



Assessment of aqueous cleaning of acrylic paints using innovative cryogels

Irene Cardaba^{a,*}, Giovanna Poggi^b, Michele Baglioni^b, David Chelazzi^b, Itxaso Maguregui^a, Rodorico Giorgi^b

^a Department of Painting, University of the Basque Country UPV/EHU, Barrio Sarriena s/n, 48940, Leioa, Bizkaia, Spain

^b Department of Chemistry & CSGI, University of Florence, Via della Lastruccia 3, 50019, Sesto F. no, Florence, Italy

ARTICLE INFO

Keywords:

Cleaning
Cryogels
Acrylic paints
Vesvelil Plus®
Modular cleaning program

ABSTRACT

Waterborne acrylic paints have been widely used by artists since their development in the late 50s. Their cleaning, i.e., the removal of mainly airborne dust and grime, is a challenging operation, because acrylics are very sensitive to solvents in a wide range of polarity. Even if aliphatic and low-molecular weight aromatic hydrocarbons are less prone to interact with the hydrophilic components of the acrylic paint layer, the use of water is necessary since it grants better cleaning performances. In this paper, three acrylic commercial paints from Liquitex® (USA) were selected and characterized using Fourier Transform Infrared spectroscopy (FT-IR) and pyrolysis – gas chromatography – mass spectrometry (Py-GC-MS). The removal of artificial soil from these paint films was carried out using novel highly retentive PVA-based cryogels that have been recently developed to avoid the uncontrolled wetting of water-sensitive artistic surfaces. Their cleaning efficiency was evaluated using Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM). Finally, an ATR-FTIR and 2D FTIR Imaging study about the residues left by the gels was carried out by comparing the cryogel with a Vesvelil Plus® emulsion, a gel-like silicone polyether copolymer used in the recent past to create a stable water-in-oil emulsion, and still available on the market to conservators. In conclusion, the cryogel granted a safe and satisfactory cleaning action and a residue-free soil removal from acrylic paint films, overcoming the drawbacks of traditional cleaning methods.

1. Introduction

Waterborne acrylic paints have been frequently used in modern and contemporary art. They usually feature high molecular weight acrylic polymers that are based on the esters of acrylic acid and methacrylic acid, and a broad range of additives including surfactants, stabilizers, wetting agents and viscosity modifiers, added to enhance stability, longevity, flow and film formation properties [1]. Different colors are obtained by the addition of either organic dyes or inorganic pigments. The usually low glass transition temperature of the acrylic resin, which results in films that are soft at room temperature [2–4] and the migration to the surface of hydrophilic additives, i.e. surfactants, upon drying [5] make acrylic paint films prone to attract airborne dust. Therefore, acrylic paintings need to be cleaned, even though this operation is particularly challenging [6]. The community has been searching for the safest and most effective procedure since 2003 [7,8]. The main problem of acrylic paints is their sensitivity to water and to organic solvents over a broad range of polarities. In fact, they show a swelling capacity of up to ten times higher than oil films [9]. It was

observed that in 3 months old samples the interaction with solvents causes the partial disruption of films' microstructure, which, in turn, induces considerable optical changes and a decrease in the mechanical strength [9]. The cleaning of acrylic paintings can also lead to the solubilization of migrated additives on the surface and extraction of additives from the bulk of the film, and their migration to the surface, resulting in changes in the physico-chemical and mechanical properties of the film [10,11]. Even if aliphatic and low-molecular weight aromatic hydrocarbons induce the lowest swelling [9] and are less prone to interact with the hydrophilic components of the acrylic paint layer [11], the use of water for the removal of airborne dust, which is mainly hydrophilic, grants better cleaning performances.

Several strategies have been recently developed to tackle the cleaning of water-sensitive artworks. The Modular Cleaning Program (MCP) [12,13] uses pre-mixed stock solutions (pH buffers, chelators, surfactants and ionic buffers) to prepare cleaning systems with controlled pH and conductivity, so to minimize the risk of changes in the acrylic films [14,15]. However, the use of gelled systems is one of the most successful strategies to achieve highly effective and non-invasive

* Corresponding author.

E-mail address: irene.cardaba@ehu.eus (I. Cardaba).

<https://doi.org/10.1016/j.microc.2019.104311>

Received 19 August 2019; Received in revised form 4 October 2019; Accepted 5 October 2019

Available online 12 October 2019

0026-265X/ © 2019 Elsevier B.V. All rights reserved.

cleaning. For instance, in order to reduce the interactions between aqueous cleaning solutions and artistic surfaces, pHEMA/PVP aqueous semi-interpenetrated polymer networks have been recently proposed [16–19]. More recently, highly retentive PVA-based cryogels have been developed for the selective removal of unwanted patinas from artistic surface [20,21]. These gels, obtained via freezing/thawing repeated cycles starting from PVA aqueous solutions, are stickier, softer and more flexible than pHEMA/PVP networks; thus, they represent a class of very promising tools for soil and grime removal from modern and contemporary paintings, which often present irregular textures and, as previously indicated, feature water-sensitive paints. A different approach involves the use of water-in-oil emulsions, where water is confined in low polarity solvents, which should be as inert as possible towards the paint layers. Among the most frequently used solvents, one can find mineral spirits [22] or low-polarity silicone-based solvents, as the continuous phase of reverse microemulsions/emulsions [23]. One commercial cleaning system that was used in recent times in cleaning case studies is Velvesil Plus®, a gel-like silicone polyether copolymer that was adopted to create stable emulsions in a silicone solvent continuous phase [24,25]. This material was selected as a suitable reference product for our study as it is still available on the market to conservators, even if other silicone polymers, such as KSG-350 z® (Shin Etsu Chemical, Japan) [26], are now used in the restoration practice.

