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Evaluating three water-based systems and one organic solvent for the removal of dammar varnish from artificially aged oil paint samples

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Abstract

A framework was developed to evaluate and compare cleaning systems and cleaning system delivery methods, collectively referred to as varnish removal methods, within art conservation practice. This framework was applied to two water-based cleaning systems, optimised for the removal of dammar varnish from an artificially aged brown earth oil paint, including the surfactant-containing microemulsion, Polar Coating B (from the Nanorestore Cleaning series) delivered via the chemical gel, Higher Water Retention (HWR) (from the Nanorestore Gel Dry series), and a surfactant-free microemulsion delivered via the microfiber cloth, Evolon. In addition, two water-based systems and one organic solvent were used to remove dammar varnish from an artificially aged lead white oil paint sample, including a xanthan gum-stabilised emulsion delivered via a synthetic brush, a surfactant-free microemulsion delivered via cotton swab rolling, and 2-propanol solvent delivered via cotton swab rolling. The evaluation framework was thus applied to two different oil paints, with different sensitivities to cleaning. Through this work, the comparative advantages and disadvantages of the varnish removal methods were demonstrated. Notably, cleaning system compatibility with multiple delivery methods afforded greater versatility, including for reducing unwanted interactions between the cleaning system and oil paint. In addition, a surfactant-free microemulsion proved to be a promising, clearance-free, inexpensive, and modifiable option within current offerings for largely water-based methods for varnish removal.

Keywords　Varnish removal, Dammar, Oil paint, Evaluation, Nanostructured fluid, Oil-in-water microemulsion, Xanthan, Organic solvent, Nanorestore HWR, Evolon

Introduction

Water-based methods for art conservation cleaning purposes have expanded considerably in the past three decades, to encompass multiple types of cleaning systems (i.e., mixtures with water as the largest component, which can be classified as homogeneous solutions or heterogeneous colloids) and delivery methods, from the introduction of aqueous approaches in the early-1990s, to the ongoing exploration of microemulsions and a range of hydrogels [1–3]. The main advantage associated with water-based methods for varnish removal is the significant decrease in the amounts of organic solvents required to remove degraded natural resins from traditional oil paintings (for example, from the 16–mid-nineteenth century). Switching from organic solvents to methods predominantly based on water is beneficial

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from an environmental and health and safety (EHS) perspective [4]. In addition, water-based cleaning is possibly less detrimental to the underlying oil paint. However, potential interactions between water-based systems and oil paints have not yet been fully established. In contrast, the swelling, diffusion and retention capabilities of organic solvents have been more extensively studied in art conservation research [5]. Furthermore, relatively simple testing schemes can be followed to find an optimal organic solvent or organic solvent mixture for the removal of a specific natural resin varnish [6]. For water-based methods to be incorporated in these treatment decision-making processes, the comparative advantages and disadvantages between water-based and organic solvent-based methods must be assessed.

In contribution to this area of research, the parameters which influence the relative success of varnish removal were identified and defined for a comparative evaluation framework for varnish removal methods, inspired by similar frameworks for surface cleaning methods [7–13]. This evaluation framework was then applied to multiple varnish removal methods, which had been optimised to remove artificially aged dammar varnish from artificially aged oil paints, according to a methodology described by Husby et al. [3]. To remove varnish from a brown earth oil paint sample: the surfactant-containing microemulsion, Polar Coating B (from the Nanorestore Cleaning series) was delivered via the chemical gel, Higher Water Retention (HWR) (from the Nanorestore Gel Dry series), and a surfactant-free microemulsion was delivered via the microfiber cloth, Evolon. To remove varnish from a lead white oil paint sample: a xanthan gum-stabilised emulsion was delivered with a synthetic brush, the surfactant-free microemulsion was delivered via cotton swab rolling, and 2-propanol was delivered via cotton swab rolling.

The Nanorestore Cleaning option, Polar Coating B (https://www.csgi.unifi.it/products/cleaning.html [accessed June 3, 2023]), is an oil-in-water (OiW) microemulsion, also referred to as a nanostructured complex fluid, and is one of a series of such systems developed for conservation cleaning purposes in the NANORESTART project (2015–2018) (http://www.nanorestart.eu/ [accessed June 3, 2023]). This microemulsion consists of nano-sized droplets of butanone and 2-butanol dispersed in water with the help of an alkyl(C_{9-11}) alcohol, ethoxylated surfactant (water content: 64–78 wt.%, total organic solvent content: 20–32 wt.% and surfactant content: 2–4 wt.%) [4, 14, 15]. The microemulsion is expected to remove the varnish through a process called dewetting where the organic solvents mobilise the polymer chains and molecules in the varnish and the water accumulates at the interface between the hydrophobic varnish and hydrophilic paint, undermining adhesion so the varnish detaches. The water is also expected to

repel solubilised varnish from diffusing into the bulk of the paint [16–18]. In addition, as water is exceptionally slow diffusing [19], these systems may cause less oil paint swelling than faster-diffusing organic solvents (providing the oil paint is not water-sensitive). However, the swelling and diffusion rates of Polar Coating B remain to be experimentally determined.

Polar Coating B was delivered to the varnished brown earth oil paint sample via the chemical hydrogel HWR (https://www.csgi.unifi.it/products/dry.html [accessed June 3, 2023]). HWR consists of a semi-interpenetrative network made from poly (2-hydroxyethyl methacrylate) and poly(vinylpyrrolidone) (pHEMA/PVP) polymers, developed as part of the NANORESTART project, and is the most solvent-retentive of the chemical gels in the Nanorestore Gel series [2]. This ability to retain solvents has been confirmed experimentally [20–22]. In addition, HWR, alongside the other gels in the Nanorestore Gel series, were designed to be compatible with the Nanorestore Cleaning systems (e.g., Polar Coating B). It is worth noting, however, that HWR can also be loaded with a surfactant-free microemulsion (as a mixture of water and alcohols) and the organic solvent (2-propanol) [23].

