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# A PRELIMINARY FTIR-BASED EXPLORATION OF THE SURFACTANT PHASE SEPARATION PROCESS IN CONTEMPORARY MURAL PAINTINGS

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## Abstract

This paper reports on a preliminary evaluation of a degradation process that may affect mural paintings created with emulsion products: the phase separation of paint additives towards film-environment and film-support interfaces. A number of mock-ups were prepared by brushing five acrylic, five vinyl and five styrene-acrylic paints on cement-lime mortar supports. A selection of these samples was stored under laboratory conditions to verify the appearance of exudation phenomena, and to compare the stability of paints having different chemical composition. Since water was suspected to influence the phase separation process, the remaining samples were deteriorated simulating the absorption of water into the mortar supports by capillary rise mechanism. This degradation process forced the paint layers to delaminate from the supports, allowing the exploration of the two interfaces (the one in contact with mortar and the one exposed to the environment) by mid-near FTIR reflection spectroscopy. According to the results, capillary rise seemed to promote surface exudation of non-ionic polyethoxylate type surfactants, but the process was also influenced by the chemical composition and the properties of the paint layers. No water-soluble paint components were detected at the film-support interface.

## 1 Introduction

Emulsion paints are one of the most common media used to create contemporary murals. In the recent years, the development of these paints has been reviewed,[1-3] and waterborne formulations have been reported as complex chemical systems consisting of numerous components. Among these, there are many additives which are included during the production of the latex binders and the subsequent formulation of the paints to satisfy manufacturing requirements and to enhance the performance of the final products. These additives are mainly freeze-thaw agents, protective colloids, coalescents, biocides, thickeners, buffers, defoamers and surfactants.

Different types of surfactants are used to properly develop the polymerization process of the binders and to stabilize polymer emulsions. Typical emulsifiers are anionic (generally alkyl sulfates and alkylaryl sulfonates) and non-ionic compounds (mainly alkylphenol ethoxylates, fatty alcohol ethoxylates and fatty acid monoethanolamide ethoxylates). Other surfactants (e.g. sulfosuccinates, ethoxylated silicone-based compounds, etc.) are included in the emulsion binders as wetting agents, to enhance the spreading of the products and the formation of continuous films on different kinds of surfaces.

During the formulation of paints, further surfactants are added to wet the pigments and to finely disperse them in the waterborne medium. Typical wetting agents are oligomeric non-ionic surfactants, characterized by hydrophobic chain lengths of 10-12 carbon atoms and hydrophilic heads of 6-8 ethylene oxide (EO) units.

Anionic surfactants (mainly polyphosphates, polyacrylic acids and polycarboxylates) and non-ionic polyethoxylated compounds (characterized by 20-

30 EO units) are employed as dispersing agents. The former are preferred to disperse inorganic pigments and the latter to disperse the organic ones, but a mixture of the two dispersant typologies is often used in the same formulation.[4]

Considering the overall composition of an emulsion paint (where water content can vary from 40 to 60% by weight), the total amount of additives is generally lower than the 10% (w/w), with surfactants varying from 1 to 3% (w/w).[1,2,4] With the exception of some volatile compounds, all these additives remain in the dry paint film and, even if their concentration is still low, they may affect the properties of the paint layers and their responses to environmental conditions or conservation treatments. A number of studies have been recently carried out on laboratory samples and real canvas paintings[5-8], with the aim of exploring these aspects.

It has been shown that non-ionic polyethoxylate (PEO)-type surfactants tend to spontaneously desorb from the bulk paint layers, leading to the formation of small rounded crystals or translucent layers at the paint-environment interface. This exudation process may be influenced by a number of factors, such as: the nature of the polymer binder and the tendency of its particles to coalesce; the type and quantity of surfactant; the binder-surfactant interactions; the film drying mechanism.[5] The process is also influenced by the environmental conditions (it is enhanced by dark storage and high temperatures)[7,9] and the properties of the support.[5] Comparing the stability of samples prepared by applying the same commercial paints on different kinds of support, the exudation of PEO-type surfactants was more evident for samples cast on Teflon rather than for samples cast on acrylic primed cotton canvas (more porous).[6] The changes to the bulk films, due to typical cleaning treatments and removal of the exuded surfactants, have been also evaluated.[6-10]

To the best of our knowledge, little attention has been paid to the study of the surfactant phase separation in the context of mural paintings. Nevertheless, the leaching of water soluble components of emulsion paints has been reported as one of the degradation processes which could affect contemporary murals,[11] and the exudation of surfactants has been proposed as one of the causes of bleaching of paint layers.[12]

This work was developed in the attempt of exploring these degradation processes, considering a number of factors which could influence the surfactant phase separation in murals. The chemical composition of the paint layers was taken into consideration, as well as the properties of the mural support and the role played by water. Most murals are outdoor works of art, directly exposed to rain or painted on supports affected by water infiltration and rising damp. On the one hand, the presence of the hydrophilic additives in the bulk film is expected to enhance water permeability of the paint layers,[13] especially if they were recently applied and the film formation process is still not complete. On the other hand, water is expected to promote the phase separation process, driving the hydrophilic paint components towards both the surface and the support. As far as this last aspect is concerned, it is remarkably that many murals are affected by delamination of the paint layer and, even if this phenomenon is often due to the properties of the mural support

itself, the adhesion of the paint could be influenced by the presence of surfactants at the support-film interface.[14]

A number of mock-ups simulating the properties of mural paintings were prepared and subjected to capillary rise cycles. This method was preferred to other degradation processes (e.g. simulation of rain) because it was likely to accelerate delamination of the paint layers, allowing the examination of the film-support interface. Previous trials also revealed that, simulating the absorption of water into the mortar supports by capillary rise mechanism, it was possible to wet the paint layers in a controlled way and to easily evaluate the permeability of the films to liquid water. The phase separation of water soluble components of the paints toward the support-film and the film-environment interfaces, was evaluated by mid-near FTIR reflection spectroscopy, which had been successfully used to study this degradation process.[7,8] The surfaces of reference mock-ups stored under laboratory conditions were also studied to verify the occurrence of exudation processes not induced by water.

