is occupied, followed by a structural stage which is dependent on polymer relaxation and restructuring before saturation is achieved. Systems which exhibit sigmoidal sorption kinetics experience Fickian diffusion with an anomalous initial stage due to a delayed establishment of equilibrium at the film surface. In some cases, Sigmoidal diffusion kinetics may be followed by two-stage sorption kinetics. Finally, Case II sorption kinetics are characterised by constant linear penetrant uptake and swelling of the polymer film, the plasticisation of the film allowing for an increase in the diffusion kinetics [34].

Studies of water intake into polymer films by single-sided NMR have been useful in confirming the theoretical models described above. Kopinga *et al.* recently showed that in highly crosslinked polyurethane films, water uptake occurs without the plasticisation of the polymer matrix below the enthalpy relaxation temperature, while water uptake *and* polymer chain mobilization occur at higher temperatures [49]. In a more practical application, Gazi and Mitchell showed that liquid diffusion profiles into polymeric coatings can be obtained during the penetration process, allowing for the visualisation of film swelling, the elucidation of the dynamics of solvent spread into the film, and the determination of preferential solvent accumulation sites within the film [45].

Specifically pertaining to solvent ingress into acrylic paints, Ulrich *et al.* used single-sided NMR spectroscopy to show that ingress of water into titanium white waterbourne acrylic paint-films is largely independent of its salt concentration when the films have not experienced any prior cleaning treatment [31]. Acrylic films that have been washed of bulk additives, however, absorbed less water than control paint-films, and this uptake decreased further with increasing salt concentration [31]. These results are in agreement with studies on swelling and surfactant extraction conducted by Dillon *et al.* who showed that changes in the volume decrease when the conductivity of the aqueous washing solution is increased [10]. Similar results have been obtained in other studies, indicating that increased salt concentration in the cleaning solution decreases swelling [9], and that removal of water-soluble paint components has the same effect [50,51].

The swelling of acrylic paint films during immersion in water or aqueous cleaning treatments is dependent on the types and amounts of additives in the paint formulation, and

therefore is brand-dependent [37,38,52]. Both thermally and light-aged acrylic paints tend to swell less than their un-aged counterparts [46], and this may be partly attributed to the photodegradation of hydrophilic surface surfactants [41]. Paints containing organic pigments may swell to a larger extent than those formulated with inorganic pigments due to the higher proportion of paint medium, and consequently, hydrophilic components [46]. Though the presence of water-extractable components in the bulk of the paint film tends to cause increased swelling, based on studies of the water self-diffusion coefficient *within* the paint-films, Ulrich *et al.* conclude that the presence of surfactant and the concentration and size of salt ions in the aqueous solution do not affect the rate of water diffusion within the paint [31]. Finally, the temperature [53] and relative humidity conditions at which the paint film has been stored, or is undergoing treatment in, are likely to have an effect on that rate of water permeability. These conditions not only affect the properties of the polymer film, but also the migration and localisation of hydrophilic surfactants in the paint [54].

3.2 Structure of Gels

It is important to note that the gels used in this study have very different physico-chemical and rheological characteristics. The retention of water and its diffusion within the gels will also differ. Agar gels are physical, strain-stiffening gels prepared from hydrogen-bonded bundles of polymer chains having porous regions within which water can diffuse as if in the bulk. Water in the agar gels can also be structured near the bundles and its diffusion can be hindered not just by chemical interactions with the polymer chains but also by physical obstruction by the bundles giving rise to increased tortuosity [55]. The pore size depends on the agar grade, the concentration, and the preparation method of the gel [56]. The gels used in this study have not been analysed for pore size, but based on other publications, we can speculate that the pores in 1 wt % agar gels will be larger and have a higher polydispersity than the pores in gels prepared with 4 wt % agar; the pores are not expected to be larger than 400-500 nm [56,57].

Methylcellulose is a form of partially methylated cellulose; the hydrophobic modification is necessary to overcome the strong intermolecular hydrogen bonding of cellulose and for its dissolution in water [58]. When dissolved in water, the hydrophobic regions of the methylcellulose fibres are encapsulated by water molecule ‘cages’, which upon heating are dispersed, allowing for the formation of hydrophobic aggregates which form into fibrils with ca. 14 nm diameters [58,59]. These fibrils then assemble into bundles of diameter

on the micrometer scale, which hold a large amount of the water within their structure [59]. The formation of a gel network at increased temperatures (ca. 60°C) is counterintuitive, and many of the fibres are lost on cooling (ca. 30°C) [58,59]. The room temperature methylcellulose solution is closer to a viscous polymer solution than a gel, with approximately 5-6 mol of bound/structured water per every repeating unit of methyl cellulose [59].

Poly(vinyl alcohol) or partially hydrolysed poly(vinyl acetate) can be crosslinked with borax in aqueous, organic, or organo-aqueous solutions to form gel-like materials [60]. The true nature of the PVA-borax systems is comparable to highly viscous polymeric solutions with transient crosslinks having a finite relaxation time. The materials are dynamic, self-healing, and mouldable yet at the same time, strain-stiffening and elastic. The combination of these characteristics yields a material which can flow and conform to complex structures and surfaces, yet maintain its shape so that removal from a surface can be achieved simply by lifting or peeling [23,24]. As in methylcellulose solutions at room temperature, PVA-borax systems act more as polymer solutions than gels under standard conditions, and the majority of water which is not bound to the polymer by hydrogen bonding is considered free. Nonetheless, the diffusion of water in polymer solutions is slower than in a true gel structure, where pores and channels which lack the hindrance of polymeric macromolecules allow for faster diffusion of the liquid [61].

Pemulen-TR2 is a polymeric emulsifier formed from a block co-polymer of hydrophilic poly(acrylic acid) and hydrophobic long-chain C₁₀-C₃₀ methacrylates [62]. Using this single polymer, non-miscible liquids can be made into oil-in-water gel-emulsions where the hydrophobic liquid is encapsulated by the methacrylate portion of the polymer, and held in a thickened aqueous polyelectrolyte gel network which forms from the poly(acrylic acid) portion of the polymer. In this way, the emulsion droplets are prevented from coalescing through a process of electrosteric stabilisation [63]. It can be assumed that the gel-portion of these systems is formed in the same manner as in Carbopol gels – when dissolved in water, some of the carboxylate groups on the polymer backbone dissociate, and through electrostatic repulsion cause the polymers to extend into a rigid form; addition of a base enhances this effect to a degree although screening of the dissociated acid groups may eventually occur, resulting in a collapse of the gel viscosity [64].

Finally, Velvesil Plus, a silicone emulsifying gel is composed of epoxy-crosslinked silicone crosspolymer gel particles and a silicone poly(ethylene)/poly(propylene oxide) copolymer [65]. This system is used to create water-in-oil emulsions with the propylene oxide chains encapsulating the water in a chemically-crosslinked hydrophobic silicone dispersion. The paste-like gel is used to deliver aqueous cleaning systems to water-sensitive surfaces, and is commonly diluted to the desired consistency using dimethicone D₄ and D₅ solvents which act to swell the crosslinked silicone gel particles [66]. The aqueous component of the dispersion comes in contact with the surface during cleaning, and if the Velvesil Plus gel is left on the surface for sufficient time, the evaporation of the dimethicone diluent and subsequent collapse of the gel particles can result in further release of the entrapped aqueous portion of the emulsion [66].

4. Results and Discussion

4.1 Solvent Ingress during Reservoir Experiments

Data obtained from the NMR MOUSE in a ‘profile’ sequence is rich with information. A higher resolution scan of the paint film can be obtained initially to localise the exact boundaries of the air-paint and paint-glass interfaces. The data is visualised in a 2D colour-intensity plot with an x-axis representative of the CPMG echo train decay, and a y-axis representative of the depth in micrometres. A vertical ‘slice’ through the 2D map at $\tau = 0$ ms on the echo train axis allows for a visualisation of the proton density through the depth of the scanned region, thus allowing for the location of the paint film. If the films were prepared from different components, these would be differentiated in such a signal amplitude profile scan.