The surfactant-free microemulsion evaluated is based on a mixture of water, 2-propanol, and 1-butanol (water content: 65 wt.% and total organic solvent content: 35 wt.%) and was recently introduced to the field of art conservation as a potential option for natural resin varnish removal [3]. This type of mixture is expected to form an OiW microemulsion through the clustering of the hydrotrope 2-propanol around 1-butanol, as 2-propanol is highly soluble in 1-butanol and poorly soluble in water, but without the micellar aggregation characteristic of a surfactant-containing microemulsion [24, 25]. Even without micelles, a thermodynamically stable dispersion of two immiscible liquids (1-butanol and water), separated by an interface (2-propanol), is expected to occur, fulfilling the technical criteria for a microemulsion, as defined by the International Union of Pure and Applied Crystallography (IUPAC) [26]. The system of water, 2-propanol, and 1-butanol included in this study was first identified as an OiW microemulsion by Wang et al. [27] using characterisation methods that have since been critically reviewed [26]. In addition, experimentation is required to verify whether this system can induce dewetting, as has been shown for surfactant-containing microemulsions [17]. The surfactant-free microemulsion, nevertheless, potentially provides a clearance-free, water-dominant option for natural resin varnish removal.

To remove varnish from the brown earth oil paint sample, the water/2-propanol/1-butanol surfactant-free OiW microemulsion was delivered via Evolon (https://prese

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rvationequipment.de/Catalogue/Restaurierungs-Material/Materialien-und-Stoffe/Evolon-Mikrofilament-Material [accessed June 3, 2023]). Using Evolon reduces the amount of cleaning mixture and the degree of mechanical action required to remove varnish. Furthermore, Evolon has been shown to limit solvent diffusion into oil paint films to a similar level as the HWR gel [22, 28]. Thus, Evolon facilitated the partial removal of varnish from the brown earth oil paint sample, with less pigment pickup than what was achieved via other delivery methods [3]. However, to remove varnish from the lead white oil paint sample, the surfactant-free microemulsion was delivered via cotton swab rolling. This delivery method involved more mechanical action but also resulted in more varnish removal than what was achieved via the other delivery methods (Nanorestore Gel series and Evolon). Cotton swab rolling was also considered a viable delivery option in this case, as the lead white oil paint sample was more resistant to pigment pickup.

A xanthan gum-stabilised emulsion was also assessed in this study. This system is essentially a gel-emulsion, formed through the addition of the polysaccharide xanthan gum, to an inhomogeneous mixture of water and organic solvent (the system evaluated in this study contained 78.5 wt.% water, 20 wt.% benzyl alcohol [BnOH], and 1.5 wt.% xanthan gum) [29]. As a thickened system, the diffusion of solvents and solubilised varnish into the underlying oil paint is theoretically inhibited [1]. However, this effect remains unconfirmed experimentally and was not found to be the case for a similar gel-emulsion (partly due to the clearance step required) [30, 31]. A xanthan gum-stabilised emulsion was included in this study as a highly modifiable, easily prepared, bio-based and affordable, water-based solvent containment system, that can substantially limit the use of organic solvents [3]. The gel-emulsion was delivered with a synthetic brush, which was continuously agitated on the sample surface to optimise varnish removal efficacy [29].

Finally, 2-propanol solvent was evaluated [6]. This solvent has intermediate swelling and diffusion rates, being slower than acetone and ethanol, but faster than water [22, 32]. Faster diffusing solvents have been linked with greater solvent penetration, which risks leaching soluble paint components and disrupting delicate surfaces [22]. For this study, 2-propanol was delivered via cotton swab rolling, as the conventional delivery method for organic solvents [6].

Experimental
Mock-up samples
Two sets of multi-layered mock-up samples were designed to approximate traditional, 16th—mid-nineteenth century oil painting, with either brown earth or

lead white oil paint as the immediate substrate to the dammar varnish. The iron oxide-based, brown earth oil paint was expected to be significantly more prone to pigment pickup than the basic lead carbonate-based, white oil paint. Oil paints containing iron oxide have been shown to lose significant strength and stiffness as hydrolysis reactions take place early in their curing process, whereas lead white oil paints tend to become increasingly stiffer with curing, and from a much higher initial stiffness than iron-oxide based paints [33, 34].

Pure linen canvases (Ulster Weavers, quality 3151, piece No. Z4377) were sized with sheep skin parchment glue (parchment from William Cowley Parchment Makers) and primed with a lead white-based ground (88.2 wt.% Stack Lead White pigment [Michael Harding Handmade Artists Oil Colours] in 11.8 wt.% cold-pressed Linseed Oil, from Sweden [Kremer Pigmente]). The brown earth oil paint was made with 78.69 wt.% iron-oxide based pigment (Brown Earth from Otranto, Kremer Pigmente) in 21.31 wt.% cold-pressed linseed oil (Linseed Oil, from Sweden, Kremer Pigmente). The lead white oil paint had the same composition as the lead white-based ground. The dammar varnish was first prepared with 16.7 wt.% dammar (Dammar, best quality, Kremer Pigmente) in 70.8 wt.% Shellsol D40 and 12.5 wt.% Shellsol A, according to an art conservation recipe [35], and then with 30 wt.% dammar in 60 wt.% Shellsol D40 and 10 wt.% Shellsol A.

The mock-up samples were aged in two stages: before varnishing (after the oil paints had cured in ambient conditions for 32–33 days) and after varnishing. Before varnishing the samples were light aged in a Sanyo Versatile Environmental Test Chamber MLR-351H, using MASTER TL-D Super 80 36W/840 1SL/25 from Philips, as the light source, with fluorescent light filter sleeves (below 400 nm): C20 from Encapsulite (around 7000 lx), at conditions of 25–30 °C and 24–50% relative humidity (RH). After varnishing the samples were light aged in a Panasonic® Versatile Environmental Test Chamber MLR-352H, using the same light source with UV filtration, at 45 °C and 57% RH. In total, light ageing was conducted over 44 days, which approximated 15 years display in standard museum conditions (calculations in Additional file 1: Table S1). It is duly acknowledged that the total artificial ageing amounts received by the mock-up samples cannot approximate an aged oil painting of the specified period of interest. Experimentation on these mock-up samples was expected to demonstrate the comparative varnish removal efficacies and potentials for inducing pigment pickup, displayed by different methods for varnish removal. A more detailed description of the mock-up preparation and layer structure can be found in Husby et al. [3].

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Methods for preparation, application, removal and clearance

The cleaning systems were optimised to remove varnish from the mock-up samples according to the methodology reported by Husby et al. [3]. From this work, the following preparation, delivery/application, removal, and clearance strategies were used for the brown earth oil paint sample (Table 1), and the lead white oil paint sample (Table 2).

