



Original article

Green solvents and restoration: Application of biomass-derived solvents in cleaning procedures



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ABSTRACT

Blends of solvents from non-renewable sources, often polluting and toxic to humans, are routinely used in the restoration of painted artifacts. Here we present the application of three different green solvents (and their mixtures) as a viable alternative to the standard triad of solvents (acetone, ethanol, and isooctane) used in the solubility test for cleaning polychromic artworks.

Solketal (SOLK), γ -valerolactone (GVL), and 2-ethylhexyl pelargonate (ARGO) were selected among the solvents achievable from bio-based synthons such as glycerol, levulinic acid, and pelargonic acid, which are mainly produced from biomass and renewable feedstocks as exhausted vegetable oils, carbohydrates, and lignocellulose. Specifically, ARGO solvent was prepared by esterification reaction and characterized by nuclear magnetic resonance (NMR) and mass spectroscopy coupled to gas chromatography (GC–MS).

Hansen solubility parameters for each solvent were determined by a group contribution method, thus enabling their placement in the Teas graph. Their penetration ability in wooden specimens was investigated by evaluating the volume retention of each solvent with different coated specimens.

The solvent ability of the selected compounds was tested by visible and UV observations on specimens prepared with film-forming substances (Dammar, Mastic, Shellac, Paraloid® B72 and linseed oil) brushed onto glass plates.

Our results pointed out the suitability of this solvent triad for application to panel painting surfaces. The effectiveness of mixtures made with the above green solvent was successfully tested to remove a terpenic varnish from a 16th century oil painting on a wooden panel.

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1. Introduction

Cultural heritage artifacts are widely recognized as invaluable assets, and their conservation and restoration are such crucial topics to capture the interest of the entire scientific community, which is increasingly focused on finding the best strategies to preserve and pass our cultural heritage to posterity. Indeed, the integrity of artworks is continually threatened by chemical and physical degra-

ation processes, which make their conservation and restoration a challenging problem [1,2]. Among restoration procedures, cleaning the surfaces of polychrome artifacts is one of the most demanding and complex, as often in addition to the removal of external agents (dust, particles, etc.) it is necessary to remove aged and damaged protective film-forming layers (e.g. finishing varnishes) whether they are original or from subsequent restorations [3–7]. Today, the cleaning of painted surfaces with aqueous methods [8–11] is widely used and exploits water-based buffered solutions with the addition of chelating agents and/or surfactants to improve their solvent ability. Even though superficial cleaning alone is not always sufficient, it is still considered an important surface-cleaning step and a procedure that simplifies the subsequent varnish removal process. Aqueous-phase solutions (W) can also be combined with

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a solvent oil-phase (O) through the creation of W/O (water is dispersed as droplets in the oil continuous phase) and O/W (oil drops are dispersed throughout the aqueous phase) emulsions, which offer a wider range of cleaning capabilities [12,13].

In addition to the cleaning procedure, the removal of unwanted varnish layers is usually performed with organic solvents, which have adequate affinity and effectiveness in removing film-forming layers, but also present many practical issues related to their penetration into polychrome surfaces (e.g. binder swelling), and selectivity towards desired layer (e.g. etching of paint layer). Furthermore, commonly used organic solvents present a risk profile due to their volatility (e.g. low flash points) and eco-toxicity, exposing the end-user and the environment to serious risks. In this scenario, numerous studies are aimed at finding new cleaning methods and selective removal substances able to face the above mentioned issues [14,15].

An eco-friendly cleaning approach for the removal of inorganic patinas and organic coatings is based on the use of bacteria and enzymes [16]. The use of bacteria, such as A29 strain of *Pseudomonas Stutzeri*, had already been successfully applied to degrade the organic matter of altered animal glue for bio-restoration and bio-cleaning by Ranalli et al. and Lustrato et al. [16,17]. Lipases, on the other hand, are used in cleaning procedures to remove oil-based coatings or even acrylic varnishes [18–21].

Concerning the problem of solvents volatility and diffusion within the paint layers, many studies propose gelling as a method to limit these issues, to lengthen surface contact times, and to reduce mechanical friction [22–25]. Among the direct gelling agents, such as the widely used cellulose ethers, other polysaccharide compounds such as agar, xanthan gum can be exploited (used also to create a water/benzyl alcohol mixture) [26], and gellan gum, mainly used for paper and manuscripts restoration [23]. Furthermore, also polyacrylic-based synthetic gels can be found, introduced in the 90s by Wolbers [10] for the preparation of solvent-surfactant gels. Other high-viscosity polymer dispersions [27] proposed as thickening agents are, for example, polyvinyl alcohol (PVA)-borax compounds, or methyl methacrylate (MMA)-based organogels [28]. Various poly-hydroxyalkanoates are also being tested for the production of gelling solutions.

Nevertheless, the most widely used approach to address the issue of the selective removal of film-forming substances is the use of the Teas ternary diagram (based on the Hansen solubility parameters), which allows organic solvents to be graphically located in a solubility triangle, based on their dispersion forces (F_d), polarity (F_p) and hydrogen bonding (F_h) values [29]. With this information, an adequate combination of solvents can be selected by targeting the solubility area of film-forming substances that need to be removed. This affinity-based approach has been applied to a practical solubility test [30], that utilizes increasing polarity combinations of non-confined solvents, in order to reach different solubility areas of the Teas chart.

As mentioned earlier, although common organic solvents are widely validated in this field, they often possess negative characteristics, such as high chemical hazard (e.g., high flammability) and ecotoxicological profiles (e.g., pollutant, acute or chronic toxicity). Therefore, identifying new sustainable solvents that can replace commonly used toxic and polluting solvents is a primary goal [31–34].

Existing bio-cleaning and eco-friendly strategies to reduce the use of hazardous compounds, discussed above, are often appropriate only for narrow applications (e.g. emulsions are poorly effective with aged varnishes; resin soaps are time-consuming to be prepared, and the use of enzymes is expensive and requires some specific condition to be effective; solvents confined in gels often require additional steps to remove gel particles). Because of these

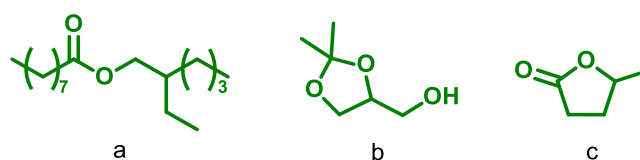


Fig. 1. (a) 2-Ethylhexyl pelargonate, ARGO; (b) (2,2-dimethyl-1,3-dioxolan-4-yl)methanol, SOLK; (c) γ -valerolactone, GVL.

circumstances, these undirected approaches have not found wide application in everyday practice by restorers.

2. Research aim

In this paper, we propose an alternative triad of solvents to perform solubility test, replacing classical and hazardous organic solvents with bio-based organic solvents (Fig. 1) and testing their solvent properties with specimens prepared *ad hoc* with widely used film-forming/coating substances.

Since the most commonly used solvents for removing aged varnishes from the polychrome layer of artifacts are acetone (Ace), ethanol (EtOH) and isooctane (i -C₈), it is reasonable to focus on a triad of solvents with similar functional groups that possess the following features: (i) synthesizable from biomass; (ii) low ecotoxicological profile; low physico-chemical hazard profile; (iii) commercially available at low cost. Thus, the following different solvents were identified:

- γ -Valerolactone–GVL (no hazards have been classified from ECHA, fp 96 °C) as an alternative to acetone (H225–H319–H336, fp –17 °C), which can be synthesized from lignocellulosic biomass;
- (2,2-dimethyl-1,3-dioxolan-4-yl)methanol – SOLK (H319, irritating to the eyes, fp 90 °C) as an alternative to ethanol (H225–H319, fp 17 °C), which can be obtained by ketalization of glycerol, which is one of the most relevant bio-based chemical platform resulting from the synthesis of biodiesel (glycerol 10% wt of the biofuel produced);
- 2-Ethylhexyl pelargonate – ARGO (no hazards have been classified from ECHA, fp 144 °C) as a substitute for isooctane (H225–H304–H315–H336–H410, aquatic acute 1–aquatic chronic 1–asp. tox. 1–flam. liq. 2–skin irrit. 2–STOT SE 3, fp –12 °C), that is an ester of pelargonic acid, which is industrially obtained from the oxidative cleavage of oleic acid and recently also directly from the oxidative cleavage of exhausted vegetable oils [35].