In this paper, three acrylic commercial paints from Liquitex® (USA) were selected because they are known to be highly swelling compared to other brands [14]. They were characterized using Fourier Transform Infrared spectroscopy (FT-IR) and pyrolysis – gas chromatography – mass spectrometry (Py-GC-MS). The removal of artificial soil from these paint films was carried out using the aforementioned novel highly retentive PVA-based cryogels, recently developed to avoid the uncontrolled wetting of water-sensitive artistic surfaces [20,21]. Their cleaning efficiency was evaluated using Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM). Finally, an ATR-FTIR and 2D FTIR Imaging study about the residues left by the gels was carried out by comparing the PVA-based cryogel with Velvesil Plus®, chosen as a commonly used physical gel reference for soil removal from modern and contemporary water-sensitive paintings.

2. Materials and methods

2.1. Materials

Glacial acetic acid (99.8–100.5%), sodium hydroxide ($\geq 97.0\%$), ammonium hydroxide solution (33%), citric acid (99.5%) were all supplied by Sigma Aldrich. Velvesil Plus® and decamethylcyclpentasiloxane, also known as cyclomethicone D5 ($\geq 97.5\%$) were both obtained from CTS (Florence, Italy). Poly(vinyl alcohol) (PVA) (HD 99+ % with $M_w = 146\text{--}186,000$, and HD 89% with $M_w = 89\text{--}124,000$) was used for the synthesis of the PVA-based cryogels. Acrylic paint mock-ups were prepared using Ultramarine Blue (LI 29), Phtalocyanine Green (LI 7) and Cadmium Red Light (LI 108) paints from Liquitex®.

2.2. Cryogels preparation

PVA-based cryogels were obtained according to the literature [20] by homogenous solubilization of PVA with different hydrolysis degree by stirring at 100 °C the solution for 2 h. To avoid water evaporation, a reflux condenser was used. PVA solutions were then cooled down to room temperature and poured in polystyrene casters. The casters were then kept at $-23\text{ }^\circ\text{C}$ for 16 h and thawed at room temperature, to obtain about 2 mm thick hydrogel films.

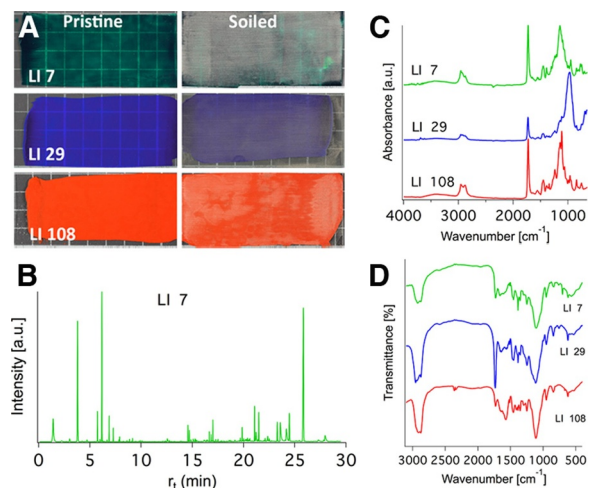


Fig. 1. (A) Acrylic paint mock-ups before (pristine) and after the application of the artificial soil (soiled). (B) Py-GC-MS spectrum of the green acrylic paint. (C) ATR-FTIR analysis of pristine acrylic paint mock-ups. (D) FTIR transmission spectrum of water-soluble additives. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. Acrylic paint film mock-ups

Acrylic paints were applied on Mylar® sheets using a paint applicator (Baker Universal Applicator from Neurtek). The average thickness of films is 150 μm . Samples were then left in a dark and dust-free environment (RH = 50%) for one year. Afterwards, as shown in Fig. 1-A, sample set was artificially soiled according to a procedure described elsewhere [27]. Cleaning tests were conducted after two months from the artificial soiling of samples.

2.4. Cleaning systems

Several stock solutions were prepared according to the Modular Cleaning Programme, MCP [13,28], as reported on Table 1. pH 5 was chosen throughout this work because a slight acidic pH minimizes the swelling of acrylic emulsion paints without hampering the cleaning action [29]. After preliminary testes, two different pH 5 cleaning solutions were selected and prepared by combining different aliquots from the stock solutions. The composition of these cleaning solutions, labelled as Solution A (SA) and Solution B (SB), is reported in Table 1. The selected aqueous cleaning solutions were loaded in the cryogels by immersion for 12 h, as described elsewhere [20].

The cryogels, loaded with the cleaning solutions, were applied on the paint layer for 30 s. Each application was repeated twice, with a 24-h interval between applications. After cleaning, a final rinse was performed with a cryogel loaded with the rinse solution (pH 5, 6000 $\mu\text{S}/\text{m}$) [28].

As a reference method, cotton swabs, soaked in the same cleaning solution loaded in the cryogels, were also used in soil removal tests. Cotton swabs were gently rolled over the paint film, three times. Each application lasted 10 s. After cleaning, a final rinse was performed with

Table 1

Name and composition of the cleaning solutions. The amount of each component in the buffer and in the citric acid (chelator) solution can be found in the published literature [28].

Components	SA	SB
Buffer (Acetic acid/NaOH, pH 5.0)	1 mL	1 mL
Citric acid solution (Citric acid/NaOH, pH 5.0)	–	1 mL
Water	4 mL	3 mL

a cotton swab soaked in the rinse solution (pH 5, 6000 $\mu\text{S}/\text{m}$) [28].

Velvesil Plus®-based systems were prepared as proposed by Wolbers and Stavroudis [24,25] dissolving 20 g of Velvesil Plus® in about 9.5 g of cyclomethicone D5. 3 g of the buffer solution were added, and the system was stirred to homogeneously disperse the aqueous phase in the silicone solvent continuous phase. Velvesil Plus® was applied for 30 s; the gel was then removed mechanically with a dry cotton swab. A final rinse was performed with a cotton swab soaked in cyclomethicone D5 [25]. The whole procedure was repeated twice, as done with the cryogels.