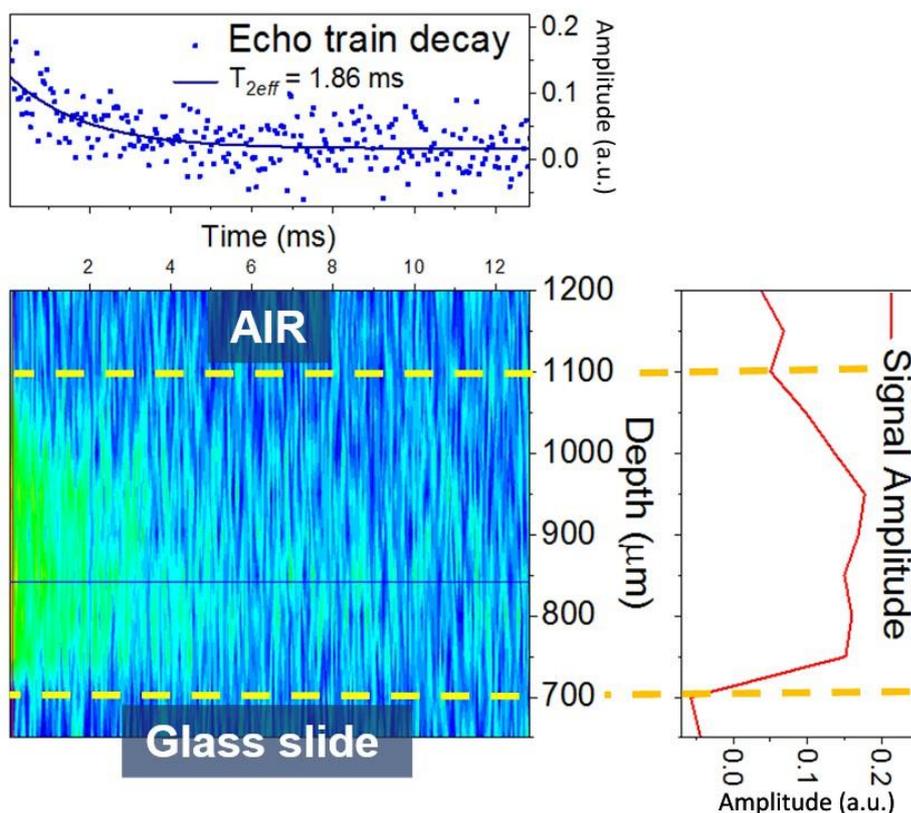


Fig. 1. An example of the 2D profile data obtained for a Hansa yellow light paint-out on a glass slide. A horizontal slice through the 2D data yields the CPMG echo train decay for each depth within the sample (top curve), while a vertical slice through the 2D data at the $\tau = 0$ yields a profile of the proton density through the scan depth (right curve).

To demonstrate how the water ingress into a sample can be monitored, a 30 second Pemulen-TR2 gel treatment test is shown in Fig. 2. The much longer relaxation time, expressed by a higher intensity for the entire echo train decay in the top slice of the paint film in the 2D map, represents the location of the water in the profile. The echo decay data from the water-laden sections of the paint film can be extracted and fitted. Of interest in these studies is the ability to obtain the y-intercept of the water signal in these layers which can be compared to the same data from free water to calculate the relative volume of water in the sensitive volume of the experiment.

The signal amplitude data in Fig. 2 also demonstrate the localisation of a much higher proton density in the top 150 μm of the paint film. Continuous scanning through the depth of the paint film, and extraction of the signal amplitude at $\tau = 0$ ms allows us to trace the movement of the water after the treatment. In the plot to the right in Fig. 2, the increased proton density from the water signal is shown to move deeper in the paint-film, whilst

simultaneously decreasing in the top layers. The drying process in these initial stages seems to include evaporation and de-swelling of the paint-film at the air-interface accompanied by diffusion of the water into the paint-film (red arrow in Fig. 2). Because these films are attached to a glass substrate, drying cannot occur from both fronts. The migration of liquid from the top paint layers deeper into the paint-film after exposure to a gel may be of relevance as it is likely that during an actual conservation treatment, the water may contain cleaning agents such as chelators or surfactants. Furthermore, although some gels are able to reabsorb part of the solubilised surface dirt and grime, some of this material may be carried further into the paint film after the gel has been removed during the drying process.

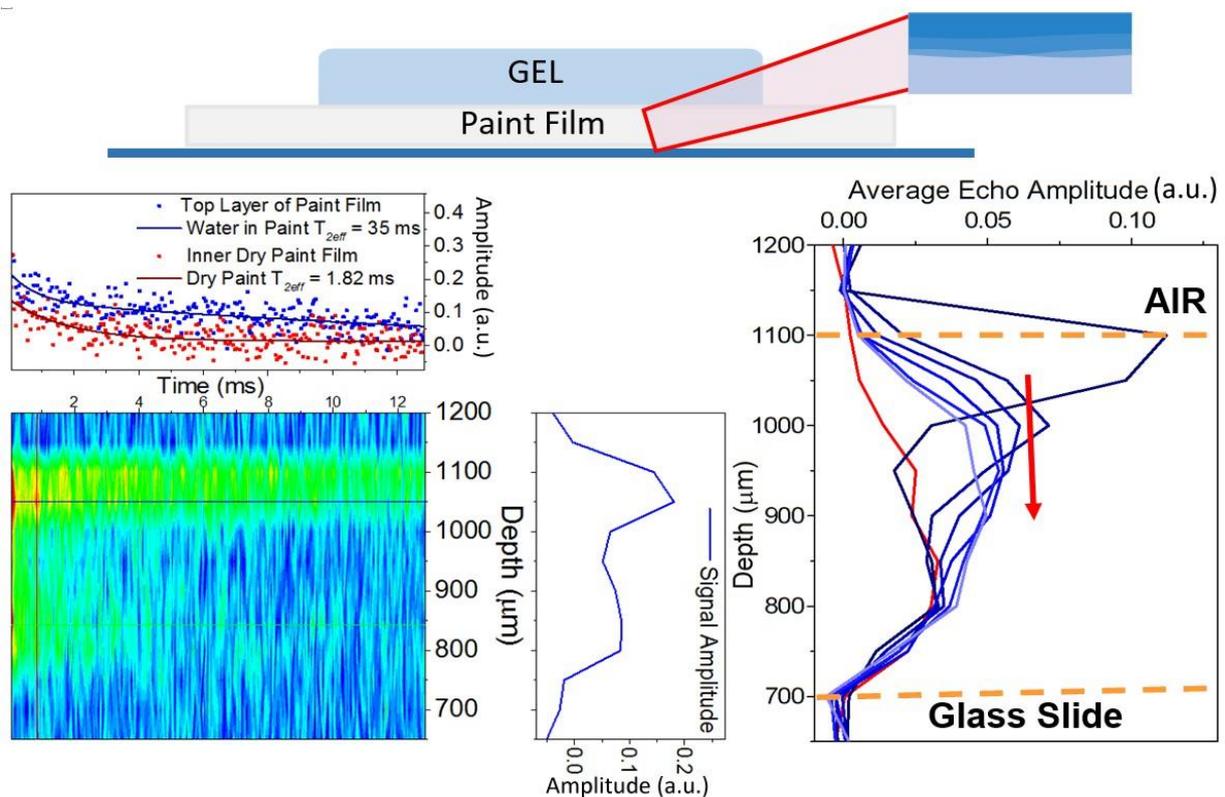


Fig. 2. An example of the 2D profile map obtained of a Hansa yellow light paint-out on a glass slide immediately after a 30 sec treatment with Pemulen TR-2. The presence of water in the 2D profile plot and CPMG echo train decays is expressed by the much longer relaxation time of the decay. The location of the water can also be visualised by the increased proton density in the top 150 µm of the signal amplitude profile; six sequential profiles obtained during the drying process have been shown to the right. The red profile signal represents the dry paint film before treatment and the red arrow shows the progression of the water signal into the depth of the film.