Once successfully tested on glass and wood specimens, the triad of solvents under investigation was applied with remarkable results on a real case study: the restoration of a XVI sec wooden panel painting, *Ecce Homo* (unknown artist, Fig. 2).

3. Materials and methods

3.1. Materials

Pelargonic acid, 2-ethylhexyl alcohol, γ -valerolactone, (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (commercial name: solketal), zinc oxide, acetone, ethanol, and isooctane were purchased from Merck Life Science and used without further purifications. The heating band was purchased from Watlow® and controlled through coupled thermocouple and thermostat. Paraloid® B72 and Klucel® G were purchased from C.T.S., granular hide glue from Bresciani, Bologna gypsum from Giosi S.r.l., umber pigment from Maimeri, raw linseed oil and turpentine essence from Lefranc et



Fig. 2. *Ecce Homo* wooden panel, unknown artist.

Bourgeois. Glass slides, wood panels (poplar), dammar resin, mastic resin and shellac were provided by the University of Suor Orsola Benincasa, Napoli (Italy). The reaction setup for the synthesis of the 2-ethylhexyl pelargonate (ARGO) is reported elsewhere [36], however, it is briefly described in the supporting information (Paragraph S1).

3.2. NMR analysis

All NMR analyses were performed with a Bruker Avance Ultrashield 400 operating at proton frequency of 400 MHz or with a Varian 500 Oxford at proton frequency of 500 MHz. Samples were prepared using deuterated solvents. The following abbreviations were used for describing NMR multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; td, triplet of doublets; tt, triplet of triplets.

3.3. GC/MS analysis

All gas chromatography analyses were performed using Agilent GC 6890, coupled with a 5973 MS detector. The column used was an HP-5 capillary column (30 m × 0.25 mm, 0.25 μm, 5% polysilarylene 95% polydimethylsiloxane). Helium was used as carrier gas, at a rate of 1.0 ml/min. The GC injector was maintained at 230 °C, while the analyzer was kept at 250 °C. The collision energy was set to a value of 70 eV, and fragment ions generated were analyzed by continuous quadrupole scanning in the mass range 40–550 m/z.

The injection temperature was 250 °C, the oven temperature was preheated and held at 60 °C for 3 min and then increased: from 60 °C to 150 °C at 10 °C/min; from 150 °C to 230 °C at 14 °C/min; from 230 °C to 280 °C at 15 °C/min. Once reached 280 °C, the temperature was held for 5 min.

Each sample was measured in triplicate. The identification of each compound was based on the combination of retention time and mass spectrum matching using Ms search-Nist 05 library software.

3.4. Glass specimens' preparation

The selected substances were brushed on glass slides after being prepared as follows:

- Dammar resin 20% wt + turpentine essence 80% wt.
- Mastic resin 20% wt + turpentine essence 80% wt.
- Shellac 10% wt + ethanol 90% wt.
- Paraloid® B72 10% wt + acetone 90% wt.
- Linseed oil 40% wt + ground umber pigment 60% wt.

The coated glass slides were air-dried for 14 days. The specimens were prepared in duplicate and half of them were subjected to an accelerated artificial aging process. Solubility tests were performed on both, the non-aged and the aged ones.

3.5. Wooden specimens' preparation

3.5.1. Support

Five panels of painting specimens were prepared by using wooden supports consisting of 15 × 10 × 1.5 cm³ aged solid poplar panels.

3.5.2. Primer and ground layer

Hide glue was used as primer and binder for the ground layer, following Cennino Cennini's recipes [37]. The granular hide glue was mixed with water in a 1:8 volume ratio; after 24 h of swelling, it was heated to 60 °C in a water bath and brushed on the wooden panels as a primer.

The same 1:8 hide glue was mixed with sifted Bologna gypsum and brushed on the primer, for a total of eight layers. This ground layer was air-dried for 48 h and then sanded to ensure planarity.

Two layers of 1:12 hide glue in water were used to isolate the ground layer before applying the oil paint.

3.5.3. Paint layer

The paint layers were prepared by manually milling 15 g of umber pigment with 10 g of raw linseed oil. This mixture was then brushed on the panels and let air-dry for 30 days.

3.5.4. Coatings

The coating substances were airbrushed onto four out of five panels after being prepared as follows:

- Dammar resin 20% wt + turpentine essence 80% wt.
- Mastic resin 20% wt + turpentine essence 80% wt.
- Shellac 10% wt + ethanol 90% wt.
- Paraloid® B72 10% wt + acetone 90% wt.

The completed specimens were air-dried for 15 more days before undergoing artificial aging.

3.5.5. Artificial aging

Photooxidative aging of the specimens was carried out under mild humidity conditions (RH 50%) and 40 °C in a forced air environmental chamber (Angelantoni SU250) equipped with a borosilicate glass-filtered low-pressure mercury UV lamp, in order to filter radiation with wavelengths lower than 300 nm, which would cause strong photochemical deterioration not representative of real aging. The irradiance spectrum of the filtered lamp is reported in Fig. S1 in the supplementary information. The power of the light emitted was about 5.5 W in the range 300–400 nm, 7.1 W in the range 400–615. Aged specimens were collected after 7 days and subjected to further characterization.

3.6. Cleaning test and cleaning performance evaluation of coated glass specimens

The tests were conducted by placing 20 μL drops of each solvent on the coated glass specimens and then removing the solvent after the appropriate time by lightly dabbing the drops away with a swab. The non-aged coatings were in contact with the solvent drops for 30 s and 3 min, while for the artificially aged coatings, the exposure time frames were 30 s, 3 min, and 10 min. The specimens were observed and photographed under 365 nm UV radiation before and after the tests.

3.7. Diffusion of solvents in coated wood specimens

The test consisted in placing 1.5 μL drops of water and of the studied solvents on each specimen and estimating their penetration by monitoring key geometrical properties of the drops during the contact time frame.

The contact angle, base width, height, and sessile volume of each drop were measured every 30 s, for a total test duration of 5 min, using a First Ten Angstroms FTA 1000 B apparatus in conjunction with the software FTA32, release 2.1.

The resulting data were then processed to extrapolate the percentage volume decrease of the drops in comparison to the initial volume. Due to the high boiling point of the tested solvents and the negligible evaporation of water during such a short time span in a controlled environment, the volume variations were considered directly related to the penetration properties of solvents or water drops.

3.8. Thermogravimetric analysis of solvents

The rate of solvent evaporation was measured by thermogravimetry (TG). An initial volume of 40 μL of solvent was introduced in the TG aluminum crucible and maintained at 30 $^{\circ}\text{C}$ for 8 h under flowing nitrogen (100 mL/min) while the weight change was constantly measured.

3.9. Ecce Homo – cleaning performance evaluation

The surface of the oil painting was observed under 365 nm UV radiation and visible light. The film-forming layer was characterized by GC–MS following the protocol described in Melchiorre et al. previous case study [38].