2.5. Infrared spectroscopy

The characterization of pristine and soiled acrylic paint films, before and after cleaning tests, was performed with Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) using a Thermo Nicolet Nexus 870 FTIR spectrometer equipped with a Golden Gate diamond cell. Data were collected with an MCT detector with a sampling area of 150 μm^2 . The spectra were obtained from 128 scans with 2 cm^{-1} of optical resolution over the range of 4000–650 cm^{-1} .

For the identification of water-soluble additives, pristine dried films were immersed in deionized water for 24 h (12 mg of acrylic paint in 15 mL of water). Water extracts were then dried and used to prepare KBr pellets. Fourier Transform Infrared spectra were acquired with a Biorad FTS-40 spectrometer, over the range of 4000–400 cm^{-1} with an optical resolution of 4 cm^{-1} , averaging 32 scans.

The presence of residues from the gels was evaluated through 2D imaging-Fourier transform infrared (FTIR) using a Cary 620–670 FTIR microscope, equipped with an FPA 128 \times 128 detector (Agilent Technologies). This set up allows the highest spatial resolution currently available to FTIR microscopes. The spectra were recorded directly on the surface of the samples (or the Au background) in reflectance mode, with open aperture and a spectral resolution of 4 cm^{-1} , acquiring 128 scans for each spectrum. A “single-tile” analysis results in a map of 700 \times 700 μm^2 (128 \times 128 px), and the spatial resolution of each imaging map is 5.5 μm (i.e. each pixel has dimensions of 5.5 \times 5.5 μm^2).

2.6. Pyrolysis – gas chromatography – mass spectrometry

Pyrolysis – gas chromatography – mass spectrometry was carried out on dried pristine acrylic paints (10–20 μg) using an integrated system composed of a micro-furnace pyrolyser (5250 pyrolyser, CDS Analytical, United States) and gas chromatograph equipped with a mass spectrometer (5975C GC/MSD System with Triple-Axis Detector, Agilent Technologies, USA) and a ZB-WAX (30 m \times 0.25 mm \times 0.25 μm) capillary column. Pyrolysis was performed at 600 $^\circ\text{C}$ [30–32]. The pyrolyser interface and injector were set at 300 $^\circ\text{C}$. The gas chromatography column temperature program used is the following: initial temperature 40 $^\circ\text{C}$, hold for 2 min, followed by an increase of 12 $^\circ\text{C}/\text{min}$ up to 250 $^\circ\text{C}$, hold for 10 min. The helium gas (99,999%) flow was set at 1.7 mL min^{-1} with a pressure of 13.7 psi. Mass spectra were recorded under electron impact ionization (EI) at 70 eV energy, in the range from 40 to 550 m/z , source temperature of 230 $^\circ\text{C}$ and quadrupole at 150 $^\circ\text{C}$. Analyzed micro-samples were weighed using a Sartorius SE2 10⁻⁷ g micro-balance (Sartorius Stedim Biotech, Germany).

2.7. Scanning electron microscope

Scanning electron microscope (SEM) pictures were acquired using a Field Emission Gun Scanning Electron Microscope SIGMA (Carl Zeiss Microscopy GmbH, Germany) with an acceleration potential of 5 kV. Acrylic paint film mock-ups were gold-metallized using an Agar Scientific Auto Sputter Coater.

2.8. Atomic force microscope

Atomic force microscope (AFM) images were acquired using a Dimension ICON Scanning Probe Microscope equipped with a NanoScope V controller (Bruker). Tapping mode was employed using an integrated silicon tip/cantilever having a nominal resonance frequency of 320 kHz and a spring constant value of 42 Nm^{-1} . Scans were performed at a scan rate of 1 Hz and a resolution of 512 lines. Through the reflection of a laser off the cantilever into a split photodiode detector, the oscillation amplitude output voltage differences were measured from the interaction of the cantilever with the surface of the samples, during the rastering of the probe across the surface of the paint with the aid of a piezoelectric z-scanner. Images of 10 \times 10 μm^2 areas were collected in height, amplitude and phase mode using NanoScope 8.15 software. Due to the soft nature of the samples, the tapping amplitude error images gave the most useful information, showing changes in the topography of the samples.

3. Results and discussion

3.1. Characterization of acrylic paints

Py-GC-MS was used to characterize the binder of the selected paint colors (see Fig. 1-B). The selected acrylic paints feature a poly n-butyl acrylate/methyl methacrylate copolymer [14]. In fact, the characteristic pyrolysis fragments of the monomers n-butyl acrylate (m/z 55) and methyl methacrylate (m/z 41) are found at 6.16 r_t (min) and at 3.78 r_t (min), respectively. Moreover, dimers (nBA-MMA, m/z 112 at 14.69 r_t ; nBA-nBA, m/z 127 at r_t 16.98), trimers (nBA-nBA-MMA, m/z 195 at 21.07 r_t ; nBA-nBA-MMA, m/z 195 at 21.48 r_t ; nBA-MMA-nBA m/z 228 at 23.26 r_t and nBA-nBA-nBA m/z 181 at 24.46 r_t) and sesquimers (nBA-MMA, m/z 143 at 14.55 r_t and nBA, m/z 115 at 16.64 r_t) derived from the pyrolysis products of both monomers were detected [33].

ATR-FTIR spectra, reported in Fig. 1-C, show the intense absorption band at 1730 cm^{-1} (carbonyl stretching), and the less intense peaks at 2982 cm^{-1} and 2952 cm^{-1} (CH stretching), and the signals at 1446 cm^{-1} and 1381 cm^{-1} (CH bending) are consistent with the presence of an acrylic binder [31]. In sample LI 29, the signals at 3690 cm^{-1} , 3620 cm^{-1} and 970 cm^{-1} are due to the inorganic ultramarine blue pigment in association with kaolinite [34], while, in sample LI 7, signals at 1389 cm^{-1} , 1305 cm^{-1} , 1155 cm^{-1} and 930 cm^{-1} are characteristic of the phthalocyanine dye [35]. As expected, the characteristic IR absorptions of Cadmium Red, which is the pigment of sample LI 108, are not detected in the investigated spectral range [35]. The presence of a cadmium-based pigment was confirmed by SEM-EDX analysis on sample LI 108 revealing the presence of cadmium, sulfur and selenium.