## 2 Experimental

### 2.1 Selection of Materials and Preparation of Samples

Samples were prepared using three professional grade artists' emulsion paints, encompassing different types of binders: (i) Flashe by Le Franc & Bourgeois, consisting of a vinyl resin; (ii) Heavy Body (H.B.) by Liquitex, consisting of an acrylic resin; (iii) Brera by Maimeri, consisting of a styrene-acrylic resin. Five paints of each commercial brand were selected, including three inorganic and two organic pigments: titanium white (PW6), ultramarine blue (PB29), an iron based yellow (PY42), phthalocyanine green (PG7) and quinacridone violet (PV19). These 15 paints were used to create film samples as well as mock-ups.

The films, cast as draw-down on Mylar® supports and having a final average thickness of 100-150 μm, were used only to assess the composition of the paints by ATR-FTIR analysis. The mocks-ups simulated the properties of real murals. The supports of the mock-ups were prepared using a commercially blended cement-lime mortar (mixed according to the technical data sheet, using clean water). A total of 60 supports were mould-shaped (5 cm x 5 cm x 2 cm) and left to cure for approximately 12 months (20 $\pm$ 2 °C, 60 $\pm$ 5% RH). Before painting, all loose particles, dirt and dust were removed and the supports were further conditioned in an oven (60 °C), until reaching constant weight ($\Delta$w% $\leq$ 0.01%) as measured day-to-day. The emulsion paints were then diluted with distilled water (paint:water ratio 4:1, by weight), and brushed on the supports until the fresh paint weight of 500 g/m$^2$ was obtained. Previous trials suggested that this amount of wet paint would result in 200 $\pm$ 50 μm thickness of dry films.

The painted samples were left to dry in laboratory conditions for 24 h and further conditioned in a T and RH controlled environment (20 $\pm$ 2 °C, 50 $\pm$ 5% RH) for 3 weeks before testing.

Four mock-ups were prepared per paint: the first one, considered as a reference, was stored in laboratory

conditions; the other three were subjected to capillary rise cycles, as a method of degradation.

## 2.2    Degradation Conditions and Experimental Method

Since water was suspected to influence the surfactant phase separation process, the mock-ups were deteriorated simulating the absorption of water into the mortar supports by capillary rise mechanism. As seen in Figure 1, each cycle was carried out by placing the back of the mock-ups in contact with filter paper soaked with distilled water. The samples were left to absorb the water for 2 h, then placed over a grating and left to dry under laboratory conditions for 24 h. At the end of each cycle the water uptake was evaluated by weighing the samples were examined using normal and raking light to detect delamination and other changes.

The degradation process was discontinued after 20 cycles, when some of the samples were clearly affected by delamination. Due to the small dimensions of these defects (diameters 0.5 - 2 mm), the paint layers were locally peeled off and the support-paint interface was studied by benchtop µ-FTIR reflection spectroscopy.

Only in two cases, degradation was discontinued earlier (after 3 cycles for sample LQPB29_1 and after 17 cycles for sample LQPY42_1), because the mock-ups showed surface variations in the form of small white crystals and translucent layers, which could be due to the exudation of surfactants. All the paint-environment interfaces were assessed by mid-near FTIR reflection spectroscopy, using a portable instrument to allow for examination of real works of art non-invasively.

The analyses were carried out on a central area (probe diameter width of 6 mm), as well as on points affected by variations detectable by naked-eye, such as white or translucent materials (probe diameter 3 mm). The surfaces of the reference mock-ups were studied in the same way.



Figure 1: Some of the mock-ups subjected to the capillary rise cycles: samples are placed with the support in contact with filter paper soaked with distilled water.

## 2.3    Instrumentation

### 2.3.1    ATR-FTIR Spectroscopy

Although it was possible to partially deduce the composition of the paints from the technical data sheets and the literature, the film samples were also characterized by ATR-FTIR analysis. The spectra were collected using a Perkin Elmer Spectrum 100 spectrometer, equipped with an Attenuated Total Reflection (ATR) accessory (diamond crystal). Interferograms were collected in the 4000-400 $cm^{-1}$ range, at a resolution of 4 $cm^{-1}$ and a total of 32 scans.

As already described, emulsion paints are known to contain a number of hydrophilic components which could affect the properties and the degradation processes of the paint layers. In an attempt to detect diagnostic peaks to assess the potential phase separation process of these components, water extracts of the paint layers were characterized.

After 6 months of storage in laboratory conditions, samples of equal size (about 0.12 g in weight) were removed from each film and subjected to extraction in 30 ml distilled water for 24 h. The water fraction was separated, left to dry on Petri dishes and subsequently analyzed using the setup described above.