By greatly reducing the number of scans, the repetition time and number of echoes in the sequence, the experiments can be extended to reflect the signal of the diffusing water-front rather than that of the paint-film (this is accomplished by the contrast function described in the Methods section). The entire profile can then be obtained in 60-90 seconds, and profiles of the paint-film with the treatment agent on the surface can be continuously obtained until full saturation of the paint-out occurs (Fig. 3a). With these parameters, we can calculate that saturation occurs when approximately 30% of the sensitive volume is occupied by water. The progression of the liquid into the paint film at different depths can be extracted (Fig. 3b and 3d). The treatment agent can then be removed, and the drying of the paint-film can be monitored using the same parameters (Fig. 3c). The penetration seems to follow uptake and drying kinetics based on a Type II sorption isotherm [35,67]. Along with the water ingress into the paint-film, an approximate 100 μm swelling of the paint surface layer is observed in Fig. 3a (green double-headed arrow). Similar swelling of the paint film is observed in YG1 samples during continuous exposure to the gel systems.

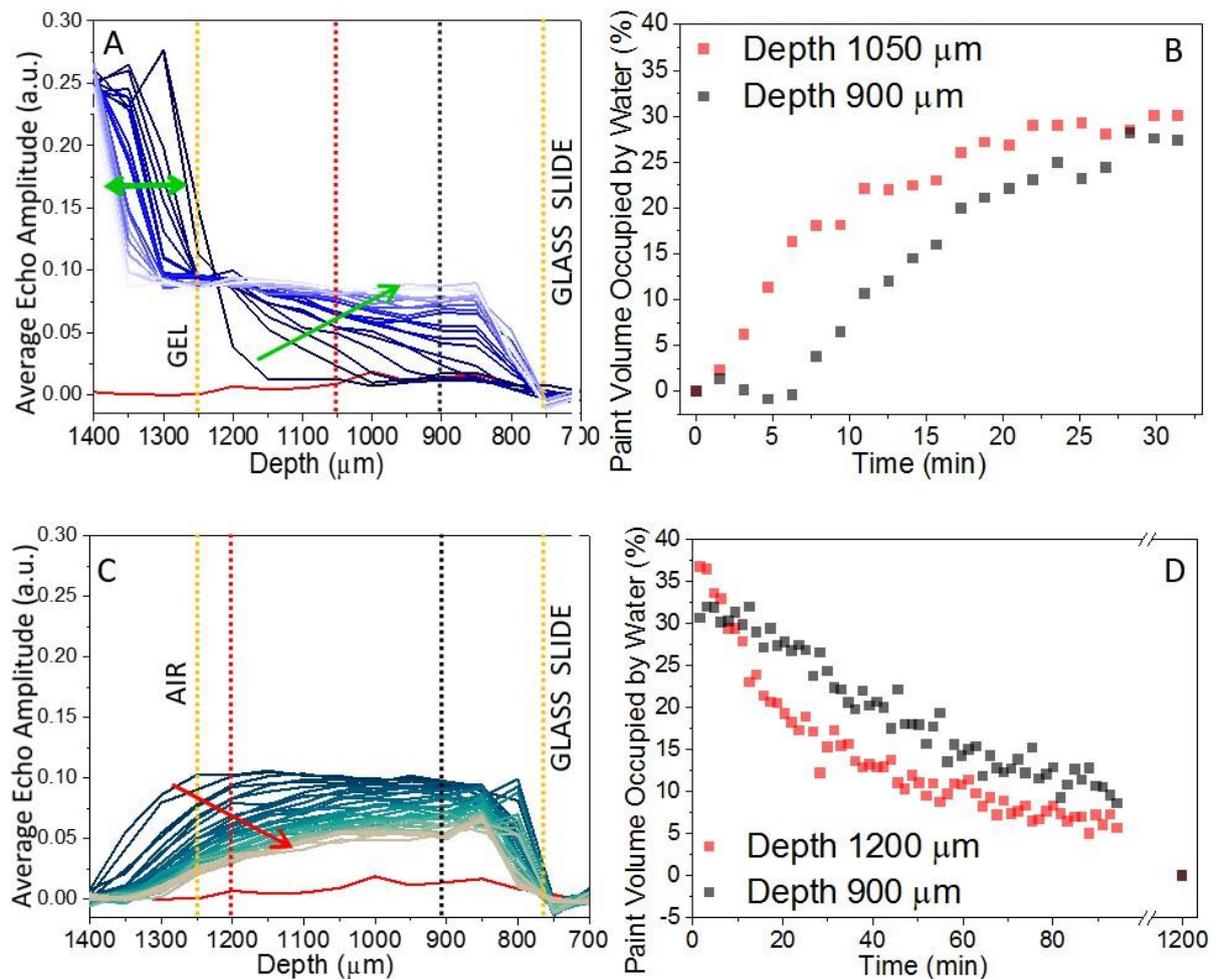


Fig. 3. Average echo amplitudes of the water signal through the depth of a 4-week old titanium white paint-out on glass with Pemulen TR-2 on the surface (A); 20 profiles were obtained before the Pemulen TR-2 was removed, and 60 profiles were obtained after removal (C). The solvent ingress (B) and egress (D) expressed as the % of the sensitive volume occupied by water are shown at two different depths for each experiment. The dry film profile is shown in red; the dashed yellow lines show the gel-paint (A), air-paint (C) and paint-glass (A and C) interfaces. The single-headed green arrow in A represents the movement of water into the paint-film, while the double-headed green arrow represents the movement of the gel-paint interface as the paint swells. The red arrow in C represents the deswelling of the paint-film through a reduction of the water signal intensity.

Obtaining a ‘horizontal slice’ through data like that presented in Fig. 3a from reservoir treatments with each gel type on 4-week old paint-outs, shows the water progression through the paint-film. Rather than monitoring saturation of the entire paint-film, this data allows for a qualitative understanding of the water flux through the paint whilst it is continuously exposed to the treatment system. The titanium white paint, with a T_g of 8.8°C absorbs water from all of the gel systems and bulk water at faster rates than the Hansa yellow light paint ($T_g = 14.5^\circ\text{C}$), (Fig. 4). Within ten minutes of exposure to the treatment system, more than 80% of the paint film has been breached by water in the young TG1 films (Fig. 4a), though this process occurs fastest with the PVAc-borax and Pemulen TR-2 gels. Similar trends are observed in the young YG1 paint films, though less than 80% of the paint film was affected by water after ten minutes (Fig. 4b). In both young paints, diffusion of free water occurred at rates comparable to or only slightly faster than from a 1% agar gel or 5% methylcellulose paste. PVAc-borax gels are formulated at pH 8, and also contain free, non-crosslinked borate ions and boric acid in the liquid part. It is possible that the increased water permeation from this gel system is due to the more basic pH [10,46]. Syneresis from PVAc-borax gels was also observed when they were placed on the Hansa yellow paint which may be a result of the larger amount of non-ionic surfactant present on the surface of this paint relative to the titanium white (*vide infra*, Fig. 7) [37].

