



Original article

Extension study of the assessment of aqueous cleaning on nBA/MMA and EA/MMA acrylic paints

Irene Cardaba*, Itxaso Maguregui

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

ARTICLE INFO

Article history:

Received 12 October 2022

Accepted 12 March 2024

Keywords:

Cleaning

Cryogels

Acrylic paints

Titan

Hyplar

Thermogravimetry

ABSTRACT

Acrylic paints became popular among artists in the late 50's. Some of the main conservation issues of these paints are inherent to their composition characteristics, for instance, their high sensitivity to water and a wide range of polar solvents. This makes difficult to establish an accurate and respectful cleaning treatment for this kind of artworks. As reported on previous studies, the application of pH and conductivity adjusted solutions using accurate methods, such as confined on chemical gels, improved this kind of procedures.

The aim of this work is to extend a previous study where the effect of water based cleaning treatments was tested on Liquitex acrylic paint mock-ups, and deepen on evaluating the alterations both on the surface and in the bulk of the paint film. In this paper, six acrylic commercial paints of two widely used paint brands, Titan Arts – Acrílico extrafino (Spain) and Hyplar Acrylic Colors® (USA), were selected to compare the effect of the cleaning treatment on their surface and binder matrix. Samples were prepared using Mylar sheets and left to dry in a dark and dust-free environment for three years. Adjusted water solutions were applied both using cotton swab and cryogels for comparison. Paints were characterized using Fourier Transform Infrared spectroscopy (FT-IR), pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS), Thermogravimetric Analysis (TGA) and Atomic Force Microscope (AFM).

All the samples showed different reaction to cleaning according to their different composition. This study revealed that those paint films where most surface alterations are observed after cleaning, are not those that suffer greater changes in the binder matrix.

Moreover, a set of samples was aged under accelerated conditions (solar radiation under controlled temperature and humidity). The accelerated ageing was carried out under isochronous sampling up to a maximum of 1426 h. This tests revealed certain degradation processes such as chain scission of the binder that coincide with those alterations observed in several mock-ups after application of the cleaning treatment.

© 2024 The Authors. Published by Elsevier Masson SAS on behalf of Consiglio Nazionale delle Ricerche (CNR).

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

Introduction

Acrylic paints have been widely used by contemporary artists since they were first introduced in 1927 as acrylic organic solvent solutions [1]. At the beginning they were developed as house paints, until late 1940s when the first acrylic solution artist paints were marketed under the name of Magna [2]. Many artists such as Rothko, De Kooning or Kenneth Noland used these paints for their artworks. Acrylic emulsion paints were introduced in 1953 by Rohn

and Haas facilitating the handling of the paint since they were water soluble. Thus, they quickly became the most popular medium among artists. Since then, numerous formulations have been incorporated into the market. To date, paint makers have constantly varied the paint formulations in order to improve their performance.

Acrylic emulsion paint is a mixture of dyes or pigments dispersed on an acrylic binder, together with a large amount of additives such as, emulsifiers, biocides, buffers and fillers [3], which dry through coalescence. The binder used in these paints is an acrylic copolymer made out of a hard acrylate such as methyl methacrylate (MMA) and a softer acrylate such as ethyl acrylate (EA) or n-butyl acrylate (nBA). Ethyl acrylate (EA) was employed as soft monomer in the earlier formulations, EA/MMA copolymer.

* Corresponding author.

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

However, since the end of the 1980s many of the resin formulations have changed to a poly (n-butyl acrylate/methyl methacrylate) copolymer, p(nBA/MMA) [4,5]. According to other studies, nBA is more flexible than EA, thus reducing the need to add large amount of plasticizers to the paint formulation [5,6]. In consequence, the resulting film formed by butyl acrylate copolymers tends to be slightly tougher and more hydrophobic than ethyl acrylate copolymers, which makes them more stable to outdoor conditions [3]. These paints contain an amount of stabilizing additives, each providing its function and contributing to the complexity of such a multi-component system. For instance, non-ionic PEO-based surfactants, which are the most abundant type detected on acrylic emulsion paints [4].

The film formation process starts with the paint in liquid form, where the acrylic polymer droplets are suspended within the water phase. During evaporation of the water phase, the polymer particles meld to form a 'honeycomb' network, finally forming a continuous film. The film formation degree can vary depending on a number of factors: ambient conditions during drying, the glass transition temperature (T_g) of the paint film, the minimum film formation temperature (MFFT), the modulus of elasticity and viscosity of the resin, as well as the type of additives that are present – all of which can affect the porosity of the final film [4].

Surfactants can be distributed quite unevenly across the paint film after drying. Long chain surfactants (20–40 PEO units), which are more hydrophilic, tend to move away from the acrylic polymer leading to the formation of local concentrations at the film-air interface and film-substrate interface. On the other hand, the more hydrophobic surfactants (short chain, less than 20 units of PEO) can be dissolved in the acrylic binder and remain trapped between polymer particles, concentrated in pockets creating hydrophilic domains, or localised on the surface of un-coalesced polymer particles [4]. It is also important to point out that surfactant distribution is not static. After drying, surfactants continue to relocate through the paint both exuding to the surface and resorbing inside the film. These movements depend on several factors, such as the film formation conditions, the mobility of the polymer itself or the influence of external factors such as temperature and humidity [7].

A previous publication summarized some of the most relevant outcomes regarding the behavior of acrylic emulsion paints [4]. Among others, some studies revealed that p(EA/MMA) based films had major amounts of surface surfactant regardless of pigment in comparison to p(nBA/MMA) paints [8], pointing out that the quantities of PEO surfactants in these paints may partially depend on the binder emulsion type. The water sensitivity of PEO-based surfactants which can be easily removed from paint surfaces has also been widely demonstrated both using water immersion and by mechanical action. Moreover, the exudation process of surfactants is ongoing, since even after removing some additives after cleaning, new surfactants have been detected on the surface.

Accelerated aging studies revealed that thermal ageing provoke the resorption of surface surfactants back into the bulk of the paint film and re-exude at a faster rate upon storage in ambient conditions [4]. At the same time, a wider study published by Ortiz-Herrero et al. [9], confirmed that the pigment type, copolymer binder and additives that are present of the paint play a crucial role in the aging tendency of the surface. This study, based on accelerated aging mock-ups, proved that there is a decrease in thermal stability of the paint, linked to the aging of the binder, which is attributed to the chain scission of the polymer and is brand dependent. While Titan and Liquitex paint brands (p(nBA/MMA) binder) samples showed a chain scission of the polymer after aging, the binder remained almost unaltered for the Hyplar paint (EA/MMA binder) sample, indicating that, under the same curing conditions, p(EA-MMA) copolymer may be more stable than p(nBA-MMA) in terms of crosslinking binder.

The pigment type also influences the surfactant migration degree, for instance, synthetic organic and iron based pigments contain more amount of dispersant on their composition, unlike cadmium-based colours, which show less presence of additives on their surface [10].

The multiple components of the paint can be heterogeneously distributed along the dried film, leading to variable physical properties and of course determining their aging tendency. The most relevant issues that affect the preservation of the acrylic paint are directly linked to its composition: the different origin of the colorants (organic and inorganic), the usually low glass transition temperature of the acrylic resin, which results in films that are soft at room temperature, the migration to the surface of hydrophilic additives, i.e. surfactants, [11] which make acrylic paint films prone to attract airborne dust and sensitive to water and organic solvents. Water sensitivity of other type of contemporary paints such as oil paints, was also analyzed on previous studies [12]. Those investigations indicate that water sensitivity of the film may be related to several factors such as a low degree of crosslinking of the medium or the type of pigment.

All these aspects should necessarily be considered when raising the cleaning of these type of paint surfaces, aspects that have been widely discussed on previous studies [3-5,13]. Thus, the high swelling capacity [8] of these films and the potential solubilization of additives in the bulk of the film, and their migration to the surface [4,14], makes it difficult for conservators and restores, to treat them without provoking changes in the physic-chemical and mechanical properties of the film [15].

Some authors explored the amount of water extractable material that is present on acrylic paints in order to determine their water-sensitivity during cleaning. For instance, Learner et al. [16] determined that after immersing the acrylic mock-ups for 24 h in water, organic pigment containing paints are those that suffer greater weight losses, concluding that may be due to several factors such as, the pigment solubility itself, the greater medium (water soluble) content needed to strengthen the tint the mixture, more amount of pigment dispersants, as well as the particle size.

Several strategies have been recently developed to tackle the cleaning of water-sensitive artworks. Water solutions with controlled pH and conductivity, have not proven to remove the risk of changes in the acrylic film [17,18]. Nevertheless, previous studies confirmed that the use of cleaning solutions imbibed in gelled systems instead of using the cotton swab is one of the most successful strategies to achieve highly effective and non-invasive cleaning [13,18-19]. However, given the number of variables that determine the behavior of these paints and the influence of the internal structure of the material (coalescence degree), it is necessary to study and compare the effects caused by these treatments at both the surface and internal levels.