### 2.3.2    Reflection Mid-near FTIR Spectroscopy

The spectra from the surface of the mock-ups were collected using a portable Bruker Alpha FTIR spectrometer. The instrument was equipped with a cube-corner RockSolid interferometer, a room temperature deuterated triglycine sulfate detector (DTGS) and an A241/D QuickSnap$^{TM}$ front-reflection module especially designed for carrying out contactless measurements at a distance between the sample and the instrument of 15 mm. The probe, characterized by a 23°/23°geometry, was kept perpendicular to the sample surface. The investigated sample area width, as determined by the probe diameter, was either 6 or 3 mm. Interferograms were collected in the interval 7500 to 360 $cm^{-1}$ at a resolution of 4 $cm^{-1}$, and a scan time of 3 min. A spectrum collected from a gold mirror was used for background correction.

The mortar-paint layer interface was studied by µ-FTIR reflection spectroscopy, using a benchtop Jasco FT-IR 4100e spectrometer coupled to an IMV-400 optical microscope, and collecting the micro-infrared spectra with a Cassegrain 16x objective. Interferograms were obtained over 4000 scans, at a resolution of 4 $cm^{-1}$, in the spectral range 7500-700$cm^{-1}$.

All the spectral data collected in reflection mode are presented as pseudo absorbance $A'=\log(1/R)$, where $R$ is reflectance.

## 3    Results and Discussion

### 3.1    Characterization of Commercial Paints

As shown in Table 1, the ATR-FTIR characterization of the film samples mainly confirmed the information inferable from manufacturers' declarations and the existing literature.

It was verified that the binder of Flashe paints was a polyvinyl acetate-vinyl versatate copolymer (PVAc-VeoVa), the binder of H.B.-Liquitex paints was a *n*-butyl acrylate-methyl methacrylate copolymer (p(*n*BA-MMA)), while that of Brera paints a *n*-butyl methacrylate-2-ethylhexylacrylate-styrene terpolymer (p(*n*BMA-2EHA-styr)).

assess of the phase separation process of paint water soluble additives (e.g. surfactants).

As can be seen in Figure 2, representing a selection of the results (specifically of the blue paints), spectra from the extracts of Flashe and H.B.-Liquitex paints were characterized by absorption bands ascribable to a polyethoxylated compound, possibly a non-ionic alkylphenol ethoxylate surfactant. The most diagnostic features of this kind of surfactants are: a characteristic C-H stretching region profile, dominated by an absorption around 2880 cm$^{-1}$ and showing two additional weak absorptions at 2741 and 2694 cm$^{-1}$ (Ar-O-CH$_2$- stretching); a small band at about 1511 cm$^{-1}$ (-C=C- ring stretching); a doublet around 1360 cm$^{-1}$ and 1342 cm$^{-1}$; a sharp band at about 1110 cm$^{-1}$ (v$_{as}$ C-O-C).

These bands were less clear for the extracts of some Flashe paints, which showed broad

| Commercial Brand | Paint Name | ID Cod | Paint Components | |
|---|---|---|---|---|
| | | | Pigment | Other components |
| Flashe (LeFranc&Bourgeois) | 001-white* | FLPW6 | titanium dioxide and possibly lithopone white (PW6-PW5) | vinyl binder p(VAc-VeoVa) |
| | 043-ultramarine blue | FLPB29 | artificial ultramarine blue (PB29), traces of kaolinite | calcium carbonate extender |
| | 302-yellow ochre | FLPY42 | Synthetic iron oxide yellow (PY42) | non-ionic surfactant (PEO type) |
| | 388-ruby red | FLPV19 | quinacridone red (PV19) | *anionic surfactant (polyacrylate type) |
| | 512-armor green* | FLPG7 | phthalocyanine green (PG7) | cellulose derivative thickener |
| Heavy Body (Liquitex) | 432-titanium white | LQPW6 | titanium dioxide (PW6) | |
| | 380-ultramarine blue (green shade) | LQPB29 | artificial ultramarine blue (PB29), traces of kaolinite | acrylic binder p(*n*BA-MMA) |
| | 332-transparent raw Sienna* | LQPY42 | synthetic iron oxide yellow (PY42) | non-ionic surfactant (PEO type) |
| | 110-quinacridone crimson | LQPV19 | quinacridone red (PV19) | *anionic surfactant (polyacrylate type) |
| | 317-phthalocyanine green (blue shade) | LQPG7 | phthalocyanine green (PG7) | |
| Brera (Maimeri) | 018-titanium white | BRPW6 | titanium dioxide (PW6) | |
| | 390-ultramarine | BRPB29 | artificial ultramarine blue (PB29), traces of kaolinite | styrene-acrylic binder p(*n*BMA-2EHA-styr) |
| | 131-yellow ochre | BRPY42 | synthetic iron oxide yellow (PY42) | cellulose derivative thickener |
| | 256-primary red magenta | BRPV19 | quinacridone red (PV19) | |
| | 321-phthalo green | BRPG7 | phthalocyanine green (PG7) | |

Table 1: The commercial names and the composition of the 15 artists' grade waterborne paints included in the study (as confirmed by ATR-FTIR analysis).

According to technical data sheets, the Flashe white paint was supposed to contain titanium dioxide (TiO$_2$, PW6) and lithopone (ZnS-BaSO$_4$, PW5) white pigments. This latter component was barely detected in the spectrum of the film sample which showed only two weak absorptions at 1083 and 1045 cm$^{-1}$ that could be assigned to barium sulfate (v$_3$ of SO$_4^{2-}$).

The spectra of the Flashe paints were characterized by some vibrational features ascribable to calcium carbonate (CaCO$_3$) extender: the strong and broad absorption around 1430 cm$^{-1}$ (v$_3$ asymmetric stretching of CO$_3^{2-}$), the strong sharp absorption around 873 cm$^{-1}$ (v$_2$ CO$_3^{2-}$ band) and the less strong but still sharp absorption around 714 cm$^{-1}$ (v$_4$ CO$_3^{2-}$).