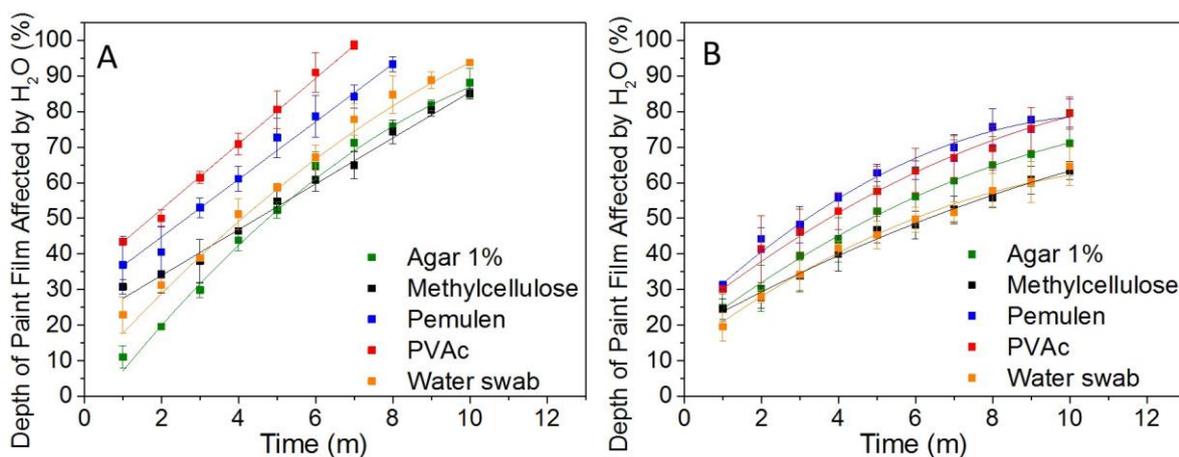


Fig. 4. Depth of titanium white TG1 (A) and Hansa yellow light YG1 (B) paint-out samples affected by water released from different gel systems or a bulk water reservoir over the course of 10 profile scans. The depth is expressed as a percentage, with 100% representing the entire thickness of the film and canvas from the air to the glass interface; experiments were performed in triplicate.

Due to sample limitation, only diffusion from a free water reservoir could be studied on the aged paint-outs. The paint layer in these samples is only ~100 μm thick in contrast to the 400-500 μm young paint-outs. The movement of water into the aged samples was visibly much slower; the profile scans obtained confirm this trend (Fig. 5 and 6) with the 2-year old paint-outs swelling faster than the 10-year naturally and artificially aged paint-outs. Within a 50-minute reservoir experiment, water had saturated the paint-layer and moved into the canvas of TG2, while only the paint-layer was saturated during this time in TG10 (Fig. 5). Surface wettability of the light-aged film was very low. FTIR-ATR characterisation (Fig. 7) of the make-up of the paint-films shows that the surface-surfactants of the TG10-LA have been almost entirely lost. Similar low wettability was observed for the TG10-TA sample, though to a lesser extent. Studies have shown that surfactants can migrate to the surface after thermal ageing [41]. The loss of surface surfactant as well as other processes such as increased polymer coalescence, crosslinking, and chain density [46], limit the penetration of water into the light-aged sample to a greater extent than any of the other aged samples (Fig. 6). Diffusion is also slower in the thermally aged sample, TG10-TA.

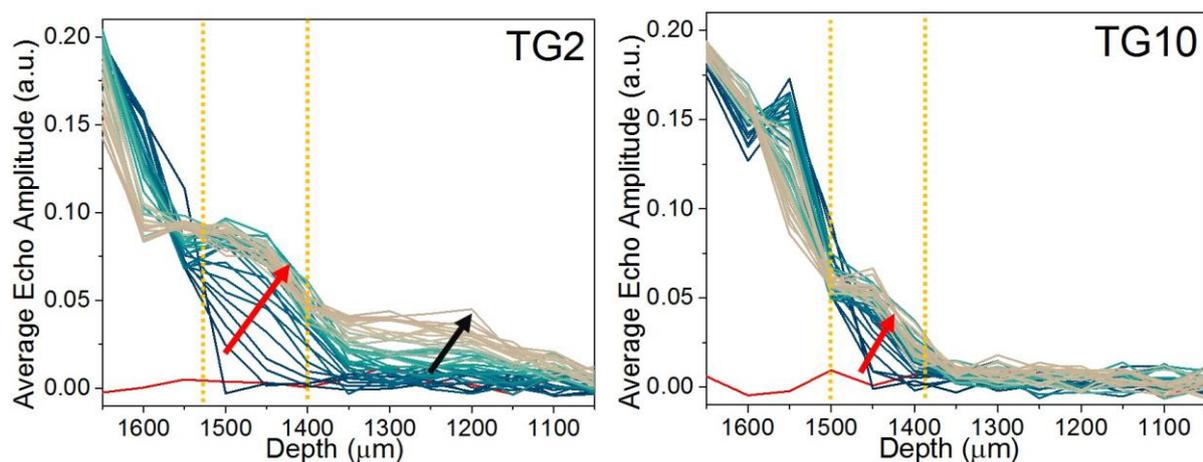


Fig. 5. Diffusion of water into 2-year old (left) and 10-year old (right) titanium white paint films. The red arrows show the movement of water into the paint layer, marked by yellow dashed-lines; the black arrow shows the movement of water into the primed canvas in the younger paint-out.

Diffusion of water and swelling occur to the greatest extent in the YG2 (2 year old yellow) sample, where signal from water in the sensitive volume in the centre of the paint-film reaches a plateau at nearly twice the value of that in sample TG2 (Fig. 6). The extent of swelling in this sample is comparable to that in the top 50 μm of the unaged, YG1 sample. It is likely that the higher medium and additive content associated with organic pigmented paints results in a larger hygroscopicity of this paint. Because of limited samples, replication of the experiments was not possible, though the YG2 experiment was carried out twice on two separate paint samples due to its anomalously large swelling capacity. The results of the second trial are comparable to the first, suggesting that YG2 absorbs much more water than TG2 and all of the ten-year old paints.

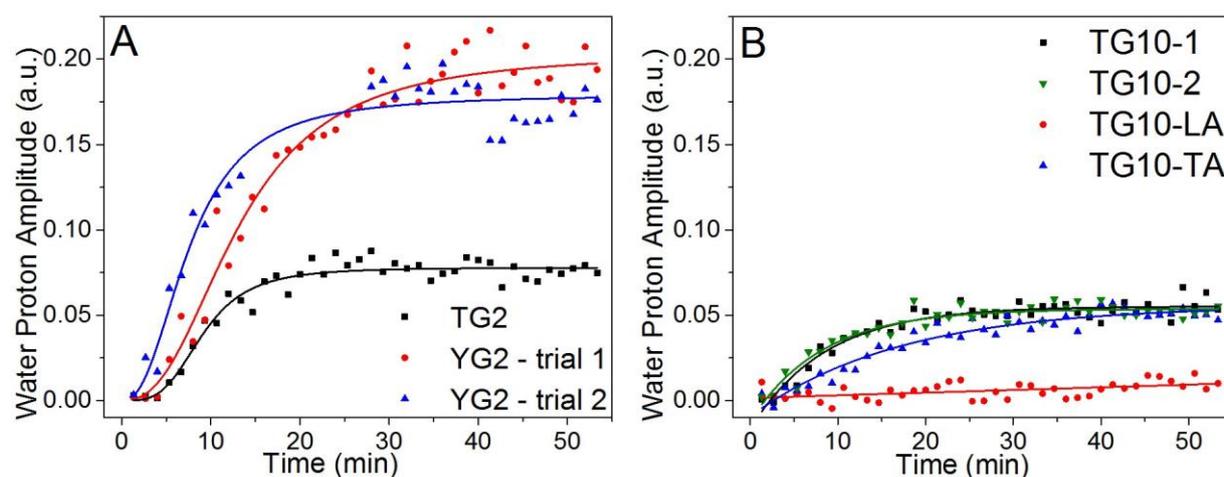


Fig. 6. Saturation by water of a 50 μm thick layer in the centre of the paint film during reservoir tests with free water; (A) two-year old paint-outs and (B) ten-year old paint-outs.