A wide range of analysis techniques has been applied to assess the efficacy and side effects of the different cleaning strategies, mainly to study the surface affections of the films [20]. For instance, ATR-FTIR is usually employed to verify the surfactant presence/absence on the paint surface [3,8,10,17,21-24], as well as to identify any organic residue of either the cleaning system [13]. Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) are usually employed to detect morphological changes on the paint surface after cleaning [25-27]. Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS) is used to characterize the organic components by identifying monomer units and thermal degradation products of the paint [9,28-30]. Other methods, such as High Performance Liquid Chromatography/Mass spectrometry (HPLC/MS) or Electrospray Ionisation Mass Spectrometry (ESI-MS) have also been used to identify water extractable materials and Unilateral Nuclear Magnetic Resonance (NMR) to monitor the rate of water penetration into acrylic paint films during cleaning [31].

Thermogravimetric techniques, on the other hand, have been used less frequently to assess the cleaning treatment. In the studies in which this technique has been used, the results served to identify the loss of weight of the volatile and soluble components [16].

Research aim

The aim of this work is to extend our initial study on the use of PVA-based cryogels [13] to the surfaces of paints exhibiting different composition dependent aging behaviour, as pointed out in our previous work [9]. Titan and Hyplar brand paintings were chosen since they have different composition and showed different aging tendency. The main objective is to study how the type of binder and the origin of the pigment affect in terms of selecting the cleaning method and if therefore, we can affirm that cryogels with confined solutions are safe for any acrylic emulsion film, despite its brand and formulation. To do that, changes at the surface level and inside the paint matrix were analysed, to verify the real side effects of the methods under study. For this purpose, same colours (red, blue and green) used in our previous work were selected for comparison. The mockups were naturally aged under indoor and dust free conditions for up to three years.

Moreover, a set of phthalocyanine green samples of both brands were aged under accelerated conditions in order to observe the different aging behaviour of each brand by means of ATR-FTIR. Green organic colour was selected according to bibliography and previous studies which have proven its instability [28]. The acrylic paint characterization as well as the assessment of the effect of the aqueous cleaning were carried out by means of Py-GC-MS, ATR-FTIR and TGA. Thermogravimetric analysis provides interesting results from which novel conclusions can be drawn regarding changes at the internal level of the paint. In this case, not only the quantity of volatile and soluble organic compounds were identified, but also the formation of a new thermal degradation step of the paint was identified after cleaning treatment of some samples. The surface of the paint film was also assessed with Atomic Force Microscopy (AFM).

Materials and methods

Sample preparation and aging

Materials

Glacial acetic acid (99.8–100.5%), sodium hydroxide ($\geq 97.0\%$), ammonium hydroxide solution (33%) and citric acid (99.5%) were all supplied by Sigma Aldrich. 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 Dark Ultramarine Blue (PB 29), Phthalocyanine Titan Dark Green (PG 7) and Cadmium Red Light (PR 108) paints from Titan and Ultramarine Blue (PB 29), Phthalocyanine Green (PG 7) and Naphthol Red (PR 112) from Hyplar®.

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 to dry in a dark and dust-free environment for three years. Tests were carried out after one year and after three years of drying (Table 1).

Accelerated ageing

A set of 19 phthalocyanine green mock-ups of both Titan and Hyplar brands were aged under accelerated conditions. The ageing procedure consisted in exposing the reference paint films ($1 \times 2 \text{ cm}$) to artificial solar radiation under controlled temperature, humidity and irradiance conditions, as reported in a previous

work [20]. A Solarbox 1500e RH equipment (Neurtek Instruments, Spain) was used, with a Xenon Lamp, which provided radiation with wavelengths between 300 and 800 nm and a nominal irradiance of 600 W m^{-2} . The camera was equipped with an indoor 310 nm UV filter and set to a black panel temperature of $55 \text{ }^\circ\text{C}$ and 50% humidity. The accelerated ageing was carried out under isochronous sampling up to a maximum of 1426 h.

Cleaning tests

A pH5 buffered water solution was prepared using Acetic acid and NaOH according to bibliography [32]. The selected aqueous cleaning solution was loaded in the Nanorestore Gels® Peggy that was provided by CSGI. These PVA-based hydrogels are used to perform the cleaning treatment under controlled conditions of water release. The gels were charged with the pH5 water buffer by immersion for 12 h, as described elsewhere [13]. The hydrogels were applied on the paint surfaces for 30 s. Each application was repeated twice, with a 24-hours interval between applications.

As a comparative reference method, cotton swabs, soaked in the same cleaning solution, were also used in soil removal tests. Cotton swabs were gently rolled for 10 s over the paint film, three times.

Analytical techniques

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 $150 \mu\text{m}^2$. The spectra were obtained from 128 scans with 2 cm^{-1} of optical resolution over the range of $4000\text{--}650 \text{ cm}^{-1}$.

Pyrolysis - gas chromatography - mass spectrometry

Pyrolysis - gas chromatography - mass spectrometry was carried out on dried pristine acrylic paints ($10\text{--}20 \mu\text{g}$) 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 ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) capillary column. Pyrolysis was performed at $600 \text{ }^\circ\text{C}$ [33–34]. The pyrolyser interface and injector were set at $300 \text{ }^\circ\text{C}$. The gas chromatography column temperature program used is the following: initial temperature $40 \text{ }^\circ\text{C}$, hold for 2 min, followed by an increase of $12 \text{ }^\circ\text{C}/\text{min}$ up to $250 \text{ }^\circ\text{C}$, hold for 10 min. The helium gas (99,999%) flow was set at $1.7 \text{ mL}\cdot\text{min}^{-1}$ 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 $230 \text{ }^\circ\text{C}$ and quadrupole at $150 \text{ }^\circ\text{C}$. Analyzed micro-samples were weighed using a Sartorius SE2 10^{-7} g micro-balance (Sartorius Stedim Biotech, Germany).

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 of 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

Table 1
Identification and description of paint mock-ups.

| ID. Sample | Paint brand | Pigment |
|------------|---|-----------------------------|
| TI 29 | Titan Arts – Acrílico extrafino (Spain) | Ultramarine Blue (PB 29) |
| TI 108 | Titan Arts – Acrílico extrafino (Spain) | Cadmium Red (PR 108) |
| TI 7 | Titan Arts – Acrílico extrafino (Spain) | Phthalocyanine green (PG 7) |
| HY 29 | Hyplar Acrylic Colors® (USA) | Ultramarine Blue (PB 29) |
| HY 112 | Hyplar Acrylic Colors® (USA) | Naphthol Red (PR 112) |
| HY 7 | Hyplar Acrylic Colors® (USA) | Phthalo Green (PG 7) |

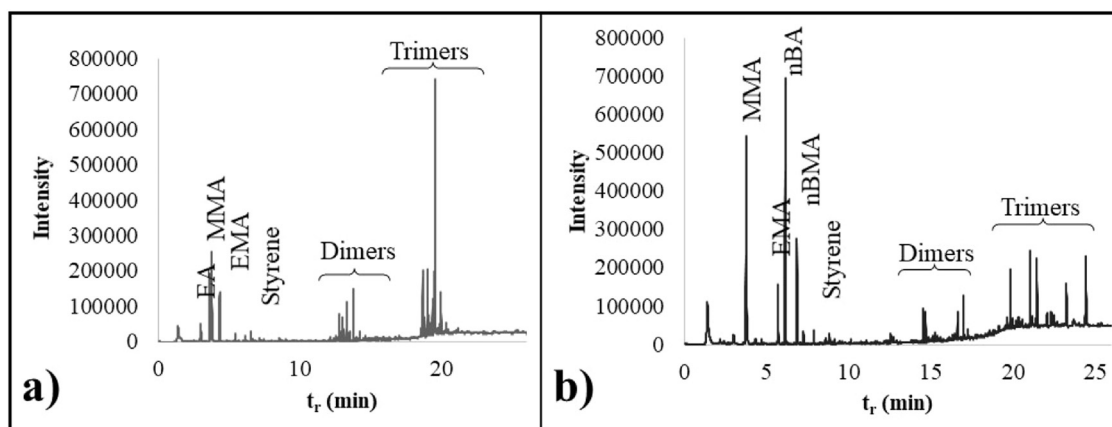


Fig. 1. Py-GC identification of Hyplar phthalocyanine green paint (a) and Titan phthalocyanine green paint (b).

across the surface of the paint with the aid of a piezoelectric z-scanner. Images of $10 \times 10 \mu\text{m}^2$ 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.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a sample is heated at a constant rate. This technique can analyse materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture) [35].