The FT-IR spectra of water-soluble additives (Fig. 1-D) revealed intense absorption bands at 1110 cm^{-1} (O–C–O stretching), and less intense peaks at 2880 cm^{-1} (CH stretching), 1511 cm^{-1} (C=C ring stretching), and 1349 cm^{-1} (CH bending) due to the presence of a nonionic alkylphenol ethoxylate surfactant [33]. In addition to that, in the two samples featuring inorganic pigments (LI 29 and LI 108), a strong band at 1550 cm^{-1} is probably due to a pigment dispersant, such as sodium polyacrylate [36].

The analyses performed on the commercial paints confirmed their acrylic nature and the presence of several water-soluble additives in the dried films, i.e., mainly nonionic surfactants and water-soluble polymers in agreement with numerous studies in the literature [10,11,15], which make them very sensitive to the action of water and polar organic solvents. Therefore, any cleaning action carried out on these materials with aqueous systems has to be very carefully controlled in order to minimize possible damages to the paint film, and, subsequently, to the artwork [14,15]

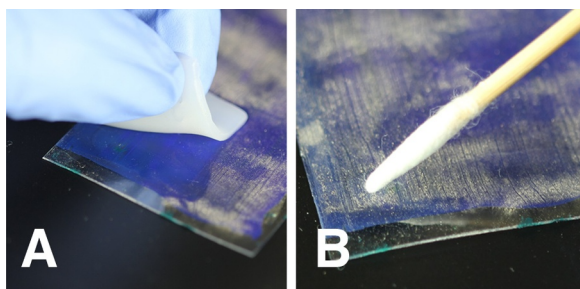


Fig. 2. Cleaning tests on the blue acrylic paint covered with artificial soil: (A) PVA-based cryogel. (B) Cotton swab. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Cleaning tests using novel cryogels

According to the results of the selected commercial paints characterization, soil removal tests conducted with PVA-based cryogels were performed with the aim of finding the optimum compromise between a good cleaning and minimum stress for the paint film. To this aim, the cryogels application time was tuned, through some preliminary testing, and the final protocol was set up, as reported in Section 2.4. PVA-based cryogels are elastic and flexible films of about 2 mm of thickness (see Fig. 2-A). Once loaded with the cleaning solution, the film can be cut with scissors to the desired size and shape, and applied on the surface to be cleaned. Before application, the gel is dried with blotting paper to remove the surface excess water, in order to have a real control on the wetting rate of the treated surface. After the application, the cryogel can be removed in a simple way, by peeling it off using tweezers or hands, if possible. A final rinse is carried out with a rinse solution-loaded hydrogel, placed on the same area for 30 s. It is worth pointing out that rinsing is only necessary to remove possible residues from the cleaning solution loaded into the gel, rather than gel residues, as in the case of “traditional” physical gels [38–40]. The rinsing step is usually performed using cryogels loaded with non-buffered water. However, in this case, we decided to follow the MCP guidelines, which suggest, for the rinsing step, using water adjusted at the same pH of the cleaning solution.

The two aqueous cleaning solutions, described in the experimental section, were tested using cryogels, and the most effective system (selected by visual assessment) for each sample was chosen for further investigations. In fact, depending on the colors and the cleaning methods, a slightly different behavior was observed using the SA or the SB solutions. As said, cotton swabs soaked in the same cleaning solutions were used as a reference cleaning method (Fig. 2-B).

As expected, the soling of the acrylic paint films significantly altered the FTIR spectrum of the surfaces, as shown in Fig. 3-A. The spectra of the red acrylic film cleaned with cotton swabs (cleaned-S) is indeed very similar to the soiled one, indicating that soil removal was incomplete. On the other hand, the spectrum of the sample cleaned with the cryogel (cleaned-C) is similar to the pristine one, as the result of a good cleaning action. In particular, in both spectra, a doublet at 1359 cm^{-1} and 1343 cm^{-1} , and a strong peak at 1114 cm^{-1} are visible, as indicated by dashed lines in Fig. 3-A. These peaks can be ascribed to a non-ionic alkylphenol ethoxylate surfactant, as previously indicated [34]. The presence of these peaks is likely to indicate that the cryogel, loaded with the MCP solution, did not alter the original composition of the paint layer. In principle, scarcely retentive confining matrices could cause partial solubilization of surfactants and their extraction from the bulk up to the surface. In this case, because PVA-based cryogels have good retentiveness [20,21], we expect the cleaning action to be limited at the gel-paint interface. Further studies could be conducted to investigate possible changes at the surface of acrylic paint films during the application of the cryogel.

Fig. 3-B shows SEM micrographs taken on some significant areas of the pristine, soiled and treated samples. The surface of the pristine sample appears homogeneous and compact, while the soiled sample is visibly covered with soil particles and crystals. Looking at the comparison between the two bottom images, i.e., taken after the cleaning tests, it is easily noticeable that the use of cotton swabs only leads to a partial removal of the soil (cleaned-S), while the original visual aspect of the surface is almost completely recovered when using the PVA-cryogel (cleaned-C). A noteworthy consideration is due: a complete cleaning could be possibly obtained even with cotton swabs, but at the price of a more energetic mechanical action, which would have eventually led to severe damages of the delicate paint film surface. In fact, an alteration of the surface morphology is induced even in the mild conditions adopted for soil removal tests, where only a gentle rolling over the surface was carried out, trying to avoid scratches or any mechanical stress for the paint layer. This was easily detected due to the paint residues remaining on the cotton swab after rolling.