Method evaluation parameters and rating criteria

Seven evaluation parameters were chosen and defined to help assess and compare the selected methods for varnish removal. Each parameter was rated on a scale from 1–5 (worst–best) (Table 3). The first four parameters were rated independently of the experimental work carried out on the mock-up samples (therefore labelled 'independent evaluation parameters' for this paper), where assessments were transferable to any varnish removal treatment. Whereas the last three evaluation parameters addressed

Table 1 Varnish removal methods optimised for the brown earth oil paint sample

Cleaning system	Delivery method	Preparation and application	Exposure time (min)	Removal and clearance
Surfactant-containing OiW microemulsion (Polar Coating B from Nanorestore Cleaning)	HWR	Gel immersed in diH$_2$O for 24 h, before pre-loading with Polar Coating B (immersion, 12 h). Gel cut to 2×2 cm. Gel blotted on each side for one second on Whatman Grade 1 paper, before placing on surface with tweezers. Contact increased by momentarily pressing gel with tweezers. System covered with polyester film (Melinex)	4	Gel removed with tweezers, followed by dry cotton swab rolling, and then wet cotton swab rolling (diH$_2$O)
Surfactant-free OiW microemulsion (65/25/10 wt.% diH$_2$O/2-propanol/1-butanol)	Evolon	Cloth cut out to 2×2 cm. Dry cloth placed on surface with tweezers with thread direction parallel to brush-strokes, before applying 8 drops of the cleaning system to the cloth using a pipette as illustrated below, Contact increased by momentarily pressing cloth with a dry brush	2	Cloth lifted with brush, followed by dry cotton swab rolling

diH$_2$O = deionised water

Table 2 Varnish removal methods optimised for the lead white oil paint sample

Cleaning system	Delivery method	Preparation and application	Exposure time (min)	Removal and clearance
Xanthan gum-stabilised emulsion (78.5/20/1.5 wt.% diH$_2$O/BnOH/xanthan gum)	Brush	Mixed until homogeneous with frothier. Applied with continuous stirring	3	Gel-emulsion removal via dry cotton swab rolling, and cleared with diH$_2$O, delivered via cotton swab rolling, as recommended by Casoli [30]
Surfactant-free microemulsion (65/25/10 wt.% diH$_2$O/2-propanol/1-butanol)	Manufactured cotton swab (Muji)	Mixed until clear by magnetic stirrer. Applied with continuous swab rolling. The swab was exchanged after 1 min of application	5	N/A
Organic solvent (2-Propanol)	Manufactured cotton swab (Muji)	Applied as above	5	N/A

diH$_2$O = deionised water

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Table 3 List of method evaluation parameters and rating criteria

	Rating of 1	Rating of 2	Rating of 3	Rating of 4	Rating of 5
Independent evaluation parameters					
Visibility	Totally obstructed	Greatly reduced by more opaque material	Moderately reduced by translucent material	Sightly reduced, or momentarily obstructed in a limited area	Completely visible
Process complexity (number of steps needed to test, prepare, apply, remove, and clear a varnish removal method)	Most steps (9 or more)	7–8	5–6	3–4	Fewest steps (1–2)
Initial cost (in EUR)	Most expensive (> 25.00)	16.01–25.00	9.01–16.00	4.00–9.00	Least expensive (< 4.00)
Health and safety measures	Rating of 2–4 + containment and fire prevention measures	Rating of 3–4 + PPE	Rating of 4 + ventilation measures	Standard laboratory practice only	No prevention measures required
Mock-up-dependent evaluation parameters					
Time (to optimal cleaning result)	Slowest (> 6 min)	5–6 min	3–4 min	1–2 min	Fastest (< 1 min)
Mechanical action (degree applied to optimal cleaning result)	Significant action to solubilise varnish	Moderate action to remove varnish + minor action to clear cleaning system	Moderate action to remove already solubilised varnish	Minor action to clear cleaning system	None
*Pigment pickup**	Most pigment pickup (> 15)	12–15	8–11	4–7	Least pigment pickup (< 4)

*The term 'pigment pickup' and the values within this parameter are explained in the following text

how well the cleaning systems performed on the specific mock-up samples (referred to as 'mock-up-dependent evaluation parameters').

'*Visibility*' is critical for monitoring the removal of varnish and detecting observable effects on the oil paint, and depends on the transparency of the cleaning material and to what extent it covers the cleaning site. Cleaning material transparency was evaluated through empirically comparing the material with five Word-generated shapes of increasing transparency, from 0–100%, with the intermediate values of 25%, 50%, and 75% (Additional file 1: Table S2).

'*Process complexity*' was indicated by the total number of steps needed to test, prepare, apply, remove, and clear each varnish removal method. A total of 12 steps were subjectively defined based on practice: (1) experimentation with exposure time, (2) formulation, (3) pre-washing, (4) pre-loading, (5) cutting, (6) blotting, (7) increasing contact, (8) covering, (9) gel/cloth removal, (10) varnish solubilisation, (11) varnish removal, (12) cleaning system clearance. Each step was counted as one, despite possible variations in the time and effort required to execute each step. Steps which might lead to ambiguous interpretations are further discussed in (Additional file 1: Table S3).

'*Initial cost*' evaluated the cost of the raw materials needed for a varnish removal method (both the cleaning system and the delivery method). Product prices were provided by Merck, Kremer Pigmente, and Deffner & Johann. The price per 1 L was used for all analytical grade chemicals. Bulk prices were used for Evolon, cotton wool wadding, and wooden sticks. The price for a single sheet of HWR was used, as the gel cannot currently be bought in bulk. Material reusability was disregarded in this assessment, as this is too dependent on the specific cleaning scenario. However, the brush used to apply the xanthan gum-stabilised emulsion (Comb Brush, No. 3/8 [Kremer Pigmente]) was estimated to cost less than 4 euro, as it cost 4.70 euro and can be used more than once without any observable changes to its properties (other options for reusability are presented in (Additional file 1: Table S4). The 'initial cost' of each method was calculated by adding the cost of the cleaning system (per 100 mL) with the cost of the delivery method (per 100 g). Results, ranging from about 3–40 euro, were rated on a scale raised to the power of two. Thus, the optimal 'initial cost' was less than 2^2 euro (i.e., < 4 euro) and the worst 'initial cost' was more than 5^2 euro (i.e., > 25 euro)This approach enabled the representation of both the considerable difference between the least and most expensive varnish

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removal methods and intermediate price variations (Additional file 1: Table S4).