The thermal behavior of the investigated acrylic paint films was studied by means of thermogravimetry (TGA-DTG), using a SDT Q600 (TA Instruments) apparatus. Sample masses ranging from 5 to 10 mg were heated from 20 to 500 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

Results and discussion

Characterization of acrylic paints

Acrylic paint binders were characterized by means of Py-GC-MS see Fig. 1a and b. Results for Titan acrylic samples showed the presence of nBA-MMA polymer while for Hyplar paint mock-ups EA-MMA co-polymer was detected. Most characteristic peaks found in Titan are those related to the monomers methyl methacrylate (MMA) at RT 3.79 (m/z 39, 41, 69, 100) and n-butyl acrylate at 6.18 (m/z 55, 56, 73). Moreover, dimers (nBA-MMA, m/z 112 at 14.69 t_r ; nBA-nBA, m/z 127 at t_r 16.98), and trimers (nBA-nBA-MMA, m/z 195 at 21.07 t_r ; nBA-nBA-MMA, m/z 195 at 21.48 t_r ; nBA-MMA-nBA m/z 228 at 23.26 t_r and nBA-nBA-nBA m/z 181 at 24.46 t_r) derived from the pyrolysis products of both monomers were detected [33].

Hyplar® paint, however, revealed the presence of a different copolymer whose main peaks correspond to MMA and ethyl acrylate (EA), which was identified at RT 3.63 min (m/z 27, 55 and 56) (Fig. 1). Ethyl methacrylate (EMA) at RT 4.33 min (m/z 39, 41 and 69) was observed as a pyrolysis product of EA. In addition to the peaks of the polymer monomers, the pyrogram of the acrylic binder is also characterized by the formation of sesquimers, dimers and trimers at higher RTs: EA-MMA sesquimer, EA-MMA dimer, EA sesquimer, EA-EA dimer, two isomers of EA-EA-MMA trimer and EA-EA-EA trimer [20].

Paint additives were also detected in all the samples. As published on previous studies, the presence of non-ionic PEO type surfactant was identified in both brands according to the detection of P-tert-octylphenol [9]. This compound is associated to the pyrolysis products of the alkylaryl poly(ethoxylated) type surfactant (octylphenyl PEO).

Methacrylic acid and acrylic acid were also detected in both brands, attributed to peaks with m/z 86 and 72 respectively. These acids are used in the polymerization process to increase the mechanical stability of the acrylic binder and reduce the surfactant content [33].

Py-GC-MS results are consistent with those obtained by ATR-FITR. As shown in figure Fig. 2, Titan samples show an intense absorption band at 1730 cm^{-1} (carbonyl stretching). 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 [20]. However, nBA/MMA medium shows two peaks at 2960 and 2877 cm^{-1} and a shoulder at 2940 cm^{-1} .

In Hyplar samples two peaks characteristic of acrylic resins were identified: a strong and sharp absorption at 1725 cm^{-1} that corresponds to the carbonyl ($\text{C}=\text{O}$) stretching vibration, followed by a strong absorption at 1150 cm^{-1} , which is related to the stretching vibration of the ester groups ($\text{C}-\text{C}(=\text{O})-\text{O}-$) [26]. The absorption band at 2954 cm^{-1} followed by a shoulder at 2912 and 2880 cm^{-1} is attributed to C-H bond stretching vibrations of EA-MMA [36].

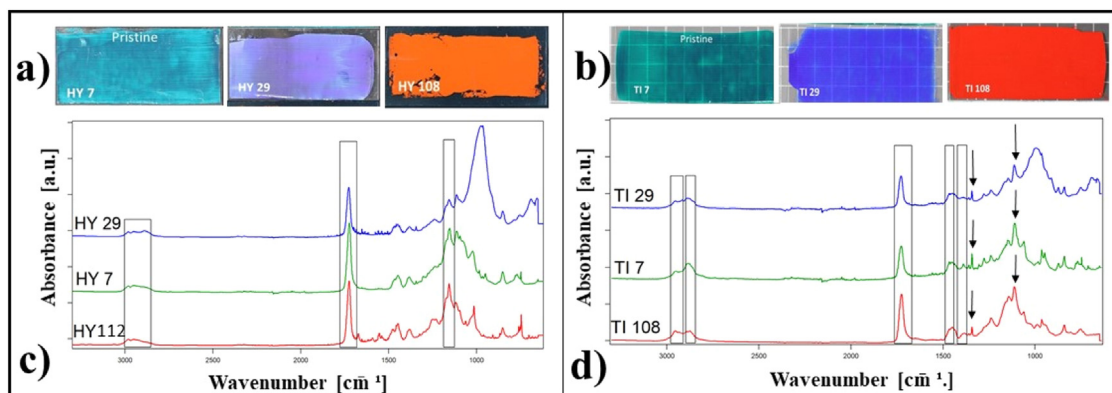


Fig. 2. Pristine Hyplar (a) and pristine Titan (b) paint mock-ups: phthalocyanine green, Ultramarine blue and Naphthol and Cadmium red. ATR-FTIR of pristine acrylic paint mock-ups. Identification of co-polymer signals inside boxes and PEO-type surfactant signals marked with arrows in (c) Hyplar (d) and Titan acrylic paints. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Both acrylic polymers contain two main absorption bands in the area of $900\text{--}1250\text{ cm}^{-1}$ that correspond to C–O stretching/C–C skeletal vibrations. The first is a peak of medium intensity at about 1239 cm^{-1} and the second one is a stronger and broader peak between 1150 cm^{-1} and 1180 cm^{-1} . In this latter region the p(EA-MMA) acrylic resin produces a doublet peak at 1178 and 1162 cm^{-1} , whereas the p(nBA-MMA) acrylic produces a single peak centered at 1170 cm^{-1} , with a shoulder at about 1153 cm^{-1} [36]. In the blue samples, the signals at 3690 cm^{-1} , 3620 cm^{-1} and 970 cm^{-1} correspond to the inorganic ultramarine blue pigment in association with kaolinite [37], while, in green samples, signals at 1389 cm^{-1} , 1305 cm^{-1} , 1211 cm^{-1} , 1155 cm^{-1} and 930 cm^{-1} are characteristic of the phthalocyanine dye [34,38]. As expected, the characteristic IR absorptions of Titan Cadmium Red, are not detected in the investigated spectral range [39]. Furthermore, in the case of Hyplar red samples, the presence of signals at 1554 , 1538 ; $1473\text{--}1457\text{ cm}^{-1}$ could be attributed to the organic Naphthol red pigment.

In the case of Titan paints, the 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) revealed the presence of a nonionic alkylphenol ethoxylate surfactant (PEO type surfactant) [37].

The mass composition of the acrylic films was analyzed using thermogravimetric analysis (TGA). As depicted in Fig. 3, there are mainly three main degradation steps below $400\text{ }^{\circ}\text{C}$ corresponding to the degradation of the different materials that conform the paint film, which has also been confirmed in other studies [40]. All the samples depict a first minimum slope that bears to the loss of water ($<0.25\%$). Between 80 and $280\text{ }^{\circ}\text{C}$, there is slight curve that corresponds to the degradation of the additives present in the paint film (around 6%). Above 280 and below $400\text{ }^{\circ}\text{C}$ the acrylic polymer degrades, and it is at these temperatures where the most remarkable differences between the tested samples were observed, corresponding both to the binder as well as to other organic materials. Thus, inorganic pigment based acrylic samples show a weight loss percentage of around $47\text{--}58\%$ while organic pigment based acrylic samples show a weight loss of around $60\text{--}80\%$. These differences stand for the distinct degradation temperature of the pigments, being the temperature for the organic pigments lower than for the inorganic ones [41]. Moreover, when comparing samples of the same pigment and colour but different brand, Titan paints showed a higher organic material content than Hyplar paints (see Table 2), which may correspond to a greater amount of dispersants in the paint mixture. As expected, cadmium red Titan samples show the highest inorganic residue percentage, corresponding to the pigment itself and other inorganic additives, as well as to the lower dispersant content of cadmium based colours [16].

Table 2

Weight loss percentages in the different ranges of temperature of each acrylic paint mock-up before and after (W) swab cleaning.

| | 0–200 °C | 200–300 °C | 300–450 °C | Residue |
|----------|----------|------------|------------|---------|
| TI 29 | 2433 | 3,46 | 51,73 | 42.3 |
| TI 29 W | 1,79 | 5,24 | 50,12 | 42.2 |
| TI 7 | 0,58 | 4012 | 60,60 | 30.4 |
| TI 7 W | 1,19 | 2,87 | 72,53 | 22.8 |
| TI 108 | 3,11 | 2,12 | 41,78 | 51.5 |
| TI 108 W | 3,45 | 2,62 | 43,30 | 52.3 |
| HY 29 | 1,50 | 1,78 | 47,44 | 48.2 |
| HY29 W | 1,12 | 1,79 | 45,60 | 50.4 |
| HY 7 | 5,21 | 2,13 | 62,64 | 30 |
| HY 7 W | 2,32 | 2,07 | 64,44 | 31.2 |
| HY 112 | 0,94 | 9,44 | 63,57 | 18 |
| HY112 W | 0,42 | 8,68 | 56,01 | 26.5 |

The effect of the cleaning on paint mock-ups. Chemical evaluation of the surface

According to previous works, cleaning acrylic paints with cryogels is safer than using cotton swab [13]. Those studies showed that, samples treated with cryogels maintain the initial surfactant content on the surface after cleaning. However, considering all the different scenarios that could be faced by a conservator when tackling this kind of cleaning procedures, the aforementioned cleaning tests have been wider applied in order to check their feasibility when dealing with different brands and diverse compositions. In this case, samples left to dry for one and three years were alternatively tested. Furthermore, the paint surfaces were also analysed 1 week after applying the treatment in order to observe the mid-short term potential effects of the cleaning treatment after full evaporation of the aqueous cleaning solution.