Then green solvents mixtures and common solvents mixtures were prepared using the following percentages and tested on the painting surface:

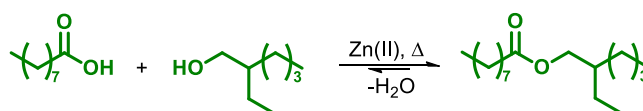
- AS3: ARGO 70% + SOLK 30%
- AG3: ARGO 70% + GVL 30%
- IA6: i-C₈ 40% + Ace 60%
- IE4: i-C₈ 60% + EtOH 40%

The tests consisted in soaking a cotton swab in the selected solvents mixture, gently rubbing it on the surface for 3 min and then removing the excess of solubilized varnish with a dry cotton swab. The surface of the painting was then observed and photographed in visible light and under 365 nm UV radiation.

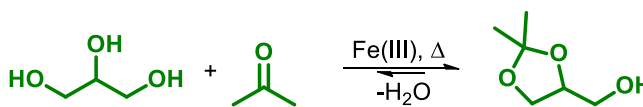
4. Results and discussion

4.1. Sustainable solvents selection

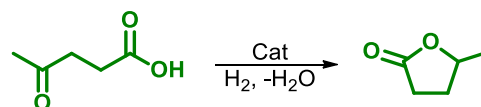
As previously described, one of the most practical approaches for polychromic surfaces restoration involves the solubility test combined with the information provided by the Teas plot. Therefore, a solvent trio was selected trying to satisfy both performance and sustainability. The choice of each solvent is discussed below.



Scheme 1. 2-Ethylhexyl pelargonate, ARGO preparation scheme.



Scheme 2. (2,2-Dimethyl-1,3-dioxolan-4-yl)methanol, SOLK preparation scheme.



Scheme 3. γ -Valerolactone, GVL preparation scheme.

ARGO was selected as a biobased and benign alternative to hydrocarbons such as i-C₈. ARGO was synthesized by the esterification of pelargonic acid with 2-ethylhexyl alcohol (Scheme 1). See Supplementary materials (Paragraph S1) for details.

Pelargonic acid is a fatty acid with nine carbon atoms obtainable from oil biomass through the oxidative cleavage of oleic acid or its triglycerides [35,39]. Furthermore, the fatty acid esterification process is a reaction of broad industrial interest and can be performed using sustainable Lewis acids such as Zn(II) ions (Scheme 1) [40]. Moreover, the esters of pelargonic acid have demonstrated high performance for the dissolution/dispersion of modified rosins used in industrial printing varnishes [41]. The relative NMR spectra and GC–MS characterization of ARGO are reported in Supplementary materials (Figs. S2 and S3).

The second selected solvent, SOLK, can be obtained through ketalization of glycerol with acetone (Scheme 2), which can be promoted by widely available and nontoxic Lewis acids such as Fe(III) ions [42].

The presence of both acetal and hydroxyl moieties makes the SOLK miscible both in water and organic solvents. It was chosen as a protic biobased solvent with low flammability (fp 90 $^{\circ}\text{C}$ – closed cup), lower evaporation pressure (0.16 mmHg at 25 $^{\circ}\text{C}$), and higher viscosity (11 mPa s at 25 $^{\circ}\text{C}$) [43] compared to ethanol (fp 13 $^{\circ}\text{C}$; vapor pressure 44 mmHg at 25 $^{\circ}\text{C}$; viscosity 1 mPa s at 25 $^{\circ}\text{C}$), which makes this solvent safer and more practical to be used with swab without confinement in a polymeric matrix. Moreover, glycerol is a chemical platform attracting great interest because of its increasing production as a by-product of biodiesel preparation [44], and its valorization is a strategy to increase the sustainability of the whole biodiesel production process [45].

The third selected solvent was GVL, which is obtainable from a lignocellulosic fraction, specifically from the reduction of levulinic acid and the lactonization of the resulting hydroxyl acid. GVL is acknowledged in many research papers as a green solvent able to replace toxic solvents (e.g. *N*-methyl pyrrolidone, dimethylformamide) [46,47]. Moreover, it is recognized as fully sustainable since it has a low-ecotoxicological profile and is biodegradable [48]. Moreover, GVL has already found application in cultural heritage as a confined solvent in polyhydroxy butyrate-based gels [49,50] (Scheme 3).

To rationalize the use of these solvents in artwork restoration, their Hansen's parameters were calculated by a group-contribution method [29], displayed in the Teas chart, and tested with a wide range of historical (mastic, dammar, shellac) and modern (Paraloid B72) filming materials and with simulated pictorial layer prepared with siccativ oil (linseed oil) and natural umber pigment.

Table 1

Normalized Hansen solubility parameters of γ -valerolactone (GVL), 2-ethylhexyl pelargonate (ARGO) and (2,2-dimethyl-1,3-dioxolan-4-yl)methanol (SOLK).

Solvent	F_d	F_p	F_h
GVL	46.1	32.8	21.0
ARGO	76.8	14.8	8.4
SOLK	42.9	20.1	37.1

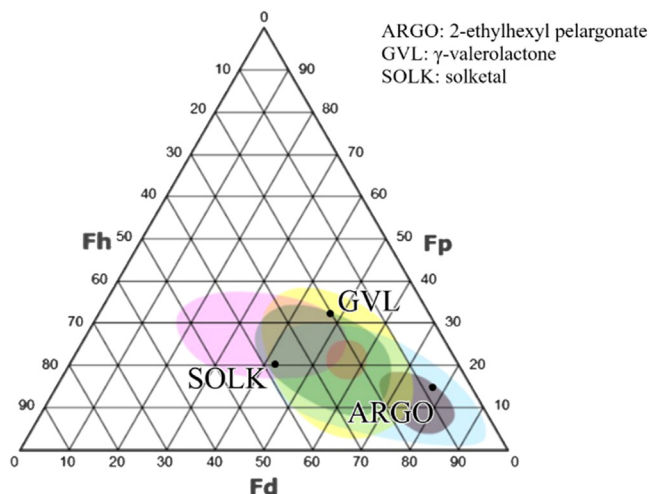


Fig. 4. Teas plot with biobased solvent trio (ARGO, GVL, SOLK) and solubilities areas: pink – proteins and polysaccharides; green – natural varnishes, yellow – synthetic varnishes, brown – aged oil paint layers, cyan – fresh oil paint layers, purple – waxes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.1.1. Hansen solubility parameters determination

The Hansen solubility parameters tend to predict the bulk solubility properties of the molecules starting from their structure using three different descriptors related to different molecular interactions: δ_d , related to the dispersion forces between molecules; δ_p , related to the dipolar intermolecular force; and the δ_{hb} , related to the hydrogen bond abilities of the molecules. There are several approaches to define these parameters, and we have chosen the model improved by Stefanis et al. [29] because its results are accurate, and mostly because it is easily applicable without the need for software. Normalized results (F_d , F_p , F_h) for each solvent are summarized in Table 1 (for complete calculation of Hansen and Teas parameters please see Tables S1–S3 in supporting material, Paragraph S2).

The Hansen parameters were so exploited to define the position of each biobased solvent on the Teas diagram (Fig. 4),¹ which also includes the solubilities area (with different colors) of the most relevant substances to be removed during restoration activities.

As can be seen from the Teas plot, the formulation of mixtures with these compounds could reach almost every part of the solubility areas reported, resulting promising for application in a relevant environment.

4.2. Cleaning tests on glass specimens

4.2.1. Film-forming substrates selection

Five film-forming substrates with a wide range of polarity were selected to understand the solvent–surface interactions. In addition, to simulate a relevant application, the substrates were chosen

¹ Figure adapted from “TriSolv – Triangolo interattivo dei solventi e delle solubilità” software, from <http://www.icr.beniculturali.it/pagina.cfm?usz&1&uid=505&umn=297>.

among those usually found on artworks as protective coatings for polychrome surfaces. Each type of varnish is described below.