'*Health and safety measures*' was assessed by reviewing the measures recommended to avoid adverse health and safety effects, i.e., the hazard classifications assigned to chemicals through the European Parliament, Council of the European Union and/or the chemical manufacturer/supplier, as defined and linked with prevention precautionary statements through the Globally Harmonised System of Classification and Labelling of Chemicals (GHS) [36, 37] (Additional file 1: Table S5). Prevention precautionary statements were categorised as relating to either standard laboratory practice (i.e., 'wash hand thoroughly after handling,' 'do not touch eyes' and 'do not eat, drink or smoke when using this product'), ventilation, personal protective equipment (PPE), containment, or fire prevention (Additional file 1: Table S6). An optimal rating was given when no prevention measures were required, and a progressively lower rating was given as additional precautionary measures were recommended (Table 3).

The *efficacy* of a varnish removal method was captured by assessing the *time* spent, and the degree of *mechanical action* applied, to reach an optimal cleaning result, as the cleaning results achieved on both mock-up samples were comparable with respect to the amounts of varnish removed (visually assessed). The exposure time was measured in minutes and rated from slowest–fastest. Degrees of mechanical action were defined and rated from 'none'– 'significant action' (Table 3).

'*Pigment pickup*' was evaluated by examining used gel-emulsions, gels, cloths, and swabs for traces of pigment. All swabs used to conduct five repeated tests were rated according to a qualitative assessment of the degree of pigment pickup, allocated with a numerical value between 0 (equal to no pigment pickup) and 4 (representing significant pigment pickup) (Fig. 1). To assess the total amount of pigment picked up via the swabs used for the five repeated tests (not the average, as different swab quantities were used depending on the cleaning system), these ratings were added together, resulting in a range of 4–16 (Additional file 1: Table S7–S11). This range was then divided evenly between the five rating criteria (Table 3).

Results from the seven evaluation parameters were represented in star diagrams made in Excel using the 'radar chart' function. Poorest ratings were positioned at the centre of the diagrams; hence, the larger the star, the more optimal the system. However, these diagrams do not illustrate the relative importance of the different evaluation parameters, which may vary with each cleaning situation [38]. The star diagrams were intended as a visual way of representing empirical testing results,
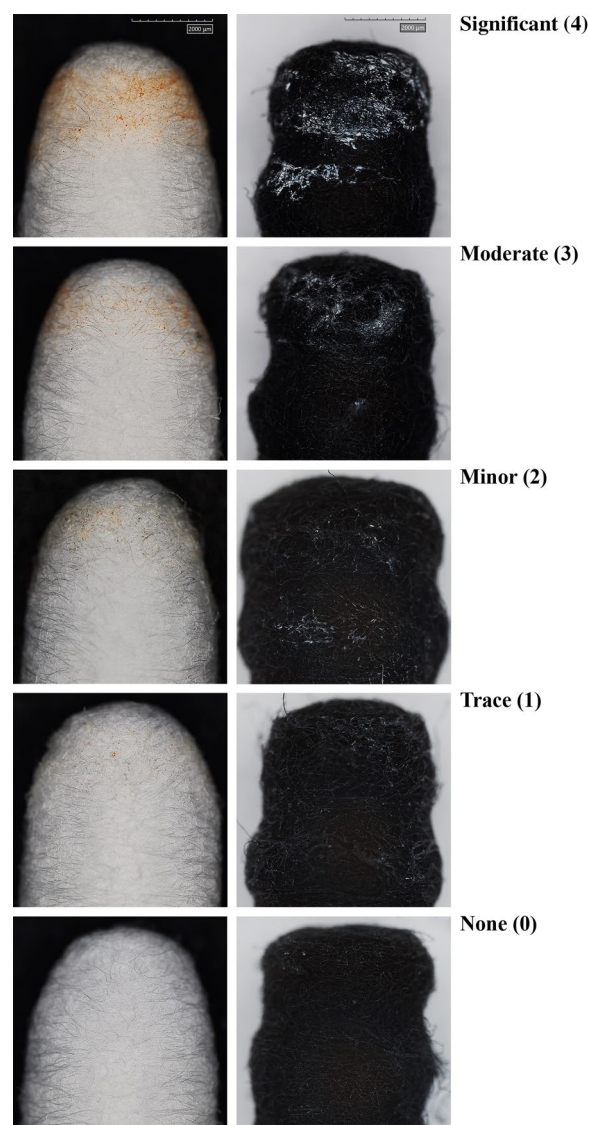

Fig. 1 Qualitative assessments of degrees of pigment pickup with corresponding numerical values. Left column: brown earth pigment on white cotton swab tips; right column: lead white pigment on black cotton swab tips. Microscopy images are in visible light, scale bar: 2000 μm, magnification: ×30

which naturally form only part of the information used by conservators in treatment decision-making processes.

Instrumentation
Digital microscopy
Varnish removal results on mock-up samples, as well as the materials applied in their execution (swabs, emulsions, gels, and cloths), were documented by high-resolution digital microscopy using a Hirox KH-8700 microscope (Hirox, Japan), with a HR-1020E lens and

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ring light illumination in visible and ultraviolet light. Images were processed using Hirox software.

Scanning electron microscopy (SEM)

The surfaces of test sites were further examined through SEM, carried out in secondary electron (SE) mode using a FEI Quanta 650 FEG. Imaging was conducted at 50–70 Pa in air (lower Pa used where samples began charging). Imaging parameters were 6 kV voltage, spot size of 3.0, using a working distance of 15 mm. Images were acquired at 50x, 200x, 500x, 1000x, and 2000×magnification.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

Xanthan gum-stabilised emulsions, used to remove varnish from lead white samples, were analysed for traces of lead white pigment using a Thermo Scientific Nicolet iZ10 spectrometer with a diamond attenuated total reflection (ATR) crystal, equipped with a deuterated triglycine sulphate (DTGS) detector. 32 scans were collected at a resolution of 4 cm^{-1} across a 3600 to 600 cm^{-1} range. Five repeat measurements were taken. Data was processed using Omnic 9 software. The spectra were manually baseline corrected and the CO_2 band at 2400–2350 cm^{-1} was removed. Measurements of the used emulsions were compared with measurements of an unvarnished lead white mock-up sample, dammar powder (Dammar, best quality, Kremer Pigmente), and xanthan gum powder (VANZAN NF-C Xanthan Gum, Vanderbilt Minerals).

Infrared reflectance spectroscopy

Detection of potential cleaning system residues was carried out with external reflectance Fourier transform infrared spectroscopy (ER-FTIR), performed using Bruker Alpha II spectrometer equipped with the External Reflectance QuickSnap module. All measurements were conducted with a measurement spot of 5.88 mm in diameter. The spectral range investigated was 4000–399 cm^{-1}, with 4 cm^{-1} resolution; 128 scans were acquired for the background using a gold flat mirror as reference, and 128 scans were recorded on the samples to optimise the signal to noise ratio. Data processing was conducted using Opus 8.7.10 software, Bruker Optik GmbH, Ettlingen, Germany.