Therefore, the same cleaning methodology used in previous studies was applied for comparison [13]. A pH 5 aqueous buffer was prepared and charged into the cryogels as described elsewhere. The same application protocol was strictly followed in all cases in order to obtain comparable results. To this aim, cryogels were applied and peeled off from the surface after 30 secs. Swabs, used as comparative reference cleaning method, were soaked on the same cleaning solutions as the cryogels and gently rolled three times, for 10 s each.

ATR-FTIR was the technique of choice to follow up on the presence or absence of absorption bands corresponding to the various materials present in the paint layer before and after applying the cleaning treatment. The ATR-FTIR spectra shown in Fig. 2 could be considered as representative of the whole surface since the small

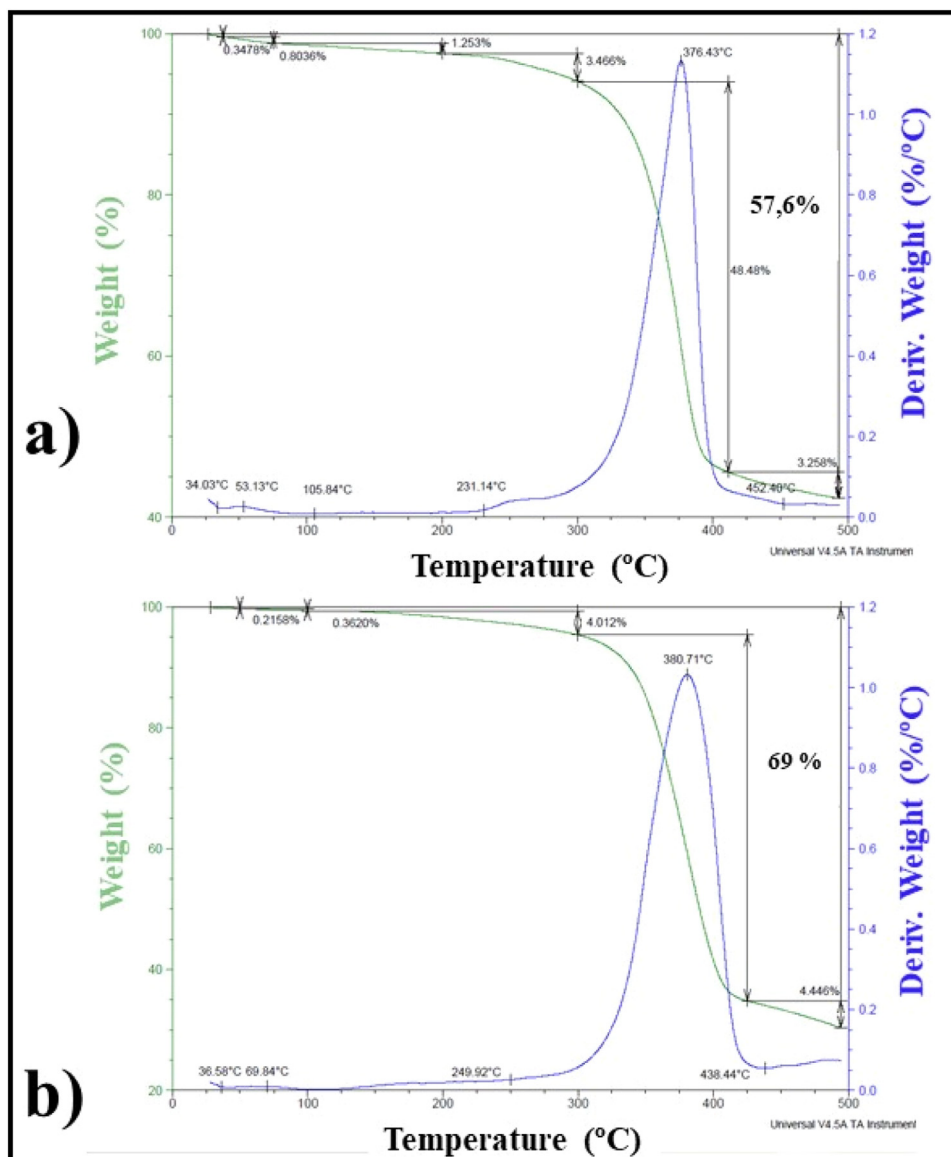


Fig. 3. TGA-DTG of Titan inorganic blue (a) and organic green (b) pristine acrylic paint mock-ups. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

irregularities in the surfactant surface concentrations did not affect the qualitative evaluation of the results. As shown in Fig. 2, one year old Titan pristine untreated paint samples present a great amount of surfactant on the surfaces and as it can be observed on the swab cleaned samples, the bands ascribed to these additives: 2880 cm^{-1} (CH stretching), 1349 cm^{-1} (CH bending) and at 1110 cm^{-1} (O–C–O stretching), nearly disappear after the cleaning procedure Fig. 4. On the contrary, cryogel effect on surfactant removal is not consistent in all the samples. As it can be observed on Fig. 4, the application of gel cleaning on both inorganic red and inorganic blue Titan samples almost completely remove surface surfactants while surfactant signals are still detected on Titan phthalocyanine organic green mock-ups. Further follow up FTIR analysis were performed on the same area of the cleaned surfaces one week after treatment, in order to observe surface behavior in the mid-short term after cleaning. Most of the surfaces remained unaltered one week after cleaning. Red and blue paints, did not show any surface change one week after either gel or swab cleaning treatments. However, results of the green mock-up surfaces revealed the absence of surfactant signal one week after gel cleaning

(Fig. 4d). Slight differences are observed by ATR-FTIR if comparing both methods. Although proven that gels incorporate less moisture than swab cleaning and do not subtract as much surfactant [13], it was observed that on those samples where additives remain on the surface after treatment, they disappear within the following days (Fig. 4d), which can be due to the resorption into the bulk of the film or their complete evaporation.

One year old Hyplar paints show less or none surfactant content on the film surface. This also demonstrates that paint's chemistry depends on the initial formulation. Therefore, since it was not possible to check the effect of cleaning on surfactant removal, Hyplar mock-ups were naturally aged for a longer period and tested after three years, under the same conditions. As shown in Fig. 5a, 3 years old Hyplar samples did show the presence of surfactants on the surface. In this case, both swab and cryogel cleaning resulted in instantaneous removal of surfactants, regardless of the colour. However, ATR-FTIR analysis of the treated area one week after cleaning, revealed the renewed presence of surfactant on the surface of Hyplar red and green mock-ups, unlike in blue colour. Therefore, we could consider that organic colour paints in either