As suggested by the bands around 3690 and 3620 cm$^{-1}$ in combination with the presence of a silicate component (970, 685 and 655 cm$^{-1}$), the three blue paints turned out to contain an artificial ultramarine blue pigment (Na$_{(6-10)}$Al$_6$Si$_6$O$_{24}$S$_{(2-4)}$, PB29) characterized by slight amounts of kaolinite (Al$_2$Si$_2$H$_4$O$_9$). Similar results have been recently presented for other artists' grade ultramarine blue acrylic paints,[15] and they are consistent with the manufacturing process of this pigment.[16]

### 3.1.1 Paint Water Soluble Components

The water extracts of the film samples were characterized by ATR-FTIR spectroscopy, with the purpose of identifying diagnostic features potentially useful to
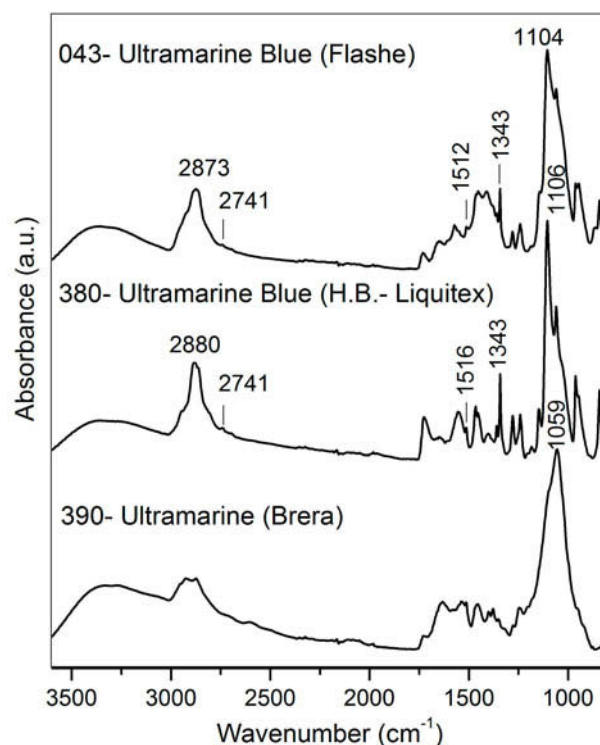


Figure 2: ATR-FTIR spectra of the water extracts of blue paints. The main spectral features to be considered in the assessment of the phase separation process of paint water soluble components are indicated.

absorption around 1100 cm$^{-1}$ that could be assigned to the ethoxylated moieties of the surfactant or to the C-O-C stretching of other additives, such as cellulose ether thickeners.

The extracts of Flashe white, Flashe armor green and H.B.- Liquitex transparent raw Sienna films showed two additional strong bands around 1550 and 1405 cm$^{-1}$ that could be assigned to the carboxylate ion stretching vibrations of an anionic pigment dispersant (such as sodium polyacrylate).

The spectra collected from the extracts of the Brera paints did not show any absorption features clearly related to a surfactant, but were dominated by a strong band between 1062 and 1053 cm$^{-1}$, which was possibly ascribable to a cellulose ether thickener.

Given the aim of the characterization, these results were considered suitable, although the majority of the spectra showed a number of weaker absorptions in the finger print region, which could not be unambiguously assigned to a specific compound.

### 3.2 The Surfactant Phase Separation Process

#### 3.2.1 Exploration of the Paint-environment Interface

No evidence of water soluble components was detected on the surface of the reference mock-ups (stored under laboratory conditions for 18 weeks), suggesting that a spontaneous exudation phenomenon was unlikely to occur, irrespective of the composition of the paint layers. The investigation of the mock-ups subjected to the degradation cycles revealed that samples cast using different paints were likely to undergo different degradation processes.

Following the 20 cycles, the water soluble components of the paints were not detected on the surfaces of Flashe and Brera samples. On the contrary, the majority of the spectra collected from the H.B.-Liquitex mock-ups were characterized by absorption bands of the alkylphenol ethoxylate surfactant. These features were particularly clear for the paints containing organic pigments (PV19 and PG7).

As an example, Figure 3 shows a portion of the spectra collected from two H.B.-Liquitex quinacridone crimson samples: while the spectrum of the reference (blue) showed only features of the bulk film constituents, the spectrum of the degraded sample (LQPV19_1, red) showed the bands of the surfactant. Due to the reflection effect, these bands had an inverted form (reststrahlen effect)[17] but the position of each minimum was in good agreement with the maximum of the absorption band in the corresponding ATR-FTIR spectrum of the paint water extracts (black). These findings indicate that the exudation of the surfactant at the paint-environment interface was possibly promoted by water, which after being absorbed in the mortar supports, wetted the paint layers and penetrated through them.