More in detail, AFM was used to evaluate the roughness of the surface in pristine samples before and after the application of cryogels and cotton swabs. The results showed a major change in the roughness of the paint surface after the use of cotton swabs. For instance, the profile roughness parameter of the green mockups showed a decrease of 46% after rolling (R_q of cleaned-S = 47.2 nm ; R_q of pristine sample = 25.5 nm), while slighter changes of just 31% decrease were observed after the application of the cryogels (R_q of cleaned-C = 201 nm ; R_q of pristine sample = 295 nm).

This result is consistent with previous studies [37], which reported that cleaning operations using gels are usually safer than those performed with cotton swabs, which are more prone to cause mechanical stresses to the acrylic paint surface.

3.3. Gel residues evaluation

The main issue connected to the use of traditional gels for cleaning purposes resides in the fact that their formulation includes non-volatile substances (mainly polymers, used as thickeners), which may remain as residues on the treated surfaces. In particular, physical gels, owing to fact that cohesion forces (between different parts of the gel) and adhesion forces (between the gel and the surface) are of the same order of magnitude, are likely to leave residues on the work of art after cleaning [38–40]. Therefore, a systematic analysis of possible residues over the cleaned areas was performed by comparing the performances of the novel cryogels and Velvessil Plus®, chosen as a reference physical gel, which has recently gained some significant attention among conservators and restorers. The surface of the acrylic paint was investigated by ATR-FTIR after cleaning it with both the gels, and the spectra were compared with the ones of neat PVA (the main component of the cryogel) and Velvessil Plus® (see Fig. 4). As can be seen in Fig. 4-A, the PVA spectrum shows several intense peaks in the investigated range, including the signals at 1737 cm^{-1} (C=O stretching, PVAc groups in PVA), 1437 cm^{-1} (CH_2 scissoring), 1374 cm^{-1} (CH_2 deformation), 1245 cm^{-1} (CH deformation), and 1088 cm^{-1} (C–O stretching) [41]. None of these peaks is present in the spectrum of the sample cleaned with the cryogel.

On the other hand, as shown in Fig. 4-B, the ATR-FTIR spectrum of the paint film cleaned with Velvessil Plus® displays a sharp peak located at 1260 cm^{-1} and a broad signal centered at 800 cm^{-1} that are not present in the pristine sample. These absorption bands are probably due to the symmetric bending of the Si- CH_3 group and to the methyl rocking mode of a silicon atom bonded to two methyl groups [42,43], indicating the presence of Velvessil Plus® residues over the cleaned surface, as already reported in the literature [44].

In order to map Velvessil Plus® residues on a treated area, 2D FTIR Imaging was carried out in reflectance mode using an FPA detector. This set up was selected as it allows discriminating compounds with different chemical composition than the substrate down to a spatial

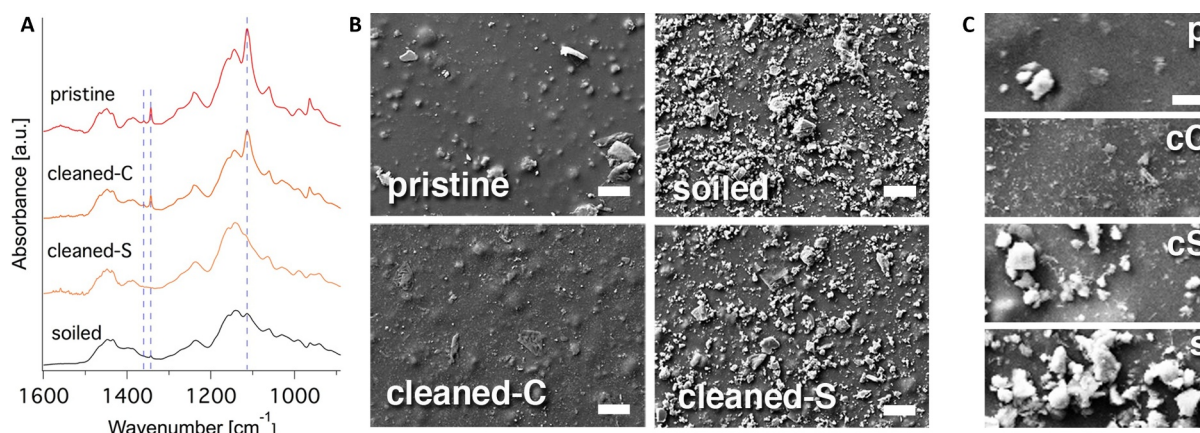


Fig. 3. (A) ATR-FTIR spectra of the red acrylic paint, before and after the cleaning tests. Dashed lines indicate the absorptions bands of polyethoxylated surfactant at 1359 cm^{-1} , 1343 cm^{-1} , and 1114 cm^{-1} . (B) SEM images (magnification $1000\times$) taken on the green acrylic paint before and after soil removal tests. The scale bar is $30\text{ }\mu\text{m}$. (C) SEM images (magnification $4000\times$) of the green acrylic paint before and after soil removal tests. The scale bar is $7.5\text{ }\mu\text{m}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