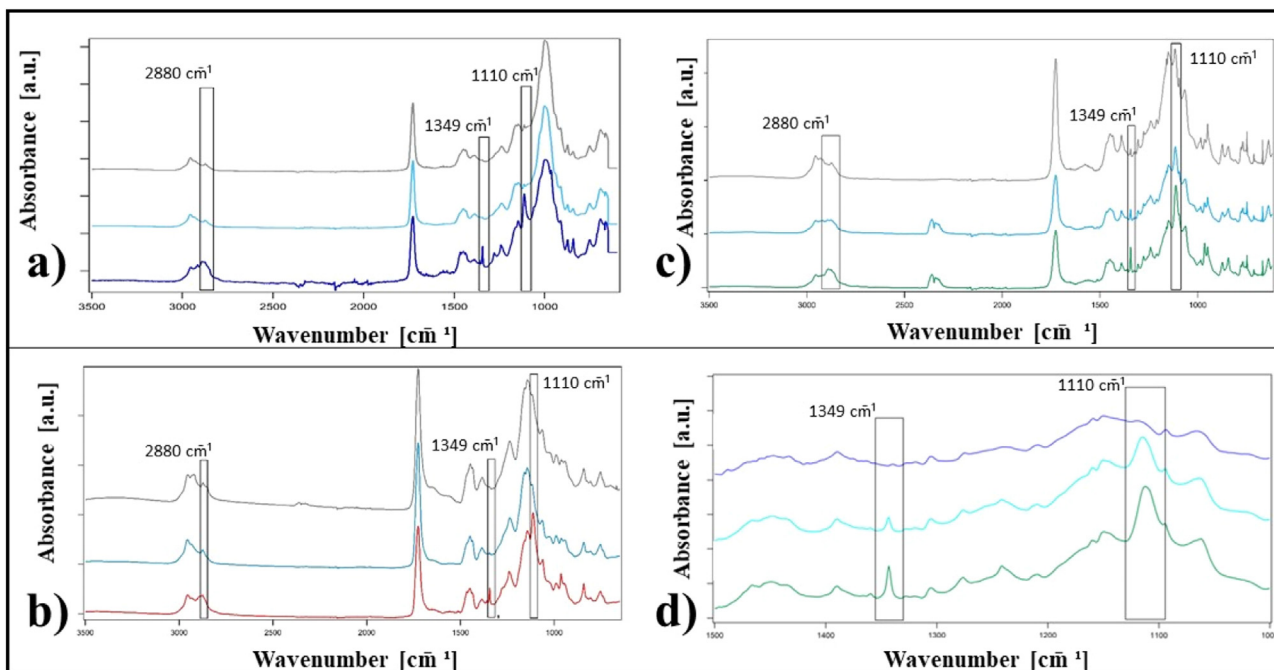


Fig. 4. ATR-FTIR of Titan blue (a) Titan red (b) and Titan phthalocyanine green acrylic paint mock-up surfaces (c). Comparison between pristine (dark blue in (a), red in (b) and green line in (c) respectively), cryogel cleaning (light blue line), and swab cleaning (grey line) methods. (d) Surfactant detection on pristine Titan green sample (green line) after cleaning with cryogel (light blue line) and one week after treatment (dark blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

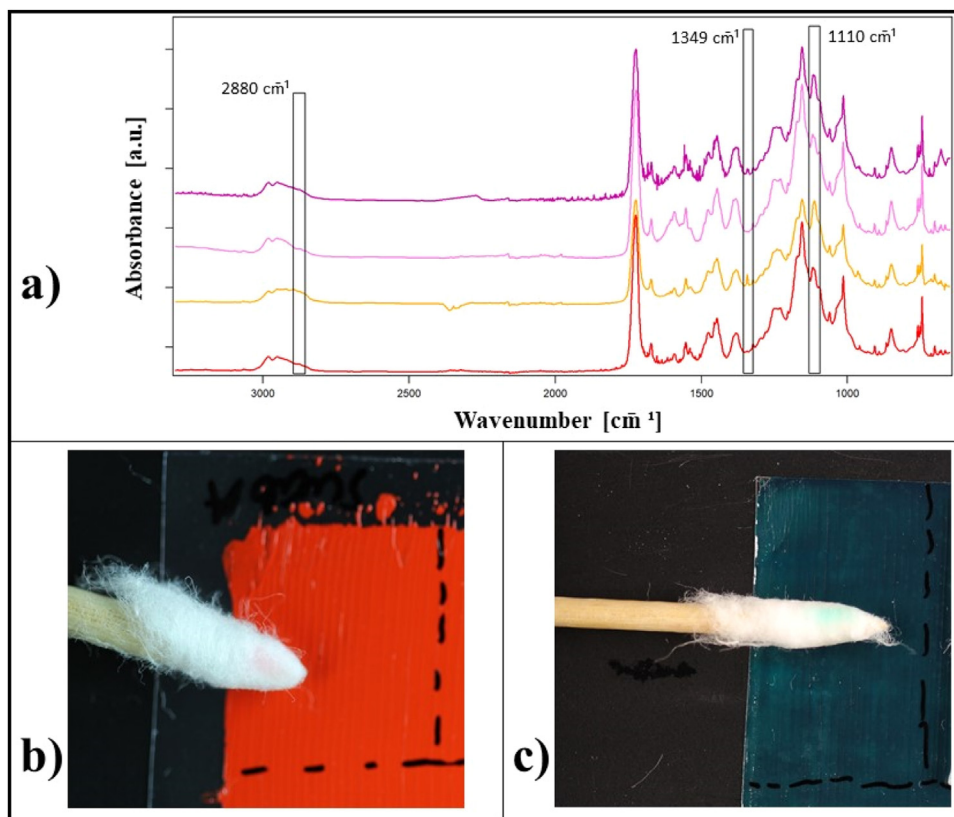


Fig. 5. (a) ATR-FTIR identification of migration and disappearance of surfactant bands on the surface of Hyplar red acrylic paint after 1 year of natural aging (red line); after 3 years of natural aging (orange line); after swab cleaning on the 3 years old mock-up (light pink); 1 week after swab cleaning on the 3 years old mock-up (deep pink). (b) Red pigment traces on the cotton swab after treatment. (c) Green pigment traces on the cotton swab after treatment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

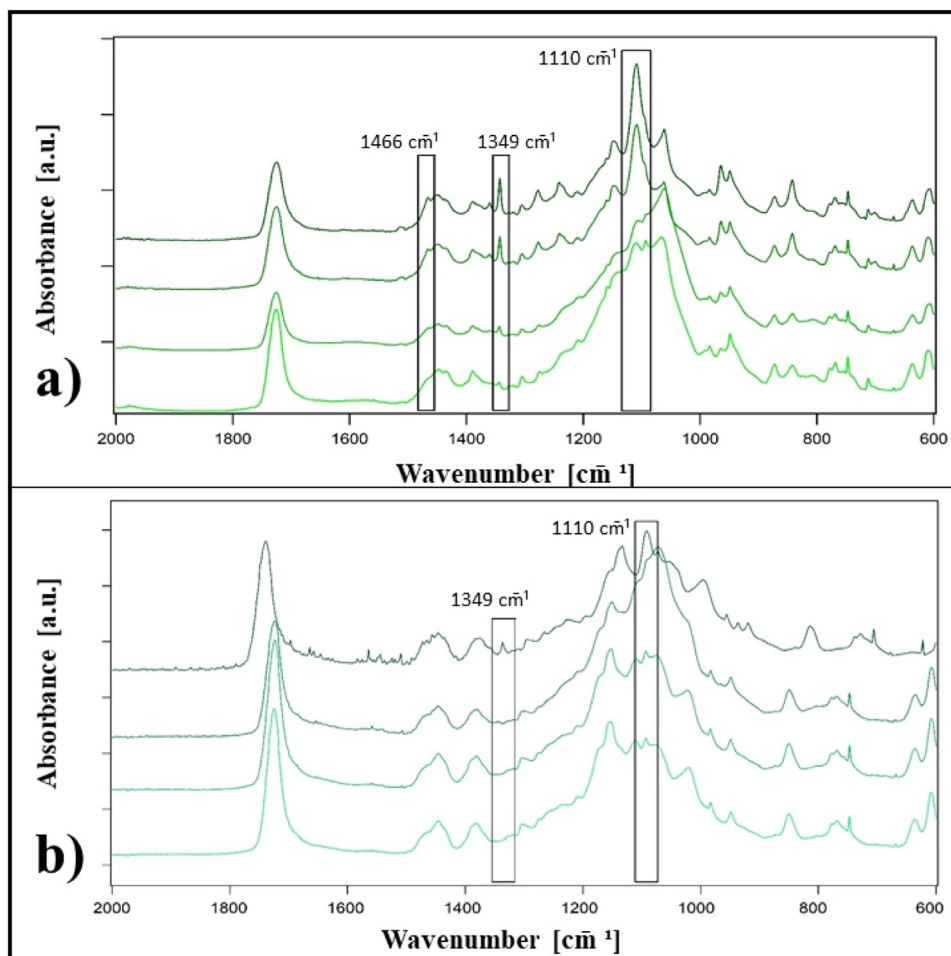


Fig. 6. ATR-FTIR of artificially aged Titan (a) and Hyplar (b) phthalocyanine green acrylic paint mock-ups. From lighter green to darker green 24 h, 192 h, 360 h and 456 h aged samples. Identification of surfactant signals that appear progressively while aging. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of the two studied brands undergo higher additive movements (migration and resorption) as a result of aqueous cleaning procedures. The movement of these additives can be ascribed to a higher amount of soluble materials, particle size and dispersant content that is needed to formulate organic pigment colours [16].

On the other hand, Hyplar paints showed an overall higher sensitivity to colour removal despite of the colour, with special-effects on green and red samples. As shown in Fig. 5b and c, pigment traces were detected in swab cleaning, under the same testing conditions as those used for the Titan mock-ups, showing that this brand is less stable against the aqueous cleaning treatment, in terms of pigment extraction.