Dammar and mastic varnishes were chosen for their frequent use as protective agents in the restoration field since the 18th century [51]; both are triterpenoid varnishes used to protect and saturate polychrome surfaces [52]. Shellac was chosen due to its solubility-position in the polar protic area of the solubility triangle and its common occurrence on gilded surfaces, historical furniture, and musical instruments as a glossy protective layer; it is an animal-based resin composed of polyesters of aliphatic acids and sesquiterpenoid acids [53]. Paraloid® B72, on the other hand, is in the polar aprotic region of the Teas plot and it has often been used as a consolidating or protective substance since the 1970s; it is an ethyl methacrylate synthetic resin that is usually dissolved in ketones or esters. The last substrate chosen was a proper painting layer simulated with linseed oil and a milled umber pigment paint layer. It was selected to evaluate the interaction between the solvents and a typical oil-painted surface prepared according to ancient recipes [54].

These five coating substances were brushed and allowed to dry onto glass slides, obtaining sufficiently thick layers (Fig. 5, columns a and b). The specimens were prepared in duplicate, and half of them were subjected to an artificial aging process (Fig. 5, columns c and d). Drops of the selected green solvents were placed on these coatings for different times (Fig. 5, columns b and d) and then removed by lightly dabbing away the solvents with a dry cotton swab, avoiding mechanical stress during the removal. Observation under 365 nm UV radiation has been used to evaluate the removal of the coating layers.

4.2.2. Solvents cleaning performances

ARGO showed an affinity with Dammar and Mastic, while Shellac, Paraloid® B72 and the oil-based paint layer did not interact with this solvent. GVL and SOLK, on the other hand, were able to solubilize all the coatings except the paint layer specimen.

The solubilization of the triterpenoid varnishes induced by ARGO, as well as GVL and SOLK, has to be linked to the wide range of behaviors of these substrates when they are freshly applied [55], while the incompatibility between ARGO and the polar coatings confirmed the theoretical assumptions on the position of the solvent in the solubility chart. The solubilization of Shellac and Paraloid® B72 when in contact with GVL and SOLK met the expectations based on their solubility area placement in the Teas triangle.

The oil and pigment layer appeared to be somewhat polymerized as it could not be dissolved by any solvent; it showed a slight interaction with SOLK and GVL, that caused the formation of minor stains after 3 min of contact.

4.2.3. Artificial aging of the filmogenic substances

Another five coated glass specimens were subjected to artificial aging to evaluate the interaction between the tested solvents and more true-to-life substrates, as over time artworks and restoration materials undergo alteration processes such as chain radical reactions, cross-linking, condensations, chain shortening, and defunctionalization, resulting in increased polarity [53,56,57]. The change in UV fluorescence of the substances after the artificial aging confirmed the alteration of the specimens.

The green solvents were tested in the same way as the previous test; a longer time frame (10 min) was added to the previous protocol to ensure a sufficient contact time for the solvents to interact with the more cross-linked materials.

GVL and SOLK solubilized every aged filmogenic substance except for the paint layer specimen, while ARGO did not interact with any substrate.

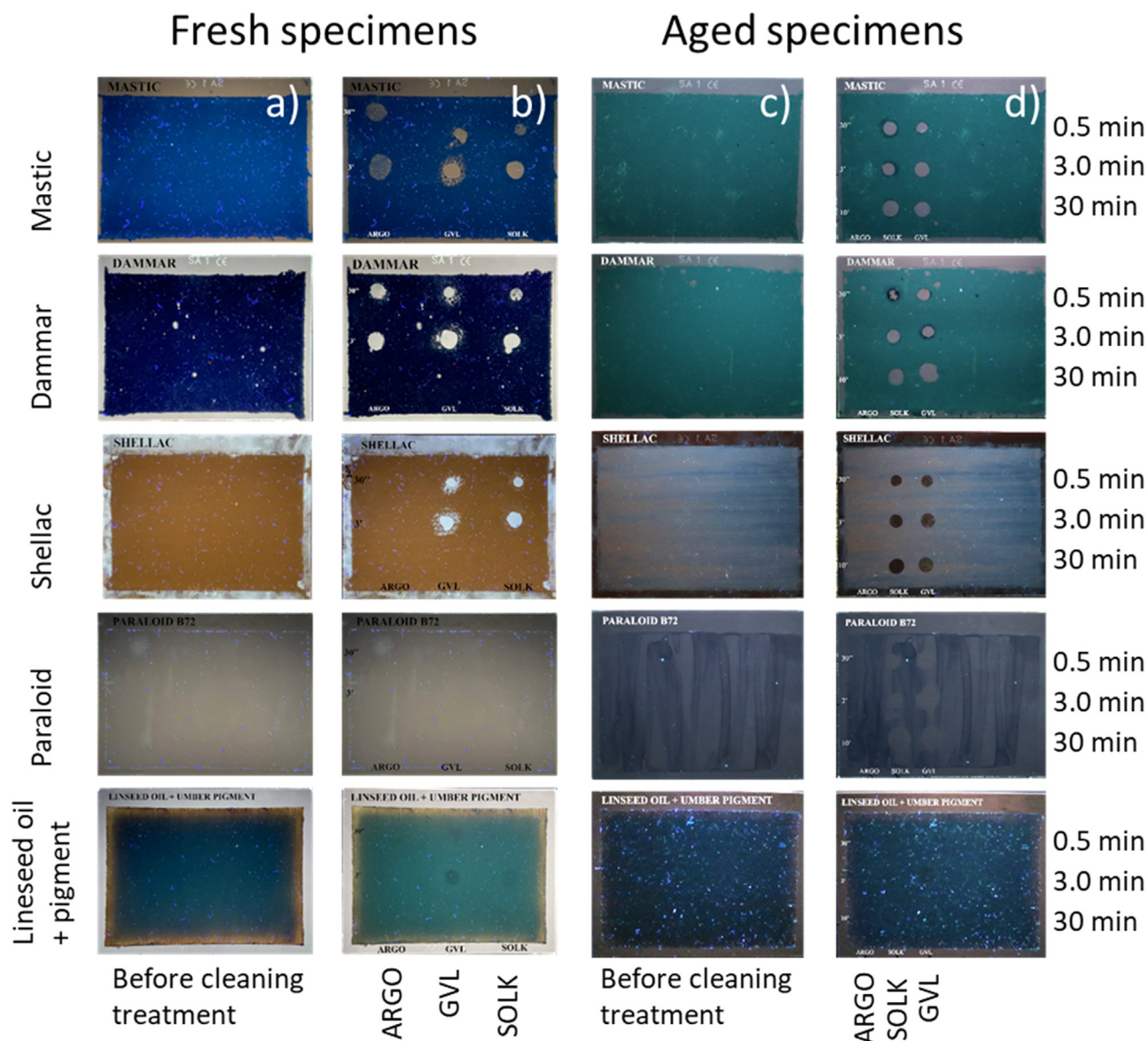


Fig. 5. (a) Fresh pristine and (b) tested glass specimens under UV light; (c) aged pristine and (d) tested glass specimens under UV light. From the top to down: mastic, dammar, shellac, Paraloid, linseed oil + umber pigment.

These results are consistent with the increased polarity of the aged coatings, particularly in the case of the terpenoid varnishes such as Dammar and Mastic, which undergo radical chain-reactions during aging that lead to the formation of carbon structures with oxygen-containing functional groups [58], preventing their solubilization by ARGO.