Results

Brown earth oil paint sample

Optimal cleaning results for the varnished brown earth oil paint sample are shown in Fig. 2, with the star diagram illustrating the evaluations made of the two water-based methods: the surfactant-containing microemulsion delivered via the HWR gel, and the surfactant-free microemulsion delivered via Evolon (as described in Table 1). The evaluation parameters 'health and safety measures' and 'time' were omitted from the star diagram, as poorly representative with respect to how well the methods for varnish removal performed. For example, each microemulsion contained two organic solvents, which increased the number and types of precautionary measures required in connection with their use. Consequently, both systems received the worst rating for 'health and safety measures,' despite considerable water dilution, which should reduce the hazard potentials of the organic solvents contained in these systems [36, 39]. 'Time' was omitted as being irrelevant to the overall success of the varnish removal method (see *Discussion*).

Among the 'independent evaluation parameters,' for 'visibility,' the surfactant-containing microemulsion+HWR outperformed the surfactant-free microemulsion+Evolon, as the HWR gel was evaluated as 'translucent,' whereas the Evolon cloth completely obstructed visibility during the application of the surfactant-free microemulsion. However, both applications (HWR and Evolon) were followed by cottons swab rolling to remove the softened varnish, during which the process of removing varnish could be monitored and pigment pickup could be detected without significant obstruction (equivalent to a rating of 4). Both methods rated poorly with respect to 'process complexity,' due to the multiple steps required to test, prepare, and apply systems delivered either via the HWR gel or the Evolon cloth. For 'initial cost,' the surfactant-free microemulsion+Evolon received a higher rating, as this method was three times less expensive than the surfactant-containing microemulsion+HWR (at the time of purchase). This result reflected both the lower cost of the surfactant-free microemulsion compared to the surfactant-containing microemulsion, and the less expensive Evolon compared to HWR (separate evaluations of cleaning systems and delivery methods are provided in Additional file 1: Fig. S1).

For the evaluation parameters conditioned by the properties of the brown earth oil paint sample, the surfactant-free microemulsion+Evolon rated better for 'mechanical action,' as this varnish removal method did not require a clearance step. On the other hand, no pigment was detected on the wetted swabs that had been used to clear the surfactant-containing microemulsion. Nevertheless, for this sample, the surfactant-containing microemulsion+HWR induced more pigment pickup in total than the surfactant-free microemulsion+Evolon across five repeated tests.
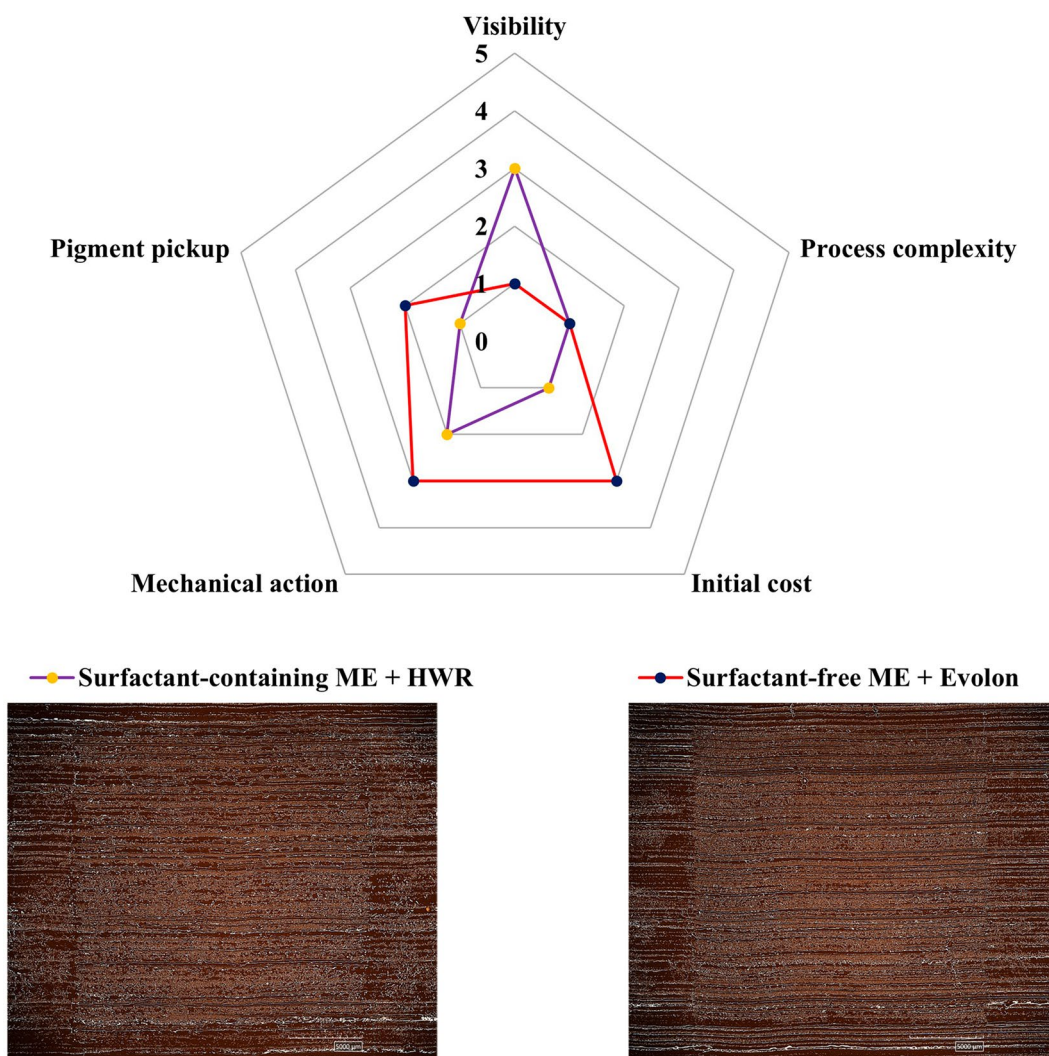
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Fig. 2 Upper: star diagram for two varnish removal methods applied to the varnished brown earth oil paint sample. Lower: Digital microscopy images of the two optimal cleaning results at 10×magnification. ME = microemulsion

Lead white oil paint sample

The optimal cleaning results produced on the varnished lead white oil paint sample are shown in Fig. 3, with the star diagram illustrating the evaluations made of the three varnish removal methods: the xanthan gum-stabilised emulsion delivered with a synthetic brush, the surfactant-free microemulsion delivered via cotton swab rolling, and the organic solvent delivered via cotton swab rolling (as described in Table 2). The evaluation parameters 'health and safety measures' and 'time' were also omitted from this star diagram, for reasons previously outlined.