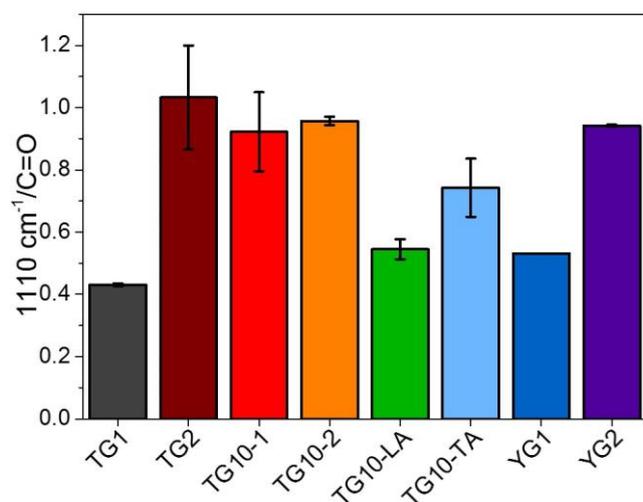


Fig. 7. ATR-FTIR measured amounts of surface surfactant on young and aged films used in this study.

4.2 Water Ingress during Simulated Treatment Experiments

Following the ‘reservoir’ tests, exposure of the 4-week old paint-films to the selected gel treatments for 30 seconds followed by a standard clearance procedure was expected to show similar trends in water delivery trends (Fig. 8). Indeed, of the gel systems tested, the agar gels release a minimal amount of liquid during the treatment test, with the 4% agar gel showing the most ‘controlled’ delivery. In opposition to many statements made regarding gel versus swab cleaning and control over the quantity of liquid delivered to the paint substrate, moistened swabs deliver very low amounts of water to the paint-film surface. In the young acrylic paint-films, swab cleaning and agar gel cleaning release approximately the same volume of water into the paint. The Velvesil Plus silicone emulsion (9 wt % water) was not found to release detectable liquid into the Hansa yellow light paint films, and a minimal amount into the titanium white paint. A test with Velvesil Plus carried out when the paint-outs were 6-weeks old showed no penetration of liquid into the titanium white paint.

Although typically within experimental error, the general trend seems to show the Hansa yellow light paint absorbing less water than the titanium white paint in the young paints. As noted earlier, the T_g of the yellow paint is approximately 7°C higher than that of the white at this stage of the drying process. Although the paints are of the same grade and

produced by the same company, there are significant differences in their composition. Most notably, the PY3 dye is an organic monoazo pigment and due to its high tinting strength requires a much lower loading than an inorganic pigment [68]. Because the pigment particles are very small and in low concentration, fillers and extenders (typically barium sulfate and calcium carbonate) are added to increase the paint coverage ability and to aid in creating the desired rheology of the paint [69,70]. However, studies have shown that Golden Heavy body acrylics contain very low concentrations of these materials [37]. Organic pigmented paints also contain larger quantities of emulsifier, surfactants, ionomers, and other hydrophilic additives. The marginally reduced propensity of the young yellow paint relative to the young white paint in absorbing water during the conservation treatments is therefore counterintuitive, though in agreement with the reservoir test results. Other factors contributing to differences in water absorption include pigment clusters, numbers of channels available for water transport, polymer chain density, surface osmotic effects, and the glass transition temperature of the films. The abnormal trend observed in this study may be a result of numerous factors, though the short drying time of these films is the most likely reason for their properties and tendency to absorb water.

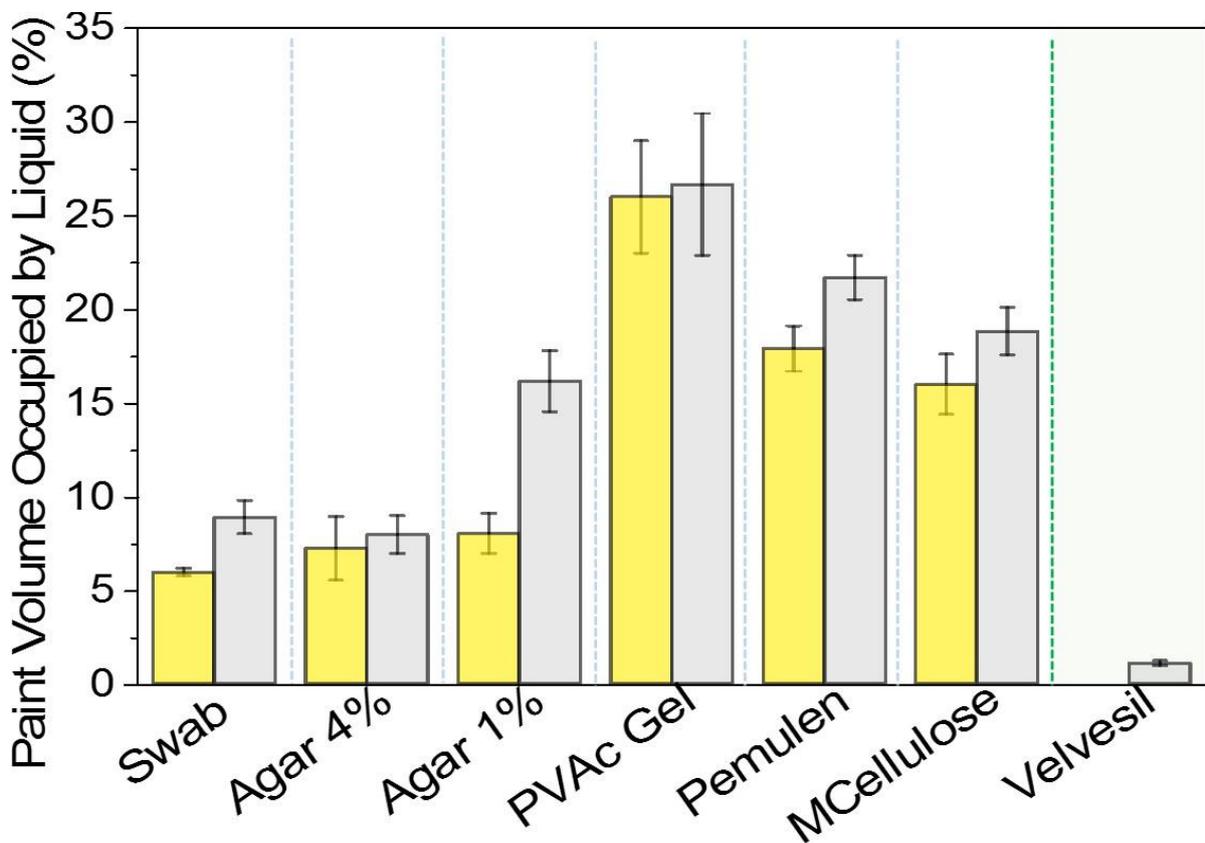


Fig. 8. Volume of entire paint film occupied by water after 30 second simulated treatments with a moistened swab or each of the listed gels on 4-week old paint films. The grey bars represent titanium white paint films on cotton canvas backing, the yellow bars represent Hansa yellow light paint films on cotton canvas backing. Standard deviation is obtained from 3-4 separate trials. Green region denotes data from Velvesil Plus simulated trials; blue dashed lines facilitate reading of the graph.

The simulated treatment tests were also performed on aged paint-outs, though only a single trial could be carried out. The treatment time was extended to 60 seconds on the two-year old and ten-year old samples because 30-second treatments delivered nearly undetectable quantities of water into the paint surface. Even with a one minute treatment, the volume of sample occupied by water was typically less than 10% (Fig. 9). Following the trends observed in the reservoir tests, the YG2 paint-outs swelled the most during the simulated treatment tests, with the PVAc-borax gel and Pemulen releasing the largest quantities of water into the paint. Both two-year old paint films, TG2 and YG2, absorbed more water during the treatments than the ten-year old samples. The light aged and thermally aged paints, TG10-LA and TG10-TA, respectively, absorbed the smallest quantities of liquid – in most cases water was not detected after the treatment in these samples. The Pemulen-TR2 treated TG10-LA sample is the only incongruous result, and may be due to experimental error or the high ionic content of this gel.