In this case, GVL and SOLK slightly interacted with the oil and pigment paint layer when in contact for 3 min or more. The classical solubility test polar solvents (acetone and ethanol) were then tested in the same way on the oil paint specimen, and the comparison of the results showed that they induce far more damage to the paint layer than the aforesaid green solvents (Fig. S4). Furthermore, the miscibility of GVL and SOLK with ARGO allows the formulation of blends with tunable polarity, to prevent the use of pure GVL and SOLK that can interact with the paint layer.

4.3. Solvent diffusion tests on wooden specimens

After testing the solvents' ability to selectively remove fresh and aged coating substances on glass specimens, further samples were

prepared on wooden panels, following Cennino Cennini's recipes [37]. These specimens were tested to get additional insight into the interaction and possible diffusion of solvents into the innermost painting layers. To address this purpose, the wooden specimens were first subjected to an artificial aging process as reported in materials and methods. Subsequently, the wetting and penetration of the solvents into the polychrome layer were evaluated by monitoring the volume change over time of a drop of each solvent (ARGO, GVL, SOLK, and H₂O as control) applied to the specimen as described in Section 3.7 (representative image of volume variation over time is reported in Fig. S5). The measured volume variation over time for each solvent tested on different aged coating (Shellac, Paraloid®, Dammar and Mastic) specimens are shown in Fig. 6. The decrease in the volume of the tested solvents was directly related to the diffusion of the solvents into the substrates. This assumption is plausible since the isothermal thermogravimetric analysis (TGA) demonstrated a negligible evaporation rate of the tested solvents within the exposure time (details are reported in supplementary information Paragraph S3 and Fig. S6).

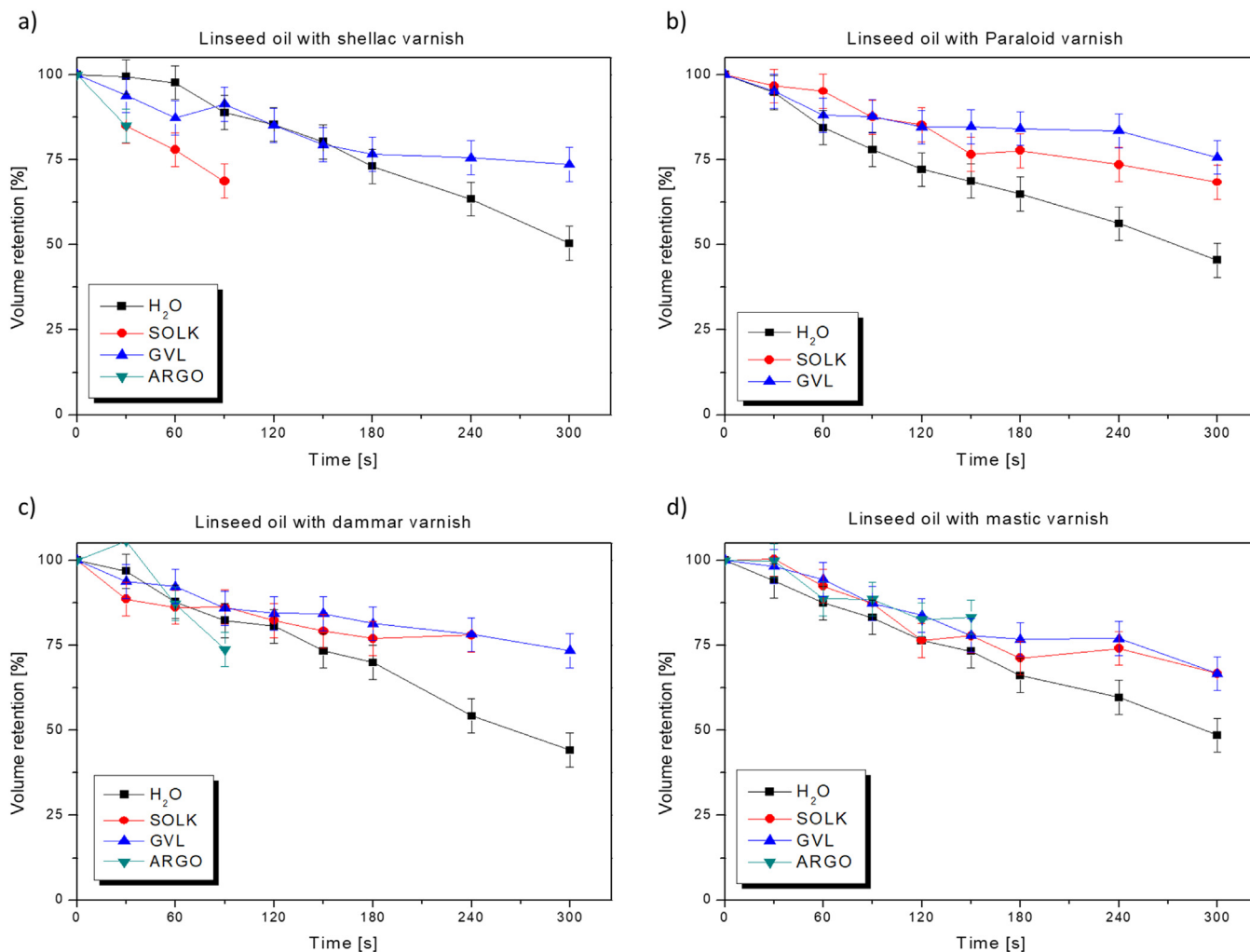


Fig. 6. Percent volume variations of solvent drops deposited on: (a) linseed oil with shellac varnish, (b) linseed oil with Paraloid varnish, (c) linseed oil with dammar varnish and (d) linseed oil with mastic varnish.

As shown in Fig. 6, the diffusion rate of water is in general higher compared to the tested solvents. In fact, the decrease in volume of the water drops appeared to be around 50% after 5 min, in all tested substrates. The diffusion rate of ARGO was difficult to measure because of its fast spreading on the substrate and the consequently low contact angle. Therefore, the drop could not fit into the frame of the measuring equipment, especially for the unvarnished and the Paraloid-coated specimens (example in Fig. S7). Hence, the apparent volume variation of this solvent seems to be related to its high affinity with the specimen surfaces, rather than its penetration in the substrate. This assumption is supported by the lack of visible solvent-substrate interaction observed during the previously reported solubility test on glass specimens. SOLK showed a volume decrease of 25–30% for Dammar, Mastic, and Paraloid-coated specimens, and it was not measurable when in contact with the unvarnished and the Shellac-coated specimens for the same reason as ARGO. GVL showed the lowest volume decrease, approximately 25% when in contact with each specimen, except for the unvarnished one, with which it showed a 45% volume decrease (Fig. S8), indicating that its diffusion into the innermost painting layers was the lowest among the green solvent tested.

Eventually, the mass variation of each proposed solvent on the surface of uncoated wooden specimens was evaluated over several

days at room temperature (Fig. S9, resulting in complete evaporation within 1 day for SOLK and GVL and 4 days for ARGO).

Considering the low interaction with the painting layer (glass specimens) and the high volume retention (wood specimens) of the pure solvent trio within a short application time (0.5–3 min), their low evaporation rate (confirmed by TGA), and their complete evaporation over 1–4 days (uncoated wood specimens), the proposed solvent trio resulted suitable to be applied on the case-study reported below

4.4. Case of study: Ecce Homo restoration

The case study consists of a 16th century panel painting that depicts an *Ecce Homo*, by an unknown Neapolitan artist. The surface of the oil painting was observed under 365 nm UV radiation and the presence of non-original green-fluorescing varnish was detected, and the GC–MS (Fig. S10) analysis confirmed the presence of an oxidized natural terpene varnish (Table S4).