Within the 'independent evaluation parameters,' the surfactant-free microemulsion+swab and the organic solvent+swab rated equally. Although, the surfactant-free microemulsion was less expensive than the organic

solvent, as indicated when only comparing the costs of cleaning systems (Additional file 1: Fig. S1). The xanthan gum-stabilised emulsion received a poorer rating for 'visibility' than the other two cleaning systems, as the gel-emulsion was 'more opaque' (evaluation illustrated in Additional file 1: Table S2), thus inhibiting visibility as it was applied and removed. The gel-emulsion was also more complicated to remove and clear, resulting in a lower rating for 'process complexity.' On the other hand, the xanthan gum-stabilised emulsion+brush proved to be the least costly option.

When evaluated within the context of varnish removal from the lead white oil paint sample, all three methods received the worst rating for 'mechanical action,' as cleaning system delivery through either the brush or swab

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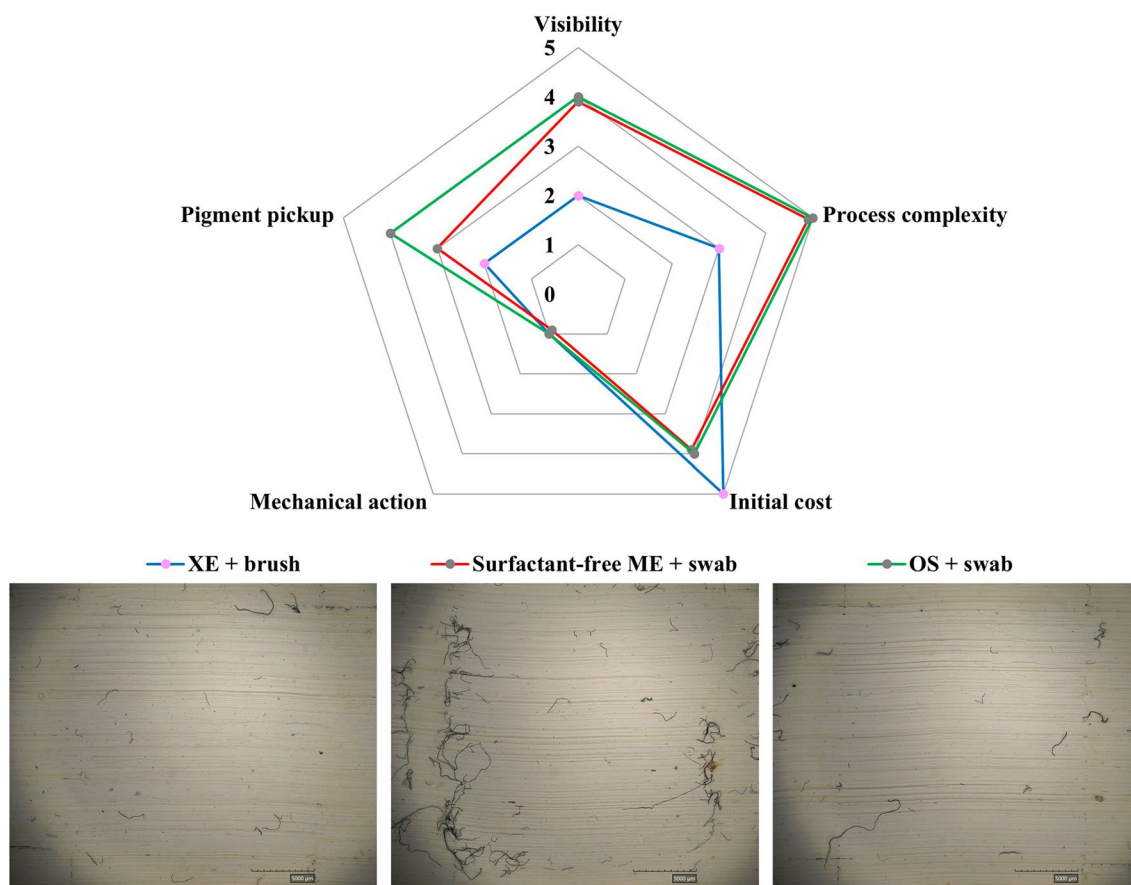
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Fig. 3 Upper: Star diagram for three varnish removal methods applied to the varnished lead white oil paint sample. Lower: Digital microscopy images of the three optimal cleaning results at 10×magnification. XE = xanthan gum-stabilised emulsion, ME = microemulsion, OS = organic solvent. Overlapping lines in the star diagram were staggered for visibility
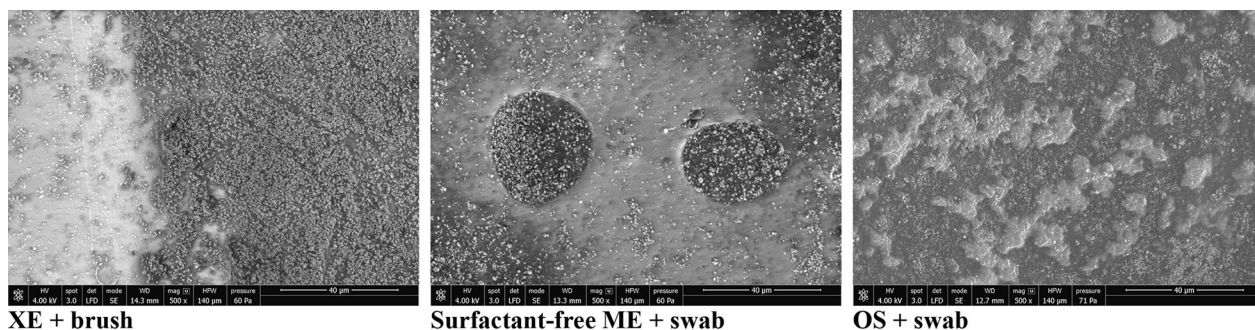