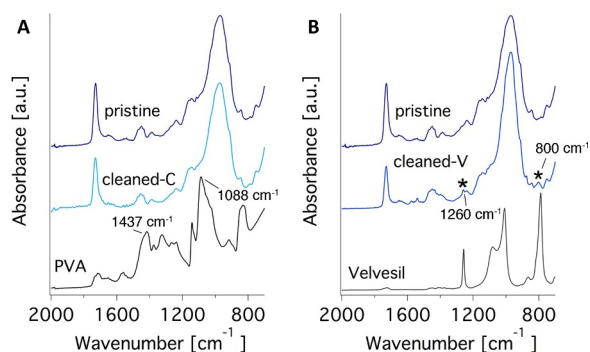
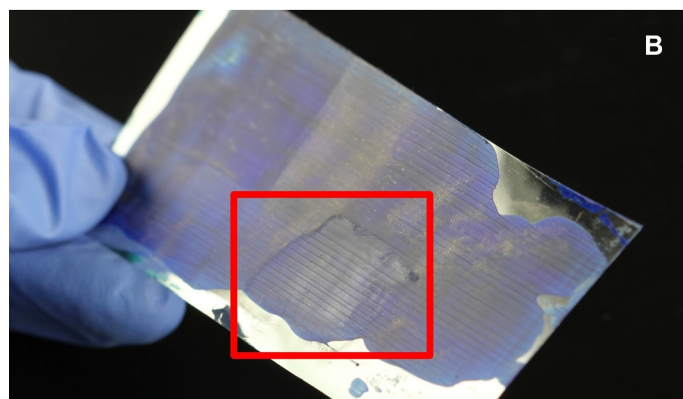
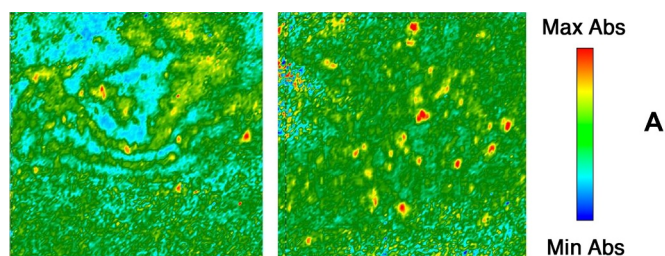


Fig. 4. ATR-FTIR spectra of the blue acrylic paint. (A) A comparison between the pristine paint film, the sample cleaned with the cryogel (cleaned-C) and PVA, which is the main component of cryogel. (B) A comparison between the pristine paint film, the paint film surface cleaned with Vesvelil Plus® (cleaned-V) and Vesvelil Plus®. Stars indicate the two peaks due to Vesvelil Plus® residues after cleaning operations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



resolution of few microns [45].

The mapping of the Si-CH₃ symmetric bending (about $1250\text{--}1260\text{ cm}^{-1}$) showed the presence of significant residues due to Vesvelil Plus® on the cleaned paint films, as can be seen in Fig. 5-A. The two maps show the presence of a siloxane compound (i.e., likely, gel residues), distributed over the analyzed surface. Changes in the acrylic paint layer due to the cleaning with Vesvelil Plus® are visible to the naked eye. In fact, as highlighted by the red square in Fig. 5-B, the area treated with Vesvelil Plus® and rinsed with cyclomethicone D5 exhibits a glossy finish altering the original visual aspect of paint film. It is worth noting that the conservation profession is still optimizing clearance for these silicone materials, and that the aforementioned KSG-350 z® (Shin Etsu Chemical, Japan) [26] has recently replaced Vesvelil Plus® in the conservation practice, even though the latter is still available on the market.

The evaluation of possible gels' residues left over the treated surface after cleaning confirms one of the main drawbacks of standard physical gels, such as the Vesvelil Plus®, i.e., the presence of residues. On the other hand, it shows that, even if PVA-based cryogels are physical gels, they behave as chemical gels, in the sense that they tend to not leave

Fig. 5. (A) 2D FTIR Imaging of the blue acrylic paint cleaned with Vesvelil Plus®. Maps were obtained mapping the peak located at $1260\text{--}1250\text{ cm}^{-1}$, corresponding to the symmetric bending of Si-CH₃ group. Each map measures about $700 \times 700\text{ }\mu\text{m}^2$. (B) The visual aspect of the paint surface after cleaning operation with Vesvelil Plus® (including the final rinse with cyclomethicone D5). The picture was taken several weeks after cleaning tests.

residues on the treated surfaces. This means that the energy of the bonds formed during the freezing/thawing cycles is high enough to overcome the adhesion forces that make the gel stick to solid surfaces.

4. Conclusions

In this work three commercial paints were firstly selected and characterized by means of FT-IR and Py-GC-MS, which show the presence of a poly n-butyl acrylate/methyl methacrylate copolymer as the binder for all the selected colors. A novel cryogel, recently developed for the cleaning of water-sensitive artistic surfaces, was then tested for the removal of artificial soil from the selected acrylic paints. The aqueous cleaning solutions, prepared according to the MCP, were loaded into the cryogels by immersion. The soil removal effectiveness of cryogels was assessed and compared to that of cotton swabs, traditionally used in conservation practice, by means of ATR-FTIR, SEM, and AFM investigations. The overall results showed that cryogels are able to clean in a more efficient and safer way than the selected traditional method. The mechanical action that can be applied by using cotton swabs without significantly harming the treated paint surface is not enough to completely remove the soil. Nonetheless, even the sole gentle rolling of swabs on the paint surface induces morphological changes, which are detectable via AFM, and represent an unacceptable damage of the paint layer. Finally, the possible presence of gel residues after the cleaning with novel cryogels and Velvessil Plus® was investigated by means of FTIR measurements. The results clearly showed that siloxane residues are found in the area treated with Velvessil Plus®, while the cleaning with cryogels is residue-free. This means that, even if the PVA-based cryogels are also physical gels, their intra-network cohesion forces are strong enough to grant that no polymer macromolecules are detectable on the treated surfaces after the application. In conclusion, we demonstrated that cryogels may grant a safe, satisfactory, and residue-free soil removal from acrylic paint films, overcoming some of the main drawbacks of commonly-used cleaning methods.

Funding

This project was partly supported by the EU Project NANORESTART (H2020-NMP-21-2014/646063), by the UniPredoctoral grant of the Basque Government, by the Erasmus+ grant, and also by the Cátedra UNESCO de Paisajes Culturales y Patrimonio mobility grant.

CRedit authorship contribution statement

Irene Cardaba: Conceptualization, Formal analysis, Writing - review & editing. **Giovanna Poggi:** Conceptualization, Formal analysis, Writing - review & editing. **Michele Baglioni:** Conceptualization, Formal analysis, Writing - review & editing. **David Chelazzi:** Conceptualization, Formal analysis, Writing - review & editing. **Itxaso Maguregui:** Conceptualization, Formal analysis, Writing - review & editing. **Rodorigo Giorgi:** Conceptualization, Formal analysis, Writing - review & editing.