The absorption features of the surfactant were barely detected in the spectra from samples consisting of inorganic pigments (PW6, PB29 and PY42), as shown in Table 2. With respect to white, blue and yellow paints, it is possible that the quinacridone crimson (PV19) and
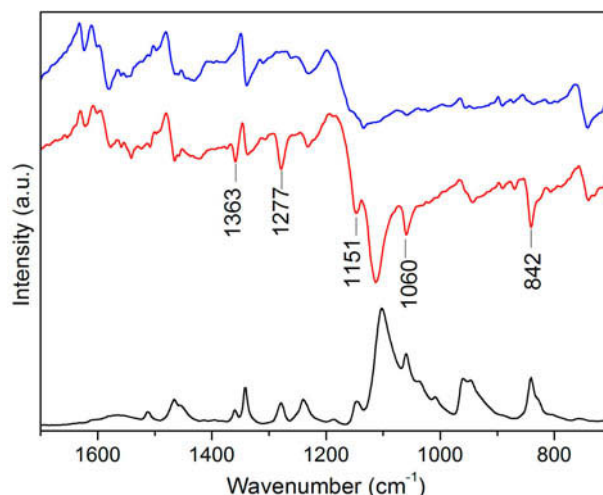


Figure 3: Reflection mid-FTIR spectra from quinacridone crimson H.B.-Liquitex mock-ups: in comparison to the reference sample (blue), the aged one (LQPV19_1, red) shows the typical features of the PEO-type surfactant, in good agreement with the ATR-FTIR spectrum collected from the paint water extracts (black).
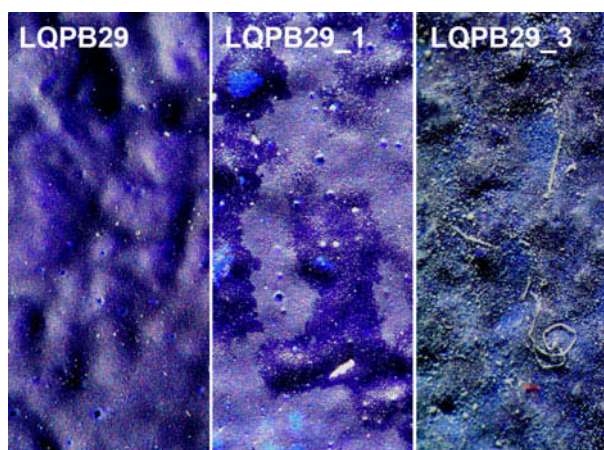


Figure 4: Micrographs (20X) comparing the surfaces of H.B.-Liquitex ultramarine blue mock-ups: the reference (LQPB29); sample LQPB29_1 which underwent 3 degradation cycles and is affected by a translucent deposit; sample LQPB29_3 which underwent 20 cycles and is affected by a white deposit.
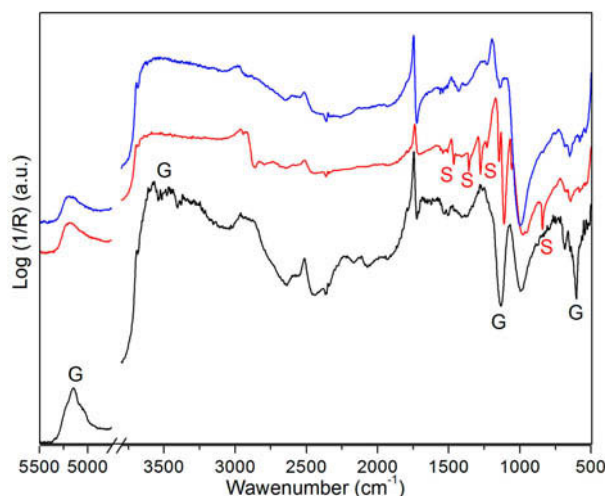


Figure 5: Reflection Mid-Near FTIR spectra from H.B.-Liquitex ultramarine blue mock-ups: the reference (blue), sample LQPB29_1 (3 degradation cycles, red); sample LQPB29_3 (20 cycles, black). S: absorption bands of the alkylphenol polyethoxylate surfactant. G: absorption bands of gypsum.

| ID | Examination Result | Support-Paint Interface | Paint-Environment Interface |
|---|---|---|---|
| LQPW6_1 | Film possibly permeable to water | G | G, S (traces) |
| LQPW6_2 | | | C, G, S (traces) |
| LQPW6_3 | Delamination | | C; G |
| LQPB29_1 | Film permeable to water. Degradation stopped after 3 cycles: translucent material on the surface | | S, C |
| LQPB29_2 | Film permeable to water | - | C, G (?) C, G close to all the edges S (?) close to only one of the edges |
| LQPB29_3 | Thinning of the paint layer. White material on the surface | | C, G, S (?) C, G close to all the edges S (traces) close to only one of the edges |
| LQPY42_1 | Film permeable to water. Degradation stopped after 17 cycles: white material on the surface | | C C, G close to the edges |
| LQPY42_2 | Film permeable to water. The surface becomes more opaque | G | C,G G close to the edges |
| LQPY42_3 | Delamination | | G G, C close to the edges |
| LQPV19_1 | | | S, C (slight amounts) |
| LQPV19_2 | Film permeable to water. White and translucent material on the surface | - | S, C C close to the edges |
| LQPV19_3 | | | S, C (slight amounts) |
| LQPG7_1 | Film permeable to water | | S, C (traces) |
| LQPG7_2 | White and translucent material on the surface | - | |
| LQPG7_3 | | | S, C C close to the edges |

Table 2: Collection of the main results obtained from the H. B.-Liquitex mock-ups. The majority of the samples underwent 20 degradation cycles. The variations detected by the naked eye and by light microscopy are reported, together with the results of FTIR analyses. C: calcium carbonate. G: gypsum. S: alkylphenol polyethoxylate surfactant. Hyphen (-) is used when no changes were detected. The question mark (?) is used when the interpretation of the spectra was uncertain. If not specified the analyses were carried out in the central area of the paint surface.

phthalocyanine green (PG7) ones were formulated using higher amounts of the alkylphenol ethoxylate surfactant. This is consistent with the reported use of non-ionic polyethoxylated compounds as the most appropriate agents to disperse organic pigments.