As proof of concept, the above selected green solvents were tested in different mixtures on the painting to remove the unwanted paint layer. The results were then compared with those obtained by using solvents commonly used by restorers.

Firstly, a solubility test was performed with mixtures of green solvents and compared with the mixtures of common solvents

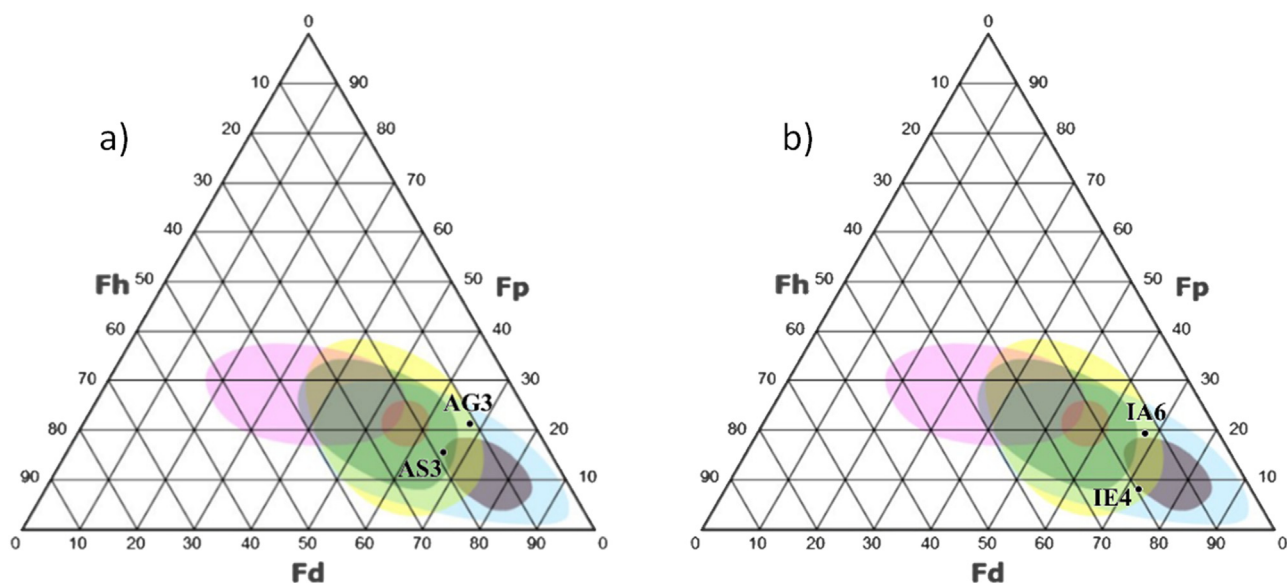


Fig. 7. (a) Teas plot with green solvents mixture; (b) Teas plot with standard solvents mixture. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

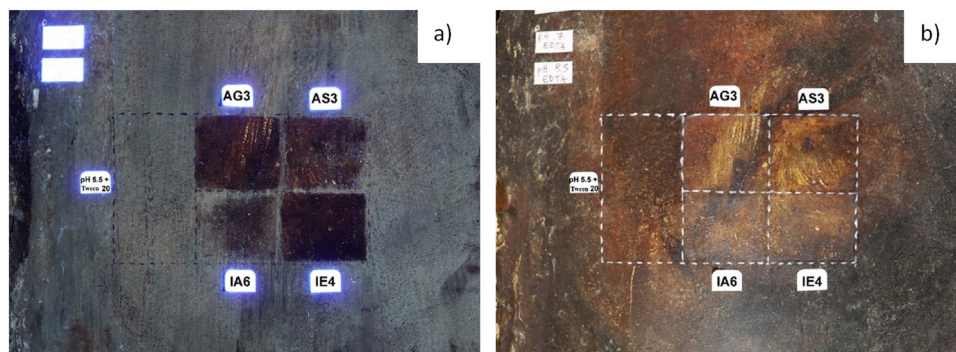


Fig. 8. Varnish removal test under (a) UV and (b) visible lights.

Table 2

Teas parameters of used mixture.

Acronym	Solvent mixture	Volume portion (%)	Teas parameters		
			Fd	Fp	Fh
AG3	ARGO/GVL	70/30	68	21	11
IA6	i-C8/Ace	40/60	68	19	13
AS3	ARGO/SOLK	70/30	67	16	17
IE4	i-C8/EtOH	60/40	73	8	19

(Ace, EtOH, i-C₈). As for the green solvents, the following mixtures were chosen:

- AG3: ARGO 70% + GVL 30%
- AS3: ARGO 70% + SOLK 30%

The two green solvent mixtures, which proved to be the least polar showing the best varnish removal, were located inside the Teas chart, to ensure that they did not intercept the solubility area of the aged oil paint (Fig. 7a). Besides the standard two-component mixture of solvents, three components mixture is possible, but their investigation is out of the scope of this work.

Therefore, classical binary solvent mixtures with the most similar solubility values (Table 2) were located in the solubility chart (Fig. 7b) and chosen as a comparison:

- IA6: i-C8 40% + Ace 60%

- IE4: i-C8 60% + EtOH 40%

Cleaning tests were carried out on the panel painting by soaking cotton swabs in each solvent mixture and then gently rubbing the swab on the surface for 3 min; the solubilized varnish left on the painting was then removed with a dry cotton swab. The effectiveness of the varnish layer removal was then evaluated by UV fluorescence and visible light inspection (Fig. 8a, b).

The comparison between AG3 and IA6, which are both polar aprotic mixtures and have very similar solubility values, showed that AG3 successfully solubilized the terpene varnish, while IA6 did not remove it completely (Fig. 8a). IA6 showed the so-called “bloom effect”, that is the partial solubilization of the varnish without complete removal, resulting in a hazy finish on the surface of the painting. This was caused by the fast evaporation of the solvent mixture, which made it impossible to maintain a sufficient contact time for the complete solubilization of the varnish. The slow evaporation rate of AG3, on the other hand, contributed to the effective removal.

As for the comparison of AS3 and IE4, the green solvent mixtures (AS3) uniformly thinned the terpene coating, even if it was less effective in completely removing the unwanted varnish layer compared with IE4. This is because the two mixtures showed some differences in solubility values (see Table 2), although IE4 mixture was chosen to have the solubility parameters as close as possible to those of AS3. On the other hand, looking at the

results obtained under visible light (Fig. 8b) it is possible to note that both the classical solvents mixtures (IA6, IE4) induced a loss of shine on the surface of the painting, while the green solvents mixtures (AG3, AS3) didn't interfere with the refractive index of the surface, restoring the painting to its natural brightness.

5. Conclusion

An innovative triad of green solvents is hereby proposed for the selective removal of covering varnishes used in cultural heritage. All of the proposed solvents can be prepared starting from bio-renewable feedstocks. Moreover, they present more user-friendly profiles compared with those of standard used solvents (isooctane, ethanol, acetone) because they are nontoxic, non-flammable, and have a low evaporation rate, making them even more practical to be used without confinement strategies.

To rationalize their use, their Hansen solubility parameters were estimated using a group contribution method and displayed in the Teas diagram. As pure solvents, they showed a high ability to solvate a wide range of fresh and aged paints. Their behavior in contact with aged wood samples was studied by monitoring their volume retention by contact angle measurements, showing a low penetration phenomenon for the exposure time.

Finally, the green-solvent triad was successfully employed in the case study of "Ecce Homo" to remove the terpenoid varnish layer from the painting while preserving the original painting. This approach led to a positive and unexpected result, including a noteworthy improvement in the gloss of the treated surfaces.

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Ethics approval and consent to participate

Not applicable.