Declaration of Competing Interest

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript

Acknowledgments

Dr. Luis Bartolomé of SGiker (Servicios Generales de Investigación) of the University of the Basque Country, is acknowledged for the py-GC-MS analysis. Dr. Nicole Bonelli is gratefully thanked for her precious support during the experimental part. The partnership of the NANORESTART project is acknowledged for the fruitful discussion

References

- [1] B.H. Stuart, *Analytical Techniques in Materials Conservation*, John Wiley & Sons, Ltd, Chichester, UK, 2007.
- [2] C. Lamb, *Acrylics: new material, new problems*, *Conserv. Mod. Paint. Introd. Notes Pap. to Be Present.* United Kingdom Institute for Conservation (UKIC) and Tate Gallery, London, UK, 1982, pp. 4–6.
- [3] L. Pomerantz, D.C. Goist, R.L. Feller, *Conservators advise artists*, *Art J.* 37 (1977) 34.
- [4] R.G. Lodge, *A history of synthetic painting media with special reference to commercial materials*, *Am. Inst. Conserv. Hist. Artist. Work. Prepr. Pap. Present. Sixth Annu. Meet.* New Orleans, Louisiana, June 1–5, 1988, 1988, pp. 118–127.
- [5] R.A. Perry, *Problems of dirt accumulation and its removal from unvarnished paintings: a practical review*, *Dirt Pict. Separated Pap. given a Conf. Held Jointly by UKIC Tate Gall. January 1990*, The United Kingdom Institute of Conservation, 1990, pp. 3–6.
- [6] E. Jablonski, T. Learner, J. Hayes, M. Golden, *Conservation concerns for acrylic emulsion paints*, *Stud. Conserv.* 48 (2003) 3–12.
- [7] A. Murray, C.C. de Berenfeld, S.Y.S.Y.S. Chang, E. Jablonski, T. Klein, M.C. Riggs, et al., *The condition and cleaning of acrylic emulsion paintings*, *MRS Proc.* 712 (2002) III.4.
- [8] B.A. Ormsby, T. Learner, *The effects of surface cleaning on acrylic emulsion paintings – a preliminary investigation*, *Surf. Clean. – Mater. Methods* (2006) 135–149.
- [9] S. Zumbühl, F. Attanasio, N.C. Scherrer, W. Müller, N. Fenners, W. Caseri, *Solvent action on dispersion paint systems and the influence on the morphology: changes and destruction of the latex microstructure*, *Mod. Paint. Uncovered Proc. from Mod. Paint. Uncovered Symp.* 2007, pp. 257–268.
- [10] B. Ormsby, T. Learner, G.M. Foster, J. Druzik, M. Schilling, *Wet-cleaning acrylic emulsion paint films: an evaluation of physical, chemical and optical changes*, *Mod. Paint. Uncovered Symp.* 2007, pp. 189–200.
- [11] B. Ormsby, T. Learner, *The effects of wet surface cleaning treatments on acrylic emulsion artists' paints – a review of recent scientific research*, *Stud. Conserv.* 54 (2009) 29–41.
- [12] D. Keynan, A. Hughes, *Testing the waters: new technical applications for the cleaning of acrylic paint films and paper supports*, *B. Pap. Gr. Annu.* 32 (2013) 43–51.
- [13] C. Stavroudis, T. Doherty, *The modular cleaning program in practice: application to acrylic paintings*, in: M.F. Mecklenburg, A.E. Charola, R.J. Koestle (Eds.), *New Insights into Clean. Paint. Proc. from Clean. 2010 Int. Conf. Univ. Politec. Val. Museum Conserv. Inst. Washington, D.C., Smithsonian Institution*, 2013, pp. 139–145.
- [14] E. Kampakali, B. Ormsby, A. Cosentino, C. Miliani, T. Learner, *A preliminary evaluation of the surfaces of acrylic emulsion paint films and the effects of wet-cleaning treatment by atomic force microscopy (AFM)*, *Stud. Conserv.* 56 (2011) 216–230.
- [15] C.E. Dillon, A.F. Lagalante, R.C. Wolbers, *Acrylic emulsion paint films: the effect of solution pH, conductivity, and ionic strength on film swelling and surfactant removal*, *Stud. Conserv.* 59 (2014) 52–62.
- [16] J.A.L. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, *Innovative hydrogels based on semi-interpenetrating p(HEMA)/PVP networks for the cleaning of water-sensitive cultural heritage artifacts*, *Langmuir* 29 (2013) 2746–2755.
- [17] J. Domingues, N. Bonelli, R. Giorgi, P. Baglioni, *Chemical semi-IPN hydrogels for the removal of adhesives from canvas paintings*, *Appl. Phys. A.* 114 (2013) 705–710.
- [18] M. Baglioni, A. Bartoletti, L. Bozec, D. Chelazzi, R. Giorgi, M. Odlyha, et al., *Nanomaterials for the cleaning and pH adjustment of vegetable-tanned leather*, *Appl. Phys. A.* 122 (2016) 114.
- [19] C. Mazzuca, G. Poggi, N. Bonelli, L. Micheli, P. Baglioni, A. Palleschi, *Innovative chemical gels meet enzymes: a smart combination for cleaning paper artworks*, *J. Colloid Interface Sci.* 502 (2017) 153–164.
- [20] R. Mastrangelo, C. Montis, N. Bonelli, P. Tempesti, P. Baglioni, *Surface cleaning of artworks: structure and dynamics of nanostructured fluids confined in polymeric hydrogel networks*, *Phys. Chem. Chem. Phys.* 19 (2017) 23762–23772.
- [21] N. Bonelli, G. Poggi, D. Chelazzi, R. Giorgi, P. Baglioni, *Poly(vinyl alcohol)/poly(vinyl pyrrolidone) hydrogels for the cleaning of art*, *J. Colloid Interface Sci.* 536 (2019) 339–348.
- [22] B. Ormsby, M. Keefe, A. Phenix, E. von Aderkas, T. Learner, C. Tucker, *Mineral spirit-based micro emulsions: a novel cleaning system for painted surfaces*, *JAIC* 55 (2016) 12–32.
- [23] C. Stavroudis, *More from CAPS3: surfactants, silicone-based solvents and micro-emulsions*, *News. (Western Assoc. Art Conserv)* 34 (2012) 24–27.
- [24] A.F. Lagalante, R. Wolbers, A.F. Lagalante, *The cleaning of acrylic paintings: new particle-based water-in-oil emulsifiers*, *Dall'Olio All'Acilico, Dall'Impressionismo All'Arte Contemp.* Il Prato, Padova, 2016, pp. 107–114.
- [25] C. Stavroudis, *Silicone-based solvents in conservation. As free solvents and components of gel systems and microemulsions*, *Dall'Olio All'Acilico, Dall'Impressionismo All'Arte Contemp.* Il Prato, Padova, 2016, pp. 176–184.
- [26] L. Angelova, B. Ormsby, J.H. Townsend, R. Wolbers, *Gel in the Conservation of Art* (2017).
- [27] B. Ormsby, A. Soldano, M.H. Keefe, A. Phenix, T. Learner, *An empirical evaluation of a range of cleaning agents for removing dirt from artists' acrylic emulsion paints removing*, *AIC Paint. Spec. Gr. Postprints*, 2013, pp. 77–87.
- [28] C. Stavroudis, *MCP Recipes - Technical Notes*, (2013).
- [29] A. Phenix, T. Learner, M.H. Keefe, B.A. Ormsby, *Evaluation of cleaning agents for*