Further conclusions may be drawn on the basis of the results collected from other H.B.-Liquitex samples. In Figure 4, the H.B.-Liquitex ultramarine blue reference (LQPB29) is compared to LQPB29_1 and LQPB29_3 samples, which underwent 3 and 20 cycles, respectively.

The surface of LQPB29_1 mock-up was affected by a translucent material identified as the PEO-type surfactant (red spectrum of Figure 5). On the contrary, the surface of the LQPB29_3 mock-up showed a white deposit, identified as gypsum ($CaSO_4 \cdot 2H_2O$). The spectrum collected from this sample (black line in Figure 5) actually showed the strong $SO_4^{2-}$ asymmetric stretching (appearing as an inverted band around 1150 cm$^{-1}$), and the highly diagnostic second-order modes of gypsum.[18] The combination of sulfate $v_1+v_3$, also gave rise to a number of bands positioned at 2114 and 2132 cm$^{-1}$, while the bands due to combinations of water stretching ($v_1$ and/or $v_3$) and bending modes ($v_2$) were shown at 5140 and 5054 cm$^{-1}$.

After 20 cycles the absorption features of the surfactant were barely detected, possibly because the concentration of the PEO-type compound was significantly lower than that of gypsum. This could be
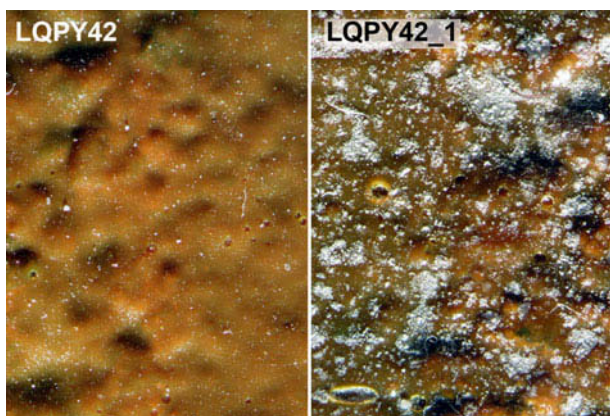


Figure 6: Micrographs (20X) comparing the surfaces of H.B.-Liquitex transparent raw Sienna mock-ups: the reference (LQPY42) and sample LQPY42_1 that, after 17 rising water cycles, is affected by a white deposit.
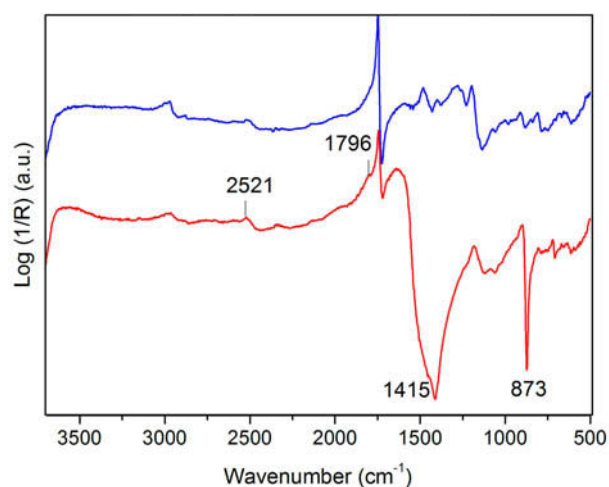


Figure 7: Reflection mid-FTIR spectra of the H.B.-Liquitex transparent raw Sienna mock-ups: in comparison to the reference (blue), sample LQPY42_1 (red, 17 cycles) is characterized by the absorption features of calcium carbonate.

also due to the fact that, as the capillary rise cycles were carried on, the exuded surfactant was partially re-dissolved by water and driven back into the paint layer during the drying process.

After 17 degradation cycles the surface of LQPY42_1 sample (Figure 6) was clearly affected by a white material. As seen in Figure 7, the spectrum from the surface of this sample (red) was characterized by the features
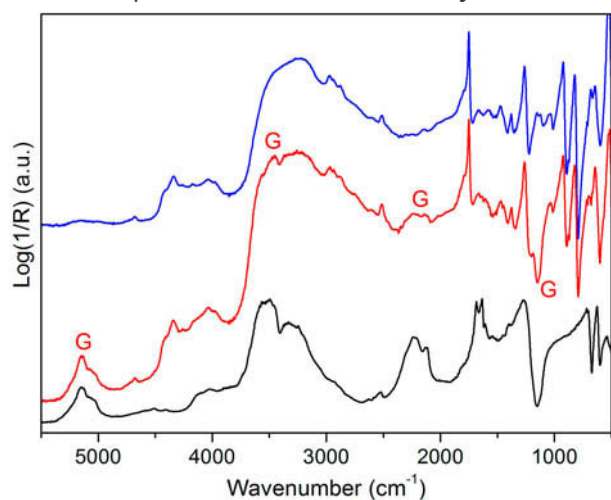


Figure 8: Reflection mid-near FTIR spectra from yellow ochre-Flashe mock-ups: in comparison to the reference sample (blue), the FLPY42_1 one (red, 20 cycles) is characterized by the absorption features of gypsum (G), whose spectrum is shown in black.

of calcium carbonate: the inverted bands at 873 ($v_2$) and 1415 cm$^{-1}$ ($v_3$), and the combination modes at 1796 cm$^{-1}$ ($v_1 + v_4$) and 2521 cm$^{-1}$ ($v_1 + v_3$).[19] It should be noted that gypsum and/or calcium carbonate were detected on the surface of all the aged H.B.-Liquitex mock-ups.