CRediT authorship contribution statement

Chiara Melchiorre: Methodology, Investigation, Writing – original draft. **Massimo Melchiorre:** Methodology, Investigation, Writing – original draft. **Maristella Marra:** Investigation, Data curation. **Emanuela Rizzo:** Investigation, Data curation. **Giancarlo Fatigati:** Validation, Supervision. **Pasquale Rossi:** Validation, Supervision. **Pierfrancesco Cerruti:** Data curation, Resources, Writing – review & editing. **Ilaria Improta:** Methodology, Writing – original draft. **Angela Amoresano:** Validation, Supervision, Resources. **Gennaro Marino:** Supervision, Visualization, Conceptualization. **Francesco Ruffo:** Conceptualization, Supervision, Funding acquisition. **Andrea Carpentieri:** Conceptualization, Supervision, Project administration.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.culher.2023.05.013](https://doi.org/10.1016/j.culher.2023.05.013).

References

- [1] P. Baglioni, D. Chelazzi, How science can contribute to the remedial conservation of cultural heritage, *Chemistry (Easton)* 27 (2021) 10798–10806.
- [2] M. Baglioni, G. Poggi, D. Chelazzi, P. Baglioni, Advanced materials in cultural heritage conservation, *Molecules* 26 (2021) 3967.
- [3] M. Raudino, G. Selvolini, C. Montis, M. Baglioni, M. Bonini, D. Berti, P. Baglioni, Polymer films removed from solid surfaces by nanostructured fluids: microscopic mechanism and implications for the conservation of cultural heritage, *ACS Appl. Mater. Interfaces* 7 (2015) 6244–6253.
- [4] M. Baglioni, Y. Jáidar Benavides, A. Desprat-Drapela, R. Giorgi, Amphiphile-based nanofluids for the removal of styrene/acrylate coatings: cleaning of stucco decoration in the Uaxactun archeological site (Guatemala), *J. Cult. Herit.* 16 (2015) 862–868.
- [5] P. Ferrari, D. Chelazzi, N. Bonelli, A. Mirabile, R. Giorgi, P. Baglioni, Alkyl carbonate solvents confined in poly (ethyl methacrylate) organogels for the removal of pressure sensitive tapes (PSTs) from contemporary drawings, *J. Cult. Herit.* 34 (2018) 227–236.
- [6] V. Rosciardi, D. Chelazzi, P. Baglioni, Green" biocomposite Poly (vinyl alcohol)/starch cryogels as new advanced tools for the cleaning of artifacts, *J. Colloid Interface Sci.* 613 (2022) 697–708.
- [7] C. Melchiorre, L. Dello Iorio, G. Ntasi, L. Birolo, G. Trojsi, P. Cennamo, M.R. Barone Lumaga, G. Fatigati, A. Amoresano, A. Carpentieri, A multidisciplinary assessment to investigate a XXII dynasty Wooden Coffin, *Int. J. Conserv. Sci.* 11 (2020) 25–38.
- [8] P. Cremonesi, E. Signorini, L'uso dei solventi organici neutri nella pulitura dei dipinti: un nuovo test di solubilità, [The use of organic neutral solvents in the cleaning of paintings: a new solubility test], *Progetto restauro* 31 (2004) 2–15.
- [9] E. Signorini, Surface cleaning of paintings and polychrome objects in Italy: the last 15 years, in: *New Insights into the Cleaning of Paintings: Proceedings from the Cleaning 2010 International Conference*, Universidad Politécnica de Valencia and Museum Conservation Institute, Smithsonian Institution, 2013.
- [10] R. Wolbers, *Cleaning painted surfaces: aqueous methods*, 2000.
- [11] R.C. Wolbers, C. Stavroudis, M. Cushman, *Aqueous methods for the cleaning of paintings*, in: *Conservation of Easel paintings*, 2020, pp. 526–548.
- [12] B. Ormsby, M. Keeffe, A. Phenix, E. Von Aderkas, T. Learner, C. Tucker, C. Kozak, Mineral spirits-based microemulsions: a novel cleaning system for painted surfaces, *J. Am. Inst. Conserv.* 55 (2016) 12–31.
- [13] T. Fardi, V. Pintus, E. Kampasakali, E. Pavlidou, K.G. Papispyropoulos, M. Schreiner, G. Kyriacou, A novel methodological approach for the assessment of surface cleaning of acrylic emulsion paintings, *Microchem. J.* 141 (2018) 25–39.
- [14] Y. Jia, G. Scitutto, A. Botteon, C. Conti, M.L. Focarete, C. Gualandi, C. Samorì, S. Prati, R. Mazzeo, Deep eutectic solvent and agar: a new green gel to remove proteinaceous-based varnishes from paintings, *J. Cult. Herit.* 51 (2021) 138–144.
- [15] A. Macchia, L. Rivaroli, B. Gianfreda, The GREEN RESCUE: a 'green' experimentation to clean old varnishes on oil paintings, *Nat. Prod. Res.* 35 (2021) 2335–2345.
- [16] G. Lustrato, G. Alfano, A. Andreotti, M.P. Colombini, G. Ranalli, Fast biocleaning of mediaeval frescoes using viable bacterial cells, *Int. Biodeterior. Biodegrad.* 69 (2012) 51–61.
- [17] G. Ranalli, G. Alfano, C. Belli, G. Lustrato, M.P. Colombini, I. Bonaduce, E. Zanardini, P. Abbruscato, F. Cappitelli, C. Sorlini, Biotechnology applied to cultural heritage: bioremediation of frescoes using viable bacterial cells and enzymes, *J. Appl. Microbiol.* 98 (2005) 73–83.
- [18] P. Cremonesi, *L'uso degli enzimi nella pulitura di opere policrome*, 1999.
- [19] Z. Kisoová, J. Pavlovič, L. Šefčíková, M. Bučková, A. Puškárová, L. Kraková, A.O. Šišková, A. Kleinová, Z. Machatová, D. Pangallo, Removal of overpainting from an historical painting of the XVIII century: a yeast enzymatic approach, *J. Biotechnol.* 335 (2021) 55–64.
- [20] R. Bellucci, P. Cremonesi, G. Pignagnoli, A preliminary note on the use of enzymes in conservation: the removal of aged acrylic resin coatings with lipase, *Stud. Conserv.* 44 (1999) 278–281.
- [21] H.E. Ahmed, S.S. Gremos, F.N. Kolis, Enzymatic removal of the oily dirt from a Coptic tunic using the enzyme lipase, *J. Textile Apparel Technol. Manag.* 6 (2010).
- [22] C. Stavroudis, T. Doherty, R. Wolbers, A new approach to cleaning I: using mixtures of concentrated stock solutions and a database to arrive at an optimal aqueous cleaning system, *WAAC Newsletter* 27 (2005) 17–28.
- [23] C. Mazzuca, L. Micheli, M. Carbone, F. Basoli, E. Cervelli, S. Iannuccelli, S. Sotgiu, A. Palleschi, Gellan hydrogel as a powerful tool in paper cleaning process: a detailed study, *J. Colloid Interface Sci.* 416 (2014) 205–211.
- [24] C. Mazzuca, G. Bocchinfuso, I. Cacciotti, L. Micheli, G. Palleschi, A. Palleschi, Versatile hydrogels: an efficient way to clean paper artworks, *RSC Adv.* 3 (2013) 22896–22899.
- [25] C. Mazzuca, L. Micheli, F. Marini, M. Bevilacqua, G. Bocchinfuso, G. Palleschi, A. Palleschi, Rheoreversible hydrogels in paper restoration processes: a versatile tool, *Chem. Cent. J.* 8 (2014) 1–11.
- [26] P. Cremonesi, Surface cleaning? Yes, freshly grated Agar gel, please, *Stud. Conserv.* 61 (2016) 362–367.
- [27] E. Carretti, C. Matarrese, E. Fratini, P. Baglioni, L. Dei, Physicochemical characterization of partially hydrolyzed poly (vinyl acetate)-borate aqueous dispersions, *Soft Matter* 10 (2014) 4443–4450.
- [28] P. Baglioni, N. Bonelli, D. Chelazzi, A. Chevalier, L. Dei, J. Domingues, E. Fratini, R. Giorgi, M. Martin, Organogel formulations for the cleaning of easel paintings, *Appl. Phys. A* 121 (2015) 857–868.
- [29] E. Stefanis, C. Panayiotou, Prediction of Hansen solubility parameters with a new group-contribution method, *Int. J. Thermophys.* 29 (2008) 568–585.
- [30] P. Cremonesi, *L'ambiente acquoso per il trattamento di opere policrome*, il prato publishing house srl, 2012.
- [31] C. Ricci, F. Gambino, M. Nervo, A. Piccirillo, A. Scarcella, F. Zenucchini, J.S. Pozo-Antonio, Developing new cleaning strategies of cultural heritage stones: are synergistic combinations of a low-toxic solvent ternary mixtures followed by laser the solution? *Coatings* 10 (2020) 466.