Finally, mock-ups of organic phthalocyanine green colour of both brands were aged under artificial accelerated conditions in order to observe changes on the surface composition. The selection was made based on previous results that revealed that this organic pigment was the most unstable. Therefore, two sets of 19 phthalocyanine green mock-ups of both brands were prepared and artificially aged in a Solarbox as described elsewhere [20]. Results demonstrated that surfactant migration on Titan paints is faster than on Hyplar paints (Fig. 6), which is consistent with the results observed after natural aging. Thus, while on Titan mock-ups the first surfactant signals are detected between the first 24 and 48 h (equivalent to around 1 year of natural aging), on Hyplar paints, PEO signals are not detectable until past 360 h of accelerated aging (equivalent to around 7 years of natural aging) [9]. Taking into account that samples were subjected to identical aging conditions,

the faster migration of additives may be caused by other factors such as the length of the surfactant chain or the polymer binder composition [7]. Along with this, TGA revealed that Titan mock-ups have more organic material than Hyplar, which may correspond to a greater amount of dispersants that might migrate faster to the surface during aging.

The effect of aqueous cleaning. Identification of binder changes according to the thermal stability

Thermogravimetric Analysis were also run in order to understand in a more thorough way the composition of the acrylic paint and the changes that they may undergo after aqueous cleaning, regardless of the application method. To do that, both pristine and swab cleaned samples were tested for comparison. All TGA-DTG curves show a similar shape with the main slope starting at 300 °C, which corresponds to the onset degradation temperature of the acrylic binder. Moreover, there is always an increase in the intensity of the TGA peak in the range of 300–450 °C, that helps identifying the binder.

DTG-TGA offered a tool to monitor the presence/absence of the water soluble components of the paint in the range of 0–200 °C (Fig. 7) before and after cleaning. In the specific case of the organic green pigment samples, the DTG curve depicts a remarkable double slope that correspond to the presence of the thermally degraded pigment and binder. As shown on Fig. 8, while no double

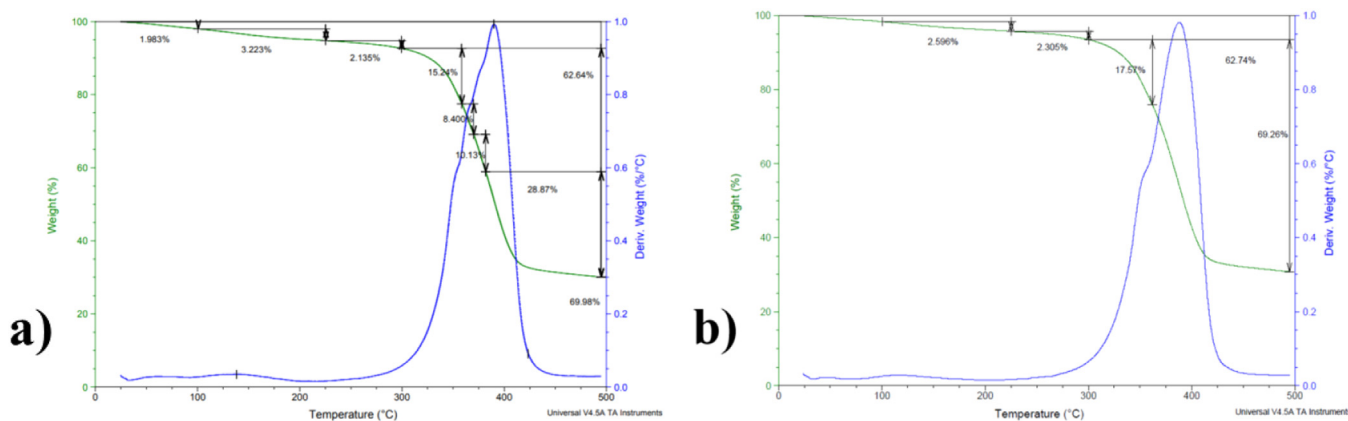


Fig. 7. TGA-DTG curves of Hyplar green acrylic paints before (a) and after (b) swab cleaning. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

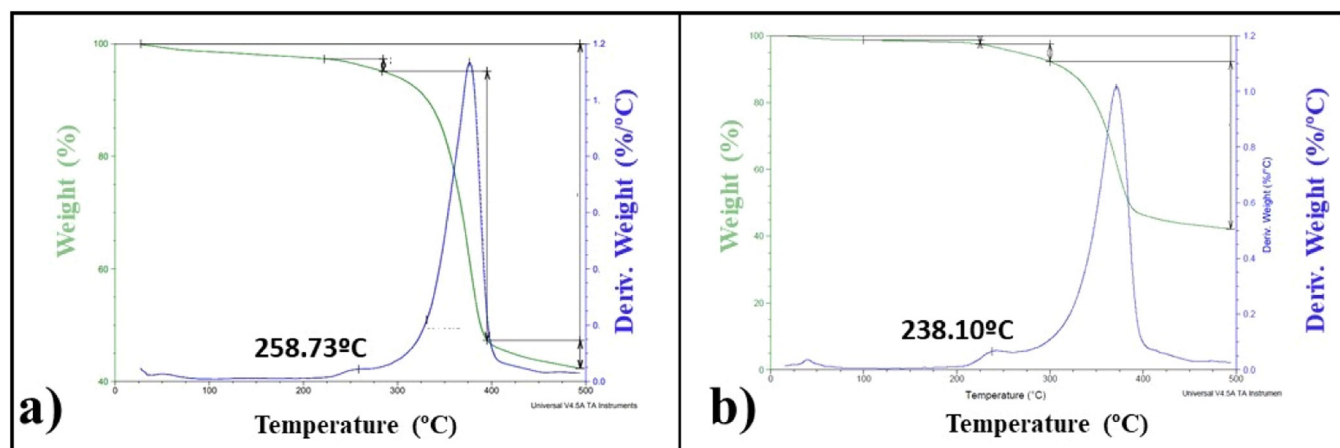


Fig. 8. TGA-DTG curves of Titan blue acrylic paint mock-ups. Formation of a new peak at around 230–260 °C in pristine sample (a) and after swab cleaning (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3

Maximum degradation temperature (Tmax) of the acrylic co-polymers before and after swab cleaning.

| | TI_29 | TI_7 | TI_108 | HY_29 | HY_7 | HY_112 |
|---------------|--------|--------|--------|--------|--------|--------|
| Tmax pristine | 376.43 | 380.71 | 383.71 | 379.80 | 389.77 | 359.68 |
| Tmax water | 371.1 | 372.21 | 376.5 | 375.1 | 380 | 360.70 |

slope in the 300–450 °C range can be observed for inorganic samples.

Samples cleaned with cotton swab were tested, to assess the effect of water on the thermal stability of the paint binder. In pristine samples the curve at 300–450 °C is sharp and high, while in swab cleaned samples, there is a notorious decrease in height and an increase in width. This is explained by the degradation of the polymer chain and the scission of PAA monomers. This is also accompanied by a decrease in the maximum degradation temperature (Tmax) of the co-polymer. This figure indicates the highest temperature at which the material completely degrades, thus interpreting that materials with lower Tmax are thermally less stable. As shown in table 3, the Tmax of Titan binder decreases more than the Tmax of Hyplar binder, leading to think that the bulk binder in this case is more prone to suffer chain-scission after water treatment, which in turn decreases the thermal stability of the paint. These results are consistent with the study of L. Ortiz et al. [9], where p(nBA/MMA) acrylic paints showed greater binder chain scission after artificial aging.

Termogravimetric analysis also depicts the formation of a new TGA curve at around 240–260 °C, after cleaning TI_29 and HY_112 paint samples (Fig. 8). The curve is more pronounced after swab cleaning on both colours and therefore does not correspond to the nature of the pigments and neither to the paint brand. Therefore, the main factor may correspond to the formation of new components coming from chain-scissions, thus interpreting that these paints are more prone to degrade in the presence of water. Organic green paints of the two brands show no significant changes on its TGA-DTG curve after swab cleaning, concluding that despite being the samples with greater additive movement, they prove to be more stable in terms of binder composition.

In this sense, TGA analysis reaffirms the fact that the side-effects of applying water based cleaning treatments on acrylic paint films should be integrally assessed (bulk and surface), since those colours that show biggest chemical surface changes (Titan acrylic mock-ups) do not coincide with those that suffer the most noticeable bulk binder alterations (TI_29 and HY_112).