Table 3 shows the results obtained from the Flashe samples. In this case, it was not possible to evaluate the surface carbonation process because the paint layers contained calcium carbonate extender. Nevertheless, traces of gypsum were detected on the surface of some samples, as seen in Figure 8 which includes the spectrum from one of the yellow ochre mock-ups at the end of the 20 capillary rise cycles (FLPY42_1, red line). No salts were detected on the surface of the aged Brera samples.

Naked-eye examinations suggested that when the deterioration process started (3 weeks after the application of the paints on the supports), some acrylic and vinyl layers were still permeable to water. The results of FTIR analyses in reflection mode (surface detection of gypsum and calcium carbonate) seemed to confirm these findings: the cement-lime mortar supports were characterized by slight amounts of water soluble components (as calcium hydroxide and various sulfates[20]), which could be dissolved by the rising water and, as the aqueous solution went through the permeable paint layers, it possibly led to the crystallization of soluble salts on the surfaces of the mock-ups (with calcium carbonate coming from the carbonation of calcium hydroxide). Similar degradation phenomena have been recently proposed in a study concerning a real mural painting.[21] The same process was not seen for the Brera samples, probably because of the higher hydrophobic character of the styrene-acrylic binder.

On some of the H.B.-Liquitex samples it was seen that capillary rise promoted separation of the alkylphenol polyethoxylate surfactant and its migration towards the paint-environment interface. Despite being characterized by the same typology of surfactant, no evidence of the exudation process was detected for the Flashe samples. As an example, a portion of the spectra collected from two Flashe-ruby red mock-ups is shown in Figure 9: the vibrational features of the PEO-type surfactant (black) were not detected, neither from the reference (blue) nor from the aged sample (red). This could be simultaneously due to different reasons:
- With respect to the H.B.-Liquitex paints, the Flashe ones contained lower amounts of the PEO-type surfactant
- Affinity of this surfactant was higher for the p(VAc-VeoVa) binder rather than for the p(nBA-MMA)
- Surface exudation was less likely to affect the vinyl paint layers because of their poor coalescence degree caused by calcium carbonate extender
- Due to the strong water sensitivity of the vinyl paint films,[22] the overall effect of the rising water on Flashe samples was to dissolve and redistribute the water-soluble components in the highly swollen paint layers. The surface detection of the PEO-type surfactant was thus prevented, because its concentration was significantly lower than that of the other paint components

| ID | Examination Result | Support-Paint Interface | Paint-environment Interface |
|---|---|---|---|
| FLPW6_1 | Film possibly permeable to water | G | G (?) |
| FLPW6_2 | Local yellowing | | - |
| FLPW6_3 | Delamination | | G close to yellow areas and to the edges |
| FLPB29_1 | Film possibly permeable to water. Darkening. Increase of surface roughness | - | - |
| FLPB29_2 | Film possibly permeable to water. Darkening. Increase of surface roughness. Local paint layer thinning | | G only close to the edges |
| FLPB29_3 | Film possibly permeable to water. Darkening. Increase of surface roughness | | G |
| FLPY42_1 | Film permeable to water | - | G in the central area and close to the edges |
| FLPY42_2 | Slight darkening | | |
| FLPY42_3 | Increase of surface roughness. | | |
| FLPV19_1 | | - | - |
| FLPV19_2 | Film possibly permeable to water | | G (?) |
| FLPV19_3 | | | G (?) |
| FLPG7_1 | | - | - |
| FLPG7_2 | Darkening | | |
| FLPG7_3 | | | |

Table 3: The main results gathered from the Flashe samples (20 degradation cycles). The variations detected by the naked-eye and light microscopy are reported, together with the results of FTIR exploration of the interfaces. G: gypsum. Hyphen (-) is used when no changes were detected. The question mark (?) is used when the interpretation was uncertain. If not specified the analyses were carried out in the central area of the paint surface.
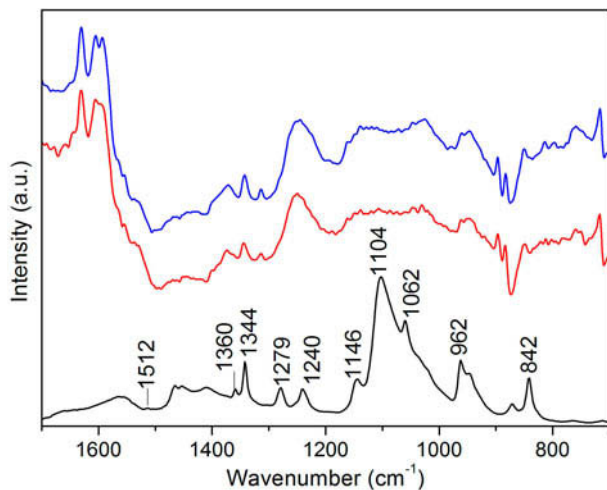
Figure 9: Reflection mid-FTIR spectra from ruby red-Flashe mock-ups: the absorption features of the PEO-type surfactant are not detected, neither on the surface of the reference (blue) nor on the surface of FLPV19_1 sample (red). In black, the ATR-FTIR spectrum of the paint water extracts.



Figure 10: Reflection μ-FTIR spectra from one of the delaminated areas of LQPY42_3 sample: the back of the paint layer (blue) and the surface of the mortar support (red). In black the ATR-FTIR spectrum from the back of the paint layer. C: calcium carbonate. G: gypsum.