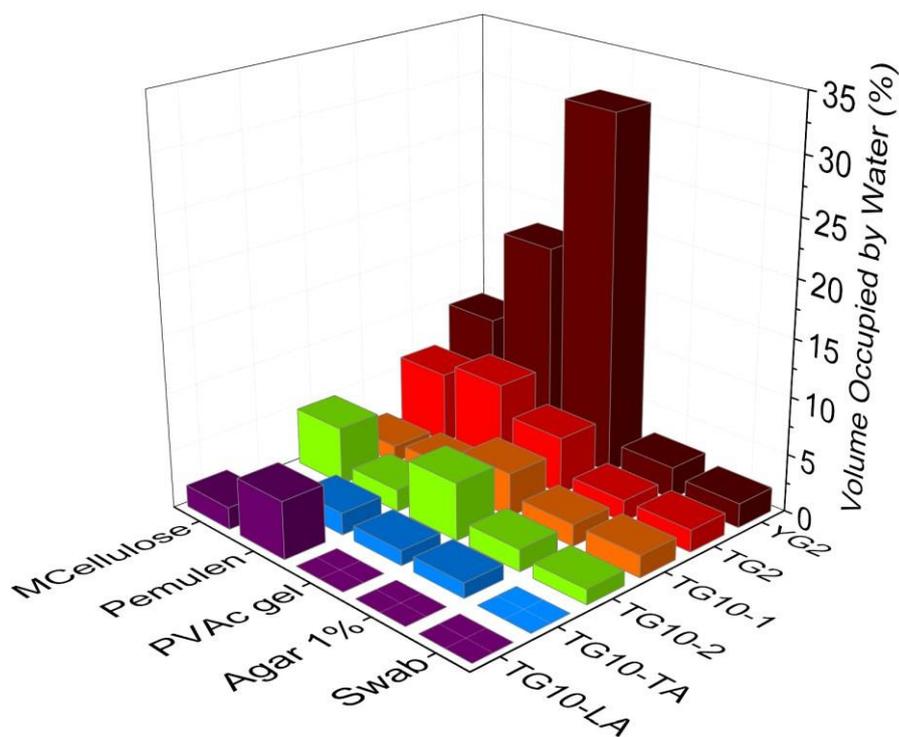


Fig. 9. Volume of aged paint-outs occupied by water after a 1 minute treatment with various gel systems and the appropriate clearance procedures.

As expected, the older samples are less prone to absorbing large quantities of water during simulated conservation treatment conditions. In addition, because the quantity of water absorbed by these samples is so small and localised only the top 50 microns of the paint layer, the drying process occurs much more quickly after the treatment (within 5 minutes, a water signal was no longer detected). As a result, the movement of water from the treatment further into the paint does not seem to occur to a large extent, though paint films can be as thin as 50 microns.

5. Conclusions

NMR relaxometry was used to evaluate water uptake in two artists' acrylic emulsion paints – Golden heavy bodied Hansa yellow light (PY3) and titanium white (PW6) – during exposure to a range of thickened and gelled cleaning treatments. The studies were carried out by following simulated treatment protocols lasting 30-60 seconds, or by exposing the paint-outs to the treatment until full water saturation of the paint was achieved. Young paints tend to absorb much more water in both set-ups than aged paints. In simulated treatments, the white aged films typically have less than 10% of their volume occupied by water after a 1

minute exposure to the gel systems, while 15-30% of the volume in the young white paints can become occupied by water after gel treatments lasting only 30 seconds. Four-week old Hansa yellow light paint films were found to absorb slightly less or the same amount of water from most treatment systems as titanium white paint films of the same age. However, Hansa yellow light paint samples which were naturally aged for two years absorbed more than twice the amount of water that two-year old titanium white paint films absorbed during extended exposure. Experiments carried out on ten-year old naturally aged, and light aged and thermally aged samples (~50 years), showed a greatly reduced propensity to absorb water during simulated treatment tests. The light aged titanium white paint absorbed the smallest amount of water in all experiments – liquid in the paint film was only detectable from two of the simulated treatment tests, occupying less than 5% of the paint volume.

Simulated treatments of both young and aged paint films showed that the use of a gently moistened swab does not result in greater release of water into the paint film than during the use of thickened systems. Of the gel treatments tested, only agar gels show water release on par with swab cleaning. However, agar gels did not *reduce* the amount of water released relative to a water swab in this study. Therefore, the main advantage to agar is reduced mechanical action relative to swab cleaning; this advantage is somewhat lost if a follow-up swab-clearance step is necessary to remove surface grime dissolved by the agar gel, or to remove chelating agents delivered to the surface by the gel. Furthermore, agar gels are commonly applied as brushed-on warm solutions which may result in a larger release of water to the paint surface, softening of the paint, and softening and melting of the surfactants. This question will be explored in future studies.

Pemulen-TR2 and PVAc-borax gels allow large quantities of water to diffuse into the paints tested, both young and aged. The cause of this has not yet been elucidated, though the pH and ionic strength of these gels may play a role. The more dynamic nature of the polymer network in these gels relative to the agar gels may also contribute, depending on its propensity for physico-chemical interactions with the paint surface. Methylcellulose gels had an intermediate effect, showing large release of water into the young paint films during simulated treatments, and release comparable to that of agar in reservoir tests. It is possible that the majority of water ingress from the methylcellulose treatment occurs during the clearance steps. The same may be true of the Pemulen-TR2 gels. The Velvesil Plus system inhibits water ingress into the paint films, though the studies presented here are very limited and do not take into account the greatly reduced quantity of water in this emulsion system.

Further experiments using thickened water-in-oil emulsion systems and on solvent-based gels will be carried out in future studies.

The results of this first study demonstrate the potential of NMR relaxometry in elucidating differences between cleaning treatment methods. As expected, large differences in water ingress from gel systems were found not only between young and aged paint films, but also depending on the ageing history of the paints. The relative propensity of gel systems for water release into substrates is likely to vary greatly and should be explored on other artists' materials. This study was also largely limited to gels that are typically water based, and the results may be different with organogels or micro-emulsion loaded systems.

Acknowledgements

LVA would like to acknowledge the Newton International Fellowship for funding this research.

Reference List

- [1] R. de la Rie, The Influence of Varnishes on the Appearance of Paintings, *Stud. Conserv.* 32 (1987) 1-13.
- [2] J.K. Delaney, E.R. de la Rie, M. Elias, L. Sung, K.M. Morales, The role of varnishes in modifying light reflection from rough surfaces - a study of changes in light scattering caused by variations in varnish topography and development of a drying model, *Stud. Conserv.* 53 (2008) 170-186.
- [3] R.S. Berns, E.R. de la Rie, The effect of the refractive index of a varnish on the appearance of oil paintings, *Stud. Conserv.* 48 (2003) 251-262.
- [4] R.L. Feller, N. Stolow, E.H. Jones, *On Picture Varnishes and their Solvents*, National Gallery of Art, Washington, D.C., 1985.
- [5] E. Kampasakali, B. Ormsby, A. Cosentino, C. Miliani, T. Learner, A preliminary evaluation of the surfaces of acrylic emulsion paint films and the effects of wet-cleaning treatment by atomic force microscopy (AFM), *Stud. Conserv.* 56 (2011) 216-230.
- [6] M. Keefe, C. Tucker, A.M. Behr, G. Meyers, C. Reinhardt, T. Boomgaard, C. Peitsch, B. Ormsby, A. Soldano, A. Phenix, T. Learner, *Art and Industry: novel approaches to the evaluation and development of cleaning systems for artists' acrylic latex paints*, *JCT Coatingstech.* 8 (2011) 30-43.