Fig. 4 SEM images at 500×magnification of a test site cleaned with the xanthan gum-stabilised emulsion (left), showing scratches, presumably from the greater amount of mechanical action used to apply, remove and clear the gel-emulsion, and a test site cleaned with the surfactant-free microemulsion (middle), with indications of dewetting (circular features), not found on a test site cleaned with the pure 2-propanol (right). XE = xanthan gum-stabilised emulsion, ME = microemulsion, OS = organic solvent. [a]Lighter areas in the SEM images were thought to be residual varnish

required significant amounts of mechanical action to solubilise the varnish. The xanthan gum-stabilised emulsion+brush initially rated 3 for 'pigment pickup,' according to the total amount of pigment observed on the swabs used to remove and clear this system across five repeated tests. However, this rating was lowered to 2 when pigment was also detected on the used gel-emulsions via ATR-FTIR (Additional file 1: Fig. S2). Furthermore, under

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higher magnification, scratches were observed on the test sites cleaned with the xanthan gum-stabilised emulsion + brush, which were not observed on the test sites cleaned with the other methods (Fig. 4). Interestingly, signs of dewetting that appeared similar to published examples using the Nanorestore Cleaning products [17, 40], were detected on the test sites cleaned with the surfactant-free microemulsion, which was not noted on the test sites cleaned with pure 2-propanol (Fig. 4). Additionally, greater quantities of black fibres (from the back cotton swabs) were deposited around the test sites cleaned with the surfactant-free microemulsion + swab. As could be expected, the surfactant-free microemulsion spread more than the other two cleaning systems, due to the surface-tension reducing action of the hydrotrope and/or the smaller solvent droplets in the microemulsion. Thus, the surrounding varnish was softened and retained the black fibres. The surfactant-free microemulsion also induced more pigment pickup than the 2-propanol, which could be attributed to these same properties.

Cleaning system residues

Neither surfactant signals from the Polar Coating B nor polysaccharide signals from the xanthan gum-stabilised emulsion were detected by ER-FTIR on the mock-up samples exposed to these systems (Additional file 1: Fig. S3–S8). No physical residues were observed using high-resolution digital microscopy (Hirox) on these mock-up surfaces. It is known, however, that ER-FTIR and other FTIR techniques have detection limits which may preclude the detection of low levels of cleaning systems, and that other more specific and/or surface-based analytical techniques should be employed to fully assess any risk of residues, alongside the ageing of cleaned samples [41].

Discussion

Evaluation parameters

Among the evaluation parameters defined for this work, the 'health and safety measures' and 'time' parameters poorly represented the objectives of varnish removal. The 'health and safety measures' parameter failed to address the synergistic effects that might have occurred with the water-based cleaning systems. Consequently, the effects of water dilution were not shown and are expected to decrease the health and safety issues associated with these systems [2, 36, 39]. The health and safety impacts of multicomponent mixtures can be estimated through calculating solvent interaction parameters or conducting specific toxicological examinations, which were beyond the scope of this study [36, 42–45].

The evaluation parameter 'time' unsuccessfully captured the primary goals of varnish removal, as the best rating was given to the varnish removal methods with the shortest exposure times, which is not always essential to the success of a varnish removal treatment. While reducing the exposure time can mitigate unwanted solvent-induced changes in oil paints [5, 19, 28, 46], so can the use of slow-diffusing solvents and/or solvent containment methods, which further limit solvent diffusion [22, 28, 46, 47]. Essentially, and this is well-known in practice, the varnish removal method that poses the least risk of harming the practitioner and the underlying oil paint will be largely preferred, regardless of the exposure time. Consequently, the 'time' evaluation parameter was omitted from the evaluation framework, as the implication of the parameter is situation specific.

Furthermore, the evaluation framework neglected two parameters, which could be critical when evaluating varnish removal methods: the risk of promoting metal soap crystallisation in oil paints prone to these reactions, and the effects of the cleaning materials on the environment. The former might be relevant, as solutions of 1–10 wt.% water in an organic solvent were recently found to promote metal soap crystallisation in oil paints with zinc white, which was attributed to the transport of water into the zinc white oil paint films via the fast-diffusing organic solvent (acetone or ethanol) [48]. Oil paints with lead white pigments, similarly to oil paints with zinc white pigments, tend to form metal soaps upon ageing, which can be accelerated in elevated RH and temperature conditions [49–51]. Although not yet investigated, metal soap crystallisation may be further promoted when these oil paints are exposed to microemulsions and gel-emulsions, which combine water with organic solvents. On the other hand, these water-based systems may involve different diffusion processes than those reported for the homogeneous water–organic solvent solutions, primarily based on a fast-diffusing organic solvent. The water-based systems included in this study are heterogeneous colloids, which incorporate considerably less and slower-swelling organic solvent(s) (except for the fast-swelling butanone in the surfactant-containing microemulsion) and are sometimes thickened or delivered via a gel or cloth [32]. Nevertheless, the experimental work conducted by Hermans et al. [48] naturally leads one to consider whether these water-based systems can likewise accelerate metal soap crystallisation in zinc- and lead white pigmented oil paints.

Awareness of the environmental effects of the materials used for conservation purposes has been increasing in the field of conservation [2, 39]. However, defining the

boundaries for this parameter is difficult, as environmental effects occur in all stages of the life of a product cycle, from raw material acquisition through production and use to end-of-life disposal, and is evaluated through various methodologies [52]. In addition, assessments would have to address the different proportions of substances used in multicomponent cleaning systems, which was beyond the scope of this study.

Water-based systems for varnish removal – summary of key findings

Xanthan gum-stabilised emulsion

A key result for the xanthan gum-stabilised emulsion was the tendency to induce pigment pickup and impart scratches on the surface of the lead white oil paint sample (Fig. 4). However, this finding partially reflected the relatively young oil paint sample used, as addressed by Husby et al. [3]. Nevertheless, the inherent opacity of the gel-emulsion, causing poor visibility during use, also contributed to these issues. In addition, the BnOH contained in the gel-emulsion is a very high swelling and retentive solvent, likely to plasticise the oil paint for a prolonged period of time and add to the risk of pigment pickup and abrasion [5, 32, 46]. This result was also attained despite the reduced solvent diffusion into the paint afforded by the thickening effect of the xanthan gum [30], and a shorter exposure time compared to the surfactant-free microemulsion+swab and the organic solvent+swab (Table 2). A more optimal result might have been accomplished if the xanthan gum-based system had been modified and applied differently, such as, by using a slower-diffusing and faster-evaporating organic solvent, reducing the concentration of organic solvent, applying the gel-emulsion without agitation, as done by Sawicki [53], or through chemically modifying the BnOH, as recently shown by Liu et al. [54]. Clearing the gel-emulsion with make-up sponges is another option, but this did not mitigate pigment pickup from the varnished brown earth oil paint sample [3]. Nevertheless, the inherent opacity of this system and the mechanical action required to remove and clear it would remain disadvantageous.