- [32] C.M. Alder, J.D. Hayler, R.K. Henderson, A.M. Redman, L. Shukla, L.E. Shuster, H.F. Sneddon, Updating and further expanding GSK's solvent sustainability guide, *Green Chem.* 18 (2016) 3879–3890.
- [33] A. Zhenova, Challenges in the development of new green solvents for polymer dissolution, *Polym. Int.* 69 (2020) 895–901.
- [34] M. Sousa, M.J. Melo, T. Casimiro, A. Aguiar-Ricardo, The art of CO₂ for art conservation: a green approach to antique textile cleaning, *Green Chem.* 9 (2007) 943.
- [35] M. Melchiorre, V. Benessere, M.E. Cucciolito, C. Melchiorre, F. Ruffo, R. Esposito, Direct and solvent-free oxidative cleavage of double bonds in high-oleic vegetable oils, *ChemistrySelect* 5 (2020) 1396–1400.
- [36] M. Melchiorre, M.E. Cucciolito, M. Di Serio, F. Ruffo, O. Tarallo, M. Trifuoggi, R. Esposito, Homogeneous catalysis and heterogeneous recycling: a simple Zn(II) catalyst for green fatty acid esterification, *ACS Sustain. Chem. Eng.* 9 (2021) 6001–6011.
- [37] C. Cennini, *Il libro dell'arte, o trattato della pittura*, Le Monnier, Firenze, 1859.
- [38] C. Melchiorre, S. Palmiero, G. Fatigati, A. Amoresano, G. Marino, A. Carpentieri, A procedure for combining the removal and the identification of patina on 15th century, Byzant. *Icon Int. J. Conserv. Sci.* 10 (2019).
- [39] M. Wang, J. Ma, H. Liu, N. Luo, Z. Zhao, F. Wang, Sustainable productions of organic acids and their derivatives from biomass via selective oxidative cleavage of C–C bond, *ACS Catal.* 8 (2018) 2129–2165.
- [40] R. Esposito, M. Melchiorre, A. Annunziata, M.E. Cucciolito, F. Ruffo, Emerging catalysis in biomass valorisation: simple Zn(II) catalysts for fatty acids esterification and transesterification, *ChemCatChem* 12 (2020) 5858–5879.
- [41] V. Benessere, M.E. Cucciolito, A. De Santis, M. Di Serio, R. Esposito, M. Melchiorre, F. Nugnes, L. Paduano, F. Ruffo, A sustainable process for the production of varnishes based on pelargonic acid esters, *J. Am. Oil Chem. Soc.* 96 (2019) 443–451.
- [42] R. Esposito, U. Raucci, M.E. Cucciolito, R. Di Guida, C. Scamardella, N. Rega, F. Ruffo, Iron(III) complexes for highly efficient and sustainable ketalization of glycerol: a combined experimental and theoretical study, *ACS Omega* 4 (2019) 688–698.
- [43] J.I. García, H. García-Marín, J.A. Mayoral, P. Pérez, Green solvents from glycerol. Synthesis and physico-chemical properties of alkyl glycerol ethers, *Green Chem.* 12 (2010) 426–434.
- [44] M. Melchiorre, A. Amoresano, P.H.M. Budzelaar, M.E. Cucciolito, F. Mocerino, G. Pinto, F. Ruffo, A. Tuzi, R. Esposito, Parts-per-million (Salen)Fe(III) homogeneous catalysts for the production of biodiesel from waste cooking oils, *Catal Lett.* (2022) 1–10.
- [45] I. Corrêa, R.P.V. Faria, A.E. Rodrigues, Continuous valorization of glycerol into solketal: recent advances on catalysts, processes, and industrial perspectives, *Sustain. Chem.* 2 (2021) 286–324.
- [46] F. Gao, R. Bai, F. Ferlin, L. Vaccaro, M. Li, Y. Gu, Replacement strategies for non-green dipolar aprotic solvents, *Green Chem.* 22 (2020) 6240–6257.
- [47] Y. Gu, F. Jerome, Bio-based solvents: an emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry, *Chem. Soc. Rev.* 42 (2013) 9550–9570.
- [48] F. Kerkel, M. Markiewicz, S. Stolte, E. Müller, W. Kunz, The green platform molecule gamma-valerolactone – ecotoxicity, biodegradability, solvent properties, and potential applications, *Green Chem.* 23 (2021) 2962–2976.
- [49] C. Samorì, P. Galletti, L. Giorgini, R. Mazzeo, L. Mazzocchetti, S. Prati, G. Sciotto, F. Volpi, E. Tagliavini, The green attitude in art conservation: polyhydroxybutyrate-based gels for the cleaning of oil paintings, *ChemistrySelect* 1 (2016) 4502–4508.
- [50] S. Prati, F. Volpi, R. Fontana, P. Galletti, L. Giorgini, R. Mazzeo, L. Mazzocchetti, C. Samorì, G. Sciotto, E. Tagliavini, Sustainability in art conservation: a novel bio-based organogel for the cleaning of water sensitive works of art, *Pure Appl. Chem.* 90 (2018) 239–251.
- [51] A. Cerasuolo, *La vernice mastice. Istanze del restauro moderno attraverso la fortuna di un materiale*, Bollettino Istituto Centrale per il Restauro (2005) 22–44 10–11.
- [52] R.W. John Mills, *The Organic Chemistry of Museum Objects*, 2nd edition, Routledge, London, 1987.
- [53] C. Coelho, R. Nanabala, M. Ménager, S. Commereuc, V. Verney, Molecular changes during natural biopolymer ageing – the case of shellac, *Polym. Degrad. Stab.* 97 (2012) 936–940.
- [54] C. Maltese, *Le tecniche artistiche*, 7th ed.
- [55] G.A.v. Doelen, *Molecular studies of fresh and aged triterpenoid varnishes*, Institute for Biodiversity and Ecosystem Dynamics (IBED), 1999.
- [56] O. Chiantore, M. Lazzari, Photo-oxidative stability of paraloid acrylic protective polymers, *Polymer (Guildf)* 42 (2001) 17–27.
- [57] I. Osticioli, D. Ciofini, A.A. Mencaglia, S. Siano, Automated characterization of varnishes photo-degradation using portable T-controlled Raman spectroscopy, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* 172 (2017) 182–188.
- [58] D. Ciofini, J. Striova, M. Camaiti, S. Siano, Photo-oxidative kinetics of solvent and oil-based terpenoid varnishes, *Polym. Degrad. Stab.* 123 (2016) 47–61.