The effect of aqueous cleaning on surface roughness

Previous studies [13,42] concluded that swab cleaning causes bigger changes to the morphology of the paint surface, in comparison to gel cleaning systems. Therefore, AFM was used to evaluate the roughness changes in both Titan and Hyplar pristine samples before and after swab and cryogel cleaning on one year old naturally aged samples. Images show remarkable morphological

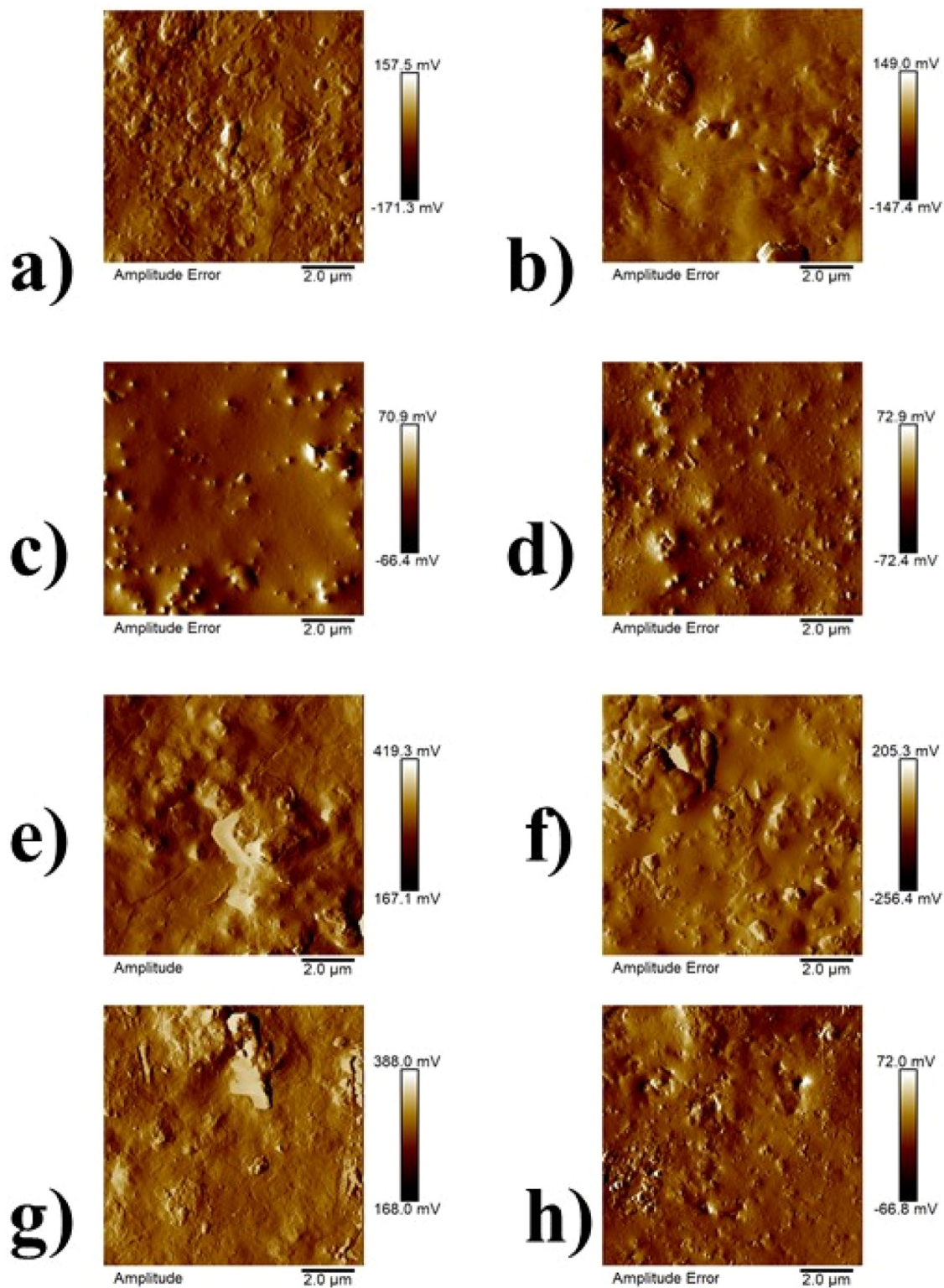


Fig. 9. AFM amplitude images of Titan blue (TI_29) pristine and swab cleaned (a-b); Titan red (TI_108) pristine and swab cleaned (c,d); Hyplar blue (HY_29) pristine and swab cleaned (e-f); Hyplar red (HY_108) pristine and swab cleaned (g-h). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

differences of the surface of the samples (Fig. 9). Regardless of the brand, pristine samples of same pigment color show similar appearance. All the results confirmed the extraction of components from the paint surface, formation of pinholes and roughness changes after application of both cleaning methods. The ma-

terials removed from the surface of each sample may differ from surfactants to pigments (Fig. 5). The root mean square roughness (Rq) value obtained as a calculation of the deviation of the roughness profile, represents the average roughness of the sample. Those values were obtained using the Nanoscope Analysis Software. The

Table 4

Profile roughness (Rq) of the unsoiled acrylic paint mock-ups before cleaning (Rq pristine), after cleaning with the cryogel (Rq gel) and after swab cleaning treatment (Rq swab).

| | TL_29 | TL_7 | TL_108 | HY_29 | HY_7 | HY_112 |
|------------------|-------|------|--------|-------|------|--------|
| Rq pristine (nm) | 107 | 104 | 109 | 278 | 63.2 | 134 |
| Rq gel (nm) | 224 | 117 | 129 | 274 | 87.2 | 252 |
| Rq Swab (nm) | 229 | 146 | 407 | 273 | 103 | 192 |

Rq of the Titan mock-ups increased in the three colors after swab rolling (ie. Rq of Titan blue, cleaned sample=229 nm; Rq of Titan blue, pristine sample= 107 nm), which can be interpreted as the removal of materials from the surface after treatment. The biggest changes are detected on red Titan surface and the smallest changes were detected on green samples. In general terms, slighter changes were observed on Hyplar brand samples (see Table 4).

These results are consistent with the surfactant removal from the one year old Titan paint samples identified by means of ATR-FTIR, presumably due to the higher amount of organic soluble material content present on the surface of the most altered mock-ups. In general terms, inorganic pigment paint colors suffer greater roughness changes than organic ones, which can be influenced by the bigger particle size.

Conclusions

In this work the analysis by ATR-FTIR, Py-GC-MS and TGA-DTG of six commercial paints from two different acrylic commercial brands proved that the existence of differences regarding the copolymers used as binders resulted in a different behavior of the surfactants present within the films. Titan paints contain a poly n-butyl acrylate/methyl methacrylate copolymer while Hyplar paints are composed of ethyl acrylate/methyl methacrylate.

This way, Titan samples show an early migration of surfactants to the surface (in less than one year) but, this phenomenon is not observed on Hyplar samples until the third year of natural aging. Accelerated aged samples showed a progressive and unequal migration of surfactants but also depicted the earlier migration of additives in Titan samples.

On the other hand, when it comes to cleaning methods both brands in all tested colors showed similar sensitivity to swab cleaning in terms of surfactant removal. Overall, the use of cryogels for cleaning proved to be more respectful than swab cleaning. Nevertheless, some surfactant removal was still observed on Hyplar samples, and on the inorganic colors (blue and red) of the Titan paints. On the contrary, the organic (green) acrylic paints seemed to be more resistant.

In general terms, the organic colour paints of both brands seem to undergo higher degree of additive migration to the surface and resorption into the bulk of the film, during and after application of the cleaning treatment.

With respect to pigment removal, Titan paints showed an overall higher stability, while Hyplar organic red and green samples left traces of color on the cotton after swab cleaning. AFM confirmed that in all the cases swab causes bigger changes in the roughness of the paint surface than cryogel, mainly due to the mechanical action. Rq results also revealed higher roughness changes on inorganic colors, presumably due to the pigment particle size.

Therefore, we can conclude that it is not possible to define a common cleaning system for all the acrylic brands and pigments. In general terms, cryogels show more respectful cleaning results compared to cotton swab. However, Hyplar organic colours for instance have demonstrated a considerable sensitivity towards colour removal while Titan inorganic colours showed higher sensitivity to

surfactant removal. These aspects should need further research in order to find a more suitable cleaning system for these cases.

Finally, TGA-DTG provided the most remarkable results for this study. The results depict the formation of a pronounce peak at 230–260 °C after swab cleaning on Titan blue and Hyplar red acrylic paints, which may correspond to the degradation or chain-scission of the polymer used as binder. This suggests that these two colors are those that suffer the biggest bulk changes. Moreover, thermogravimetric analysis confirmed major decreases of the degradation temperature of the Titan acrylic paint binder after the application of a water based cleaning treatment, which may correspond to the chain scission of the monomers. Thus, paints that suffer bigger changes on their surface after treatment, are not necessarily those that have undergone major changes on the bulk of the paint film. Leading us to conclude that in some cases, such as Hyplar blue and titan red acrylic paint films, the stability of the paint surfaces does not always guarantee an innocuous effects of water based or gel cleaning systems, since bulk changes can lead to diminish the thermal stability of the paint film. Therefore, although preliminary analysis leads us to think that the gel method causes less change in the paint binder, further analysis would be needed to confirm this hypothesis by means of TGA-DSC.

Funding

This project was partly supported by the UniPredoctoral grant of the Basque Government.