Surfactant-free microemulsion

Assessments made of the surfactant-free microemulsion provided an initial exploration into the suitability of this type of system for natural resin varnish removal. Notably, the surfactant-free microemulsion was shown to effectively remove dammar varnish, possibly via a dewetting process (Fig. 4), despite the exclusion of a classical surfactant in the formulation. On the other hand, the surfactant-free microemulsion induced more pigment pickup than the pure organic solvent, when both cleaning systems were delivered via five minutes of cotton swab rolling (Table 2). This result was attributed to the higher inherent activity of the microemulsion, due to the larger interfacial area of the nano-sized droplets of dispersed 1-butanol, compared to the non-dispersed 2-propanol [2]. Additional research is required to assess the interactions between microemulsions (surfactant-free as well as surfactant-containing) and aged oil paints, as acknowledged by Giorgi and Carretti [55]. Nevertheless, the surfactant-free microemulsion appears to be a promising, modifiable (within the OiW region of its phase diagram [3]), clearance-free and inexpensive option within the group of water-based methods evaluated for dammar varnish removal.

Conclusion

A primarily empirical framework was developed to evaluate and compare varnish removal methods within art conservation practice, including both cleaning systems and delivery methods. Parameters and criteria were defined and graphically represented, which can be used to help evaluate the success (or potential success) of a varnish removal method. Through the application of this framework, several key points were demonstrated: limitations to the applicability of the xanthan gum-stabilised emulsion, the advantages and disadvantages of the various delivery methods, and the potential suitability of one surfactant-free microemulsion for natural resin varnish removal. The greatest disadvantage associated with the xanthan gum gel-emulsion was obstructed visibility during application and removal. While this system was highly modifiable, this property of the gel-emulsion may limit its applicability in conservation practice. The delivery methods HWR and Evolon were found to be useful for their ability to mitigate pigment pickup. Conversely, both HWR and Evolon contributed to the complexity of a varnish removal method and are costly, whereas swabs and brushes are uncomplicated to prepare and apply and are relatively inexpensive. The surfactant-free microemulsion was found to be a very promising yet unexplored method for natural resin varnish removal. In addition to being inexpensive, modifiable and clearance-free, this system also more than halved the total amount of organic solvent required for varnish removal when compared to conventional methods using exclusively organic solvents. Another advantage, which was also applicable to the surfactant-containing microemulsion and the liquid organic solvent, was compatibility with multiple delivery methods, which afforded versatility, as the delivery method could be modified to a specific paint surface. Consequently, both types of microemulsions appear promising as predominantly water-based options for dammar varnish removal. However, more research on and evaluation

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of water-based varnish removal methods is required with respect to extending modification options, characterising modes of removal action on coatings, and investigating interactions with aged oil paints through mock-up samples and case studies. In addition, the evaluation framework can be extended to assess methods for the removal of other coatings (e.g., other natural resin and synthetic varnishes) from oil or other types of paint.

Abbreviations

ATR-FTIR	Attenuated total reflectance Fourier transform infrared spectroscopy
BnOH	Benzyl alcohol
diH$_2$O	Deionised water
EHS	Environmental, health and safety
ER-FTIR	External reflectance Fourier transform infrared spectroscopy
EUR	Euro
GHS	Globally Harmonised System of Classification and Labelling of Chemicals
HWR	Higher Water Retention (chemical hydrogel from the Nanorestore Gel Dry series)
IUPAC	International Union of Pure and Applied Crystallography
ME	Microemulsion
OiW	Oil-in-water, referring to a type of microemulsion
OS	Organic solvent
pHEMA/PVP	Poly(2-hydroxyethyl methacrylate) and poly(vinylpyrrolidone)
PPE	Personal protective equipment
RH	Relative humidity
SEM	Scanning electron microscopy
XE	Xanthan gum-stabilised emulsion

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-023-01077-1.

Additional file 1: Table S1. Artificial ageing converted to years in standard museum conditions. **Table S2.** Material transparencies from 0–100%. From left to right: dry Evolon (10 × MAG), wet xanthan gum-stabilised emulsion (30 × MAG), dried HWR (10 × magnification), surfactant-free microemulsion (no magnification). **Table S3.** Steps needed to test, prepare, apply, clear, and remove cleaning systems and delivery methods. **Table S4.** 'Initial cost' calculated for cleaning systems and delivery methods. **Table S5.** Organic solvents used for four cleaning systems with hazard categories and prevention precautionary codes. **Table S6.** Precautionary categories, codes and phrases linked to the organic solvents in Table S5. **Table S7.** Pigment pickup from five repeated tests with the surfactant-containing microemulsion + HWR on the brown earth oil paint sample. **Table S8.** Pigment pickup from five repeated tests with the surfactant-free microemulsion + Evolon on the brown earth oil paint sample. **Table S9.** Pigment pickup from five repeated tests with the xanthan gum-stabilised emulsion + brush on the lead white oil paint sample. **Table S10.** Pigment pickup from five repeated tests with the surfactant-free microemulsion + swab on the lead white oil paint sample. **Table S11.** Pigment pickup from five repeated tests with the organic solvent + swab on the lead white oil paint sample. **Figure S1.** Star diagrams for the independent evaluation parameters shown separately for cleaning systems and delivery methods. **Figure S2.** ATR-FTIR spectra of: **a** xanthan gum-stabilised emulsions used to remove dammar varnish from the lead white oil paint sample, **b** lead white, **c** xanthan gum and **d** dammar. **Figure S3.** ER-FTIR of a varnished, brown earth oil paint sample (mock-up I3) exposed to Polar Coating B via HWR (tests 7 to 9). **Figure S4.** ER-FTIR of a varnished, brown earth oil paint sample (mock-up I3) unexposed to cleaning. Figure S5. ER-FTIR of a HWR gel after immersion in Polar Coating B. **Figure S6.** ER-FTIR of a varnished, lead white oil paint sample (mock-up D3) exposed to the xanthan gum-stabilised emulsion with BnOH (tests 3 to 5). **Figure**

S7. ER-FTIR of a varnished, lead white oil paint sample (mock-up I9) unexposed to cleaning. **Figure S8.** ER-FTIR of the xanthan gum-stabilised emulsion with BnOH.

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