- [7] B. Ormsby, T. Learner, M. Schilling, J. Druzik, H. Khanjian, D. Carson, G. Foster, M. Sloan, The effects of surface cleaning on acrylic emulsion paintings: A preliminary investigation, *Tate Papers* 6 (2006).
- [8] E. Jablonski, T. Learner, J. Hayes, M. Golden, The conservation of acrylic emulsion paintings: A literature review, *Tate Papers*, 2 (2003).
- [9] A. Murray, C.C. de Berenfield, S.I.S. Chang, E. Jablonski, T. Klein, M.C. Riggs, E.C. Robertson, W.M.A. Tse, The condition and cleaning of acrylic emulsion paintings, In: P.B. Vandiver, M. Goodway, J.L. Mass (Eds.) *Materials Issues in Art and Archaeology VI*. Materials Research Society, Warrendale, PA, 2001, pp. 83–90.
- [10] C.E. Dillon, A.F. Lagalante, R.C. Wolbers, Acrylic emulsion paint films: the effect of solution ph, conductivity, and ionic strength on film swelling and surfactant removal, *Stud. Conserv.* 57(1) (2014) 52-62.
- [11] R. Wolbers, *Cleaning Painted Surfaces: Aqueous Methods*, Archetype Publications, London, 2000.
- [12] J. Warda, I. Bruckle, A. Bezur, D. Kushel, Analysis of agarose, carbopol, and laponite gel poultices in paper conservation, *J. Am. Inst. Conserv.* 46 (2007) 263-279.
- [13] R. Wolbers, Gel media in aqueous cleaning methods on paper, Lecture from the Wellcome Intitute, London, 19 June, 2013. https://www.youtube.com/watch?v=mu7_nS-zF1c
- [14] N. Ravendel, Pemulen® TR-2: An emulsifying agent with promise, *WAAC Newsletter*. 32(3) (2010) 10-12.
- [15] F. Gorel, Assessment of agar gel loaded with micro-emulsion for the cleaning of porous surfaces, *CeROArt web journal*. (2010) (accessed 14 Sept. 2015). <https://ceroart.revues.org/1827>
- [16] D. Gulotta, D. Saviello, F. Gherardi, L. Toniolo, M. Anzani, A. Rabbolini, S. Goidanich, Setup of a sustainable indoor cleaning methodology for the sculpted stone surfaces of the Duomo of Milan, *Heritage Science*. 2 (2014) 1-13.
- [17] Winterthur/University of Delaware Program in Art Conservation Blog, *New Methods for Cleaning Historic Textiles*, 28 August, 2012, (accessed 14 Sept. 2015). <https://wudpac2014.wordpress.com/2012/08/28/new-methods-for-cleaning-historic-textiles/>
- [18] S. Iannuccelli, S. Sotgiu, Wet treatments of works of art on paper with rigid gellan gels, *B. and Pap. Gr. Annu. J.* 29 (2010) 25-39.
- [19] C. Mazzuca, L. Micheli, E. Cervelli, F. Basoli, C. Cencetti, T. Coviello, S. Iannuccelli, S. Sotgiu, A. Palleschi, Cleaning of paper artworks: development of an efficient gel-based material able to remove starch paste, *Appl. Mater. Interfaces*. 6 (2014) 16519-16528.

- [20] G. Pizzorusso, E. Fratini, J. Eiblmeier, R. Giorgi, D. Chelazzi, A. Chevalier, P. Baglioni, Physicochemical characterization of acrylamide/bisacrylamide hydrogels and their application for the conservation of easel paintings, *Langmuir*. 28 (2012) 3952-3961.
- [21] J.A.L. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, Innovative hydrogels based on semi-interpenetrating p(hema)/pvp networks for the cleaning of water-sensitive cultural heritage artifacts, *Langmuir*. 29 (2013) 2746-2755.
- [22] J. Domingues, N. Bonelli, R. Giorgi, P. Baglioni, Chemical semi-IPN hydrogels for the removal of adhesives from canvas paintings, *Appl. Phys. A-Mater*. 114 (2014) 705-710.
- [23] L.V. Angelova, B.H. Berrie, K. de Ghetaldi, A. Kerr, R.G. Weiss, Partially hydrolyzed poly(vinyl acetate)-borax-based gel-like materials for conservation of art: Characterization and applications, *Stud. Conserv.* 60 (2015) 227-244.
- [24] I. Natali, E. Carretti, L. Angelova, P. Baglioni, R.G. Weiss, L. Dei, Structural and mechanical properties of "peelable" organoaqueous dispersions with partially hydrolyzed poly(vinyl acetate)-borate networks: applications to cleaning painted surfaces, *Langmuir*. 27 (2011) 13226-13235.
- [25] A. Casoli, Z. Di Diego, C. Isca, Cleaning painted surfaces: evaluation of leaching phenomenon induced by solvents applied for the removal of gel residues, *Environ. Sci. Pollut. R.* 21 (2014) 13252-13263.
- [26] V. Dorge, *Solvent Gels for the Cleaning of Works of Art. The Residue Question*, Getty Publications, Los Angeles, 2004.
- [27] E.A. Willneff, B.A. Ormsby, J.S. Stevens, C. Jaye, D.A. Fischer, S.L.M. Schroeder, Conservation of artists' acrylic emulsion paints: XPS, NEXAFS and ATR-FTIR studies of wet cleaning methods, *Surf. Interface Anal.* 46 (2014) 776-780.
- [28] P. Baglioni, E. Carretti, D. Chelazzi, Nanomaterials in art conservation, *Nat. Nanotechnol.* 10 (2015) 287-290.
- [29] G.R. Fife, B. Stabik, A.E. Kelley, J.N. King, B. Blümich, R. Hoppenbrouwers, T. Meldrum, Characterization of aging and solvent treatments of painted surfaces using single-sided NMR, *Magn. Reson. Chem.* 53 (2015) 58-63.
- [30] B. Blümich, F. Casanova, J. Perlo, F. Presciutti, C. Anselmi, B. Doherty, Noninvasive testing of art and cultural heritage by mobile NMR, *Acc. Chem. Res.* 43 (2010) 761-770.
- [31] K. Ulrich, S.A. Centeno, J. Arslanoglu, E. Del Federico, Absorption and diffusion measurements of water in acrylic paint films by single-sided NMR, *Prog. Org. Coat.* 71 (2011) 283-289.
- [32] P.A.J. Donkers, H.P. Huinink, S.J.F. Erich, N.J.W. Reuvers, O.C.G. Adan, Water permeability of pigmented waterborne coatings, *Prog. Org. Coat.* 76 (2013) 60-69.
- [33] V. Baukh, H.P. Huinink, O.C.G. Adan, S.J.F. Erich, L.G.J. van der Ven, Water-polymer interaction during water uptake, *Macromolecules*. 44 (2011) 4863-4871.