- artists' acrylic paints with the aid of high-throughput (HTP) testing, *Paint. Spec. Gr.*, Milwaukee, Wis, 2010.
- [30] P. Schossler, I. Fortes, J.C.D. de, F. Júnior, F. Carazza, L.A.C. Souza, Acrylic and vinyl resins identification by pyrolysis-gas chromatography/mass spectrometry: a study of cases in modern art conservation, *Anal. Lett.* 46 (2013) 1869–1884.
- [31] D. Scalarone, O. Chiantore, Separation techniques for the analysis of artists' acrylic emulsion paints, *J. Sep. Sci.* 27 (2004) 263–274.
- [32] T. Learner, The analysis of synthetic paints by pyrolysis–gas chromatography–mass spectrometry (PyGCMS), *Stud. Conserv* 46 (2001) 225–241.
- [33] V. Pintus, S. Wei, M. Schreiner, UV ageing studies: evaluation of lightfastness declarations of commercial acrylic paints, *Anal. Bioanal. Chem.* 402 (2012) 1567–1584.
- [34] M. Melchiorre Di Crescenzo, E. Zendri, C. Miliani, F. Rosi, A preliminary FTIR-based exploration of the surfactant phase-separation process in contemporary mural paintings, *E-Preservation Sci.* 10 (2013) 10–18.
- [35] D.O. Hummel, *Atlas of Plastics Additives*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2002.
- [36] B.A. Ormsby, E. Kampsakali, C. Miliani, T. Learner, An FTIR-based exploration of the effects of wet cleaning treatments on artists' acrylic emulsion paint films, *E Preserv. Sci* 6 (2009) 186–195.
- [37] T.T. Duncan, B.H. Berrie, R.G. Weiss, A comparison between gel and swab cleaning: physical changes to delicate surfaces, in: L.V. Angelova, B. Ormsby, J. Townsend, R. Wolbers (Eds.), *Gels Conserv. Art*, Archetype Publications, London, UK, 2017, pp. 250–256.
- [38] A. Burnstock, R. White, A preliminary assessment of the aging/degradation of Ethomeen C-12 residues from solvent gel formulations and their potential for inducing changes in resinous paint media, *Tradit. Innov. Adv. Conserv. Contrib. to Melb. Congr.* 10–14 Oct. 2000, Melbourne (AUS), ICC, 2000, p. 38.
- [39] D. Stulik, D. Miller, H. Khanjian, N. Khandekar, R. Wolbers, J. Carlson, et al., Solvent gels for the cleaning of works of art: the residue question, *The Getty Conservation Institute - J. Paul Getty Trust*, Los Angeles, USA, CA, USA, 2004.
- [40] A. Casoli, Z. Di Diego, C. Isca, Cleaning painted surfaces: evaluation of leaching phenomenon induced by solvents applied for the removal of gel residues, *Environ. Sci. Pollut. Res.* 21 (2014) 13252–13263.
- [41] E.F. dos Reis, F.S. Campos, A.P. Lage, R.C. Leite, L.G. Heneine, W.L. Vasconcelos, et al., Synthesis and characterization of poly (vinyl alcohol) hydrogels and hybrids for rMPB70 protein adsorption, *Mater. Res.* 9 (2006) 185–191.
- [42] A.L. Smith, *The Analytical Chemistry of Silicones*, Wiley, New York, NY, 1991.
- [43] B.C. Smith, *Infrared Spectral Interpretation: A Systematic Approach*, CRC Press, Boca Raton, 1999.
- [44] B. Ormsby, J. Youn Chung, A. Burnstock, K. Jan van der Berg, J. Lee, An Investigation of Options for Surface Cleaning Unvarnished Water Sensitive Oil Paints Based on Recent Developments for Acrylic Paints, *ICOM-CC*, 2017.
- [45] A. Cincinelli, C. Scopetani, D. Chelazzi, E. Lombardini, T. Martellini, A. Katsoyiannis, et al., Microplastic in the surface waters of the Ross Sea (Antarctica): occurrence, distribution and characterization by FTIR, *Chemosphere* 175 (2017) 391–400.