Acknowledgements

Dr. Luis Bartolomé of SGIker (Servicios Generales de Investigación) of the University of the Basque Country, and Dr. Laura Ortiz Herrero are acknowledged for the Py-GC-MS analysis. Dr. Lourdes Irusta and Dr. Alba Gonzalez of the Chemistry Faculty of the University of the Basque Country are acknowledged for the FTIR-ATR and TGA-DTG analysis. Dr. Nicole Bonelli and Dr. Rodorico Giorgi of CSGI (Universita degli Studi di Firenze) are acknowledged for the cryogels.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.culher.2024.03.008](https://doi.org/10.1016/j.culher.2024.03.008).

References

- [1] H.A.L. Standeven, *House Paints, 1900-1960. History and use*, Research in Conservation, Getty Conservation Institute, Los Angeles, 2011.
- [2] J. Crook, T. Learner, *The Impact of Modern Paints*, Tate Gallery Publishing, Ltd, Millbank, London, UK, 2000.
- [3] E. Jablonski, T. Learner, J. Hayes, M. Golden, Conservation concerns for acrylic emulsion paints, *Stud. Conserv.* 48 (2003) 3–12.
- [4] 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.
- [5] A. Solbes-Garcia, J.M. Miranda-Vidales, A. Nieto-Villena, L.S. Hernandez, L. Narváez, Evaluation of the oxalic and tartaric acids as an alternative to citric acid in aqueous cleaning systems for the conservation of contemporary acrylic paintings, *J. Cult. Herit.* 25 (2017) 127–134.
- [6] D.R. Karsa, *Surfactants in Polymers, Coatings, Inks and Adhesives*, Blackwell Pub, Florida, US, 2003.
- [7] J.L. Keddie, A.F. Routh, *Fundamentals of Latex film formation. Processes and Properties*, Springer laboratory, 2010.
- [8] B. Ormsby, T. Learner, G.M. Foster, J. Druzick, M. Schilling, Wet-cleaning acrylic emulsion paint films: an evaluation of physical, chemical and optical changes, *Mod. Paint. Uncovered Symp.* (2007) 189–200.
- [9] L. Ortiz-Herrero, I. Cardaba S. Setien, L. Bartolomé, M.L. Alonso, M.I. Maguregui, OPLSmultivariate regression of FTIR-ATR spectra of acrylic paints for age estimation in contemporary artworks, *Talanta* 205 (2019) 120114.
- [10] B. Ormsby, P. Smithen, F. Hoogland, T. Learner, C. Miliani, A scientific investigation into the surface cleaning of acrylic emulsion paintings, in: *ICOM Committee for Conservation, 15th Triennial Conference Preprints Vol. II*, New Delhi, 22–26 September, 2008, pp. 857–865.

- [11] R. Perry, Problems of dirt accumulation and its removal from unvarnished paintings: a practical review, in: *Dirt Pict. Separated Pap. Given a Conf. Held Jointly by UKIC Tate Gall*, 1990, pp. 3–6.
- [12] J. Lee, I. Bonaduce, F. Modugno, J. La Nasa, B. Ormsby, K.J. Van den Berg, Scientific investigation into the water sensitivity of twentieth century oil paints, *Microchem. J.* 138 (2018) 282–295.
- [13] I. Cardaba, G. Poggi, M. Baglioni, D. Chelazzi, I. Maguregui, R. Giorgi, Assessment of aqueous cleaning of acrylic paints using innovative cryogels, *Microchem. J.* 152 (2020) 104311.
- [14] 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).
- [15] 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, in: *Mod. Paint. Uncovered Proc. from Mod. Paint. Uncovered Symp.*, 2007, pp. 257–268.
- [16] T. Learner, O. Chiantore, D. Scalzone, Ageing studies of acrylic emulsion paint, in: *ICOM Committee for Conservation, 13th Triennial Meeting Preprints Vol. II, Rio de Janeiro 20–27 September, 2002*, pp. 911–919.
- [17] 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.
- [18] 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.
- [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] D. Scalzone, O. Chiantore, Separation techniques for the analysis of artists' acrylic emulsion paints, *J. Sep. Sci.* 27 (2004) 263–274.
- [21] B. Ormsby, R. Barker, R. Hellen, P. Smithen, Cleaning acrylic emulsion paintings: case study treatments, evaluation and reflections, in: *M.D.C. Mundici (Ed.), What's Changing: Theories and Practices in the Restoration of Contemporary Art Symposium, Castello di Rivoli Museo D'Arte, 10–11 February 2012, Contemporanea, Turin, Thames & Hudson, 2012*, pp. 227–242.
- [22] E. Kampsakali, B. Ormsby, A. Phenix, M. Schilling, T. Learner, A preliminary study into the swelling behaviour of artists' acrylic emulsion paint films, in: *ICOM Committee for Conservation, 16th Triennial Conference Preprints, Portugal, 2011*, pp. 1–8.
- [23] R. Ploeger, H. Shurvell, E. Hagan, A. Murray, Infrared analysis of materials leached by water from acrylic paint films, in: *M. Picollo (Ed.), The Sixth Infrared and Raman Users Group Conference (IRUG6), Il Prato, Florence, 2005*, pp. 46–51.
- [24] R. Wolbers, A. Norbutus, A. Lagalante, Cleaning of acrylic emulsion paints: preliminary extractive studies with two commercial paint systems, in: *M.F. Mecklenburg, A. Charola, R. Koestler (Eds.), New Insights into the Cleaning of Paintings, 2010, Smithsonian Contributions to Museum Conservation, Number 3, Smithsonian Institution Scholarly Press, Washington DC, 2013*, pp. 147–157.
- [25] O. Chiantore, D. Scalzone, The Macro- and Microassessment of Physical and Aging Properties in Modern Paints, in: *Mod. Paint. Uncovered Proc. from Mod. Paint. Uncovered Symp.*, 2007, pp. 96–103.
- [26] E. Kampsakali, B. Ormsby, A. Cosentino, C. Miliani, T. Learner, An 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) 216–223.
- [27] D. Scalzone, M. Lazzari, V. Castelvetro, O. Chiantore, Surface monitoring of surfactant phase separation and stability in waterborne acrylic coatings, *Chem. Mater.* 38 19 (2007) 6107–6113.
- [28] L. Ortiz-Herrero, A.C. de Almeida Assis, L. Bartolomé, M.L. Alonso, M.I. Maguregui, R.M. Alonso, J.S. Seixas de Melo, OPLS multivariate regression of FTIR-ATR spectra of acrylic paints for age estimation in contemporary artworks, *Chemom. Intell. Lab. Syst.* 207 (2020) 104187.
- [29] T. Learner, The analysis of synthetic paints by pyrolysis–gas chromatography–mass spectrometry (PyGCMS), *Stud. Conserv.* 46 (2001) 225–241.
- [30] P. Schossler, I. Fortes, J. Cura D'Arts de Figueiredo, F. Carazza, L.Cruz Souza, Acrylic and vinyl resins identification by pyrolysis-gas chromatography/mass spectrometry: a study of cases in moderna art conservation, *Anal Lett* 46 (2013) 1869–1884.
- [31] T. Fardia, V. Pintus, E. Kampsakalia, E. Pavlidou, K.G. Papaspyropoulos, M. Schreinerb, G. Kyriacou, A novel methodological approach for the assessment of surface cleaning of acrylic emulsion paints, *Microchem. J.* 141 (2018) 25–39.
- [32] 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, *AIC Paint. Spec. Gr. Postprints* (2013) 77–87.
- [33] T. Fardi, V. Pintus, E. Kampsakali, E. Pavlidou, M. Schreiner, G. Kyriacou, Analytical characterisation of artist's paint systems based on emulsion polymers and synthetic organic pigments, *J. Anal. Appl. Pyrolysis* 135 (2018) 231–241.
- [34] M.F. Silva, Analytical Study of Accelerated Light Ageing and Cleaning Effects On Acrylic and PVAc Dispersion Paints Used in Modern and Contemporary Art, *Universitat Politècnica de València, 2011 PhD Thesis*.
- [35] H.M. Ng, M.S. Norshahirah, O. Fatin Saiha, K. Ramesh, S. Ramesh, S. Bashir, Thermogravimetric Analysis of Polymers, *Encyclopedia of Polymer Science and Technology*, 2018.
- [36] T. Learner, *Analysis of Modern Paints*, Getty Publications, 2004.
- [37] 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-Preserv. Sci.* 10 (2013) 10–18.
- [38] D.O. Hummel, *Atlas of Plastics Additives*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2002.
- [39] S. Vahur, U. Knuutinen, I. Leito, ATR-FT-IR spectroscopy in the region of 500–230cm⁻¹ for identification of inorganic red pigments, *Spectrochim. Acta Part A* 73 (2009) 764–771.
- [40] S. Parvate, P. Mahanwar, Insights into the preparation of water-based acrylic interior decorative paint: tuning binder's properties by self-crosslinking of allyl acetoacetate - hexamethylenediamine, *Prog. Org. Coat.* 126 (2019) 42–149.
- [41] C.H. Hare, Thermal degradation, Part 2: pigments, *J. Protect. Coat. Linings* 16 (1999) 10.
- [42] 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.