- [34] G. van der Wel, O. Adan, Moisture in organic coatings - a review, *Prog. Org. Coat.* 37 (1999) 1-14.
- [35] V. Baukh, Water Transport in Multilayer Coatings, PhD thesis, Eindhoven University of Technology, 2012.
- [36] B. Ormsby, A. Soldano, M.H. Keefe, A. Phenix, T. Learner, An empirical evaluation of a range of cleaning agents for removing dirt from artists' acrylic emulsion paints. *23* (2013) 77-87.
- [37] B. Ormsby, T. Learner, G. Foster, J. Druzik, M. Schilling, Wet-cleaning acrylic emulsion paint films: an evaluation of physical, chemical, and optical changes. In: T.J.S. Learner, P. Smithen, J.W. Krueger, M.R. Schilling (Eds.) *Modern Paints Uncovered*, Tate Modern, Getty Conservation Institute, Los Angeles, 2007, pp. 187-198.
- [38] R. Wolbers, A. Norbutus, A. Lagalante, Cleaning of acrylic emulsion paints: preliminary extractive studies with two commercial paint systems, In: M.F. Mecklenburg, A.E. Charola, R.J. Koestler (Eds.) *New Insights into the Cleaning of Paintings: Proceedings from the Cleaning 2010 International Conference*, Universidad Politécnica de Valencia and Museum Conservation Institute, Smithsonian Institution Scholarly Press, Washington, D.C., 2013 147-157.
- [39] Golden Artist Colors, Inc., Just Paint: Technical Notes on Drying, (accessed 14 Sept. 2015) http://www.goldenpaints.com/technicalinfo_drying
- [40] C. Stavroudis, Pemulen revised: pHuck the pH meter, *WAAC Newsletter.* 34(2) (2012) 19.
- [41] B. Ormsby, E. Kampasakali, C. Miliani, T. Learner, An FTIR-based exploration of the effects of wet cleaning treatments on artists' acrylic emulsion paint films, *e-Preservation Sci.* 6 (2009) 186-195.
- [42] H.Y. Carr, E.M. Purcell, Effects of diffusion on free precession in nuclear magnetic resonance experiments, *Phys. Rev.* 94 (1954) 630-638.
- [43] S. Meiboom, D. Gill, Modified spin-echo method for measuring nuclear relaxation times, *Rev. Sci. Instrum.* 29 (1958) 688-691.
- [44] J. Perlo, F. Casanova, B. Blümich, Profiles with microscopic resolution by single-sided NMR, *J. Magn. Reson.* 176 (2005) 64-70.
- [45] E. Gazi, S.J. Mitchell, Nuclear magnetic resonance profiling of chemical warfare agent simulatant mass-transport through a multilayered polymeric coating, *J. Coat. Technol. Res.* 9 (2012) 735-743.
- [46] B. Ormsby, T. Learner, The effects of wet surface cleaning treatments on acrylic emulsion artists' paints - A review of recent scientific research, *Rev. Conserv.* 10 (2009) 29-41.

- [47] D.Y. Perera, Effect of pigmentation on organic coating characteristics, *Prog. Org. Coat.* 50 (2004) 247-262.
- [48] A. Sundaramoorthi, Fundamental understanding of physicochemical properties of ultra-thin polymer films, PhD thesis, Georgia Institute of Technology, 2011.
- [49] H. Zhu, H.P. Huinink, S.J.F. Erich, V. Baukh, O.C.G. Adan, K. Kopinga, High spatial resolution NMR imaging of polymer layers on metallic substrates, *J. Magn. Reson.* 214 (2012) 227-236.
- [50] P. Whitmore, H.R. Morris, V.G. Colaluca, Penetration of liquid water through waterborne acrylic coatings, In: T.J.S. Learner, P. Smithen, J.W. Krueger, M.R. Schilling (Eds.) *Modern Paints Uncovered*, Tate Modern, Getty Conservation Institute, Los Angeles, 2007, pp. 217-223.
- [51] R. Ploeger, A. Murray, S. Hesp, D. Scalarone, Morphological changes and rates of leaching of water-soluble material from artists' acrylic paint films during aqueous immersions, In: T.J.S. Learner, P. Smithen, J.W. Krueger, M.R. Schilling (Eds.) *Modern Paints Uncovered*, Tate Modern, Getty Conservation Institute, Los Angeles, 2007, pp. 201-207.
- [52] C. Tumosa, M.F. Mecklenburg, Moisture isotherms of acrylic emulsion paints, *WAAC Newsletter.* 26(3) (2004) 12-14.
- [53] G. Brown, J. Scullin, Water penetration of emulsion polymer films, *Ind. Eng. Chem.* 45 (1953) 743-745.
- [54] I. Ziraldo, K. Watts, A. Luk, A.F. Lagalante, R.C. Wolbers, The influence of temperature and humidity on swelling and surfactant migration in acrylic emulsion paint films, *Stud. Conserv.* DOI: 10.1179/2047058414Y.0000000156 (2015) Advance article.
- [55] E. Davies, Y. Huang, J.B. Harper, J.M. Hook, D.S. Thomas, I.M. Burgar, P.J. Lillford, Dynamics of water in agar gels studied using low and high resolution ¹H NMR spectroscopy, *Int. J. Food Sci. Tech.* 45 (2010) 2502-2507.
- [56] J. Narayanan, J. Xiong, X. Liu, Determination of agarose gel pore size: Absorbance measurements vis a vis other techniques, *J. Phys. Conf. Ser.* 28 (2006) 83-86.
- [57] N. Pernodet, M. Maaloum, B. Tinland, Pore size of agarose gels by atomic force microscopy, *Electrophoresis.* 18 (1997) 55-58.
- [58] L. Li, P.M. Thangamathesvaran, C.Y. Yue, K.C. Tam, X. Hu, Y.C. Lam, Gel network structure of methylcellulose in water, *Langmuir.* 17 (2001) 8062-8068.
- [59] J.R. Lott, J.W. McAllister, M. Wasbrough, R.L. Sammler, F.S. Bates, T.P. Lodge, Fibrillar structure in aqueous methylcellulose solutions and gels, *Macromolecules.* 46 (2013) 9760-9771.

- [60] L.V. Angelova, M. Leskes, B.H. Berrie, R.G. Weiss, Selective formation of organo, organo-aqueous, and hydro gel-like materials from partially hydrolysed poly(vinyl acetate)s based on different boron containing crosslinkers, *Soft Matter*. 11 (2015) 5060-5066.
- [61] R. Bai, P.J. Basser, R.M. Briber, F. Horkay, NMR water self- diffusion and relaxation studies on sodium polyacrylate solutions and gels in physiologic ionic solutions, *J. Appl. Polym. Sci.* 131 (2014) DOI 10.1002/app.40001.
- [62] M. Budai-Szűcs, Formulation and Investigation of gel-emulsions containing polymeric emulsifiers, PhD thesis, University of Szeged, 2008.
- [63] S. Simovic, S. Tamburic, J. Milic-Askrabic, D. Rajic, An investigation into interactions between polyacrylic polymers and a non-ionic surfactant: an emulsion preformulation study, *Int. J. Pharm.* 184 (1999) 207-217.
- [64] D.Q.M. Craig, S. Tamburic, G. Buckton, J.M. Newton, An investigation into the structure and properties of Carbopol-934 gels using dielectric-spectroscopy and oscillatory rheometry, *J. Control. Release*. 30 (1994) 213-223.
- [65] Momentive, Velviesil* Plus Emulsifiable Silicon Gel, Momentive Marketing Bulletin. 2011 (accessed 14 Sept 2015)
<https://www.momentive.com/Products/selectorresults.aspx?taxids=1831&sort=Ascending&tab=2>
- [66] J. Newton, S. Postiaux, C. Stoller, V. Verhelst, S. Lin, M. Starch, Silicone technologies as delivery systems via entrapment or encapsulation, Dow Corning. 2009 (accessed 14 Sept 2015) <http://www.dowcorning.com/content/publishedlit/27-1178-01.pdf>
- [67] V. Baukh, H.P. Huinink, O.C.G. Adan, S.J.F. Erich, L.G.J. van der Ven, Predicting water transport in multilayer coatings, *Polymer*. 53 (2012) 3304-3312.
- [68] F. Schulte, K. Brzezinka, K. Lutzenberger, H. Stege, U. Panne, Raman spectroscopy of synthetic organic pigments used in 20th century works of art, *J. Raman Spectrosc.* 39 (2008) 1455-1463.
- [69] S.Q. Lomax, The application of x-ray powder diffraction for the analysis of synthetic organic pigments. Part 2: artists' paints, *J. Coat. Techn. Res.* 7 (2010) 325-330.
- [70] S.Q. Lomax, T. Learner, A review of the classes, structures, and methods of analysis of synthetic organic pigments, *J. Am. Inst. Conserv.* 45 (2006) 107-125.