### 3.2.2    Exploration of the Paint-support Interface

After 20 degradation cycles, some of the samples prepared with Flashe white, H.B.-Liquitex titanium white and H.B.-Liquitex transparent raw Sienna paints, showed delamination (blisters). In the attempt of assessing the cause, the paint layers were locally peeled off and the film-support interfaces were studied by μFTIR-reflection spectroscopy. The water soluble components of the paints were not detected, neither on the back of the paint layers nor on the surface of the mortar supports.

As an example, the results collected from one of the delaminated areas of LQPY42_3 sample are shown in Figure 10. The spectrum from the back of the paint layer (blue) was characterized by absorption features that could be ascribed to the bulk film, to calcium carbonate (one of the main components of the support) and gypsum. The spectrum collected from the surface of the support (red) revealed the presence of gypsum.

The back of the paint layer was also explored by ATR-FTIR (black), confirming the results of previous investigations: bands at 3530, 3400, 1685, 1622, 1112, 673 and 603 cm$^{-1}$ were assigned to gypsum; bands at 1796, 1402, 872 and 713 cm$^{-1}$ to calcium carbonate; that at 1006 cm$^{-1}$ to silicon-based sand in the mortar support. Similar results were gathered from all the samples, suggesting that delamination is due to the sub-surface crystallization of water soluble salts originating from the supports, rather than to the presence of paint additives.

### 4    Conclusions

The experiments presented in this work contributed to better definition of the degradation processes that affect contemporary mural paintings, through a preliminary assessment of phase separation of the water soluble components of different emulsion paints using FTIR reflection spectroscopy.

No evidence of paint additives was detected on the surface of the reference samples stored under labora-
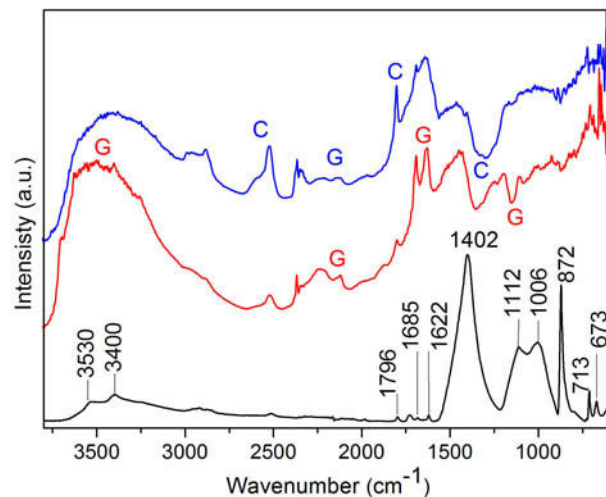
tory conditions for 18 weeks. This possibly suggests that indoor murals, created on supports which are not affected by damp and water infiltration, would not be affected by early exudation phenomena. Since the desorption of some components of the paints from the bulk films to the paint-environment interface may develop considering longer periods of time, it would be interesting to continue monitoring the condition of the surface of the reference samples.

The investigation of the mock-ups subjected to the rising water cycles suggested that phase separation could be promoted by water absorbed into the support and wetting the paint layers.

Different results were collected from samples prepared using different paints, possibly depending on the chemical composition of the paint layers. The H.B.-Liquitex samples were prone to the process, with the PEO-type surfactant (presumably an alkylphenol ethoxylate one) which desorbed from the acrylic bulk films, leading to the formation of patchy translucent layers at the paint-environment interface. Consistently with the reported use of non-ionic compounds as the most appropriate agents to disperse organic pigments, the highest amounts of the surfactant were detected on the surfaces of the aged quinacridone crimson (PV19) and phthalocyanine green (PG7) samples.

Besides being characterized by the same typology of surfactant, the Flashe samples seemed not to undergo the exudation process. This could be due to many causes: brand dependency reasons (the amount of surfactant used to formulate the paints), the interaction between the paint components, the degree of coalescence of the paint films, the response of the paint layers to water.

Considering outdoor real murals, the paint layers are often wetted by rising water or rain. Depending on the composition of the paint layers, this may lead to an early exudation of the water-soluble components (such as the PEO-type surfactants). Nevertheless, it is rather unlikely that this process is the main cause of the bleaching of paint layers, with accretions of white materials possibly due to other degradation mecha-

nisms. The results collected from H.B.-Liquitex and Flashe samples suggested that, since the mortar supports are characterized by water soluble components, the rising water may become the vehicle of soluble salts, leading to surface crystallization processes.

Neither phase separation nor surface salt crystallization were detected in the Brera mock-ups. The higher stability of these samples was presumably due to the hydrophobic character of the paint layers, characterized by a styrene-acrylic binder. On the other hand, most of the relatively fresh (3 weeks old) acrylic and vinyl paint layers were permeable to liquid water.

The sensitivity of the paint layers to water is possibly enhanced by hydrophilic additives. If phase separation occurs it is probably better to remove the exuded compounds from the surface of the paintings. However, it is reasonable to assume that after being exuded, the additives will rapidly deteriorate due to outdoor weathering conditions (exposure to rain and UV radiation).[5,7]

No evidence of paint water-soluble components was detected at the film-support interface, with data suggesting that the delamination of the paint layer was mainly caused by the sub-surface crystallization of water soluble salts. In contrast to what is observed on canvas paintings, the additives of emulsion paints seem to play a minor role in affecting the stability of mural paintings. In these, degradation processes are primarily influenced by the condition and the properties of the supports.

## 5        Acknowledgements

## 6        References

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